Apparatus for Visual Study of Corrosion by Hot Water

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The design and operation of a windowed autoclave suitable for studying corrosion of materials by pressurized hot water are described. The technique for taking time-lapse motion pictures of a specimen from the instant of contact with the high-temperature water until the corrosion is complete is explained, and a set of typical pictures is presented showing the progress of the attack. Pressure and temperature measurements provide a means for rough computation of corrosion rates, as is shown by the results of two tests of uranium specimens subjected to pressurized hot water.

A windowed autoclave was designed and constructed to permit visual study of the reaction of a corrosion specimen with high-temperature water. Although similar research is being done elsewhere, several features of the Battelle device are unique. One advantage is that the upper temperature is limited only by stresses in the pressure vessel, rather than by corrosive attack on the glass windows. Another is that the hot water can be made to contact the specimen suddenly, and thus a more interpretable test is provided than in the case where the specimen is subject to attack during the time the system is being heated and pressurized.

APPARATUS

The Viewing Autoclave

Figure 1 shows a cross section of the autoclave. There are two windows, one for illumination and one for viewing. These are mounted in the bottoms of water-cooled legs in order to permit cooling without introducing convection currents, which would distort the image.

The body of the pressure vessel is surrounded by eight Cromalox strip heaters, so arranged as to provide a slightly higher temperature at the top than at the bottom. These help to ensure that the image will not be distorted by convection currents or by rising steam bubbles. The heaters are surrounded by about 1 in. of thermal insulation. The temperature at the test specimen is maintained at the desired value by a controller which responds to a thermocouple located in the heating jacket. This method of control minimizes temperature cycling and accompanying pressure cycling. The temperature of the water in the vicinity of the specimen is measured by a second thermocouple located in the thermocouple well.

All parts of the autoclave were machined from type-304 stainless steel, with the exception of the copper window gaskets and cooling coils, the serrated nickel main gasket, the main thrust ring of oil-die steel, and the alloy-steel set screws. Heliarc welding was used for all welded joints.

The Herculite glass windows were cemented to the window heads, by means of a thin coating of water-resistant adhesive. The neoprene 0 rings were added to a standard Bridgman window seal, as shown, to permit the vessel to be evacuated without danger of dislodging the windows. These 0 rings are not intended to seal, but merely to act as spacers. The seal is formed between the glass and the window head, as well as at the copper gasket.

The upper seal is a standard pressure closure, utilizing a serrated nickel gasket compressed between a closure head and the body of the pressure vessel. The thermocouple well, welded to the closure head, serves also to hold the specimen mount, thereby providing a convenient arrangement for inserting and removing specimens.

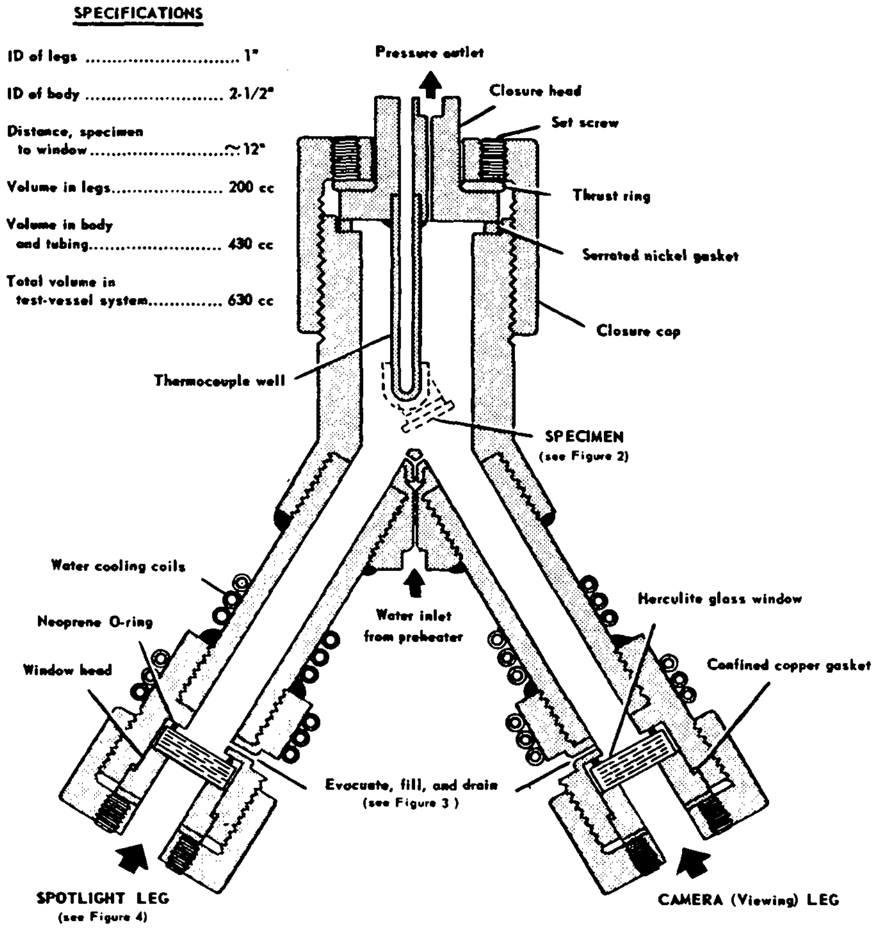

Fig. 1. Cross section of windowed autoclave.

Specimen Mount

The closure head with a test specimen mounted on the end of the thermocouple well is shown in Figure 2. The mounting permits sufficient rotating and sliding adjustments to position the specimen for maximum lighting and to center it along the axis of sight. Early trials with polished specimens gave images which showed only a narrow band of specularly reflected light. This difficulty was remedied by using a frost-gold background, as shown in Figure 2, and putting a satin finish on the specimen with emery paper. The

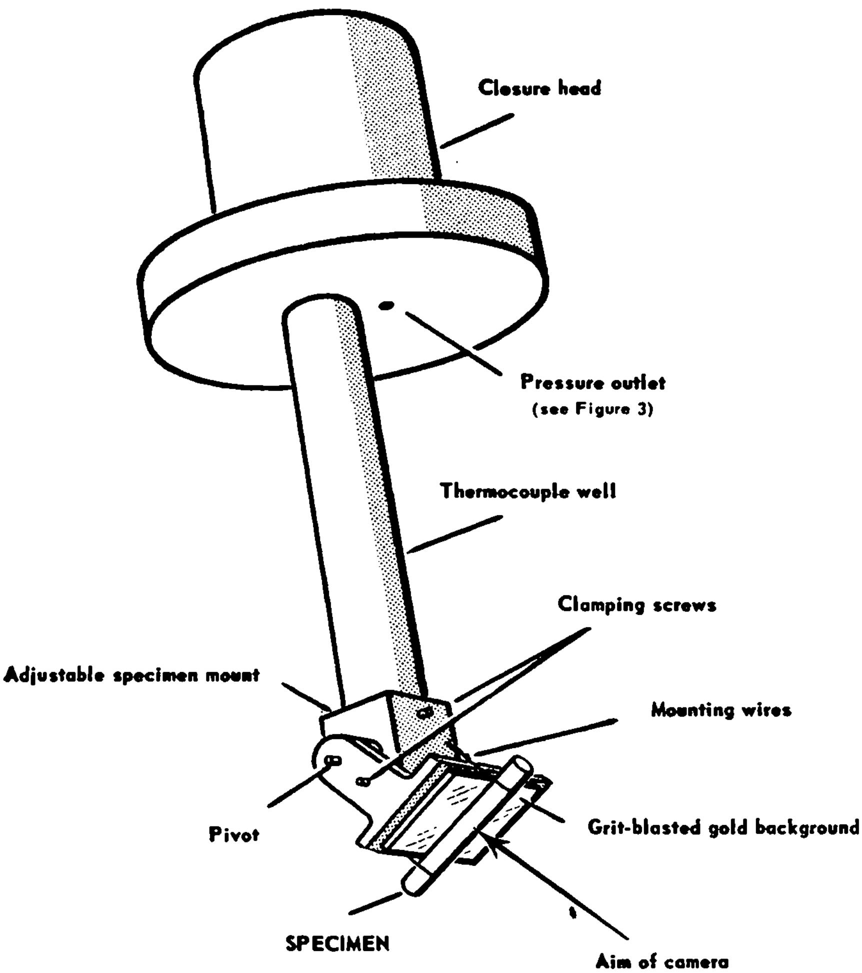

Fig. 2. Closure head for windowed autoclave, with specimen mounted.

resulting image is much clearer, and the edges of the specimen are more sharply defined.

In cases where the specimen has a corrosion-resistant shell, it is fastened to the mount with Nichrome wires as shown. Bare specimens must be placed in a wire basket or in a stainless steel boat wired to the mount, in order to keep the specimen from falling into the cooled legs before the corrosion is complete. With bare specimens, viewing is considerabу more difficult and often impossible, because either the specimen container or the corrosion débris obscures the view.

Preheat Autoclave and Pressure System

Figure 3 is a diagram of the pressure system. The independently controlled 1,000-cc. water-preheating autoclave is fitted with two outlets, one of which extends to the bottom of the vessel. It is thus possible to transfer the water to the previously heated test vessel as a liquid. The valving allows the legs of the test vessel and the preheat autoclave to be charged independently with predetermined amounts of water and then evacuated to outgas the water and to remove air.

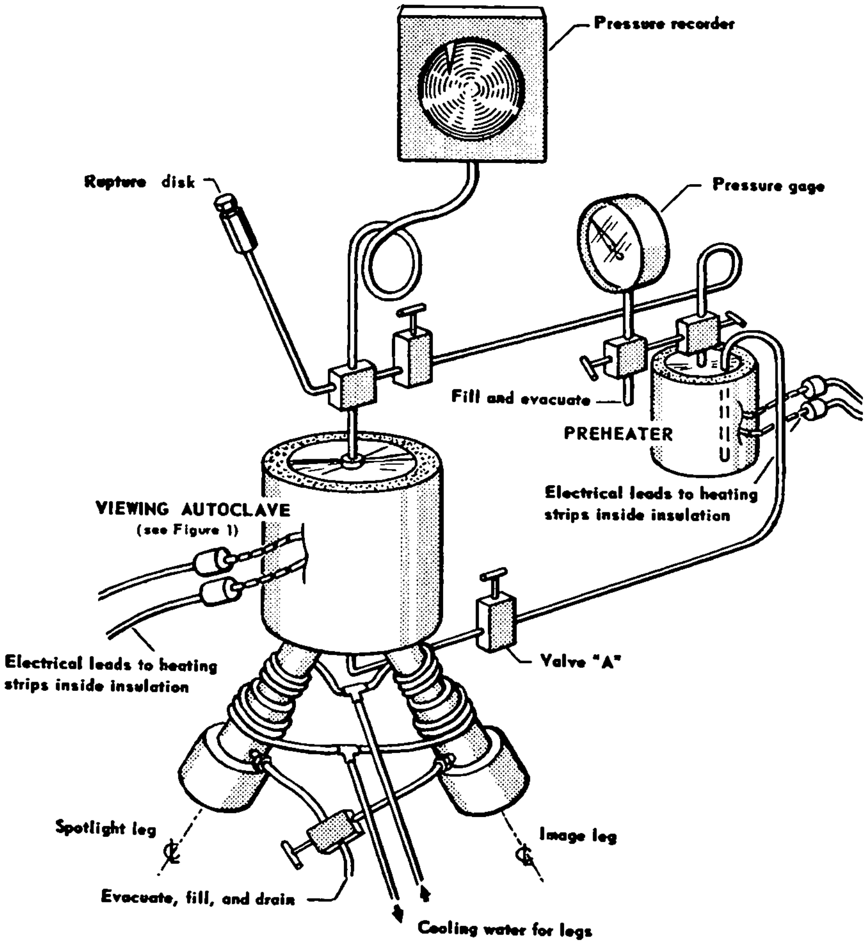

Fig. 3. Windowed-autoclave system.

Camera Setup

Figure 4 is a sketch of the arrangement used to obtain time-lapse pictures of the specimen during the corrosion process. The light source illuminates a 1-in.-diam. circular area of specimen and background. The mirror at the end of the viewing leg is positioned so that the camera sees the specimen and the digital clock simultaneously. A beam-splitter is positioned in front of the camera lens so that a small fraction of the light is reflected at right angles to the photographic axis. This arrangement allows the operator to follow the progress of the corrosion visually without disturbing the picture taking. The camera used is a 16-mm. Paillard-Bolex, fitted with an external electric motor and spring drive and a 63-mm. Ektanon Kodak lens. The time-lapse control and actuating solenoid is a Samenco movie control, capable of 1-, 2-, 4-, and 6- to 1,200-sec. intervals between frames.

TEST PROCEDURE

The specimen is prepared and mounted in the desired position, and then the test vessel is closed and sealed. Next 100 cc. of deionized water is introduced into the water-cooled legs to protect the glass

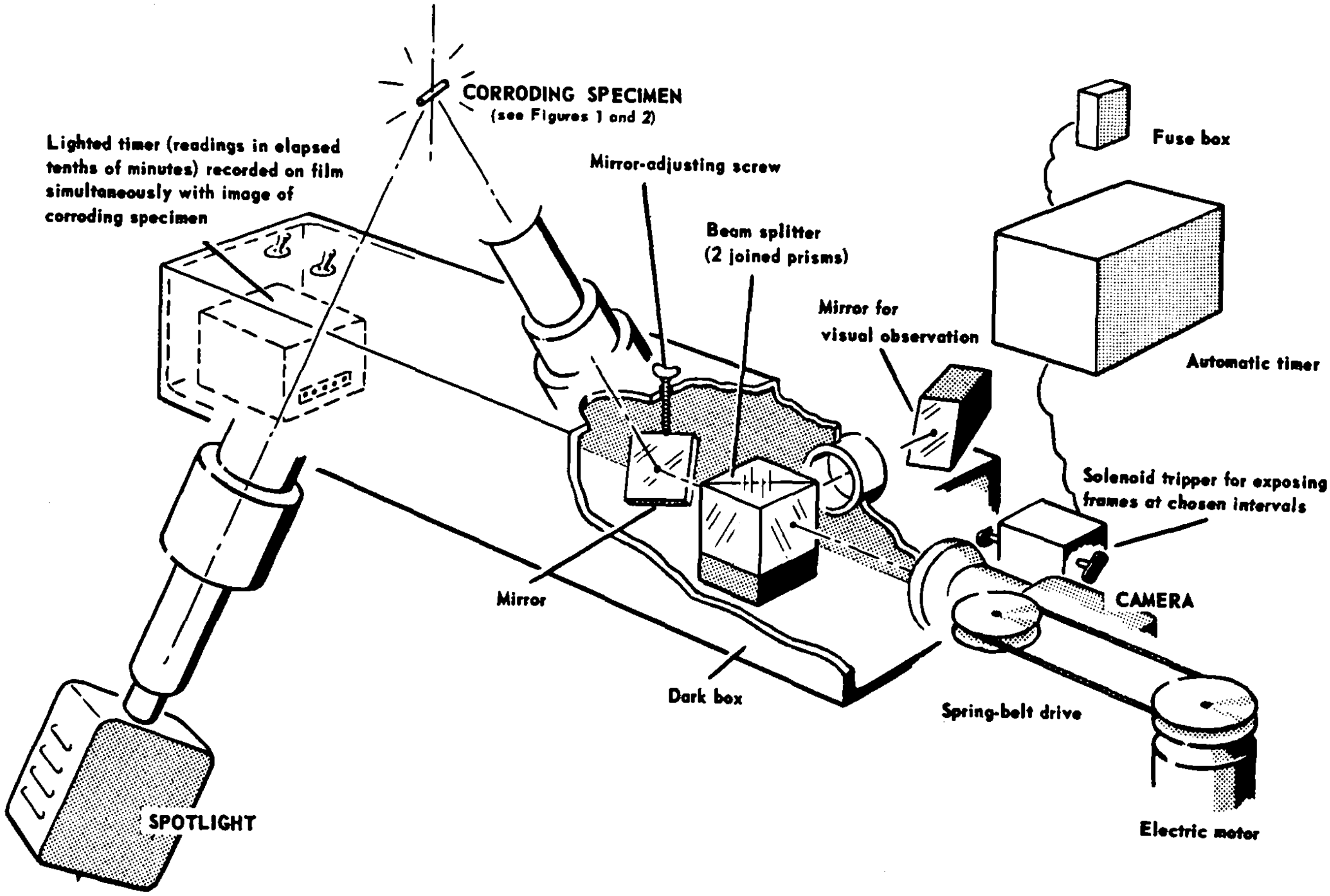

Fig. 4. Photographing and observation system.

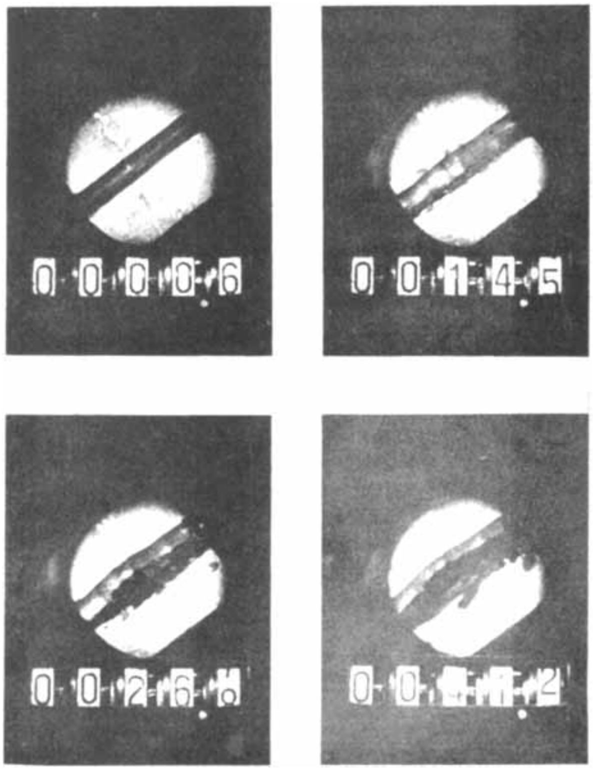

Fig. 5. Representative reproductions from films of test.

during the preheat period. The preheat autoclave is loaded with 550 cc. of water and the entire system evacuated to outgas the water. With all valves in the system closed, the preheat and viewing autoclaves are heated independently to the test temperature. The test is initiated by turning on the pressure recorder and then opening valve *A* (*see* Figure 3) to allow approximately 300 cc. of preheated water to enter the viewing autoclave and engulf the test specimen. At 600°F. this transfer is accomplished in less than 30 sec. The preheat vessel is then allowed to cool, as it has no further function in the experiment. Simultaneously with opening the valve, the time-lapse control and the specimen and timer lights are turned on. From this time until the corrosion is complete, the operation is entirely automatic. When the test is over, the heaters and camera controls are turned off and the system is allowed to cool. The pressure record is continued until the system has cooled to room temperature. Then the quantity of water emptied from the window autoclave is measured.

TYPICAL RESULTS

A selection of four frames from an actual test has been reproduced in Figure 5. This particular specimen contained a

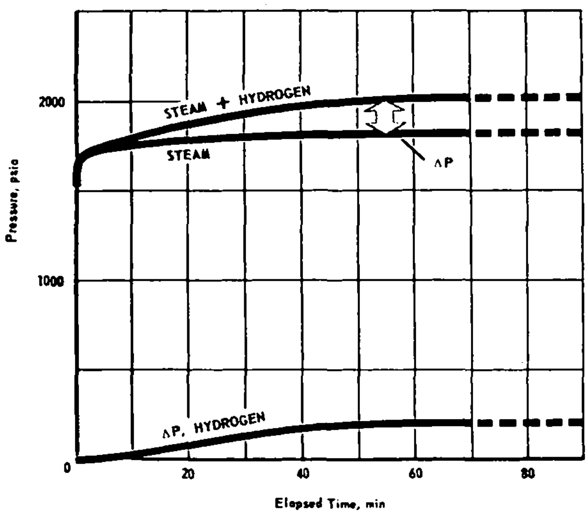

Fig. 6. Typical plot, pressures vs. time.

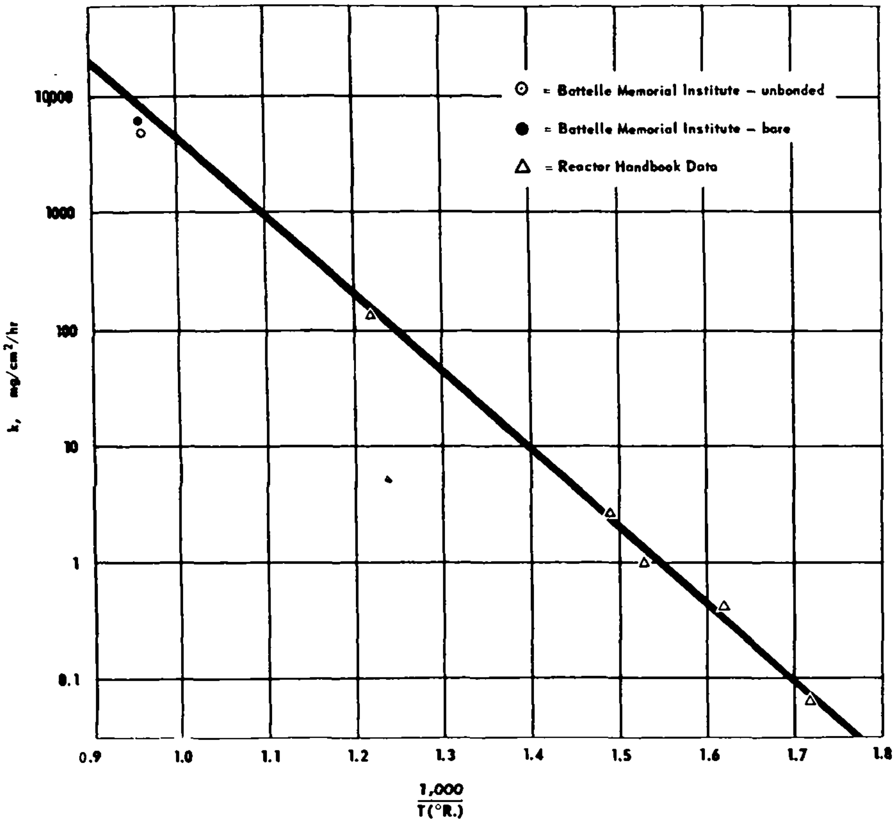

Fig. 7. Corrosion rate of uranium vs. temperature.

uranium rod welded to zirconium plugs and slipped into a shell which was bonded to the rod and plugs. The 0.010-in. hole drilled in the shell is visible in Figure 5. The numbers at the bottom of each frame represent the respective times, in tenths of minutes, that the specimen had been in contact with 600°F. water. The progress of the corrosion is easily followed from the swelling and subsequent cracking and bursting open of the shell. Bubbles of hydrogen are visible in some of the pictures, although the progress of any one bubble can rarely be traced on the film because of the time interval between frames.

Figure 6 is a graph plotted to show the manner in which the amount of hydrogen evolved may be obtained. The calibration curve shows the pressure history inside the test vessel when it is filled with 600°F. water with no specimen in place. This is necessary as it takes a finite length of time for pressure equilibrium to be reached (in this case, about 40 min.). The difference in pressure between a test with a specimen in place and a test without is, therefore, attributable to evolved gas. Of course, allowance must be made for the hydrogen which dissolves in the water and that which is lost by diffusion through the walls of the test vessel. By the use of suitable geometric equations which relate the area open to attack to the volume of material corroded, the hydrogen-evolution rate may then be translated to a corrosion rate.

This method has been employed to obtain the corrosion rates listed in Table 1. A comparison has been made in Figure 7 of the data in Table 1 with literature data reported at lower temperatures. The line shown (*1*) has the equation

$$\log_{10} k(\text{mg. cm.}^{-2}\,\text{hr.}^{-1}) = -\frac{6{,}710}{T(°R.)} + 10.34$$

TABLE 1. SUMMARY OF CORROSION DATA

Bonding condition	Temperature, °F.	Corrosion rate (k), mg./(sq. cm.)(hr.)
Bare	587	6,260
Unbonded	582	4,910

DISCUSSION

Clarity of detail in the pictures is limited primarily by the grain size in the film and the intensity of the illumination. In the tests made thus far, type Kodachrome *A* film has been used, and, even though the grain size is not as small as is obtainable with Super XX, it was felt that the identification of color would compensate for the lack of definition and at the same time show up any characteristic color of the reaction products.

Thus far the accuracy of the calculated corrosion rates, based on hydrogen-evolution data, is no better than 20%, owing largely to the extreme sensitivity of steam pressure to small changes in temperature. This could be improved by substantially more precise control of steam temperature. In any event, the windowed autoclave affords a relative evaluation of the influence of such variables as geometry, alloying, type of bonding, water temperature, and water impurities on corrosion rate. The most important advantage of this instrument is, however, that it provides a pictorial representation of the corrosion phenomenon while it is occurring.

LITERATURE CITED

1. "Reactor Handbook," vol. 3, U. S. Atomic Energy Commission, U. S. Gov't Printing Office, Washington, D. C. (1955).

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