

CORROSION RESISTANCE OF DUPLEX AND 4-6% MO-CONTAINING STAINLESS STEELS IN FGD SCRUBBER ABSORBER SLURRY ENVIRONMENTS

B. S. Phull

LaQue Center for Corrosion Technology, Inc.
702 Causeway Drive, Wrightsville Beach, NC 28480, USA

W. L. Mathay

Nickel Development Institute
111 Amesbury Drive, Pittsburgh PA 15241

R. W. Ross

Nickel Development Institute
P. O. Box 7007, Huntington, WV 25774-7007

ABSTRACT

Field tests using specimen racks were performed in six operating flue gas desulfurization (FGD) scrubber absorbers to determine the corrosion resistance of a 22Cr-5Ni duplex alloy, a 4% Mo-containing (Type 317LMN) stainless steel, and a 6% Mo-containing stainless steel. Type 316 stainless steel and alloy C-276 specimens served as highly susceptible and highly-resistant controls, respectively. The chloride levels in the six absorber slurry environments ranged from 9000 to 70,000 ppm. The pH was typically -5.5 with the slurry temperature in the 120 - 154°F (~49-68°C) range. Duplicate specimens were tested with "loose" and "tight" crevices for two exposure periods.

Keywords : Stainless steels, alloy C-276, corrosion, FGD absorber, limestone slurry, field testing

INTRODUCTION

It is widely accepted that sulfur dioxide (SO₂) is probably the most serious man-made atmospheric pollutant and a precursor to acid rain. Flue gas desulfurization (FGD) represents an important technology for scrubbing SO₂ emissions generated by electric power plants burning sulfur-bearing fossil fuels. Among the various scrubbing methods, the most developed, economical, and widely used technique is based on wet limestone slurry. FGD systems are operated like "mini" chemical plants and typically have a number of common features. The acidic SO₂, entrained in the hot flue gas, is scrubbed chemically in an absorber vessel, where it comes in counter-current contact with a spray of limestone (calcium carbonate, CaCO₃) slurry. Gypsum (calcium sulfate, CaSO₄) is the principal by-product which is either removed from the system as waste sludge or recovered for use in wall-board manufacturing. The scrubbed flue gas passes through mist eliminators and outlet ducting and is finally discharged to the atmosphere through a stack.

When first conceived some 35 years ago, it was predicted that FGD environments would be benign and that bare carbon steel would probably suffice as a construction material. However, when the first FGD scrubbers were built and operated, severe corrosion problems were encountered which proved these predictions to be erroneous. Thus, from a

Copyright

©2000 by NACE International. Requests for permission to publish this manuscript in any form, in part or in whole must be in writing to MACE International, Conferences Division, P.O. Box 218340, Houston, Texas 77218-8340. The material presented and the views expressed in this paper are solely those of the author(s) and are not necessarily endorsed by the Association. Printed in U.S.A.

construction materials standpoint, FGD systems have "evolved" over the last 25 years, from coated carbon steel to non-metallics to solid or clad stainless steels and high nickel alloys¹⁴. This evolution has been facilitated and supported by extensive research and testing, both in the laboratory⁵⁻¹³ and in the field¹⁴⁻¹⁷, under sponsorship by alloy producers, coating vendors, the Electric Power Research Institute (EPRI), and end-users. Although much progress has been made, some questions remain unanswered. Even as materials are improved and developed, new challenges continue to arise because of increased corrosivity due to closed loop operation and higher service temperatures -- dictated by environmental discharge restrictions and upstream process efficiency enhancements, respectively.

The most corrosive conditions in FGD systems exist at the wet-dry interface where hot flue gas first comes in contact with the limestone slurry-. Very harsh conditions result from the high temperatures and crevices under deposits where aggressive species, specifically acidic chlorides, concentrate; other corrodents such as H_2SO_4 , H_2SO_3 , HCl, and HF may also be present. Another very corrosive zone is in the outlet ducting where scrubbed flue gas forms acidic condensates. Corrosion problems at the wet-dry interface and in outlet-duct environments have been largely resolved by use of highly corrosion-resistant alloys, and improved design and operation.

Previously, conditions in absorbers (gas inlet wet-dry zone excepted) were considered relatively benign because of low to moderate chloride levels, near neutral pH, and abstemious temperatures. However, with increasingly stringent regulations requiring zero discharge, closed loop operation has increased chloride concentrations by orders of magnitude, and often into the 20,000 - 70,000 parts per million (ppm) range. Reportedly, in recent years, the Nickel Development Institute (NiDI) has received a number of inquiries from architect-engineering firms and electric utilities about the suitability of duplex and 4 to 6% Mo-containing stainless steels for construction of FGD absorber modules for these highchloride slurry environments. Since previous information on how these alloys would perform in such environments in FGD systems was limited, NiDI and a number of other organizations decided to sponsor a research project to develop corrosion data to address this question. The list of sponsoring organizations is provided in the Acknowledgments section of this paper.

PROCEDURE

It was decided to prepare and expose multiple test racks in six operating FGD scrubbers identified and selected by the co-authors of this paper.

Materials

The primary 4 - 6% Mo-containing alloys of interest were : Type 317LMN stainless steel, a 2205-type duplex stainless steel, and a 6-Mo stainless steel. Based on previous experience, Type 316L stainless steel and alloy C-276 were selected as baseline materials -- the former a corrodible control and the latter a highly resistant one, in the subject environments. The five alloys were purchased from commercial vendors as nominally 0.25" (6.4 mm) thick, 4 x 8 ft (~1.2 x 2.4 m) plates. Reportedly, the stainless steel plates had been hot-rolled, annealed, and pickled; while alloy C-276 was in the hot-rolled, descaled, and solution-treated condition. The nominal compositions of the five alloys are shown in Table 1. Independent spectrographic analysis confirmed that the compositions complied with respective standard ranges for the alloys. Actual compositions are not divulged in this paper to preclude frivolous "guessing" of alloy producers' identities -especially for the duplex and 6-Mo stainless steels.

Panels of each alloy, nominally 3" x 12" (~76 x 305 mm), were sawcut from the 4' x 8' (~1.2 x 2.4 m) plates and butt welded at the mating 12" (305 mm) sides, using pulsed gas metal arc welding (GMAW-P) process. The filler metals are listed in Table 2.

Specimen Preparation

Test coupons, nominally 2" x 3" (~50 x 76 mm) were saw cut from the welded panels as illustrated schematically in Figure 1. Coupon edges were ground using a 120-grit silicon carbide belt sander. Two mounting holes were drilled on opposite sides of the weld as shown in Figure 2. All cut, ground, and drilled edges were deburred and the coupons stamped with identification numbers. The coupons were glass bead blasted to remove weld heat tints, chemically cleaned in a 10% HNO_3 + 2% HF mixture at 110° F (~43° C) for 2 minutes to remove any remnant heat tint and embedded iron, rinsed with distilled water, air dried, and weighed to a precision of ± 0.001 g.

The initial appearance of the coupons was carefully recorded to preclude ambiguous interpretation of post-test examination results. The initial examination revealed the following: Type 316L and duplex stainless steel coupons had smooth surfaces; Type 317LMN stainless steel coupons had minute indentations; 6-Mo stainless steel coupons had a directional, "wood grain" surface; and alloy C-276 coupons exhibited a "sand blasted" finish.

Test Rack Design

Test rack hardware was manufactured from alloy C-276. Two types of test racks were prepared for each host scrubber absorber. The coupons were electrically isolated from each other and from the test rack hardware in both types of racks, using PTFE sleeves and spacers. In the "standard" type of field rack, the test specimens were mounted rigidly such that there was no free movement; the specimens in this type of rack were designated "tight-crevice specimens" because a tight crevice was formed between part of the test alloy surface and a PTFE spacer, on each side of each mounting hole in the specimen.

In the other type of rack design, the test specimens were mounted such that each specimen was free to move about $\frac{1}{8}$ " (~3 mm) on either side; this type was designated as a rack with "loose-crevice specimens". The purpose of this arrangement was to determine alloy resistance to localized corrosion in the absence of tight, artificial crevices -- which are sometimes denounced as being unrealistically severe and non-representative of "natural" crevices, such as may develop under process-generated scale or deposits. Critics have argued that severe crevice attack under artificial crevices "fails" some materials which otherwise have given satisfactory performance in many service applications that do not contain tight, artificial crevices.

Figure 3 depicts the appearance of a typical, assembled, ready-to-expose test rack. Close-up views in Figures 5 and 6 illustrate the arrangement of tight-crevice and loose-crevice specimens, respectively. In each rack, there were duplicate specimens of each of the 5 alloys, i.e., 10 specimens per rack. Instead of mounting them next to each other, duplicate specimens of each alloy were "dispersed" to preclude alloy bias with respect to position within a rack. Brackets with eyelets were provided at both ends of the rack to facilitate rack mounting by bolting, wiring, or tack welding in the host absorbers.

Exposure Duration

Four test racks, two with tight- and two with loose-crevice specimens, were prepared for each host site. The original plan was to initiate exposure of four test racks concurrently at any given test site during a scheduled outage. It was anticipated that one rack of each type would be removed after nominally 6 months and the second set after nominally 12 months' exposure to discern any propagation of corrosion attack. It was recognized that the 6- and 12-month target exposure times would probably not be achieved precisely because of the unlikelihood of host utilities shutting down their FGD systems just to install or remove test racks.

Exposure Conditions

The host utilities were requested to provide data on slurry chemistry -- especially, chloride, fluoride and pH -- and operating temperature and exposure duration. The test racks were placed in clean, protective plastic bags and shipped to the host sites. Since the host scrubber utility personnel generally expressed a preference to "hang" the test racks from spray piping in the absorber, rather than bolting or tack welding to the sidewalk $\frac{1}{16}$ " (~1.6 mm) thick alloy 686 wire was supplied with the racks. Figure 6 shows a typical test rack mounted in one of the absorbers.

Post-Exposure Evaluation

When the test racks were received from the host sites, they were photographed and samples of scale saved for analysis. The racks were disassembled and the coupons chemically cleaned in 30% HNO_3 at room temperature to remove gypsum scale and any corrosion products. The test specimens were carefully examined visually. Localized attack in the form of pitting and/or crevice corrosion was documented by measuring depths of attack with the aid of a dial depth gauge. Edge attack was ignored because cut edges are not normally exposed in a fabricated FGD absorber. The specimens were reweighed to determine mass loss in test. Corrections were made for the very small metal loss associated with chemical cleaning. For specimens that exhibited significant localized corrosion, the mass loss was not converted to corrosion rates to preclude the risk of erroneous inferences by end users.

TEST RESULTS

Environment

The list of six scrubber absorber host sites and a summary of the slurry chloride concentration, pH, temperature, and test rack exposure duration are presented in Table 3.

Alloy Corrosion Data

The corrosion data for duplicate test specimens of each alloy exposed in the six FGD scrubber absorbers are presented graphically in Figures 7-12. The sequence of these Figures represents increasing "average" chloride level in the slurry. Each Figure depicts the measured maximum depths of crevice corrosion under the PTFE spacers for both tight and loose crevices, and maximum depth of bold surface pitting (at non-crevice areas, i.e., away from the spacers).

PSI Energy - Gibson Station, IN (Figure 7)

The two exposure periods were 167 and 377 days, respectively. For both periods, the average chloride content of the slurry was ~9,100 ppm, pH ~5.4, and temperature ~128°F (53°C). Moderate amounts of beige, chalky, gypsum scale bridged across some of the specimens in the first set of racks removed from test but it was virtually absent in the second set. For Types 316L and 317LMN stainless steels, crevice corrosion under the tight-crevice spacers tended to affect relatively larger areas compared to those associated with loose crevices. However, attack in the latter case tended to be in the form of solitary but deeper pits. With tight crevices, depth of attack was considerably less on 317LMN than 316L. No localized corrosion was observed on duplex and 6-Mo stainless steel and alloy C-276 either under the tight crevices or loose crevices. In the case of the rack with the loose crevices, "wear" marks were observed where the spacers had rubbed or vibrated against the specimen surfaces around the mounting holes. These wear marks were excluded when characterization localized corrosion damage.

With the exception of a single 40-mil (~1 mm) deep pit near the heat affected zone on one Type 316L specimen, there was little indication of bold surface pitting under the chalky scale. At first sight, alloy C-276 exhibited a surprisingly high mass loss relative to the other materials. While this is attributed to general etching of the surface, the calculated corrosion rate is negligible, <0.3 mpy (<7.5 μm/yr). A side-by-side comparison of the five alloys is illustrated in Figure 13 (top row : 316 L, 317LMN, duplex; bottom row: 6-Mo and C-276). For each alloy, the most "affected" test specimen was selected for this photographic comparison.

NYSEG - Kintigh Station, NY (Figure 8)

The average chloride concentration in the slurry for the two exposure periods, 196 and 388 days, respectively, was 19,500 ppm; the pH ~5.6, and temperature ~120°F (49°C). Chalky scale bridging the specimens was particularly prominent on 3 of the test racks. Although the reported slurry average chloride level was higher at this test site compared to PSI's Gibson Station, the overall corrosion behavior of the test alloys was quite similar in the two scrubber. There was somewhat more etching at local areas under the scale on specimens exposed at Kintigh. While there was some localized attack on Types 316L and 317LMN stainless steels, it was not very severe. Apart from some very light attack at solitary spots, the duplex and 6-Mo stainless steels exhibited very good corrosion resistance. There was some general but very superficial etching of alloy C-276. The lower mass loss for all the test specimens exposed in this scrubber compared to PSI (Gibson Station) can be attributed, at least partly, to the smaller size of the test specimens exposed. Just as in the case of the PSI's Gibson Station, no significant differences in corrosion behavior were observed between specimens with tight and loose crevices. A side-by-side comparison of the five alloys is illustrated in Figure 14.

Seminole Electric, FL (Figure 9)

The average slurry chloride for the second set of racks (30,000 ppm; 200 days) was higher than for the first set (24,000 ppm; 365 days); the average temperatures for the two exposure periods were ~125°F (52°C) and 130°F (54°C), respectively; and the pH ~5.5. The test specimens were heavily encrusted/encapsulated in hard, but "waxy-looking" scale.

There was significant crevice corrosion of Type 316L stainless steel under the tight spacers and pitting on bold surfaces as well as some localized attack on welds. While Type 316L specimens were not immune to corrosion under loose

crevices, there was noticeably less attack, for the most part, compared to specimens with tight crevices. Type 317LMN stainless steel exhibited greater overall resistance to localized attack compared to 316L. There were some "wear" marks on several loose-crevice specimens. There was minimal localized attack on the duplex and 6-Mo stainless steel specimens, evident as very shallow solitary pits or as local etching. Alloy C-276 exhibited only very superficial surface etching. A side-by-side comparison of the five alloys is illustrated in Figure 15.

Santee Cooper - Cross Station, SC (Figure 10)

The average slurry chloride (12,960 ppm) for the second set of racks (157 days) was lower than for the first set (27,900 ppm; 687 days), presumably due to slurry blowdown. The average pH and temperature for both exposure periods were ~5.5 and 124°F (51° C), respectively. The second set of racks were encapsulated in heavy, hard, adherent, lightbrown scale. Type 316 stainless steel incurred severe crevice attack and bold surface pitting. Crevice attack tended to be quite pronounced even on specimens with loose crevices. There was also local surface etching on several specimens. Type 317LNIN stainless steel exhibited considerably less overall attack compared to 316L; and attack under loose crevices was minimal compared to tight crevices. With the exception of some superficial underscale etching and a solitary pit 17 mils (432 µm) deep, duplex stainless steel exhibited good corrosion resistance. No localized attack was observed on the 6-Mo stainless steel and alloy C-276. On both these alloys there was etching that resulted in a bright shiny surfaces. The general corrosion rate calculated from mass loss was <0.4 mpy (<10 µm/y) for these alloys. A side-by-side comparison of the five alloys is illustrated in Figure 16.

RWE - Weisweiler, Germany (Figure 11)

While the reported average temperature of the slurry in this absorber was at least 26°F (14°C) higher than at the other test sites, the average chloride content of the slurry (35,000 ppm) was half the value that had been anticipated (70,000 ppm); similarly, even though a pH of <4 was expected, it actually turned out to be higher, i.e., ~5.2. Only one set of racks was returned after 656 days' exposure. Apparently, at the time of removal, the racks were heavily encapsulated by gypsum scale which was reportedly removed by plant personnel before returning the racks. There were some signs of mechanical damage on the racks and scratches on several specimens, probably caused when the hard scale was removed on site.

The depths of attack on all the affected specimens were very small. Although relatively minor, there was more attack under tight-crevice conditions; even the duplex and 6-Mo stainless steels exhibited very slight susceptibility. There was some superficial, localized; under-scale type etching on 316L, 317LMN and duplex stainless steel. Alloy C-276 had a matt gray appearance, but no signs of localized attack. The general corrosion rate for C-276, calculated from mass loss, was <0.1 mpy (2.5 µm/y). A side-by-side comparison of the five alloys is illustrated in Figure 17.

Orlando Utilities - Stanton Energy Center, FL (Figure 12)

Curiously, all four test racks were removed and returned by this utility after 270 days' exposure during which the slurry average chloride content was 70,000 ppm, the pH ~5.6, and the temperature ~130°F (54°C). The reason given was that the next scheduled outage probably would not take place for another year or more -- such that recovery of the second set of 2 racks in the absorber would otherwise be delayed significantly. As regards slurry parameters, the utility provided information only on the range of values; the "averages" were assumed to be the mid-points of these ranges. There was relative absence of chalky scale. Rust-colored corrosion products were apparent, particularly on Type 316L specimens.

Corrosion attack on Type 316L stainless steel was the most severe compared to that at any of the other test sites, with some of the specimens undergoing complete perforation. Crevice corrosion on a 316L specimen with loose crevices was almost as severe as one with tight crevices. Localized attack incurred by 317LMN stainless steel was considerably less than that suffered by 316L stainless steel, but nevertheless still quite severe. One of the duplex stainless steel specimens exhibited fairly moderately severe crevice corrosion under a tight crevice. Some of the other duplex stainless steel specimens exhibited under-scale type etching. In contrast, the 6-Mo stainless steel and alloy C-276 displayed very good corrosion resistance. A side-by-side comparison of the five alloys is illustrated in Figures 18.

As a secondary observation, it was noted that the mating surfaces of mounting brackets and end-plates on one of the racks had incurred fairly severe crevice corrosion. Similar surfaces on the other 3 test racks exhibited only very minor to no attack. Reasons for the severe attack at metal-to-metal crevices was on one rack are not known, especially in view of

the fact that no localized corrosion was observed on the actual C-276 coupon test specimens, mounted very close by in the same rack. A semi-quantitative materials check by energy dispersive spectroscopy (EDS), in a scanning electron microscope, was used to verify that the affected rack hardware was indeed alloy C-276.

Scale Analysis

Representative samples of scale removed from the test racks were analyzed by EDS. The major peaks for scale samples from all 6 scrubbers were for Ca, S, and O -- attributable predominately to the gypsum (CaSO_4) scale. Appreciable fluoride (F) levels were detected in the scale samples from Orlando Utilities (~16%) and Santee Cooper's Cross Station (~2%). It is noteworthy that Type 316L and 317LNIN stainless steel test specimens incurred most severe attack in both these locations compared to the other 4 test sites for which no F was detected in the scale samples.

DISCUSSION

While field testing has a lot of appeal and credibility because exposures are made in actual environments, however, test variables are often difficult to control precisely to study effects of single variables. In other words, operating and environmental conditions can vary dynamically over wide ranges. Additional limitations imposed by test specimen design, exposure location, test duration as affected by ease of retrieval, and so forth. Many of these nuances were encountered in this test program. For instance, before exposure, the conditions at RWE - Weisweiler were anticipated as average slurry chloride concentration 70,000 ppm, pH ~4, and temperature ~176°F (80°C) -- potentially a very severe FGD-absorber environment. However, the conditions actually reported as corresponding with the exposure of the first set of test racks turned out to be : average slurry chloride concentration ~35,000 ppm (range 20,000 - 45,000 ppm), average pH 5.2 (range 5.0 - 6.5), average temperature 154°F (68°C; range 147 - 156°F, 64 - 69°C). Plant personnel reported that the test racks were encapsulated in 2" (50 mm) thick, hard, dense scale (gypsum), which probably accounts for the minimal corrosion attack observed even on the 316L control specimens (Figure 11); no localized corrosion was evident on C-276. Furthermore, plant personnel also indicated that the environment where the racks were mounted in the absorber was not the most corrosive. Apparently, this location had been chosen for "safety" reasons -- another nuance of field testing. The effect of higher temperature (by >26°F, >14°C) at RWE-Weisweiler, on corrosion behavior compared to the other hostscrubber absorber sites, also seems to have been negated by the foregoing factors.

The reported slurry average chloride levels (20,000 ppm) in NYSEG's Kintigh Station turned out to be higher than the anticipated range of 15,000 - 17,000 ppm. Even with 20,000 ppm chloride, there was more localized corrosion on 316L and 317LMN, though not very severe in absolute terms, compared to RWE - Weisweiler which had a much higher chloride (35,000 ppm average) concentration. Although there was some localized corrosion on the duplex and 6-Mo stainless steels, the absolute degree of attack was very minor. There was no evidence of localized attack on alloy C-276.

At Seminole Electric the average chloride was reported as 24,000 ppm for the first set of racks (200 days' exposure) and 30,000 ppm for the second set of racks (365 days' exposure); before exposure, the anticipated chloride range was 30,000 - 40,000 ppm. Attack on the 316L was severe and on 317LMN only moderate. The notably better performance of the Type 317LMN can probably be attributed to its higher Mo content ($\geq 4\%$) and N addition compared to Type 316L. The average slurry chloride level at Santee Cooper's Cross Station was reported as 27,900 ppm for the first set of racks (157 days); this apparently dropped to an average of 12,960 ppm for the second set (687 days). Significant localized corrosion occurred on Type 316L and to a lesser extent on 317LMN specimens, in both sets of racks. It could be argued that even though the average chloride concentration decreased for the second set of coupons, localized corrosion probably initiated and propagated on these materials predominately during the higher chloride first period. With the exception of one 17-mil (432- μm) deep, solitary pit on a single specimen, and some localized superficial etching, the duplex stainless steel exhibited good corrosion resistance. There was no measurable localized attack on the 6-Mo stainless steel and alloy C-276. Overall, the corrosion behavior at Seminole Electric and Santee Cooper was quite similar, with attack on 316L and 317LMN more severe at the latter test site.

Even though the average chloride level at PSI's Gibson Station was only on the order of 9000 ppm, attack on Types 316L and 317LMN, while not very severe, was greater than that at RWE-Weisweiler (average chloride 35,000 ppm). This may be explained on the basis of relatively thinner, discontinuous scale formation on the racks at PSI's Gibson Station versus RWE-Weisweiler, where the racks were encapsulated in thick, hard, dense scale. The scale formed on the specimens/racks at PSI's Gibson Station was fairly similar to that observed at NYSEG's Kintigh Station; however, the latter had a higher slurry average chloride concentration (20,000 ppm) which may account for the minor localized attack

observed on the duplex and 6-Mo specimens. In comparison, the duplex and 6-Mo stainless steel exhibited no measurable localized corrosion susceptibility at PSI's Gibson Station.

The most severe localized corrosion attack occurred on Types 316L stainless exposed in the Orlando Utilities' FGD absorber, attesting to the aggressiveness of the 70,000 ppm chloride environment. Type 317LNIN was also affected but to a lesser degree. Although susceptible to some attack, the duplex stainless steel displayed better corrosion resistance than 317LMN. There was no measurable localized corrosion on the 6-Mo stainless steel and alloy C-276 specimens. As stated earlier, the severe metal-to-metal crevice corrosion on mating alloy C-276 end-plates and mounting-bracket surfaces on only one rack from this exposure site is puzzling. In comparison, some of the other end plates and mating brackets exhibited only very slight to no attack. Recall that alloy C-276 coupons with the tight metal-to-PTFE crevices were unaffected at the crevice areas. More severe attack at metal-to-metal crevices compared to metal-to-nonmetal crevices has also been reported in some non-FGD situations¹⁸. A very conservative guideline from the foregoing discussion may be that very tight metal-to-metal crevices should be avoided in FGD-system design, especially at very elevated chloride levels, even for high Ni-based alloys.

A simple "go, no-go" delineation for chloride versus corrosion-susceptibility is not apparent from the test results. The most likely reasons for this include influence of scale and severity of local environments within the absorbers where the test racks were exposed. Besides, the different exposure durations and stochastic nature of localized corrosion precludes normalizing penetration rates. However, overall, it can be stated that the 6-Mo stainless steel and alloy C-276 exhibited excellent resistance to localized corrosion in FGD-absorber environments with slurry average chloride levels of up to 70,000 ppm, pH ~5.5, and temperature of 130°F (54°C). The 2205-type duplex stainless steel tested in this program exhibited some susceptibility to attack at this high chloride levels, such that its long-term performance may be of some concern. It is possible that super-duplex stainless steels could alleviate this concern. With the exception of some relatively minor solitary pits, the duplex and 6-Mo stainless steels also performed very well at all chloride levels ranging from ~9000 ppm at PSI's Gibson Station to ~28,000 ppm at Santee Cooper's Cross Station. Good performance for these stainless steels at RWE-Weisweiler (35,000 ppm chloride) is not surprising since the 316L control and 317LNIN specimens also incurred only very minor attack -- ascribed to encasement in protective scale. These observations attest to the importance of site-specific testing where possible.

The possibility that F⁻ may have contributed to significant localized corrosion of 316L stainless steel, in particular at Orlando Utilities and Santee Cooper, is tantalizing because it has been raised previously in the literature¹⁹⁻²¹, albeit in acidic (e.g., pH <3) FGD outlet duct condensates. However, the influence of F⁻ remains somewhat controversial. For example, it has been argued that in the presence of Ca (readily "available" from limestone or gypsum in FGD slurries) or certain other elements, such as Al, no free F⁻ ions exist; instead, fluoride is present either as part of insoluble salts (e.g., CaF₂) or as complexes (e.g., AlF). In these forms (i.e., no free ions), fluoride is stated to be innocuous²²⁻²³.

While pitting attack was incurred on some welds and within heat affected zones, primarily on 316L and 317LMN at Seminole Electric and Santee Cooper, the bold surfaces were also affected. In other words, there was no indication of corrosion exclusively at welds.

The results of this test program also demonstrated that the presence of loose crevices between specimens and nonmetallic (PTFE) spacers does not necessarily preclude crevice attack because severe crevices can also form under scale deposits. In fact, an undesirable feature of loose-crevice specimens is that vibration can cause wear of metal areas where the specimens "rub" against the spacers. This could potentially confound corrosion damage evaluations in some cases.

CONCLUSIONS

The following conclusions are based on exposure of 24 test racks in 6 operating FGD-scrubber absorbers with different slurry chloride concentrations, but nominally similar pH values and temperatures :

1. 6-Mo stainless steel exhibited good corrosion resistance at slurry average chloride levels ranging from about 9000 to 70,000 ppm.
2. Duplex stainless steel (type-2205) exhibited good corrosion resistance at slurry average chloride levels ranging from about 9,000 to 35,000 ppm. Although localized corrosion on this alloy at 70,000 ppm chloride in this test program

was not very severe, its long-term corrosion resistance in such environments may be questionable. Superduplex stainless steels are expected to give better performance than the type-2205 material at such high chloride levels.

3. Alloy C-276 exhibited excellent localized-corrosion resistance at all chloride levels in the 9,000 to 70,000 ppm range. Although general surface etching contributed to relatively "high" mass loss on the test specimens, the calculated general corrosion rate was very low, for example, <0.8 mpy (<20 $\mu\text{m}/\text{y}$), even in the worst case.
4. Type 316L stainless steel incurred localized attack varying from modest to very severe. Type 317LMN stainless steel specimens also incurred localized corrosion but less than for Type 316L.
5. Although there was pitting on some welds and in heat-affected-zone areas on Type 316L and 317LMN at two exposure locations, corrosion exclusively at welds was not observed.
6. Loose-crevice-specimen rack design did not preclude localized corrosion attack when process scale (gypsum) bridged the gaps between the PTFE spacers and the metal coupon surfaces. Loose crevice specimens were susceptible to wear by vibration.
7. Thick, hard, adherent process-scales (gypsum) may protect underlying metal surfaces. For example, the test racks exposed in the RWE-Weisweiler FGD-scrubber absorber in Germany, were completely encased in such scale. In this case, relatively minor corrosion attack was observed even on Type 316L stainless steel specimens, despite slurry average chloride levels of 35,000 ppm. However, in practice, reliance cannot be placed on scale formation for corrosion protection in FGD-scrubber absorbers.
8. Because nuances associated with differences in operating conditions and local variations in environmental conditions, site-specific testing is recommended, where possible, to generate the most useful and relevant data.

ACKNOWLEDGMENTS

The following organizations are recognized for their joint funding of this research program: ABB Environmental Systems, Allegheny Ludlum Steel, Avesta Sheffield, Creusot-Loire Industrie, Electric Power Research Institute, Special Metals, International Molybdenum Association, Nickel Development Institute, N. V. KEMA Inspection Technology, and Outokumpu Polarit Oy; the host utilities mentioned in the paper where the test racks were exposed are also recognized. The project was co-managed by Nickel Development Institute (NiDI) consultants, Messrs. W. L. Mathay and R. W. Ross who provided helpful discussions. The hands-on assistance of LaQue Center personnel involved in this project, in particular Messrs. S. J. Pikul, A. C. Hewitt, and R. Lee Graham, is also appreciated.

REFERENCES

1. D. C. Agarwal, W. L. Silence, "Evolution of Reliable FGD Components and Technology -- A Chronological Review", Solving Corrosion Problems in the Air Pollution Control Industry, Proceedings of the 1987 Air Pollution Control Seminar, APCA/IGCI/NACE/EPRI, Buffalo, NY, October 14-16, 1987, (Houston, TX: NACE International, 1987).
2. G. H. Koch, J. A. Beavers, N. G. Thompson, W. E. Berry, "Literature Review of FGD Construction Materials", EPRI Report CS-2533, August, 1992.
3. R. Dille, V. L. Kunzweiler, "Scrubber Materials: What Works and What Doesn't", 38th Annual Conference, (Montrose, CO: Association of Rural Electric Generating Cooperatives, June, 1987).
4. R.W. Ross, Jr., "The Evolution of FGD Materials Technology", CORROSION/93, paper no. 414, (Houston, TX: NACE International, 1993).
5. W. L. Silence, P. E. Manning, "Laboratory and Field Corrosion Test Results Related to Flue Gas Desulfurization Systems", CORROSION/83, paper no. 185, (Houston, TX: NACE International, 1983).

6. E. A. Lizlous, *Materials Performance* 17, 3(1978): p. 36.
7. E. A. Tice, *Materials Performance* 13, 4(1974): p. 26.
8. T. S. Lee, R. O. Lewis, *Materials Performance* 24, 5(1985): p. 25.
9. T. S. Lee, B. S. Phull, "Use of a Model Limestone SO₂ Scrubber to Evaluate Slurry Chloride Effects on Corrosion Behavior", *Solving Problems in Air Pollution Control Equipment, Proceedings of the 1984 Air Pollution Control Seminar, APCA/IGCI/NACE, Orlando, FL, December 5-7, 1984, (Houston, TX: NACE International, 1984).*
10. G. H. Koch, N. G. Thompson, J. M. Spangler, "The Effects of SO₂ Scrubber Environments on Alloy Corrosion", *EPRI Report CS-4697, July 1986.*
11. G. H. Koch, J. A. Beavers, "Materials Testing in Simulated Flue Gas Desulfurization Duct Environments", *EPRI Report CS-2537, August 1982.*
12. E. L. Hibner, R. W. Ross Jr., "Localized Corrosion Behavior of Nickel Alloys in Model Scrubber Environments", *CORROSION/87, paper no. 251, (Houston, TX: NACE International, 1987).*
13. A. K. Agarwal, G. H. Koch, "Investigation of Corrosion Resistance of Duplex and 4-6% Mo-Containing Stainless Steels in FGD-Scrubber Absorber Slurry Environments", *Report on laboratory results conducted by CC Technologies Laboratories, Inc., December, 1995.*
14. E. C. Hoxie, G. W. Tuffnell, *Resolving Corrosion Problems in Air Pollution Control Equipment, (Houston, TX: National Association of Corrosion Engineers, 1976), p. 65.*
15. *The Corrosion Resistance of Nickel-Containing Alloys in Flue Gas Desulfurization and Other Scrubbing Processes, Corrosion Engineering Bulletin, CEB-7, (New York, NY: The International Nickel Company, 1980).*
16. R.W. Schutz, C. S. Young, *Materials Performance* 24, 9(1985), p. 28.
17. G. H. Koch, C. W. Kistler, W. Mirick, C. E. Dene, "Evaluation of Linings in the Mixing Zone of R. D. Morrow Sr., Generating Plant", *Solving Problems in Air Pollution Control Equipment, Proceedings of the 1984 Air Pollution Control Seminar, APCA/IGCI/NACE, Orlando, FL, December 5-7, 1984, (Houston, TX: NACE International, 1984).*
18. R. M. Kain -- private communication.
19. G. H. Koch, J. A. Beavers, *7th Symposium on Flue Gas Desulfurization, EPA/EPRI, May 17-20, 1982, Hollywood, FL.*
20. E. L. Hibner, "Laboratory Investigations on the Effect of Ca²⁺, Mg²⁺, SO₃²⁻, SO₄²⁻, and F⁻ ions and Flyash on the Resistance of Nickel Alloys to Localized Corrosion in SO₂ Scrubber Environments", *CORROSION/84, paper no. 298, (Houston, TX: NACE International, 1984).*
21. B. S. Phull, T. S. Lee, "The Effect of Flyash and Fluoride on Corrosion Behavior in a Model SO₂ Scrubber", *CORROSION/85, paper no. 39, (Houston, TX: NACE International, 1985).*
22. D. E. Thomas, H. B. Bomberger, *Materials Performance* 22, 11(1983), p. 29.
23. G. H. Koch, N. G. Thompson, J. L. Means, "Trace Elements in Flue Gas Desulfurization Environments and their Effect on Corrosion of Alloys", *CORROSION/84, paper no. 297, (Houston, TX: NACE International, 1984).*

TABLE 1
TEST MATERIALS' COMPOSITIONS (weight %)

Alloy	UNS No.	C	Cr	Mn	Mo	N	Ni	P	S	Si	others
316L	S31603	0.03 max.	16.0-18.0	2.00 max.	2.0-3.0	--	10.0-14.0	0.045 max.	0.030 max.	1.00 max.	
317LMN	S31726	0.03 max.	17.0-20.0	2.00 max.	4.0-5.0	0.10-0.20	13.5-17.5	0.045 max.	0.030 max.	0.75 max.	Cu 0.75 max.
Duplex SS (2205-type)	S31803	0.03 max.	21.0-23.0	2.00 max.	2.5-3.5	0.08-0.20	4.5-6.5	0.030 max.	0.020 max.	1.00 max.	
6-Mo	*	0.03 max.	19.5-22.0	2.00 max.	6.0-7.0	0.18-0.25	17.5-26.0	0.040 max.	0.030 max.	1.00 max.	Cu 0-1.5
C-276	N10276	0.02 max.	14.5-16.5	1.00 max.	15.0-17.0	--	balance	0.030 max.	0.030 max.	0.05 max.	W 3.0-4.5 V 0.35 max

* There are a number of 6 % Mo stainless steels, e.g., AL-6XXN (UNS N08367), 254SMO (UNS S31254), 20-Mo6 (UNS N08026) 25-Mo6 (UNS N08925) ; the identity of the proprietary alloy was not disclosed in this test program.

**TABLE 2
WELD FILLER METALS AND WELDING PARAMETERS**

Alloy	Filler Metal
316L	AWS A5.9 ER317L
317LMN	AWS A5.14 ERNiCrMo-3
Duplex (2205-type)	AWS A5.9 ER2209
6-Mo	AWS A5.14 ERNiCrMo-3
C-276	AWS A5.14 ERNiCrMo-4

**TABLE 3
HOST FGD SCRUBBER ABSORBER SITES AND ENVIRONMENTAL CONDITIONS**

Absorber Location	Cl, ppm	pH	Temp. °F (°C)	Exposure Days
PSI-Gibson Station, Indiana (Unit 4)	5,742 - 13,537 Avg. 9,070 5,742 - 13,537 Avg. 9216	5.05 - 6.26 Avg. 5.4 4.95 - 6.26 Avg. 5.4	125 - 130 (52 - 54) Avg. 127.5 (53) 125 - 130 (52 - 54) Avg. 127.5 (53)	167 377
NYSEG-Kintigh Station, New York; (Module A)	range not provided Avg. 20,000 15,800 - 20,500 Avg. 19,000	Avg. 5.6 5.4 - 5.8 Avg. 5.6	Avg. 120 (49) 92 - 124 (33 - 51) Avg. 120 (49)	196 388
Seminole Electric Florida (Unit 2, Module A)	20,000 - 30,000 Avg. 24,000 range not provided Avg. 30,000	5 - 6 Avg. 5.5 Avg. 5.5	120 - 130 (49 - 54) Avg. 125 (52) 125 - 135 (52 - 57)	200 365
Santee Cooper-Cross Station, South Carolina (Unit 2A)	20,000 - 30,000 Avg. 27,900 3,200 - 28,000 Avg. 12,960	5.2 - 5.8 Avg. 5.5 5.2 - 5.8 Avg. 5.5	122 - 126 (50 - 52) Avg. 124 (51) 122 - 126 (50 - 52) Avg. 124 (51)	157 687
RWE - Weisweiler, Germany (Block H, Unit 1)	20,000 - 45,000 Avg. 35,000	5.0 - 6.5 Avg. 5.2	147 - 156 (64 - 69) Avg. 154 (68)	656
Orlando Utilities-Stanton Energy Center, FL (Module A)	60,000 - 80,000 Avg. 70,000	5.5 - 5.6 Avg. 5.6	range not provided Avg. 130 (54)	270

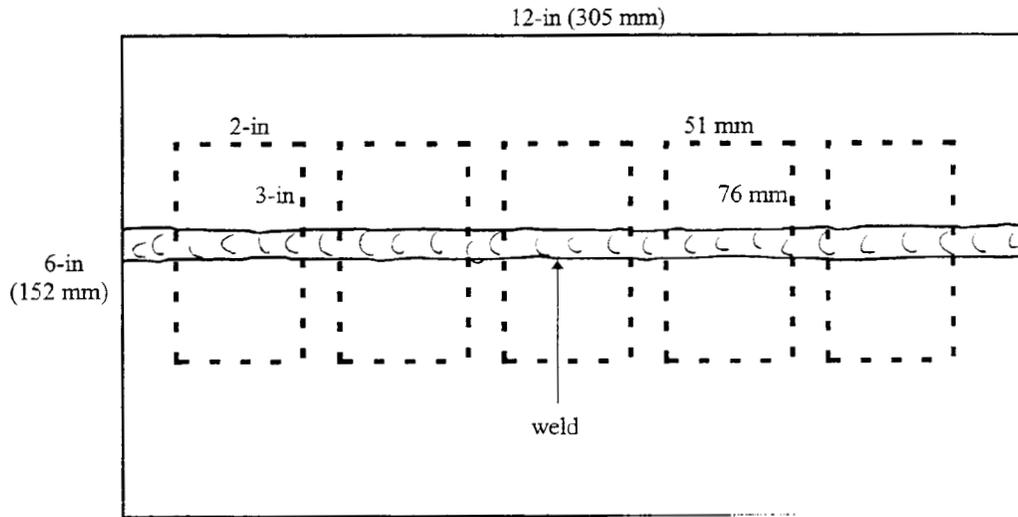


FIGURE 1 - Illustration of how test specimens were cut from welded plates.

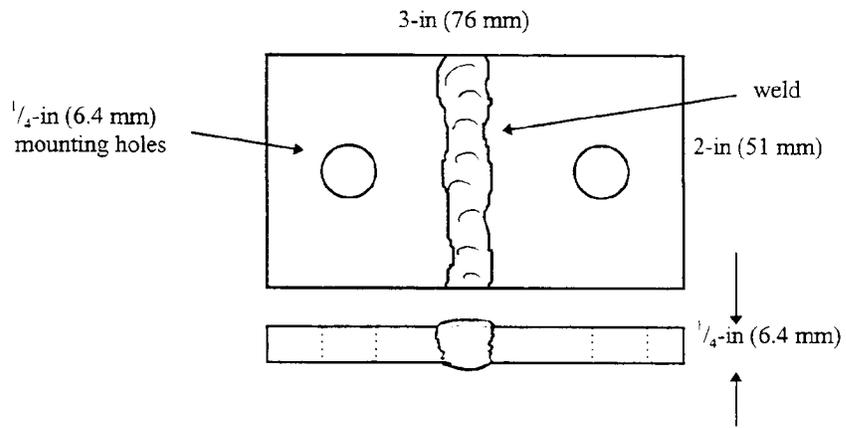


FIGURE 2 - Dimensions of individual test specimens.

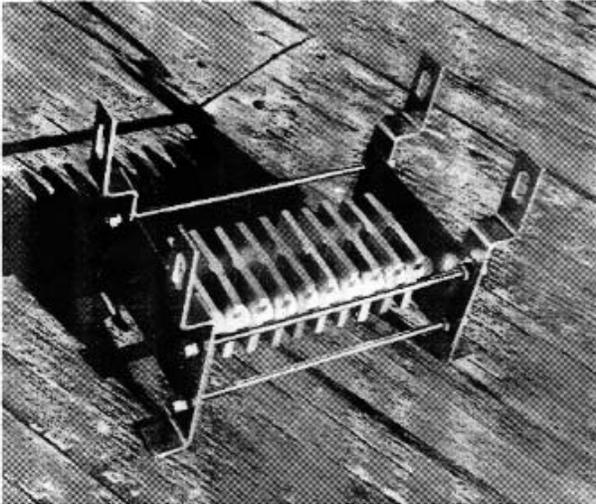


FIGURE 3 - View of fully assembled test rack.

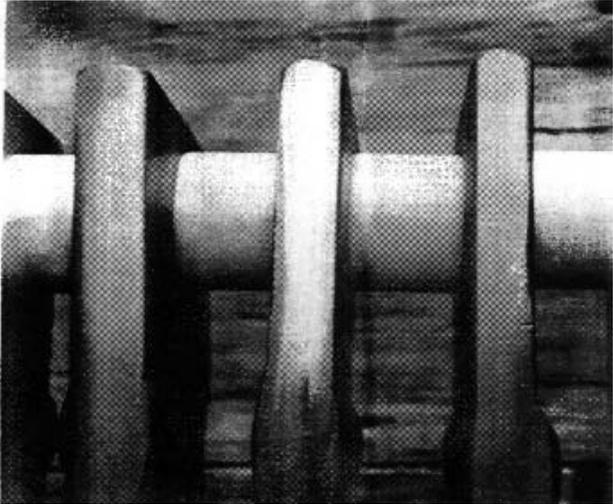


FIGURE 4 - Close-up view of tight-crevice specimen arrangement.

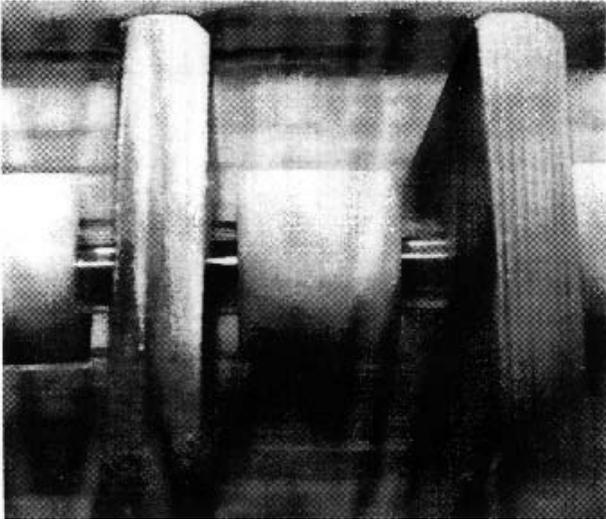


FIGURE 5 - Close-up view of loose-crevice specimen arrangement.

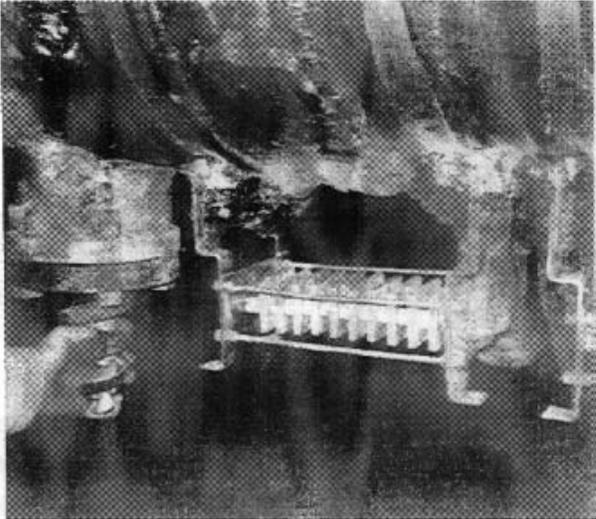


FIGURE 6 - Typical illustration of test rack exposed in FGD absorber.

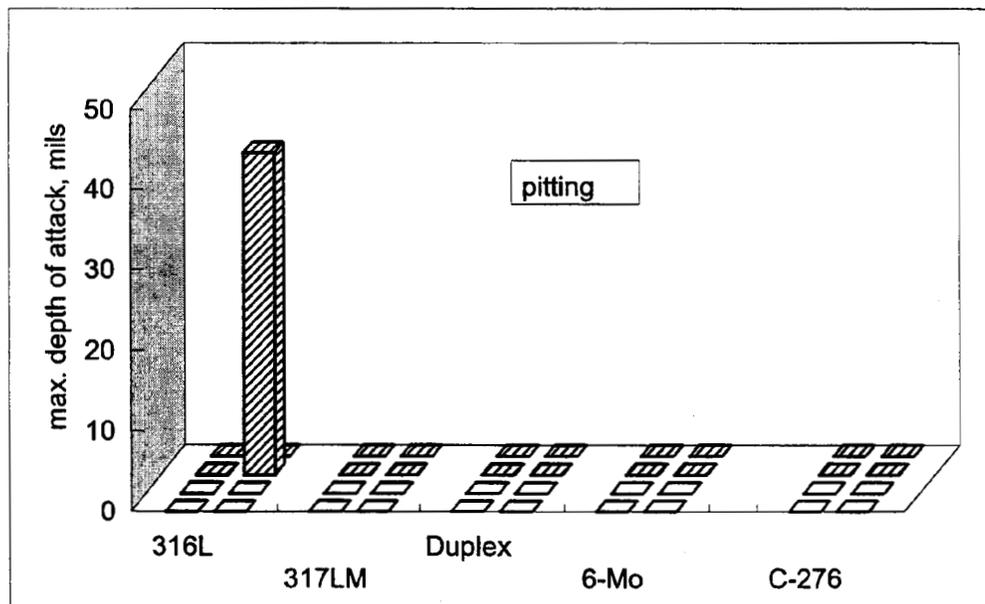
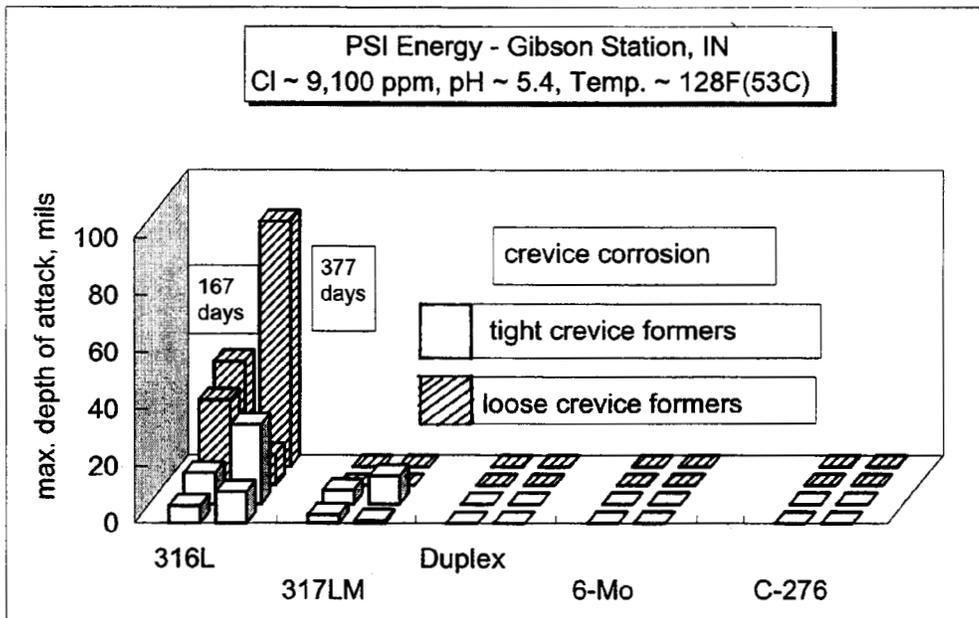


FIGURE 7 - Maximum depths of crevice corrosion and bold surface pitting. For each alloy, the 1st set of columns (going from front to back) represents 167 days' and the 2nd set 377 days' exposure. The open and shaded bars represent data for duplicate specimens with tight and loose crevice formers, respectively. (1 mil = 0.0254 mm).

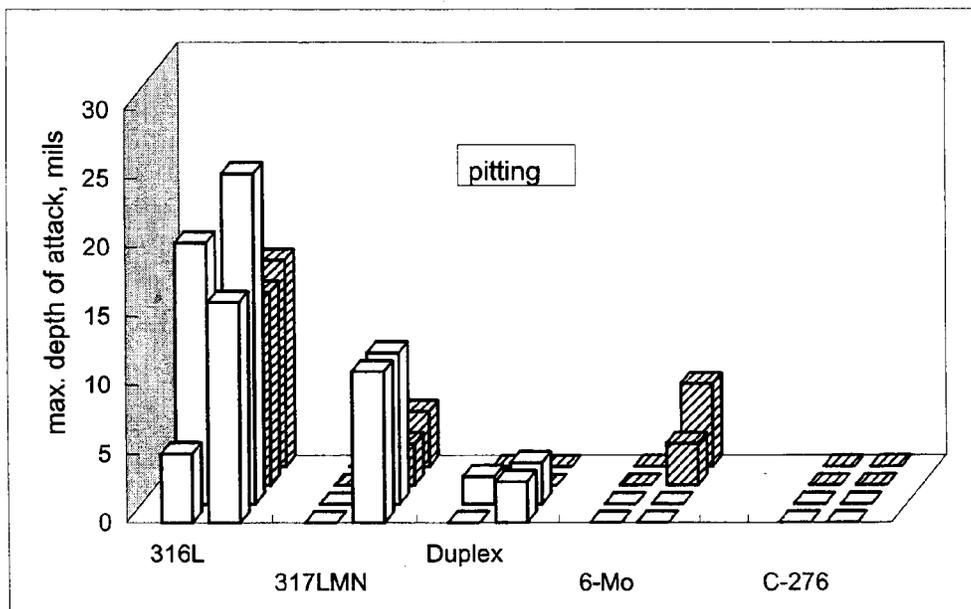
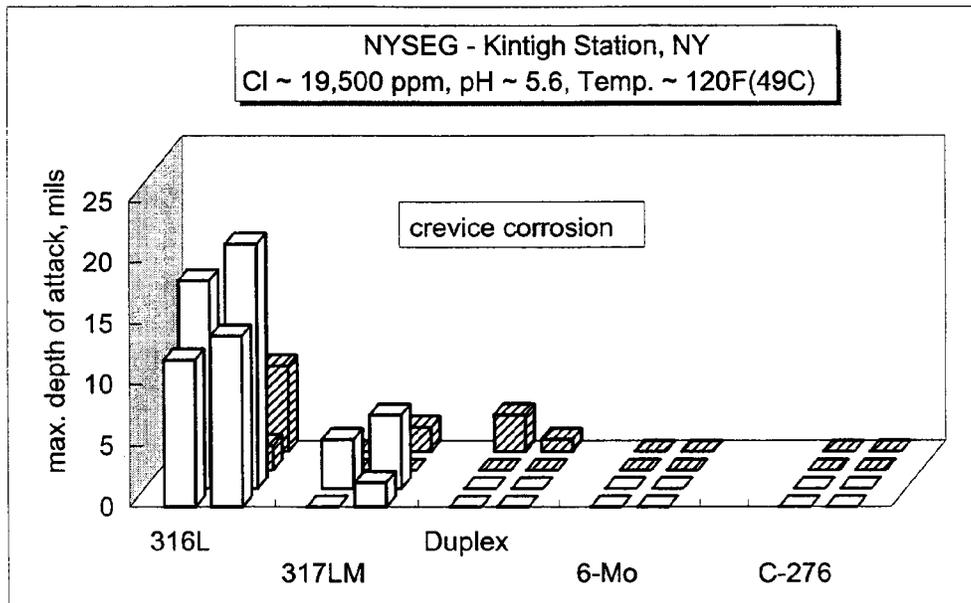


FIGURE 8 - Maximum depths of crevice corrosion and bold surface pitting. For each alloy, the 1st set of columns (going from front to back) represents 196 days' and the 2nd set 388 days' exposure. The open and shaded bars represent data for duplicate specimens with tight and loose crevice formers, respectively. (1 mil = 0.0254 mm).

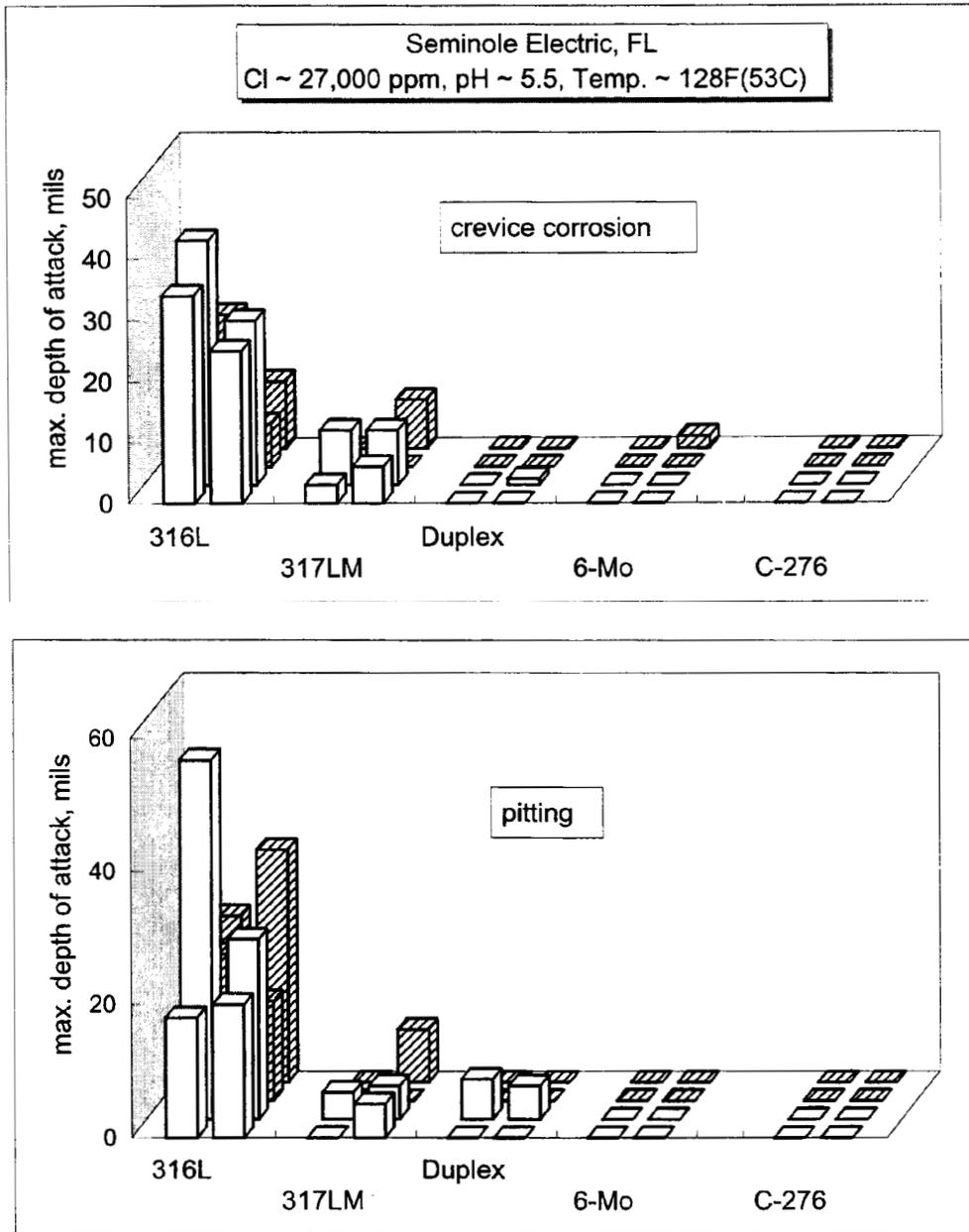


FIGURE 9 - Maximum depths of crevice corrosion and bold surface, pitting. For each alloy, the 1st set of columns (going from front to back) represents 200 days' and the 2nd set 365 days' exposure. The open and shaded bars represent data for duplicate specimens with tight and loose crevice formers, respectively. (1 mil = 0.0254 mm).

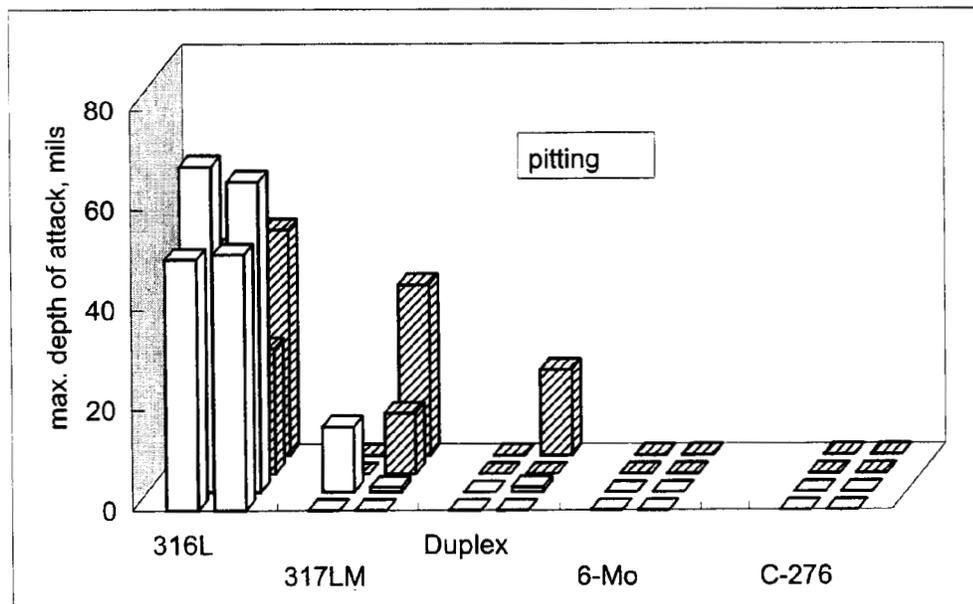
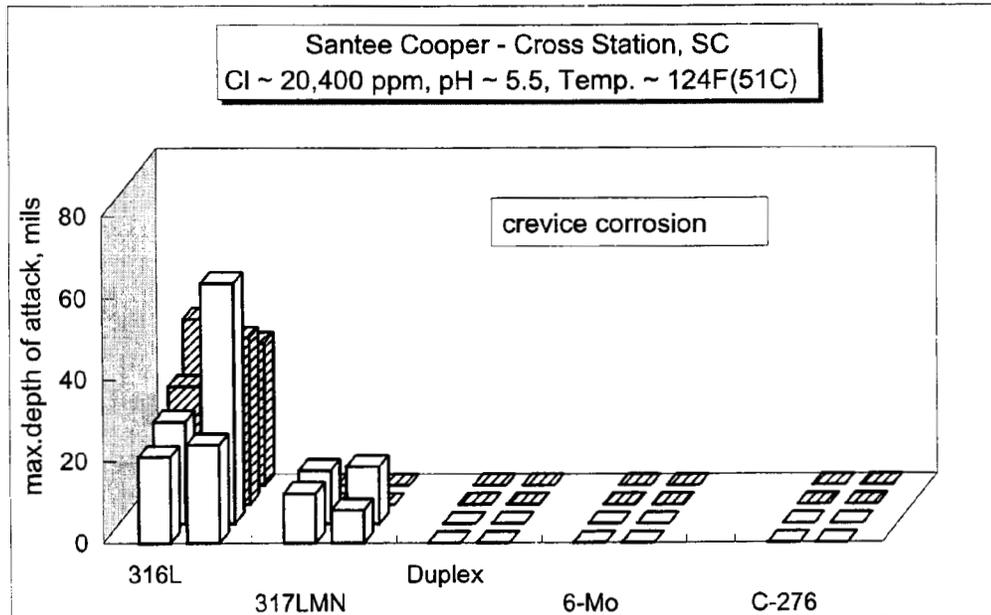


FIGURE 10 - Maximum depths of crevice corrosion and bold surface pitting. For each alloy, the 1st set of columns (going from front to back) represents 157 days' and the 2nd set 687 days' exposure. The open and shaded bars represent data for duplicate specimens with tight and loose crevice formers, respectively. (1 mil = 0.0254 mm).

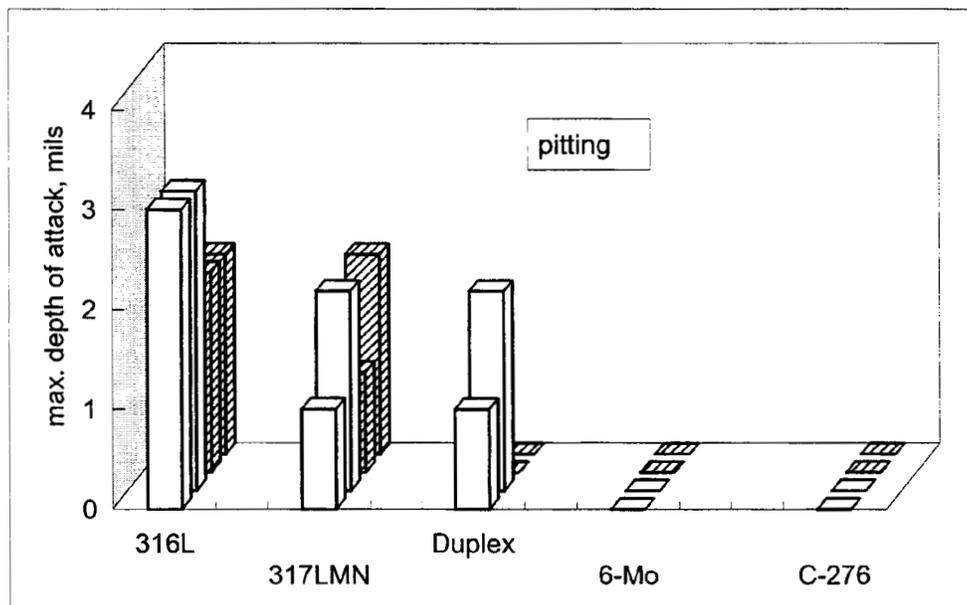
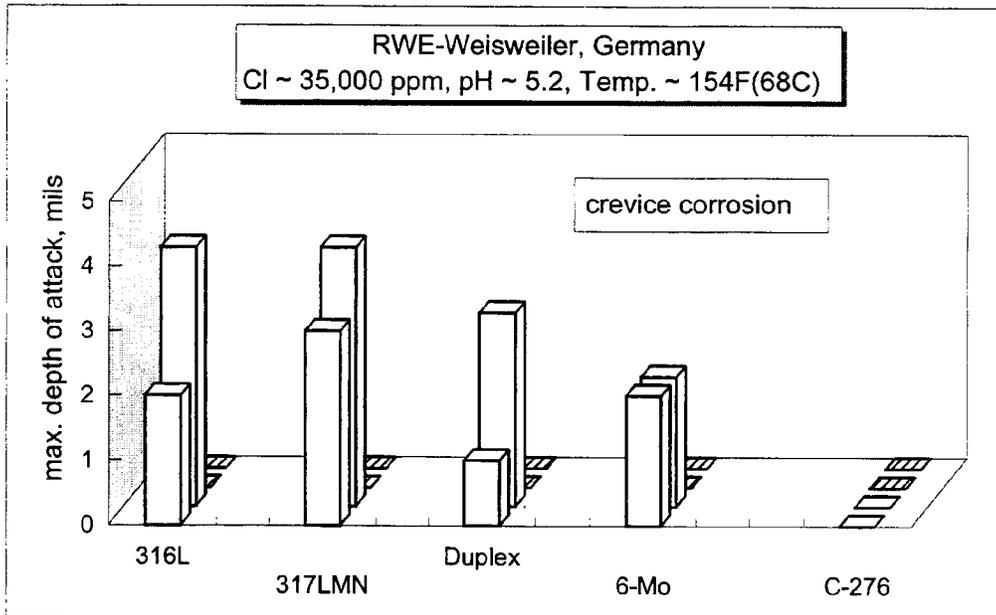


FIGURE 11 - Maximum depths of crevice corrosion and bold surface pitting. For each alloy, the open and shaded bars represent data for duplicate specimens with tight and loose crevice formers, respectively; 656 days' exposure. (1 mil = 0.0254 mm).

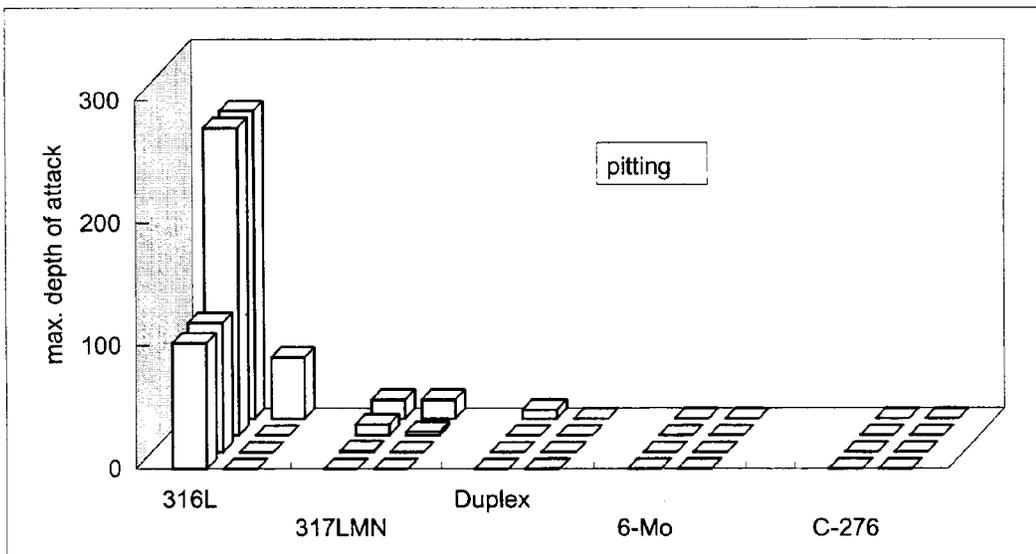
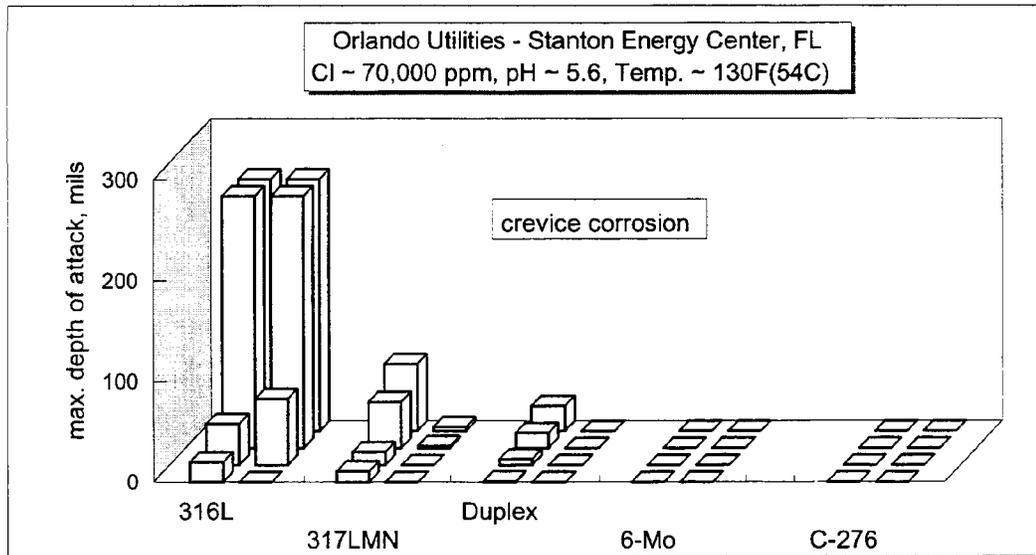


FIGURE 12 - Maximum depths of crevice corrosion and bold surface pitting. For each alloy, the 1st set of columns (going from front to back) represent data for replicate specimens with tight crevice formers and the 2nd set for those with loose crevice formers. The exposure duration for all specimens in this scrubber was 270 days. The tallest 4 bars for crevice corrosion and the tallest 2 for pitting correspond to specimen perforation by corrosion. (1 mil = 0.0254 mm).

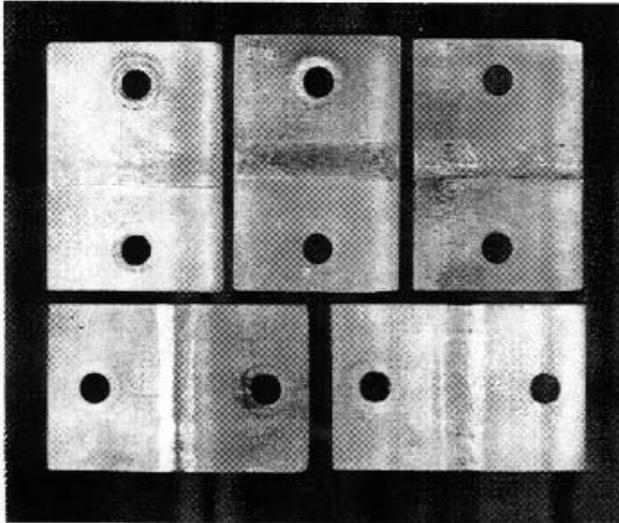


FIGURE 13 - Side-by-side comparison of 316L, 316LMN, Duplex (top row); and 6-Mo and C-276 (bottom row); 377 days' exposure at PSI-Gibson Station, IN; after-cleaning appearance.

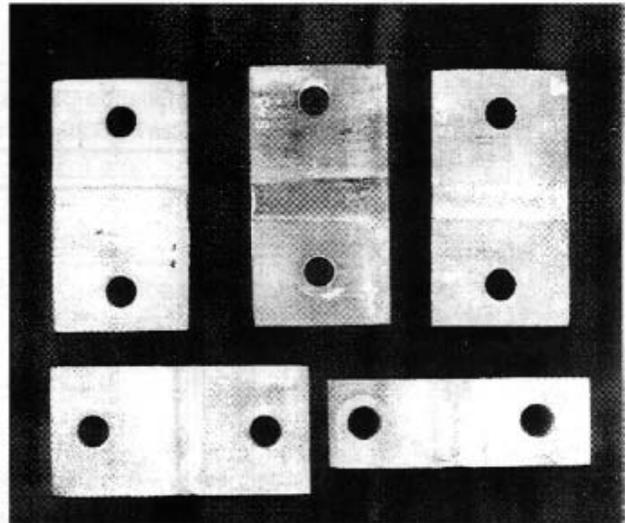


FIGURE 14 - Side-by-side comparison of 316L, 317LMN, Duplex (top row); and 6-Mo and C-276 (bottom row); 388 days' exposure at NYSEG-Kintigh Station, NY; after-cleaning appearance.

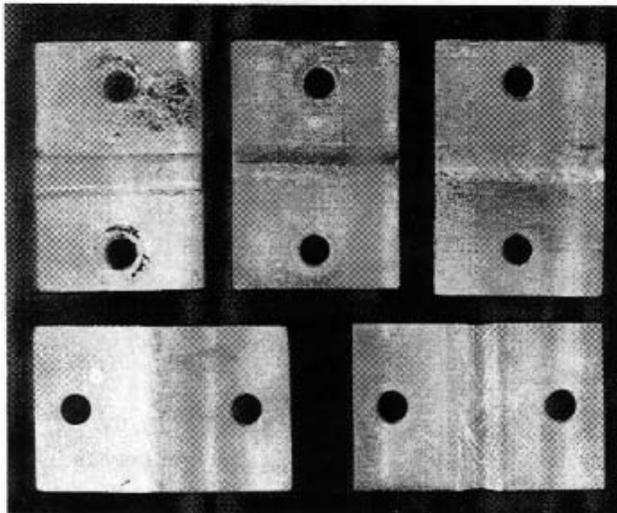


FIGURE 15 - Side-by side comparison of 316L, 317LMN, Duplex (top row); and 6-Mo and C-276 (bottom row); 365 days' exposure at Seminole Electric, FL; after-cleaning appearance.

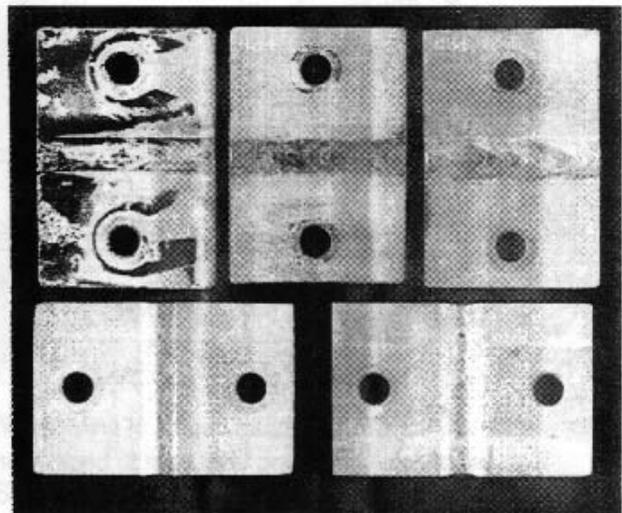


FIGURE 16 - Side-by-side comparison of 316L, 317LMN, Duplex (top row); and 6-Mo and C-276 (bottom row); 157 days' exposure at Santee CooperCross Station, SC; after-cleaning appearance.

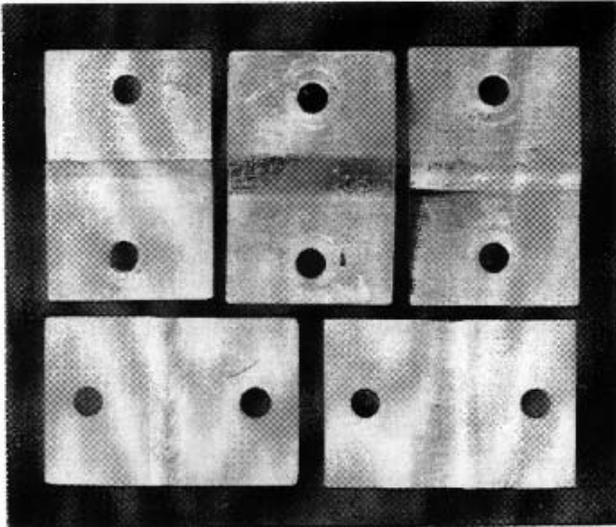


FIGURE 17 - Side-by-side comparison of 316L, 317LMN, Duplex (top row); and 6-Mo and C-276 (bottom row); 656 days' exposure at RWE-Weisweiler, Germany; after-cleaning appearance.

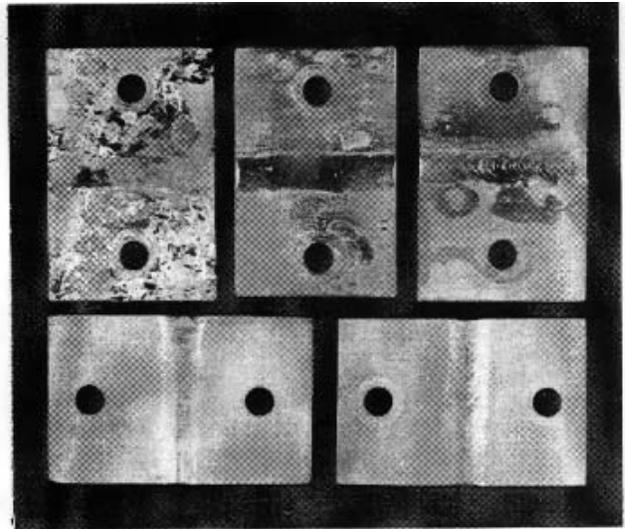


FIGURE 18 - Side-by-side comparison of 316L, 317LMN, Duplex (top row); and 6-Mo and C-276 (bottom row); 270 days' exposure at Orlando Utilities - Stanton Energy Center, FL; after-cleaning appearance.