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STRESS-CORROSION CRACKING PROBLEMS IN THE HOMOGENEOUS REACTOR TEST

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ABSTRACT

Chloride-induced stress-corrosion cracking has been encountered in the Homogeneous Reactor Test during the preliminary testing. The reactor is constructed of austenitic stainless steels. It is unique in that it will operate at 250 to 300°C with an aqueous uranyl sulfate solution fuel containing 200 to 500 ppm of dissolved oxygen.

The cracking has occurred in a secondary system used for detecting leaks in the flanged joints of the primary systems and in the grooves of flanges in the primary systems. Tubing used in the leak-detection system was found to be contaminated with chloride introduced during manufacture. Examples of cracking of tubing and flanges are shown.

In the laboratory it has been demonstrated that stress-corrosion cracking of austenitic stainless steels does not occur in oxygenated uranyl sulfate solutions unless chlorides are present. Results of the laboratory studies and studies in engineering loop experiments are discussed.

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STRESS-CORROSION CRACKING PROBLEMS

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Twenty-two years ago Dixon¹ described a phenomenon which he termed "alligator markings" which resulted in failures of 18-8 stainless steels used in oil-refinery heat exchanger and condenser tubes. These "alligator markings" were soon recognized as evidence of stress-corrosion cracking, a familiar type of failure for many other metals². In the intervening years this type failure of many so-called stainless steel alloys has been observed in such diverse environments as potable water in the neighborhood of the boiling point³ and 80% alkali at 650°F⁴. Applications in which stress-corrosion cracking failures have been encountered have ranged from steam-jacketed coffee cookers⁵ to steam power plants. More recently stress-corrosion cracking of stainless alloys has been the source of considerable concern in some nuclear power programs. Its occurrence and effect on the ORNL Homogeneous Reactor Test program are described below.

Stress corrosion may be defined as failure by cracking due to the simultaneous action of stress and localized corrosion. In the case of the austenitic stainless steels the alloys are usually very resistant to the environment involved in terms of generalized attack, and the cracks are generally transgranular in nature.

Early in the Homogeneous Reactor Project investigation of austenitic stainless steels for reactor application, several staff metallurgists pointed

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out the susceptibility of these alloys to stress-corrosion cracking. The point was well taken in view of the fact that the uranyl sulfate solution which has been the primary fuel solution under consideration is an acid solution which must be oxygenated to maintain uranyl ion stability. In addition, the particularly aggressive nature of chloride ion in promoting stress cracking of stainless alloys in oxygenated acidic solutions was cause for concern in view of the ease with which contamination by this prevalent ion could be encountered. In consequence, this cause of failure was given serious consideration in all aspects of the materials investigation program. Tests with stress specimens of various kinds were performed in laboratory beaker experiments, high-temperature autoclaves, 100-gpm dynamic test loops, and in-pile loops without encountering evidence of stress cracking by uranyl sulfate solutions in the absence of added chlorides. Over 200,000 hours of dynamic loop operation have been accumulated over widely varying conditions of concentration (0 to 1.3 m), temperature (100 to 340°C), and added reagents (O_2 , H_2 , H_2SO_4 , $CuSO_4$, $CrO_4^{=}$) with no failure attributable to stress-corrosion cracking by uranyl sulfate solutions containing normal-impurity-level chloride concentrations (< 5 ppm).

However, transgranular cracking has been observed in parts of more complex systems in use in the engineering development portions of the program with no added chloride. Of course, the presence of additional chlorides at some time could not be excluded; so the exact reason for these failures has been difficult to establish. A few general remarks on results obtained in corrosion experiments may help explain this difficulty.

In one experiment⁶ a number of type 347 stainless steel stress specimens were exposed in boiling uranyl sulfate solution and in the vapor above

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it for over 7000 hours with no signs of cracking. After completion of this exposure 60 ppm of chloride as sodium chloride was added to the solution and the test continued. All previously exposed specimens remained in test, and, in addition, two new specimens were included, one in the solution phase and one in the vapor phase. Examination of all the specimens 500 hours later showed cracks developing in the new liquid-phase specimen but none in any of the others, including the new vapor-phase specimen. This situation continued for 3000 hours of additional exposure: the new solution specimen cracked badly but all the others showed no signs of cracks.

In another series of tests⁷ with boiling uranyl sulfate solutions with added chloride, no cracking was observed at a concentration of 10 ppm Cl^- , extensive cracking and pitting were observed at 25 and 50 ppm, and extensive generalized attack but no cracking was observed at 100 ppm. This maximum cracking tendency at intermediate concentrations of the aggressive reagent is not inconsistent with the observation that stress-corrosion cracking usually occurs where over-all corrosion is absent or very small⁸.

In a different series of tests⁹ carried out under slightly different experimental conditions, no cracking of liquid-phase specimens was observed, but many instances of cracking of vapor-phase specimens were observed with only 5 to 10 ppm chloride ion added to the uranyl sulfate solution.

Thus stress-corrosion cracking of austenitic stainless steels in uranyl sulfate solutions containing chloride ions is a very complex phenomenon. As in other chloride environments which promote stress cracking of stainless steels, such things as previous history, concentrations of reagents, particular

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experimental conditions, and many other variables may affect the result obtained in a particular situation. As a result, the occurrence of stress-corrosion cracking in a complex assembly of equipment, where conditions are, generally speaking, favorable, is difficult to predict. Such was the case in the Homogeneous Reactor Test. In fact, the cracking here did not stem from conditions in the primary system, but from chloride contamination in a secondary system.

The Homogeneous Reactor Test is a two-region aqueous fluid-fuel reactor being developed at the Oak Ridge National Laboratory in connection with its long-range investigation directed at development of a two-region breeder. The process piping and equipment, which are made of type 347 stainless steel, are joined by means of O-ring flanges fitted with annealed type 304 and 347 stainless steel ring gaskets. Since the circulating fuel contains in excess of 30 curies of fission-product activity per cubic centimeter under operating conditions, absolute control of leaks must be achieved. Figure 1 shows how this was done in the case of the flange joints.

First, the O-ring fit in the grooves was made such that a seal was obtained on both sides of each groove. Second, the V-grooves in the two flanges were connected by holes drilled through the O-ring as shown. Third, a 1/8-inch-diameter hole was drilled to the V-groove of one of the flanges. All such holes were connected to a sectionalized header system by means of 1/4-inch 0.065-inch-wall, type 304 stainless steel tubes. The headers, tubing, and flange grooves were completely filled with water at a pressure ~ 500 psi above the design operating pressure of the reactor, to assure leakage into the system should a leak across the gasket to the interior occur.

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In August, before the system had been operated at all and during tests of remote maintenance procedure, it was noted that the fluid that came from the gooves in a flange which was opened was dark green in color. As a result the entire leak-detector system was drained; 40 liters of solution were withdrawn. Subsequent chemical analysis of the solution showed the composition presented in Table 1.

TABLE I
COMPOSITION OF SOLUTION FROM HRT LEAK-DETECTOR SYSTEM

	<u>γ/ml</u>
Fe	320
Ni	83
Cr	287
Cl	1070
F	1
Total Solids	2800

pH = 3.1

These analytical results necessitated a thorough investigation which produced the following information:

1. As other flanges were opened it was shown that the chloride contamination was widespread. Also, examination of flange grooves and O-rings showed that the solution was corrosive to the 347 alloy, varying pitting attack being observed.
2. Several leak-detector lines, which had been installed as spare shield penetrations and never used, were inspected. A green solution, similar to that withdrawn from the leak-detector system, was obtained by passing water through one

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of these tubes. With continued flushing, the chloride concentration in the effluent rapidly became less than could be measured (< 1 ppm). However, a chloride concentration of 28 ppm was again obtained when the water was allowed to stand in the tube overnight.

3. On splitting one of the type 304 stainless steel tubes longitudinally, the interior surfaces were found to be coated with a green colored material. There were also numerous small, sponge-like brown deposits which were fragile and easily broken. The green material turned brown after ~ 10 days exposure to air.
4. Metallographic examination¹⁰ of the tubing showed that the inner surface of the tube had a honeycomb structure ~ 1 mil thick, as shown in Figure 2; the voids in this structure were filled with the material described above. This structure accounted for the difficulty encountered in trying to wash the chloride out completely. A grain-boundary precipitate, shown to be carbides by etching with Vilella's reagent, also extended about 4 to 5 mils into the metal as shown in Figure 3. No cracks were found in any tubing examined at this time.

The tubing which was the source of the trouble, based on these observations, consisted of one lot of 5000 feet which was ordered in 45-foot lengths to minimize the number of joints required in making runs. Unfortunately, this lot of tubing was used in making practically all the shield-wall penetrations, so that almost every line in the leak-detector system contained a segment which had some of the chloride contaminant in it. This accounted for the widespread distribution of the colored solution described above.

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It has been hypothesized that the substantial contamination of the tubing may have occurred in the following way: Because of the unusual length and small, 1/8-inch-diameter bore, drawing compound from the mandrel, usually a chlorine-containing organic compound, was not completely removed in degreasing. During annealing this residue was decomposed with resultant attack and carburization of the inside surface of the tubing. The nitric-hydrofluoric acid pickle solution used would then produce surface roughening and grain-boundary attack. Subsequent repetition of the cycle with this surface in achieving the final product could be expected to aggravate the situation until the condition observed in metallographic section resulted.

As a result of these findings the 200-odd flanges in the system were opened and the leak-detector system was exhaustively flushed with water. This flushing was carried out over a period of two months, each line being flushed in 48-hour intervals until an intervening 24-hour soak sample gave less than 1 ppm chloride. The flange grooves were thoroughly cleaned and, if necessary, lapped; and the O-rings were re-machined.

In the interim it was also decided to run the leak-detector system pressurized with gas. Since high-pressure oxygen was already available it was the gas chosen. A corollary decision was that the leak-detector system would be thoroughly dried out and kept dry while in operation. Unfortunately, in practice this was not possible, particularly during shakedown operations when leaks were frequent. The process of locating a leak involved closing off all the lines connected to a given header and then opening them again, one by one, until a pressure drop indicated the line through which leakage was taking place.

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In the interim, of course, that line leaked down to fuel-system pressure, and if there was a later rise in fuel-system pressure, water was forced back into the leak-detector line. However, shakedown operations continued.

After approximately 100 hours of non-radioactive testing operation had been logged, leaks began to show up in leak detector lines. The first leak was in a weld connection and was attributed to a poor weld, which was ground out and repaired in the field. The next leak, however, appeared in a straight section of tubing; it was cut out for metallographic examination. Transgranular crack failures characteristic of stress-corrosion cracking of stainless steel were found as shown in Figure 4. While this examination was in progress, several more leaks developed in leak-detector tubing; so the reactor was shut down for further examination.

It was noted that the leak-detector-tubing leaks were in portions which were at relatively high temperatures due to proximity to hot process piping. This pointed to the flange grooves as areas of particular concern.

Three flange joints were cut from the reactor system for exhaustive examination. Two showed pits but no cracks, but the third, which was chosen because it showed a number of pits (Figure 5) which were not observed during the exhaustive wash and cleanup several months before, gave quite a different picture. This flange was first examined with fluorescent penetrant. The results are shown in Figure 6, which shows one of the more definite areas; in other areas difficulty was encountered in distinguishing between the very short cracks, deep pits, and machining marks. Macro-etches with both hydrochloric acid (Figure 7) and sulfuric acid showed considerable surface cracking as short

irregular cracks. A metallographic examination revealed the typical trans-granular stress-corrosion cracks as shown in Figures 8 and 9. While found on all groove surfaces below the seal line, the cracks were concentrated primarily near the corners of the grooves, where the stresses were highest. The maximum crack depth observed in eight metallographic sections of this 3-1/2-inch, 2500-psi flange was approximately 25 mils.

Thus the examination of three flanges of the 200-odd in the reactor suggested that many flanges may have cracks started in them. This conclusion was reinforced when careful microscopic and fluorescent penetrant examination of the 15-inch flange grooves and O-ring of the top closure of the reactor pressure vessel showed evidence of cracks. Figure 10 is an ultraviolet-light photograph of the crack indication obtained on the O-ring with the fluorescent penetrant, and Figure 11 is the confirmatory metallographic section.

Unfortunately, the experience obtained in the above examinations rather conclusively demonstrated that no technique of non-destructive testing in the field could be relied on to distinguish between sound and cracked flanges. This was particularly true where surface attack had taken place. In view of this present lack of knowledge of suitable non-destructive testing methods and of the similar state of knowledge concerning the propagation of cracks in stainless steel once they have been formed, it appears necessary to consider replacement of the leak-detector system and all flanges in the reactor. Materials have been ordered for this purpose. Unfortunately, three flanges are considered irreplaceable: the pressure-vessel flange discussed above and the tube-sheet closures of the two heat exchangers. These three closures have

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been equipped with individual, circulating leak-detection systems in which O_2 will be minimized by a scavenger and chloride will be eliminated by fluid replacement. The pressure-vessel flange grooves were also lapped so that they gave no further indication of cracks by fluorescent penetrant examination.

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BIBLIOGRAPHY

1. Thum, E. E., The Book of Stainless Steels, 2nd Ed., American Society of Metals, Cleveland, 1935, E. S. Dixon, "Petroleum Refineries", p. 590.
2. Symposium on Stress-Corrosion Cracking, published by ASME and AIME, Philadelphia and New York, 1944.
3. Benneck, H., "Spannungskorrosionerscheinungen bei Eisenlegierungen", Korrosion u Metallschutz 20, p. 133, 1944.
4. Brush, E. G., The Behavior of Type 347 Stainless Steel in Sodium Hydroxide at Elevated Temperatures, Knolls Atomic Power Laboratory, Memo-EGB-22.
5. Ellis, O. B., Symposium on Stress Corrosion Cracking, published by ASME and AIME, Philadelphia and New York, p. 421, 1944.
6. Griess, J. C., English, J. L., et al., Quarterly Report of the Solution Corrosion Group for the Period Ending October 31, 1956, Oak Ridge National Laboratory, Central Files No. 56-10-13 (to be issued).
7. Griess, J. C., English, J. L., et al., HRP Dynamic Solution Corrosion Studies, Quarter Ending July 31, 1956, Oak Ridge National Laboratory, Central Files No. 56-7-52, p. 36.
8. Nathorst, H., Stress Corrosion Cracking of Stainless Steels, Part I, Welding, Research Council Bulletin Series, No. 6, p. 1, October, 1950.
9. Moore, G. E., Summary of Laboratory Corrosion Tests, Oak Ridge National Laboratory, Central Files No. 55-12-70, December 12, 1955.
10. Adamson, G. M., Kegley, T. M., et al., Metallurgical Examination of HRT Flanges and Leak-Detector Tubing, Oak Ridge National Laboratory, Central Files No. 57-1-109 (to be issued).

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Fig.1 Ring Joint Flange Equipped with Leak Detector

Fig. 2 Section of Leak-Detector Tubing Showing Honeycomb Structure of Inside Surface (750X).

Fig. 3 Section of Inner Surface of Leak-Detector Tubing Etched With Vilella's Reagent to Show Carbides (750X).

(250X)

Fig. 4 Section Through Wall of Straight Portion of Leak-Detector Tubing Showing Transgranular Crack Penetrations(50X).

Fig. 5 Pits in Side of Groove in Flange A-101 (15X).

Fig. 6 Ultraviolet-Light photograph of Fluorescent Penetrant Examination of Flange A-101.

Fig. 7 Hydrochloric Macro-etch of Flange A-101 Showing Surface Cracking (15X).

Figure 8

Figure 9

Metallographic Sections of Flange A-101 Showing Transgranular Cracks at Bottom Corners of Grooves.

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Fig. 10 Ultraviolet-Light Photograph of Crack Indication
in Reactor Pressure-Vessel Flange O-Ring.

Fig. 11 Metallographic Section of Reactor Pressure-Vessel O-Ring Showing Transgranular Crack (100X).