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CORROSION MEASUREMENTS ON MATERIALS OF CONSTRUCTION FOR A ROLLING CYLINDER LATENT HEAT STORE USING GLAUBER'S SALT

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SUMMARY

A variety of stainless steels, titanium, bronze, and aluminum resist corrosion by saturated sodium sulfate solution at pH 7.0 well enough to be used in rolling cylinder heat storage construction. In the absence of oxygen, 1010 mild steel has an acceptably low overall corrosion rate. Unfortunately it does experience the occasional formation of a tiny corrosion pit. It is likely that solid sodium sulfate trapped in a number of such pits will promote crystal growth adherance to the cylinder wall, resulting in a serious degradation of heat transfer performance. Mild steel is therefore unlikely to be satisfactory for use in sodium sulfate sytems at pH 7.0.

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KEY WORDS

corrosion, heat storage, rolling cylinder, Glauber's salt, solar heating

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CORROSION MEASUREMENTS ON MATERIALS OF CONSTRUCTION FOR A ROLLING CYLINDER LATENT HEAT STORE USING GLAUBER'S SALT

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INTRODUCTION

The rolling cylinder has been demonstrated to be a prospective high performance latent heat storage device when used with Glauber's salt (sodium sulfate decahydrate).(1,2) During normal use, heat is stored by melting a portion of the solid decahydrate; heat is withdrawn from storage by refreezing the melt to the solid decahydrate.

The melt is a two-phase mixture of small sodium sulfate crystals (solid) plus an aqueous solution saturated with sodium sulfate (approximately 9 N). Aqueous sodium sulfate is well known to corrode a wide variety of metals, while the solid crystals of both sodium sulfate and Glauber's Salt are potential causes of metal erosion. This report is an evaluation of both possibilities.

If rolling cylinder heat storage apparatus is to achieve a lifetime in the range of 20 to 30 years, then the average combined corrosion/erosion rates must not exceed 2 mils/yr if initial cylinder wall thickness is to remain reasonable. Combined rates of 0.2 mil/yr would be much preferred to minimize material costs.

General corrosion rates for numerous materials in aerobic concentrated sodium sulfate are readily available in handbooks.(3,4) From these sources and under these conditions, steels and other common metals and alloys appear to be unsatisfactory. Materials such as aluminum, silicon iron, glass, rubber, and Karbate* plastic impregnated graphite appear to be satisfactory.

Many corrosion studies have been conducted in dilute solutions, some of which may point to remedies for the corrosion problem. As in other systems, corrosion rates in sodium sulfate increase as the concentration decreases.(5) Corrosion rates for lead under dilute conditions when extrapolated to concentrated conditions suggest it would be satisfactory.(6) When lead is coupled to iron, however, the iron will corrode unacceptably.(7)

A series of papers by Mayne et al.(8–12) describes the corrosive effect of 0.1 N solutions of various sodium salts on iron. Corrosion inhibition was observed under some conditions with borate, hydroxide, carbonate, acetate, and benzoate anions. Fujii et al.(13,14) reported decreased corrosion rates on iron in deaerated solutions with a protective film of magnetite. It is not known whether either protective mechanism is operative in saturated sodium sulfate solutions.

Average or general corrosion rates have significance only in the absence of localized corrosion mechanisms which produce either pits or stress corrosion cracking. Both types of corrosion can lead to catastrophic failure of metal structures.

Pitting corrosion can occur with iron in dilute sulfate solutions.(15–17) Stress corrosion cracking by sulfate ion is reported for the cases of one steel and one admiralty brass.(18,19)

For a time, our laboratory-sized experimental rolling cylinders were constructed of FERNICO† alloy (iron, nickel, and cobalt). Rapid corrosion was evident from the apparent buildup of ferric oxide. When oxygen was excluded, as by a nitrogen purge of the gas space above the solution, then the corrosion rate was dramatically reduced. It is possible to build the rolling cylinder as a hermetic system having no material exchange with its surroundings. In particular, it is possible to exclude oxygen during the cylinder filling operation and during the cylinder operating lifetime. The literature does not offer any clear guidelines for corrosion behavior under these operating conditions. Experimental determinations are therefore necessary to provide an accurate estimate of rolling cylinder corrosion problems.

Measurements have been made of erosion or abrasion of metals by sodium sulfate crystals.(20–22) Due to the very low particle velocities relative to the rolling cylinder interior surfaces, erosion by sodium sulfate will very probably be negligible. The same is true of erosion by sodium sulfate decahydrate. Solar heating system simulations performed in this laboratory do suggest that the sodium sulfate form will predominate in the rolling cylinder heat store about 90% of the time.

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STATIC CORROSION TESTS

Test coupons of selected metals were exposed to agitated saturated aqueous solutions of sodium sulfate at room temperature. Mallinckrodt analytical reagent grade anhydrous sodium sulfate was dissolved in distilled water and adjusted to pH 7.0 with sodium hydroxide prior to use. Two identical sets of coupons were tested: one in an open vessel covered with a thin natural rubber membrane through which oxygen could pass freely (the aerobic test), and the other in a closed vessel from which oxygen was excluded by a continuous flow of nitrogen gas having less than 3 ppm oxygen content (the anaerobic test). Figure 1 shows the arrangement of equipment for the anaerobic test. The oxygen content of the exit nitrogen was monitored continuously by a Beckman model 715 instrument (100 ppm sensitivity) to assure thorough purging and to guard against back-diffusion. Throughout the test period the measured oxygen concentration remained below 100 ppm; however, the actual concentration very probably remained below 3 ppm.

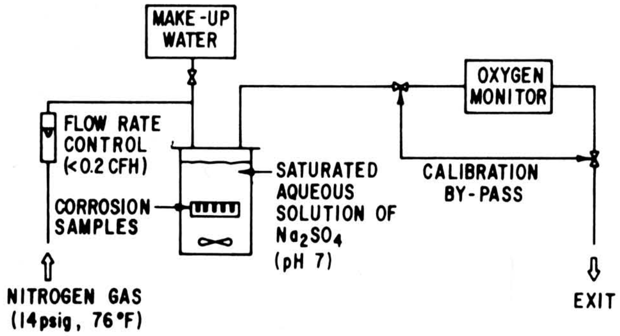

Figure 1. Anaerobic corrosion test equipment.

Two kinds of metal coupons were tested. Firstly flat coupons of sheet metal, generally 1.5 inches long by 0.5 inch wide, were mounted on edge by sliding into slots cut in a polymethacrylate ring 1/8-inch thick. Secondly stress corrosion cracking evaluation specimens were prepared for the restrained U-bend test, as described in ASTM G30-72, and mounted in the same manner.

Each test (aerobic and anaerobic) contained one flat coupon of each of the following metals:

1010 mild steel
chromized steel
50-50 Pb-Sn on 1010 steel
410 stainless steel
304L stainless steel
Allegheny 6X stainless steel
Allegheny 26-1 stainless steel
aluminum
bronze (87 Cu, 13 Sn)
titanium

and one U-bend specimen of:

410 stainless steel
304L stainless steel
Allegheny 6X stainless steel
Allegheny 26-1 stainless steel.

The aerobic test lasted 276 days and the anaerobic test 253 days.

ROLLING CYLINDER CORROSION TESTS

Flat coupons cut from sheet metal to about 1.5 inches long and 0.5 inch wide were inserted in an operating rolling cylinder at the beginning of lifetest #1. The sodium sulfate was commercial grade obtained from Ashland Chemical Company neutralized to pH 7.0 with sulfuric acid. At all times, the corrosion coupons were completely immersed in slightly fluidized sodium sulfate particles of 0.02- to 0.05-inch diameter and effective density about 1.1. Coupons of the following metals were included:

1010 mild steel
410 stainless steel
304L stainless steel
Allegheny 6X stainless steel
Allegheny 26-1 stainless steel

This cylinder completed 135 freeze-melt cycles over a period of 210 days of continuous operation.

At the conclusion of each test, all flat coupons were rinsed with distilled water, dried, photographed, scrubbed with detergent to remove surface coatings, dried, and weighed. Those with significant new features were sectioned, mounted, and polished for microscopic examination. Weighing was done on an analytical balance to the nearest 0.1 milligram.

RESULTS OF CORROSION EXPERIMENTS

Stress Corrosion

None of the stress corrosion U-bend specimens showed any variation or enhancement of corrosion or any sign of cracking in the stressed area beyond that experienced in the unstressed areas. This was true under both the aerobic and anaerobic test conditions. In the unstressed areas, corrosion followed the same pattern to be reported later for the flat coupons.

The work described here constitutes only a general screening test for stress corrosion cracking. Therefore one can conclude only that none of the group of stainless steels composed of 430, 304L, Allegheny 6X, and Allegheny 26-1 show any gross tendency toward accelerated corrosion under stress in concentrated sodium sulfate solution.

Aluminum

In the aerobic test, aluminum developed a visible uniform surface coating which was most probably stained by the presence of ferric oxide generated by corrosion of companion coupons of ferrous metals. It was equivalent to a base metal loss of 0.21 mil/yr. Under anaerobic conditions, the corrosion was equivalent to 0.30 mil/yr and was marked by some variations in surface layer thickness (see Figure 2).

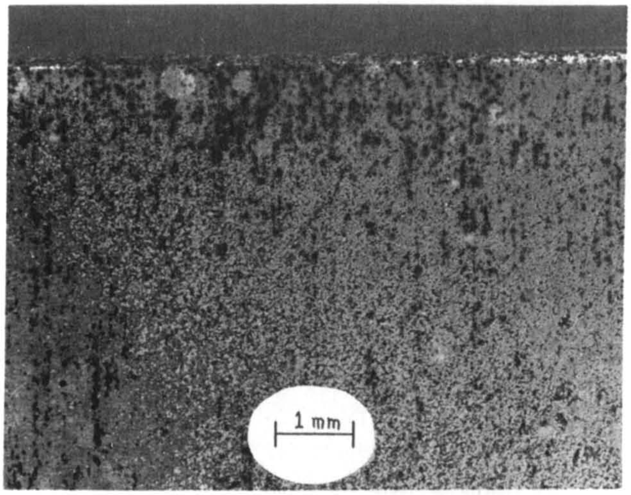

Figure 2. Variations in surface layer thickness on aluminum in the anaerobic experiment.

Bronze

The bronze (87Cu, 13Sn) coupon developed a very light uniform surface coating in aerobic sodium sulfate equivalent to a 0.10 mil/yr loss of metal. In the anaerobic test, a few tiny spots of surface coating could be seen which were equivalent to 0.013 mil/yr loss. The surface finishing marks were still visible on both sides of this coupon. There was visible staining of the surface in the confined areas between coupon and support.

Titanium

Under aerobic test conditions, the titanium coupon lost metal equivalent to 0.010 mil/yr. Under anaerobic test conditions, the sample lost no weight at all (to the nearest 0.1 mg). The lifetest coupon showed no weight loss either.

Allegheny 6X and 26-1

Neither of these Allegheny Ludlum Company stainless steel alloys experienced any weight loss at all (to the nearest 0.1 mg) in both the aerobic and anaerobic tests. No change in surface appearance was noted, and no surface films were visible. The lifetest sample had no weight change.

304L Stainless Steel

In the aerobic test this coupon had a loss rate of 0.002 mil/yr. In the anaerobic test it lost weight at the rate of 0.005 mil/yr. No visible changes occurred in the coupon except for a darkening in the center portion of one side. The lifetest sample experienced no weight change.

1010 Mild Steel

Corrosive attack on all of the foregoing metals appeared to be uniform in nature. In all of the steel samples, pitting corrosion dominated the observations. In the aerobic test, extensive attack on the coupon was evident (see Figure 3). The principal feature of this attack was the frequent formation of pits of fairly uniform depth, about 0.12 mm (see Figure 4).

In the anaerobic test, pit-formation still dominated the results; however, the frequency of occurrence was much lower, as shown in Figure 5. The pit depth was much reduced, to about 1 μm (see Figure 6).

The sample immersed in the lifetest cylinder also showed a few pits in the surface (see Figure 7). Estimates made by microscopy suggest a pit depth of about 17 μm.

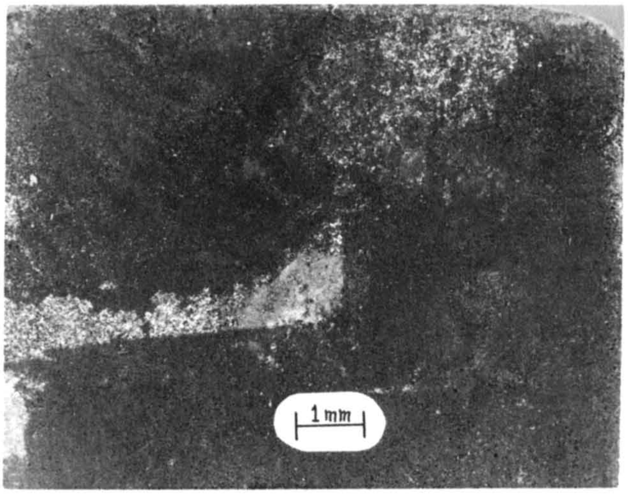

Figure 3. Extensive attack on 1010 mild steel surface in the aerobic experiment.

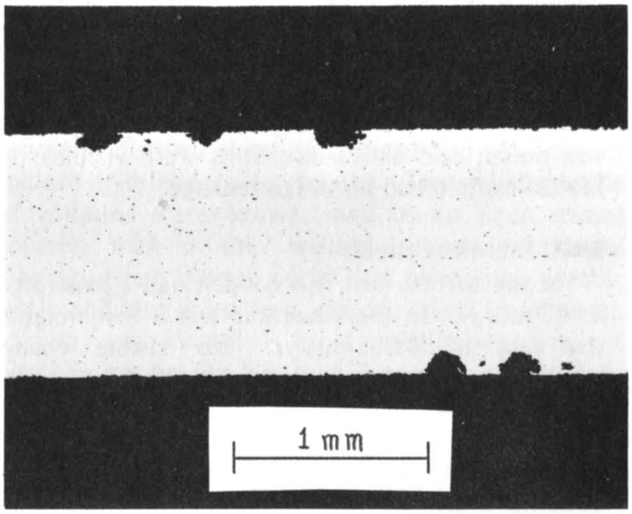

Figure 4. Cross sectional view of pits in 1010 mild steel in the aerobic experiment, vertical illumination.

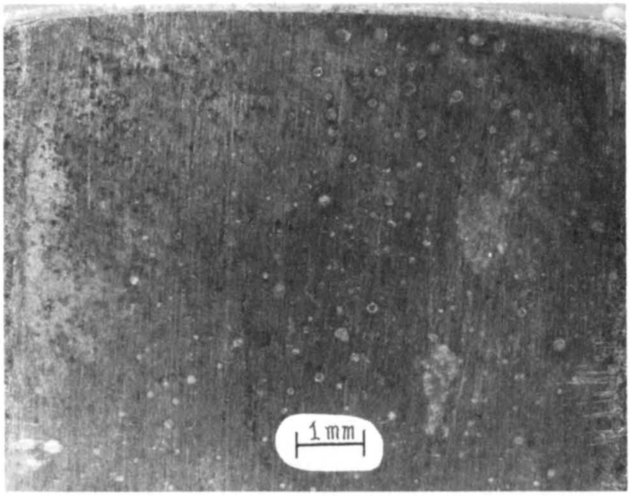

Figure 5. 1010 mild steel surface after the anaerobic experiment.

Chromized Steel

A chromized surface on 1010 mild steel did not protect the base metal from the action of sodium sulfate solution. In aerobic medium, the chromized surface layer was completely removed from about 10% of the area. Figure 8 shows some of the many pits which formed in 1010 steel just below the chrome surface layer during anaerobic testing. The frequency of pit formation in 1010 steel seemed to be greatly increased by the presence of the chrome surface layer.

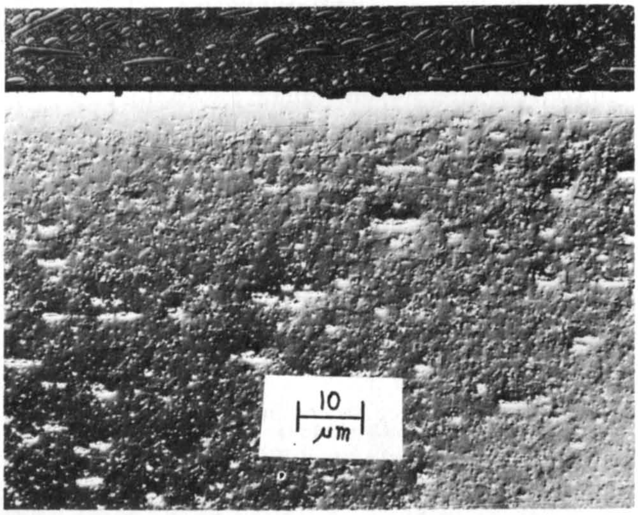

Figure 6. 1010 mild steel cross section after the anaerobic experiment, Nomarski interference contrast.

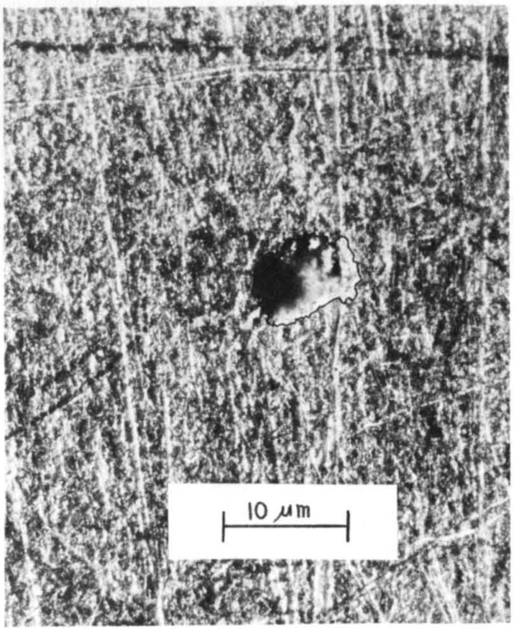

Figure 7. 1010 mild steel surface pit after the lifetest immersion in an operating rolling cylinder, oblique illumination (retouched to accent the pit opening).

Lead-Tin Coated 1010 Steel

Under aerobic conditions, the 50-50 Pb-Sn coating disappeared from about one-half the sample area, leaving the base metal exposed. Under anaerobic conditions, smaller portions of the coating

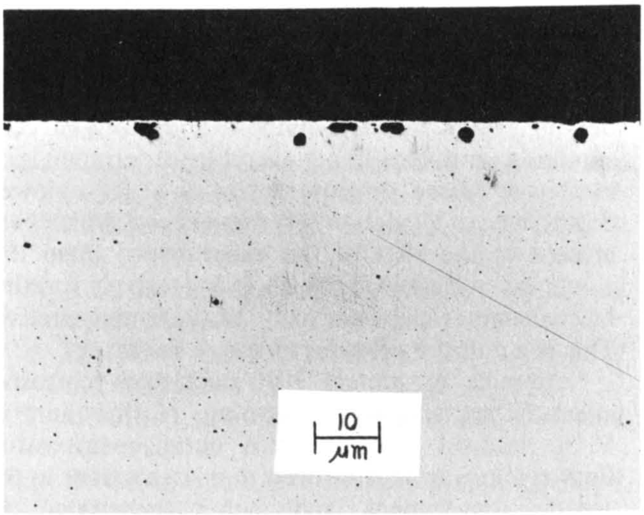

Figure 8. **Cross section of pits formed just below the surface of chromized steel, anaerobic experiment, bright field.**

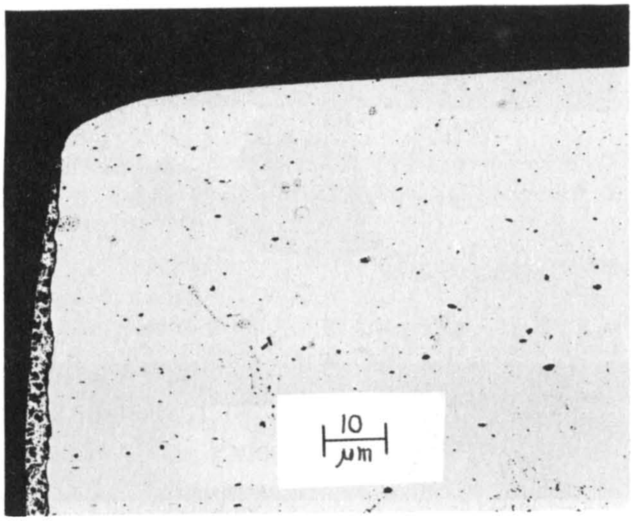

Figure 9. **Partial disappearance of Pb-Sn layer initially covering 1010 steel anaerobic experiment, cross section, bright field.**

seemed to disappear (see Figure 9); however, the weight loss was modest and base metal attack was slight (possibly it was just beginning). In an earlier experiment, galvanized steel (Sn on 1010) was heavily attacked.

410 Stainless Steel

In the aerobic experiment, 410 stainless suffered crevice corrosion. Heavy pitting attack was observed, particularly in the confined area between coupon and support (see Figure 10). Extensive subsurface pit growth was observed, as shown in Figure 11 where the pit depth is estimated to be 50 μm.

In the anaerobic experiment very little attack was observed during a metal loss of 0.006 mil/yr.

In the lifetest experiment, no weight loss was measurable.

DISCUSSION

The uniform corrosion rates measured in the aerobic and anaerobic tests are listed in Table 1. Pitting corrosion was observed in four materials during the aerobic tests and in three materials during the anaerobic tests. Pitting is highly nonuniform and is usually not satisfactorily described by a constant corrosion rate. Therefore the existence of the pitting phenomenon is noted in Table 1 in place of a corrosion rate where appropriate.

Those materials which have a listed corrosion rate less than 1 mil/yr are satisfactory for rolling cylinder construction.

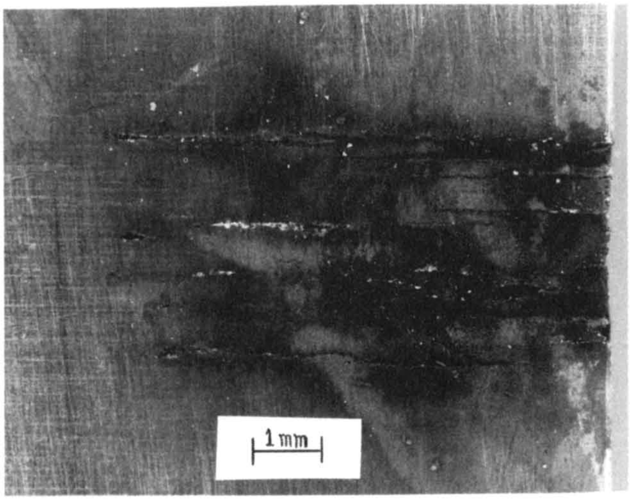

Figure 10. **410 stainless steel surface degradation after the aerobic experiment.**

Materials in Table 1 which experience pitting corrosion are unsuitable for rolling cylinder construction. In cases where the pits are too shallow to pose any apparent threat of structural weakness or liquid leakage (such as the 1010 mild steel in the anaerobic tests, for example), the material is still unsuitable for use in rolling cylinders due to the potential entrapment of colloidal size sodium sulfate particles in the pits. Such entrapment would provide anchor points to attach growing Glauber's salt crystals firmly to the cylinder walls. The heat transfer performance would be significantly

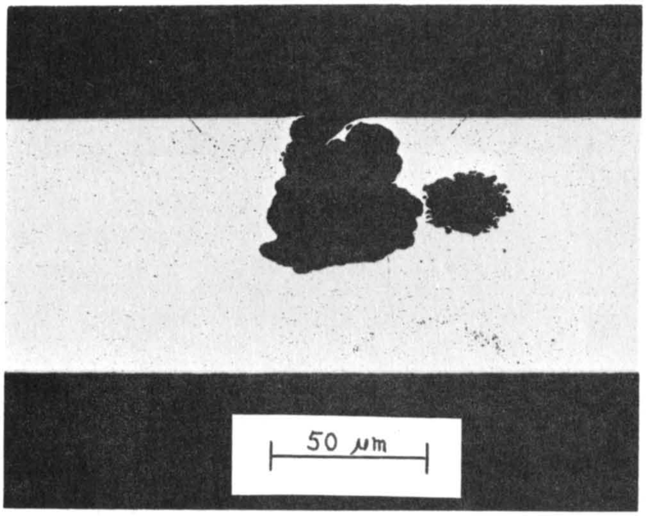

Figure 11. 410 stainless steel cross section showing extensive pit after the aerobic experiment, bright field.

Table 1

MEASURED CORROSION RATES IN SATURATED AQUEOUS (SODIUM SULFATE AT ROOM TEMPERATURE AND pH 7.0)

Material	Aerobic Conditions (mil/yr)	Anaerobic Conditions (mil/yr)
304L stainless steel	0.002	0.005
Allegheny 6X stainless steel	0.000	0.000
Allegheny 26-1 stainless steel	0.000	0.000
410 stainless steel	pits	0.006
Aluminum	0.21	0.30
Bronze (89Cu,13Sn)	0.10	0.013
Titanium	0.010	0.000
1010 mild steel	pits	pits
Chromized steel	pits	pits
50-50 Pb-Sn on 1010 steel	pits	pits

degraded, and an important advantage of the rolling cylinder would be lost.

The 304L stainless steel and the aluminum experienced somewhat larger corrosion rates as oxygen partial pressure was reduced. On the other hand, the two Allegheny stainless steels, along with the bronze and titanium, decreased in corrosion rate as the oxygen decreased. The pitting of 1010 mild steel also decreased markedly when oxygen was substantially absent. One can speculate that pit formation in 1010 steel is accomplished by oxygen consumption and that the anaerobic experiment pits may have ceased to grow in size or at least slowed down due to depletion of the oxygen which was present at the start of the experiment. If so this would be a marked contrast with most pit forming mechanisms which normally are self-regenerative. This is a point to consider in future work.

Attempts to protect 1010 steel from corrosive attack by applying surface coatings of chromium or 50-50 lead-tin (solder) were quite unsuccessful. Both coatings were destroyed to a large extent in the aerobic experiment and either penetrated or removed in the anaerobic experiment.

Aluminum in oxygen free conditions had the highest uniform corrosion rate of the metals tested. It is well below the acceptable limit and could be readily accommodated by design allowances during cylinder fabrication.

The 410 stainless steel provided the greatest contrast with the presence or absence of oxygen. In the presence of oxygen, the pitting corrosion is catastrophic in nature; in the absence of oxygen, pitting disappears to be replaced by a uniform low corrosion rate. Anaerobic rolling cylinder designs which incorporate 410 stainless steel will risk some degree of material failure if oxygen enters the cylinder during its operational lifetime.

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