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Final Report on PCRV Thermal Cylinder Axial Tendon Failures

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FINAL REPORT ON PCRV THERMAL CYLINDER AXIAL TENDON FAILURES

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JANUARY 1976

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FINAL REPORT ON PCRV THERMAL CYLINDER AXIAL TENDON FAILURES

D. A. Canonico, J. C. Griess, and G. C. Robinson[1]

ABSTRACT

The post-test examination of the failed tendons from the PCRV thermal cylinder experiment has been concluded. Failures in the wires are attributed to stress-corrosion cracking. The cause of the tendon failures has not been unequivocably established, but they may have been due to nitrates in the duct. The wires employed in the manufacture of the tendons will crack in less than 72 hr in a 0.2 *M* solution of ammonium nitrate at 70°C. The quality of the wires is poor, and surface cracks were detected. These could have acted as concentrating sites for both stress and the deleterious contaminants. We feel that the factors that led to the failures in the thermal cylinder experiment were unique. An improper formulation of the epoxy resin did not provide the tendon anchor plate seal that was desired; indeed, the improper formulation is responsible for the high level of nitrogen in the ducts of the failed tendons.

INTRODUCTION

In May 1973 the Prestressed Concrete Reactor Vessel (PCRV) thermal cylinder test was terminated. During detensioning it was found that nearly all of the inner row ASTM A 416 prestressing tendons had failed during the lifetime of the experiment. An in-depth study sought the cause of the tendon failures. Previous work was reported in two interim reports. The first[2] discussed the PCRV thermal cylinder experiment. The second[3] presented the results of preliminary observations and studies and serves as the background for this final report. It specifically discussed the tendon failures up to the time of its issuance. The summary from that report is provided.

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[1] Reactor Division.

[2] G. D. Whitman, *Interim Report on PCRV Thermal Cylinder Axial Tendon Failures*, ORNL-TM-4763 (December 1974).

[3] D. A. Canonico, *Second Interim Report on PCRV Thermal Cylinder Axial Tendon Failures*, ORNL-TM-4764 (November 1974).

> "The posttest examination of the tendons from the PCRV thermal cylinder tests is continuing. It has been shown to date that the failures have occurred both before and after the hot-spot test. The failures occur in the inner row and do appear to be due to a stress corrosion phenomenon. The evidence to date tends to minimize the probability that hydrogen embrittlement is responsible for the tendon failures. A successful stress-corrosion cracking (SCC) test has been conducted; however, the conditions were extremely severe. Failure occurred in 420 hr. The final failure is by ductile mode; there is no evidence of a brittle failure mechanism. A cup-cone fracture, initiated by a loss of cross section, is the prevailing morphology.
>
> The tendons that have failed contain wax that is enriched in chlorine and nitrogen. Further, an aqueous liquid has been obtained and analyzed. It too has a high nitrogen content. It is certain that moisture entered the ducts surrounding the tendon. There is evidence that the epoxy resin was incorrectly formulated and that free ammonia was present in the region of the bottom anchor plates. An SCC mechanism incorporating the free ammonia and carbon dioxide from the atmosphere has been postulated and tests to prove this theory are under way."

Since the issuance of the interim report in November 1974, additional studies have been conducted to explain the cause of the tendon failures. This report addresses itself to the results and conclusions that were derived from these studies, and constitutes the completion of the metallurgical examination of the failed tendons.

REVIEW OF PRIOR EXAMINATION

Figure 1 is a sketch of the axial tendon assemblies. The tendons were enclosed within the duct as shown. The wires (ASTM A 424) were coated with NO-OX-ID "A" by the manufacturer of the tendons,* and the ducts were filled with Mobilwax 2300-T5L6 during the assembly of the thermal cylinder experiment. Tendon failures occurred randomly during the lifetime of the experiment, as shown by the load-time curves obtained with instrumented tendons (see Figs. 9 thru 16 of Ref. 2). An example of a typical fracture is shown in Fig. 2. All the wire failures contained a flat semi-elliptical initiation site and a ductile cup-cone fracture when the net area of the wire was not able to withstand the stressing load. (The initiation site in the wire shown in Fig. 2 contained sulfur, but this was not necessarily true of all of the failures.) The wax in the ducts of the disassembled thermal cylinder test was chemically analyzed, and the results are given in Table 1. For comparison, the as-received NO-OX-ID "A" Special and Mobilwax 2300-T5L6 are included. It is evident that the wax in the tendon ducts contained large quantities of nitrogen. Although the chemical form of nitrogen was not determined,

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*Corrosion inhibitor manufactured by Dearborn Chemical Division of W. R. Grace and Company.

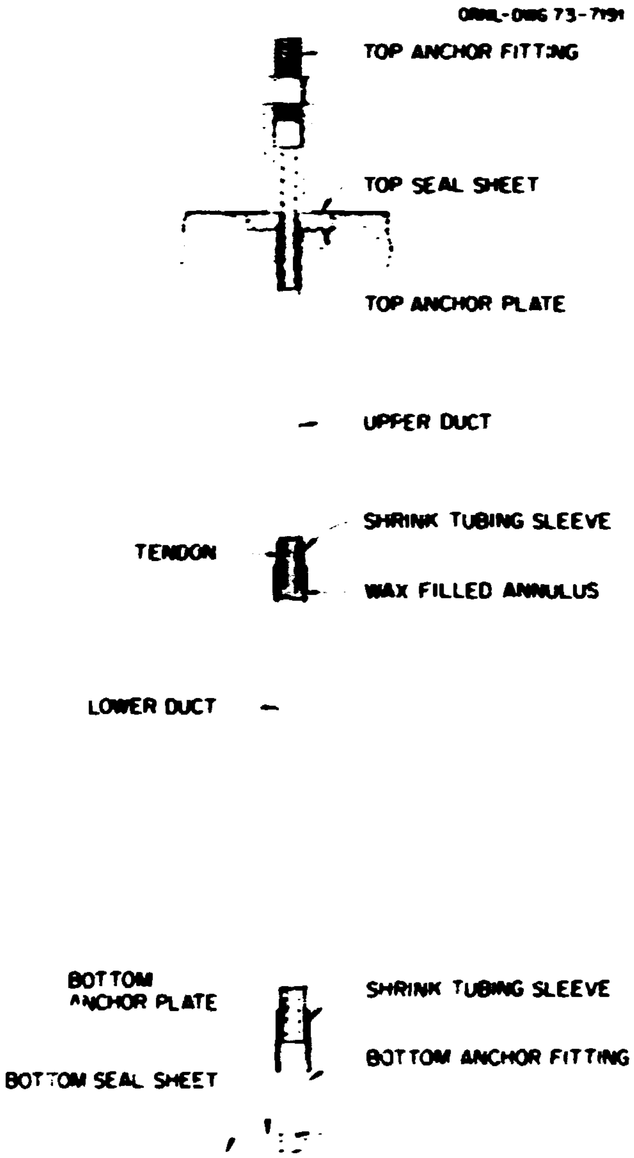

Fig. 1. Axial Tendon Subassembly.

the wax had a strong odor of ammonia when it was initially removed from the ducts. This was true for the wax from ducts that contained failed tendons (tendons 19 and 28) as well as for that taken from a duct in which the tendon did not fail (No. 44). The presence of nitrogen in the wax could not be explained on the basis of its presence in the NO-OX-ID (high nitrogen but very little NO-OX-ID was used to coat the wires) or in the Mobilwax (where large quantities are used but the nitrogen level was low). A review of the experimental procedure revealed that the presence of nitrogen and perhaps the high moisture content could probably be traced to an improper formulation of the epoxy sealer.

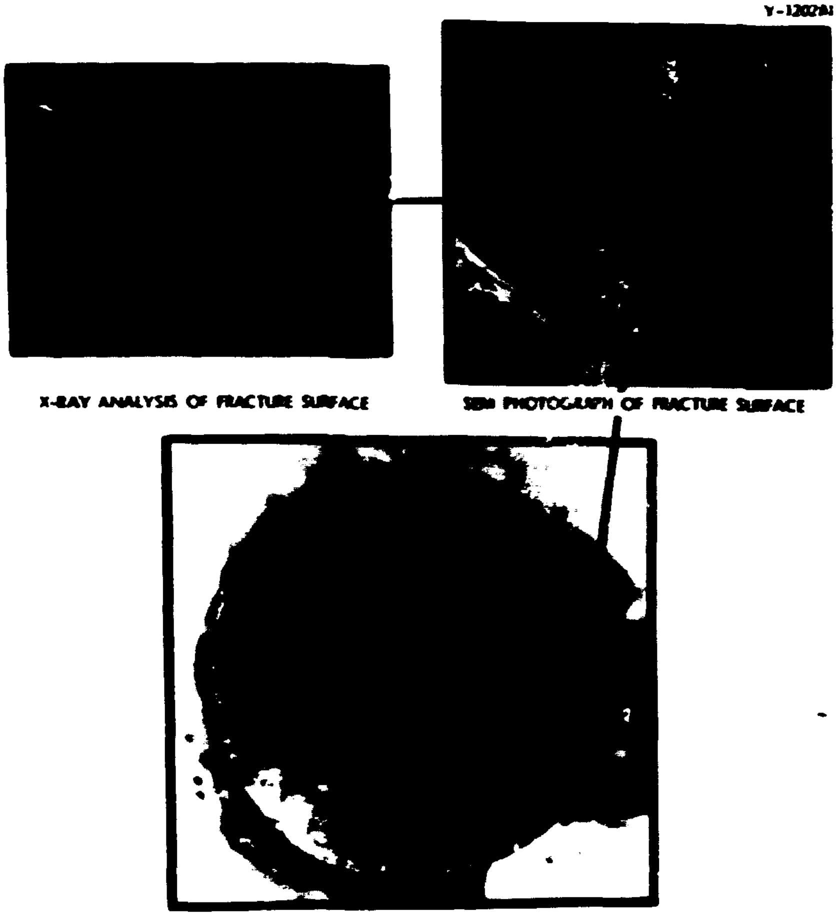

Fig. 2. Fractographic Examination of Failure Surface in a Wire from Tendon 1. The flat area in the photomacrograph was viewed and analyzed in the scanning electron microscope. There is a definite indication of sulfur in the flat area of the fracture surface.

Further, visual inspection of the polyvinyl fluoride shrink tubing on several of the removed tendon assemblies indicated that the seal design was ineffective in preventing water ingress from the concrete.

RESULTS OF RECENT STUDIES

During the past year we have investigated the probable mechanism(s) that could explain the tendon wire failures. In addition, the effect of the temperature difference between the outer row and inner row tendons on the preferential location of the failures was studied, and some randomly selected wires (from the seven-wire tendons) were examined metallographically.

Table 1. Chemical Analysis of the PCRV Thermal Cylinder Test Wax

Identification of Source of Wax	Level of Contaminant, ppm			
	Cl	S	N	H_2O
As-received NO-OX-ID	3.1 3.1 2.4	1900	785	76
As-received Mobilwax 2300-T5L6	3.6 7.6 2.7	3200	200	32
Wax Removed From				
Tendon 19[a]			840	1,900
Tendon 28[a]			6400	25,585
Tendon 44[b]			1000	24,800

[a] Inner row tendon that contained failed wire(s).

[b] Outer row tendon that did not contain a failed wire.

Experimental Stress-Corrosion Cracking Studies

As previously[2] indicated, a strong ammonia odor was associated with the moist wax from the disassembled ducts of the thermal cylinder test. Subsequent analysis of some of the liquid showed it to be an aqueous solution containing nitrogen, chlorine, sulfur, and perhaps other substances. The nitrogen appeared to be mostly in the form of ammonia (or perhaps a volatile amine), but in a few cases low levels of nitrate (<50 ppm) were also present. Because of the small volumes of solution, complete analysis was not possible. From the above observations and the known applied stress levels in the tendons, stress-corrosion cracking appeared to be the most likely cause of failure.

The ammonia apparently originated from the incorrect formulation of the epoxy sealer used to coat the bottom seal plates and the top concrete surface of the thermal cylinder. Excess hardener was used in preparation of the sealer. Hardeners used with epoxy resins contain organic amines, which can hydrolyze in the presence of water to produce ammonia.

Various ammonium salts, such as nitrate and carbonate, are known to be capable of producing stress-corrosion cracking in steels. To determine whether the steel in question was susceptible to cracking in such environments, several U-bend specimens of the steel were exposed to various solutions that contained certain ammonium salts and the epoxy mixtures.

One test environment was the incorrectly formulated epoxy resin used in the thermal cylinder test. A mixture with a large excess of hardener (large enough that the mixture did not harden) was placed on a shelf in a closed container, and under it was placed the same volume of water. After equilibration for one week the ammonia concentration of the water was 0.2 M. At that time samples of both the water and the resin were taken for use as test solutions. Then carbon dioxide was added to the system, and after a week both phases were resampled. Other test environments included 0.2 and 2.0 M and saturated ammonium nitrate, 0.1, 0.2, 0.5, and 1.0 M and saturated ammonium carbonate, and the same carbonate solutions with 50 ppm nitrate (as $NaNO_3$) added.

The test specimens were made from the center wires of uncracked circumferencial tendons taken from the thermal cylinder experiment. These were centerless ground to a diameter of 0.060 in. (1.5 mm). Then 3-in. (76-mm) lengths of the steel were bent into small-radius U's, and the legs were held essentially parallel by insertion in short pieces of sintered aluminum oxide insulation containing two holes. The wires were both plastically and elastically deformed. Figure 3 shows a typical test specimen. The small U-bends were placed in 25-ml Pyrex bottles containing 15 ml of test solution. Plastic-lined screw-top lids sealed the containers against evaporation. The bottles were placed in a small oven held at the desired temperature.

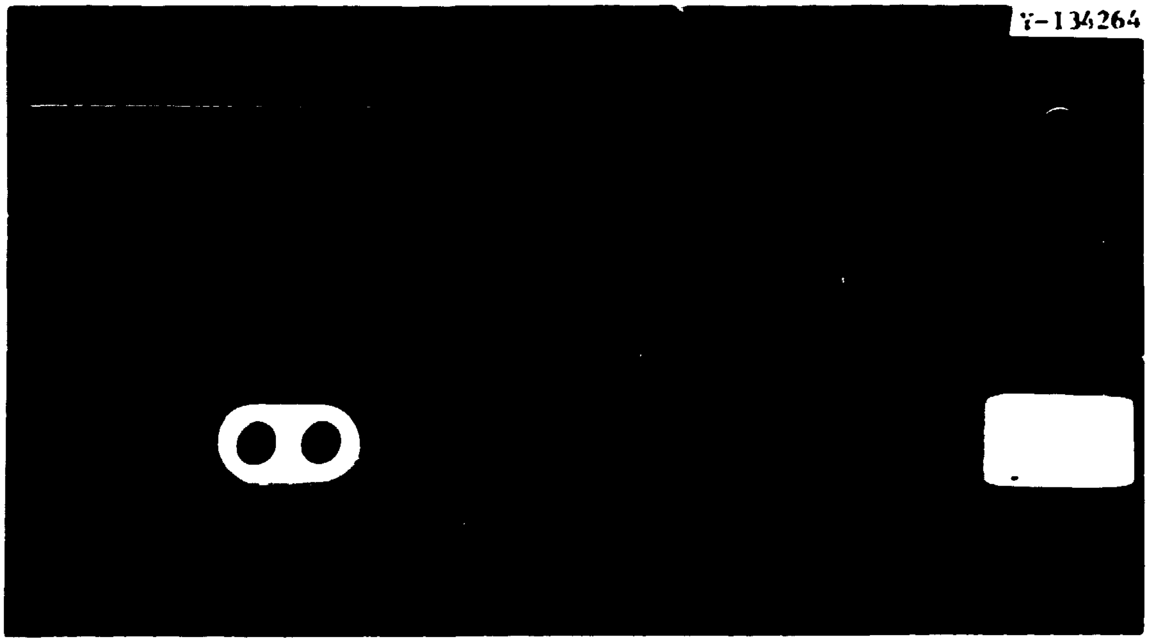

Fig. 3. The U-bend Specimen Used in the Stress-Corrosion Studies. The 0.060-in.-diam (1.5-mm) steel test section was ground from a sound area of a wire removed from a tendon in which individual wires had failed. The wire is bent into the U configuration, and its ends are placed in the refractory retainer.

No cracks were found in the specimens exposed in either epoxy mixture (with or without CO_2) or in the water equilibrated with them during exposures that lasted 94 days at 70°C. Similar tests in the same environments to which 50 ppm nitrate had been added produced the same results during a 100-day test at 66°C. Also cracking was completely absent in all concentrations of ammonium carbonate solutions under the above conditions, either with or without 50 ppm nitrate added.

Cracking was noted only in the 0.2 and 2.0 M ammonium nitrate solutions. In the 0.2 M solution at 70°C duplicate specimens cracked in three days. Under the same conditions the one specimen exposed to the 2.0 M solution cracked in the time interval between 7 and 10 days. A failed specimen is shown in Fig. 4. Failures in the other two U-bend specimens looked almost identical to the one shown. The one specimen exposed to the saturated solution of ammonium nitrate at 70°C did not crack during the 94-day test.

The above results show that the steel from which the tendons were made is susceptible to stress-corrosion cracking in 0.2 and 2.0 M ammonium nitrate, but not in very dilute solutions (50 ppm) or in very concentrated solutions (saturated at test temperatues). However, in certain regions along the tendons higher concentration of the dilute nitrate solution could have occurred, in which case cracking certainly could have resulted. Although our results do not allow one to conclude unequivocally that ammonium nitrate was responsible for the observed cracking, they do not exclude the possibility that cracking resulted from nitrate present in the aqueous environment.

Retension Tests

As previously noted, the observed failures were associated with the inner row of tendons. This implies either a preferential location for the corrodent(s) or a sensitivity to the slight difference in temperature experienced by the outer and inner row of tendons [52 vs 38°C (125 vs 100°F)]. A test was prepared to examine sensitivity to temperature. We assumed that the corrodent(s) was still present in the ducts and that a reversal in the radial temperature gradient would, in time, result in a failure of an outer-row tendon. On these premises, two pie-shaped segments were removed from the PCRV thermal cylinder test, one including tendons 15 and 39, the other tendons 20 and 45 (see Fig. 5).

Each segment was outfitted on the outside cylindrical surface with silicone rubber electric strip heaters and on the radial cuts immediately adjacent to the inside circumferential surface with Panelcoil heat exchangers as shown in Fig. 6. Each tendon was equipped with a calibrated load cell, the output of which was continuously recorded by a multipoint recorder. Thermocouples were embedded in the inner and outer cylindrical faces of the segments; temperatures were continuously recorded by a multipoint recorder. Heater input was controlled by manually adjustable Variac voltage control and by a temperature controller.

On August 20, 1974 tendons 20 and 45 in one segment and tendon 39 in the second segment were retensioned. Tendons 45 and 39 were retensioned to the design load of 36,200 lb (162.2 kN). At that load tendon 39 showed

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Y-126814

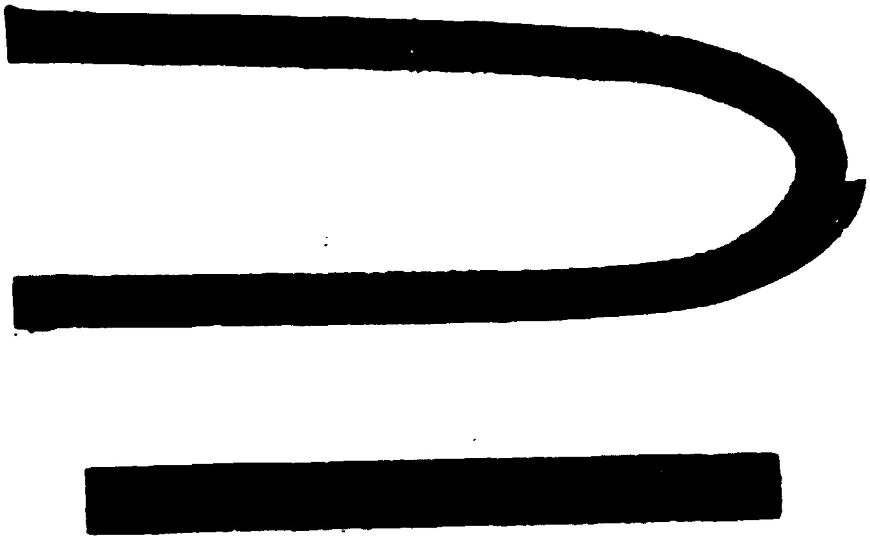

Fig. 4. Failed U-bend Stress-Corrosion Specimen. This specimen failed in a 0.2 *M* ammonium nitrate solution in 72 h at 70°C.

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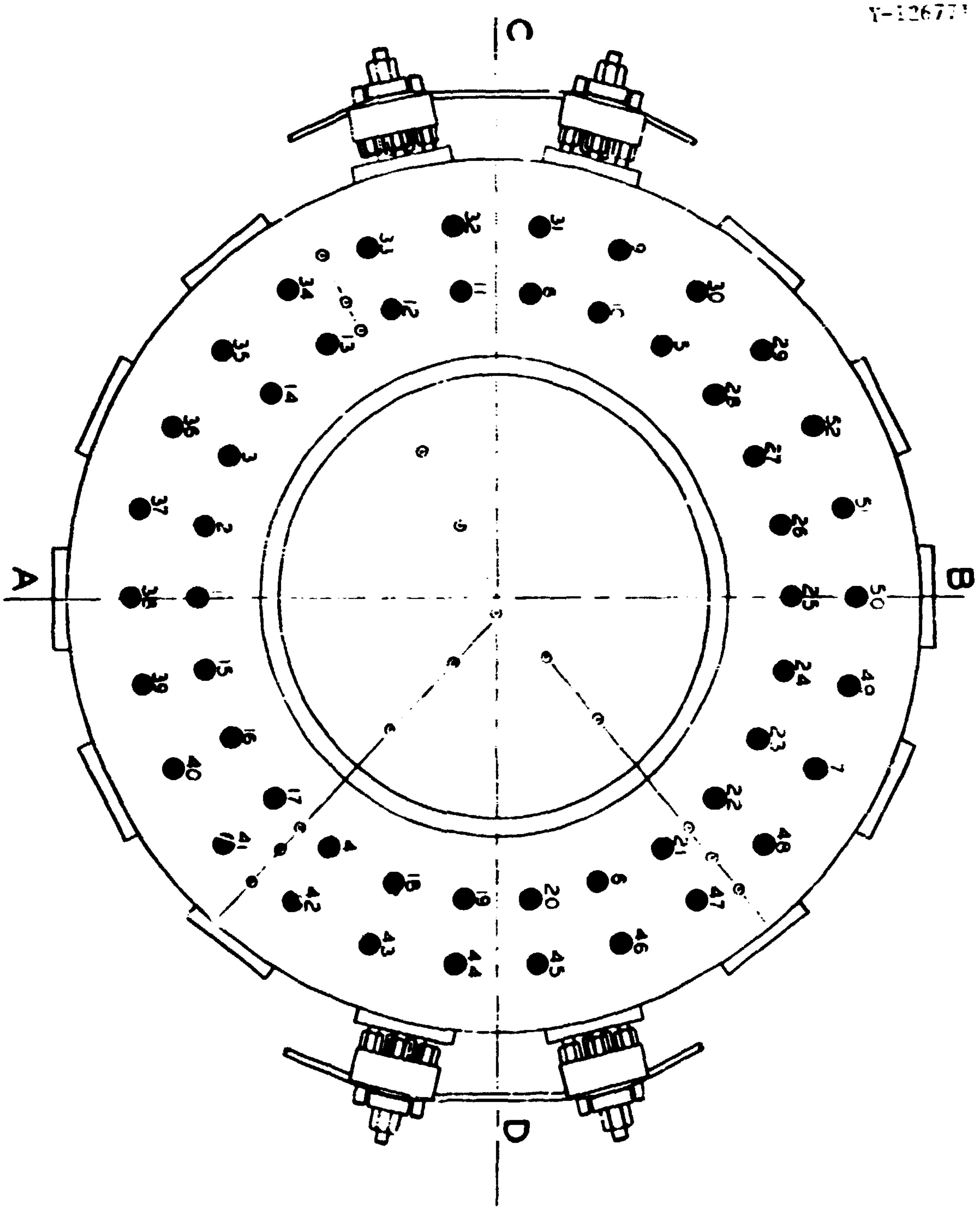

Fig. 5. Location of Tendon Assemblies in the Prestressed Concrete Reactor Vessel Thermal Cylinder Test.

Fig. 6. Panelcoils and Electric Strip Heaters on Segments of Thermal Cylinder Test Before Being Insulated.

distress, as indicated by audible popping sounds. Following transfer of the load to the concrete anchors, the load in tendon 39 dropped to 18,900 lb (84.1 kN), thereby indicating that several wires had broken. Tendon 20 was subjected to a reduced loading of 19,500 lb (86.7 kN) because of observed departures from measured linear load-extension response. Tendon 15 was not stressed since it had failed during the earlier detensioning of the thermal cylinder model.

Upon completion of the restressing operation the heat exchangers for the two concrete segments were descaled and passivated. Corrosion inhibition was initiated and the prescribed thermal conditions of 66°C (150°F) on the outside and 24°C (75°F) on the inside were instituted on August 30, 1974. The loads on the tendons and temperatures of the segments were then monitored continuously until termination of this task.

During the intervening period no significant changes in load occurred. Apparently, the factors leading to the previously observed failures were no longer active or never existed in the ducts tested. The load loss exhibited by tendon 39 during retensioning was probably a consequence of the environmental conditions existing during operation of the thermal cylinder test. The reversed thermal gradient imposed on the segments had no observable effect.

Assessment of Wire Quality

During the course of this investigation, numerous incidences of poor wire quality were noted. Some of these observations were previously[5] reported. Since the release of the interim report additional studies of randomly selected wires have revealed that the wires in the tendons used in the thermal cylinder test were of questionable quality. Locating defective areas in the wires is fortuitous. Radiographic examinations of randomly selected wires removed from archive (unused) tendons did not reveal any evidence of defects in the wires. However, metallographic examination of these "acceptable" wires revealed fine hairline cracks. Figures 7 and 8 contain typical photomicrographs of the types of defects observed. These cracks are not detectable by the usual examination standards. The most damning evidence was obtained during the centerless grinding of the wires before the preparation of the U-bend stress corrosion test specimens. During grinding one wire sample separated into two pieces; a metallographic examination of the wire revealed the quality shown in Fig. 9. These fissurelike cracks could serve as both locations for concentrating any contaminants present and stress concentrating sites. Thus, these cracks could have contributed to the failures observed in the thermal cylinder test.

CONCLUSIONS

1. The tendon corrosion problem experienced during the Thermal Cylinder Experiment is fairly unique because of the particular combination of materials employed. A similar set of conditions should not occur in a prototype Prestressed Concrete Reactor Vessel. In general,

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[5] D. A. Canonico, *Second Interim Report on PCRV Thermal Cylinder Axial Tendon Failures*, ORNL-TM-4754 (November 1974).

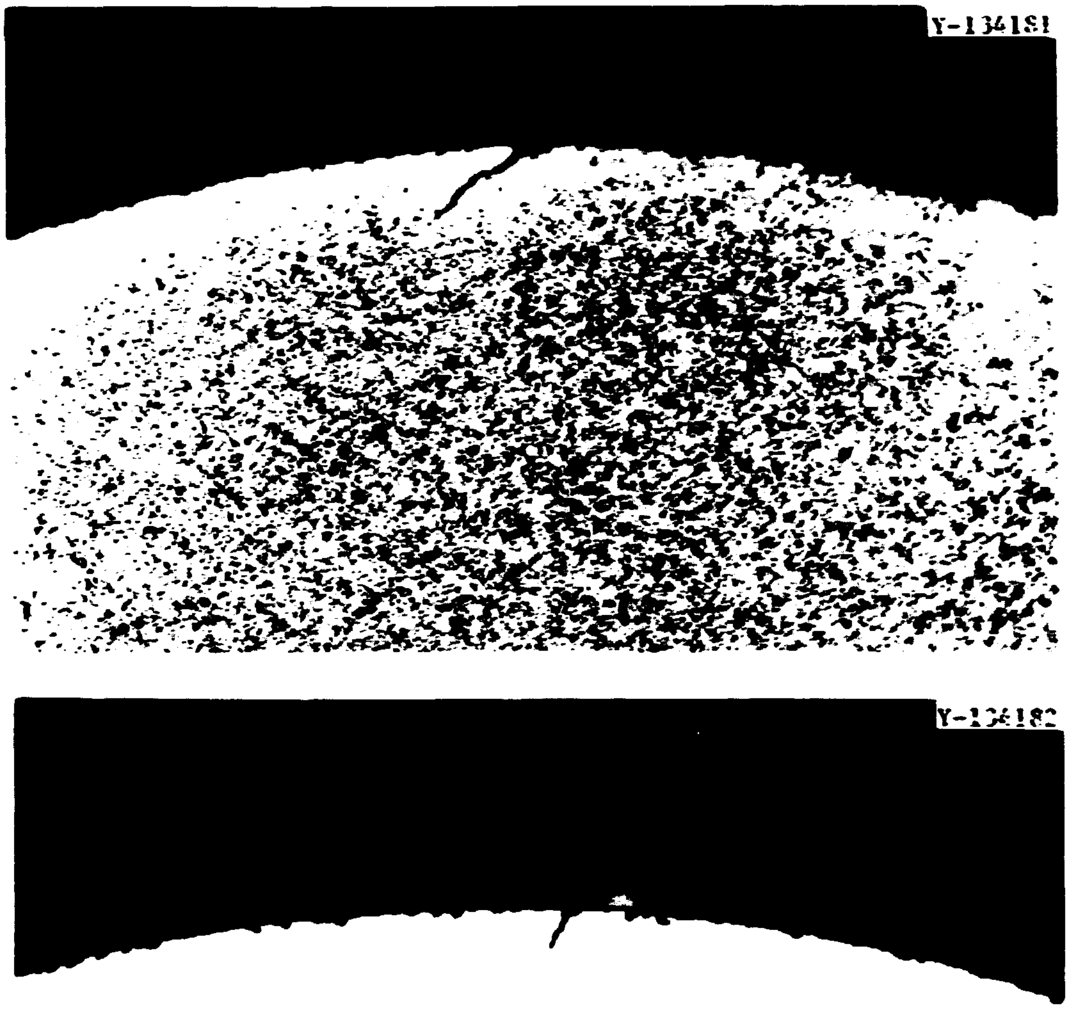

Fig. 7. Surface Defects in a Wire Used in the Manufacture of Tendons. 100×. These surface laps could serve as concentrating sites for contaminants that cause stress-corrosion cracking.

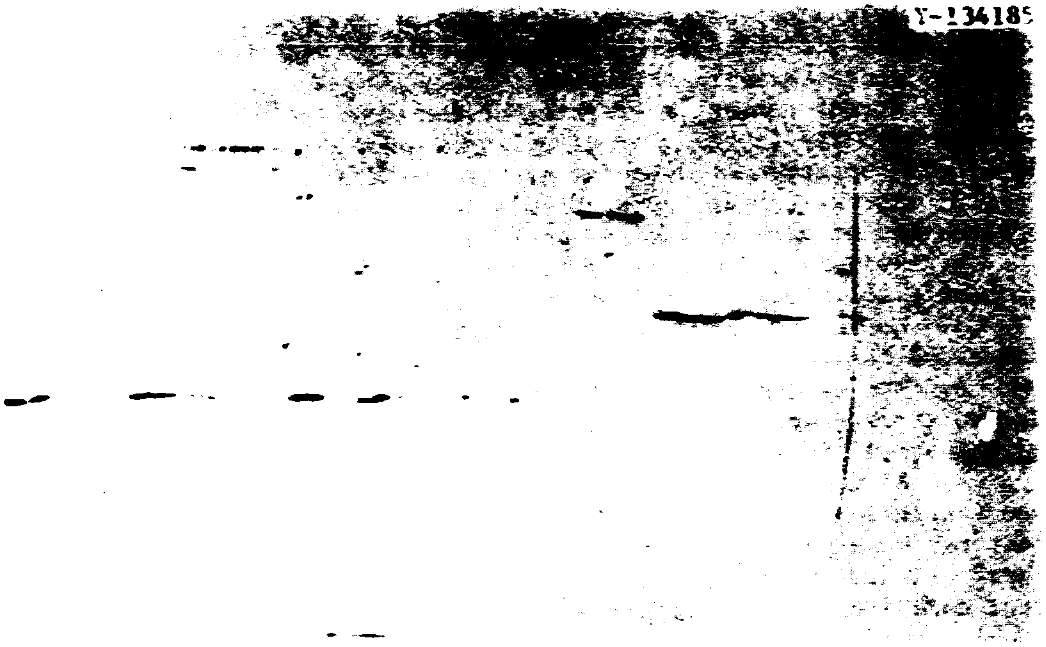

Fig. 8. Sulfide Stringers in the Interior of a Randomly Selected Section of Archive Tendons Employed in the Thermal Cylinder Test. 500×.

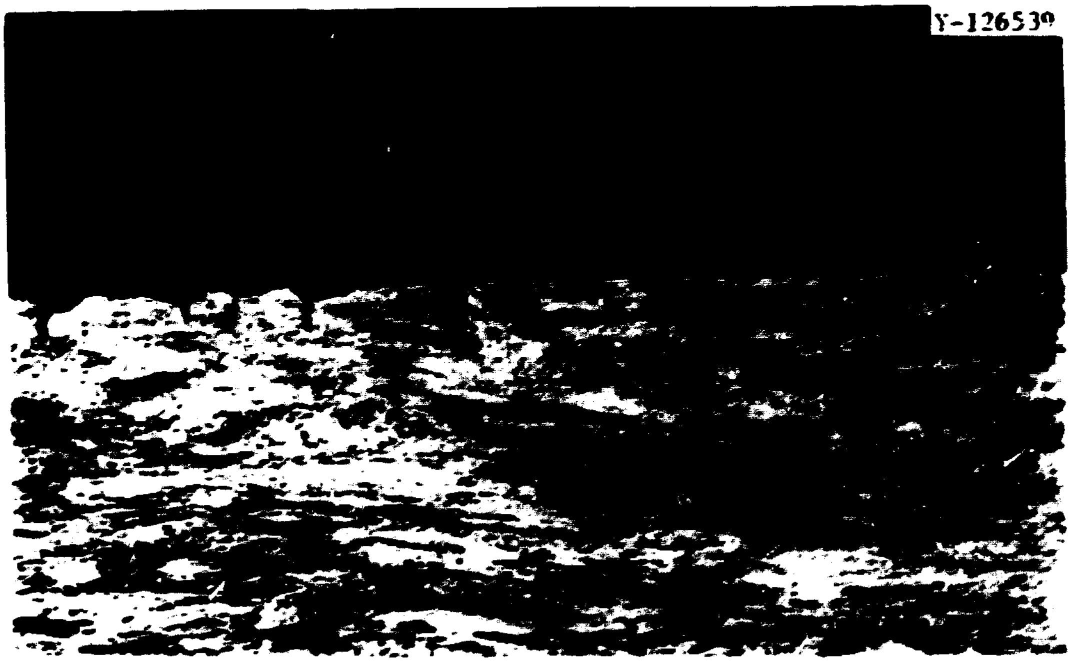

Fig. 9. Photomicrograph of a Wire that Separated During a Centerless Grinding Operation. The cracks, which are perpendicular to the longitudinal axis of the wire, could contribute to premature failure.

the presently accepted tendon protection procedures employing hermetically sealed ducts and protective coatings should prevent the type of corrosion problems encountered in this particular experiment.

2. Stress-corrosion cracking of the wires used to manufacture the tendons employed in the thermal cylinder test occurred in 72 hr or less in a 0.2 M solution of ammonium nitrate at 70°C.

3. Stress-corrosion cracking of the wires did not occur in either a saturated or very dilute (50 ppm) solution of ammonium nitrate at 70°C.

4. Failure did not occur in U-bend specimens exposed to ammonium carbonate solutions of any concentration for over 94 days at 70°C.

5. Adding 50 ppm nitrate to the ammonium carbonate solutions did not cause failure during a 100-day exposure at 66°C.

6. The tendon failures in the thermal cylinder test were probably due to stress-corrosion cracking, possibly assisted by the poor quality of the steel wires in the tendons.

7. An improper formulation of the epoxy resin (excess hardener, see Conclusion 1) used to coat the bottom plates of the thermal cylinder test may have produced an environment that led to the cracking. This improper formulation resulted in a high level of nitrogen in the liquid that came into contact with the tendons. Although chemical analysis showed most of the nitrogen to be ammonium nitrogen, low levels of nitrate nitrogen were present.

8. Reversing the thermal gradient for 14 months on two retensioned segments from the thermal cylinder test had no observable effect on the load-carrying capacity of the tendons; cracking did not occur.

9. The quality of the wires used to manufacture the tendons employed in the thermal cylinder test is questionable. Laps, cracks, and other evidence of metallurgically poor wire quality were observed. (It should be emplasized that these wires represent the manufacturing practices employed in the mid-1960s and may not represent current practice.)

RECOMMENDATIONS

1. The constructors of prestressed concrete reactor vessels should be alerted to the consequences of an improper formulation of an epoxy resin sealant. Ordinarily, epoxy would not be employed in PCRV construction, but there is evidence of its use in England to repair voids or concrete honeycombing in the tendon anchorage region of a vessel. In cases where similar "protective" procedures are employed, extreme care should be exercised to ensure that the tendon ducts are sealed and that excessive hardener is not employed in the epoxy mixture.

2. A critical assessment should be made of the wire(s) that are used in prestressing tendons. There is evidence that suggests that the wires used in the manufacture of the ASTM A 416 tendons employed in the Thermal Cylinder Experiment were of questionable quality. A study should be undertaken to determine whether or not the wires used in this study represent current metallurgical quality.

3. An extensive parametric study should be conducted to determine the threshould levels of contaminants that are not detrimental to the load-carrying capacities of the tendons.

ACKNOWLEDGMENTS

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