

**NEQ REPORT**  
(Nuclear Environmental Qualification)

**WYLE LABORATORIES**

SCIENTIFIC SERVICES AND SYSTEMS GROUP  
HUNTSVILLE, ALABAMA

Rochester Gas and Electric Corporation  
89 East Avenue  
Rochester, New York 14649

REPORT NO. 17490-2  
WYLE JOB NO. 17490  
YOUR P.O. NO. N-BU-17089  
DATE January 15, 1982

ANALYSIS OF THE DECOMPOSITION EFFECTS OF  
VINYLCEL INSULATION ON 304 SST FACINGS  
IN A DESIGN BASIS ACCIDENT

STATE OF ALABAMA } California Professional  
COUNTY OF MADISON } ss. Engineering Reg. No. 2635  
James F. Gleason

, being duly sworn,  
deposes and says: The information contained in this report is the result of complete and  
carefully conducted analyses and is to the best of his knowledge true and correct in all  
respects.

SUBSCRIBED and sworn to before me this 18th day of January, 1982

Joyce Klutts (formerly Joyce Oliver)  
Notary Public in and for the State of Alabama at large.

My commission expires June 3, 1982  
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PDR

Wyle shall have no liability for damages of any kind to person or property, including special or  
consequential damages, resulting from Wyle's providing the services covered by this report.

PROJ. ENGINEER M. Bruce  
M. Bruce  
APPROVED BY E. P. Sweeney  
E. P. Sweeney  
WYLE O.A. M. Kimbrell  
M. Kimbrell



## 1.0 PURPOSE

This analysis was prepared by Wyle Laboratories for Rochester Gas and Electric Company.

As requested by RG&E, this report provides additional analysis to supplement Section 8.3 of Wyle Report 17490-1.

## 2.0 SCOPE

The scope of this investigation includes literature search and analysis of applicable data to estimate the time it would take for the 304 SST facing panels to be corroded by the decomposition of vinylcel insulation during a design basis accident at the Robert E. Ginna Nuclear Power Plant.

## 3.0 APPLICABLE VINYLCEL INFORMATION

Further information regarding the 19-mil facing panels was provided by RG&E: Gilbert Associates, Inc., Bill of Materials, GAI W.O. 4155 (Attachment 1).

## 4.0 ANALYSIS

As the accident temperature declines and the total radiation dose to the vinylcel increases, HCL gas will begin to evolve. Wherever moisture is available on interior surfaces of the 304 stainless steel facing panels, aqueous HCL will form. Neutralization of this acid will be most effective in the areas most accessible to the containment chemical spray, that is, along panel edges and around retaining bolts. Less accessible areas will be exposed to hydrochloric acid at pH levels that will vary depending on chemical spray penetration between the insulation and facing. Welded areas that might be sensitized to corrosion are protected by acid-resistant paint (Attachment 3).

Reference 21, Wyle Report 17490-1, reports a corrosion rate of 10 mils per year for 304 stainless in 0.4% HCL (Calc pH = 3) at 80°F (Attachment 2). Below about pH 4 increasing acid concentration does not greatly accelerate corrosion of carbon steel (see Section 8.2 of Wyle Report 17490-1). Though no specific data was located, a similar insensitivity to acid concentration can be expected for the 304 stainless in acid environments.

Temperatures following a DBE at Ginna are postulated to be higher than the temperature for which a corrosion rate was given. Corrosion at higher temperatures would be more rapid. Because the initial transient temperature phase is short (slightly over 1 day) and HCL generation will not occur until the radiation dose to the insulation has reached  $5 \times 10^6$  rads, only the 150°F post-accident ambient is considered. Reference 20 of Report 17490-1 reports that the rate of iron corrosion by HCL (at low pH) doubles for each 10°C rise above ambient temperature. Low pH will persist in the least accessible central section of the panels. Assuming the acceleration

#### 4.0 ANALYSIS (CONTINUED)

factor for iron/HCL applies for 304SS/HCL and extrapolating the known 10-mil per year corrosion rate at 80°F (26.66°C) to Ginna's 150°F (65.55°C), corrosion rates in those areas could be as high as 160 mils per year. Penetration of the 19-mil facing could occur in 1.4 months. Neutralizing chemical spray could then enter through these penetrations and retard or prevent further corrosion.

Along panel edges and around panel penetrations for retaining bolts, chemical spray is assumed to enter behind panels and completely or partially neutralize HCL evolved from the insulation. Fully neutralized areas would not be subject to rapid corrosion. Slightly less accessible areas where only partial neutralization occurs would be subject to acid corrosion. Reference 20 in Report 17490-1 indicates that corrosion by solutions of pH 4-10 is limited by oxygen diffusion and that corrosion rates approximately double for each 30°C increase above ambient. Extrapolating the known rate of 10 mils per year at 80°F to Ginna's 150°F, the expected corrosion rate, in slightly to moderately acid areas, would be about 30 mils per year. Panel penetration could occur in about 7.5 months. As with penetrations in lower pH areas, these areas would then become more exposed to neutralizing chemical spray and further corrosion would be inhibited.

Thus, for the panels to fail, it would take 7.5 months to penetrate the panel in the areas of the retaining bolts.

The bolts are analyzed per the following. The chemical spray may neutralize the HCL in the areas of the bolts. For purposes of this analysis, it is assumed that only partial neutralization occurs and the 30 mils per year corrosion rate applies. The amount of corrosion of the bolts which could result in failure of the bolt due to exceeding the failure shear load is calculated as follows:

Shear stress calculations in panel mounting bolts:

##### Assumptions

- o Panel is unsupported by frame work.
- o 6 studs carry full panel weight.
- o Studs are in pure shear across threads.
- o Panel weight is evenly distributed on studs.

##### Given

- o Panel size: 44" x 84" x 0.019" Tp 304SS
- o Insulation: 44" x 84" x 1½" density 4 lb/ft<sup>3</sup> bonded to panel
- o Studs: 6 ea. 10-24, Tp 304SS

4.0 ANALYSIS (CONTINUED)Calculations

## Panel Weight:

- Steel:  $(44") (84") (0.019") (0.29 \text{ lb/in}^3) = 20 \text{ lb}$
- Insulation:  $(44") (84") (1\frac{1}{4}") (1/1728 \text{ ft}^3) (4 \text{ lb/ft}^3) = 11 \text{ lb}$
- Total:  $20 \text{ lb} + 11 \text{ lb} = 31 \text{ lb}$
- Per Stud:  $31 \text{ lb}/6 \text{ studs} = 5 \text{ lb/stud}$

## Stud Load:

- Tensile stress area of stud  $0.0175 \text{ in}^2$
- Shear stress  $\tau = 5 \text{ lb}/0.0175 \text{ in}^2 = 286 \text{ psi}$
- Allowable stress  $S_u/8 = (66,200 \text{ psi})(1/8) = 8,275 \text{ psi}$
- Failure stress  $S_y/2 = (25,000 \text{ psi})(1/2) = 12,500 \text{ psi}$

## Minimum Stud Area at Failure

- $A_{\min} = 5 \text{ lb}/\tau_{\text{failure}} = 5 \text{ lb}/12,500 \text{ lb/in}^2 = 0.004 \text{ in}^2$
- Diameter  $= \sqrt{4A/\pi} = \sqrt{4(0.004/\pi)} = 0.022 \text{ in.}$

Original minimum diameter of 10-24 thread = 0.136 in.

Depth for failure =  $(0.136 - 0.022)/2 = 0.057 \text{ in.}$

Source for calculations: Boiler & Pressure Vessel Code  
ASME Section III, Div. 1, Appendices, 1980

1. Design Requirements for Bolted Joints - XVII, 2460
2. Shearing Stress of Austenitic Steels - XVII, 2461.2  
 $F_{vb} = 0.62S_u/5 = 1/8 S_u$
3.  $S_u(200^\circ\text{F})$  - Table I-3.2
4.  $\tau_{\max}(200^\circ\text{F})$  - Table I-2.2

The time to reduce the minimum bolt diameter by 57 mils at 30 mils per year corrosion rate is 1.9 years.

## 5.0 ADDITIONAL INFORMATION

Additional information was located on actual corrosion of 304 stainless in acid environments containing chlorides (see Attachments 4, 5, and 6).

Attachment 4 reports field corrosion studies for 304SS (unstressed samples) in wet scrubber systems. General corrosion rates are not reported, but the maximum depth of pitting/crevice corrosion was 55 mils after 5.3 months in a refuse incinerator scrubber in which the process fluid contained recirculated unneutralized hydrochloric acid. A maximum penetration depth of 47 mils was achieved by 4 months exposure in another scrubber system which used a highly oxidized fluid at a pH of 4.5 and a 1,400 ppm chloride concentration.

As noted in Attachment 2, acid chloride solutions (pH below 7) could induce stress corrosion cracking in austenitic steels at Ginna's 150°F ambient (residual or applied tensile stress for the steel is required). Data from Attachment 5 indicates that if the acid is hydrochloric, general corrosion is dominant. A solution containing 0.8% NaCl and HCL at a pH of about 2.2 and a temperature of 141°C did not show cracking for U-bend specimens after 10 days exposure. Cracking did occur after 30 days, but may have been due to evaporation of the test solution during that period. When the acidifying agent was phosphoric or citric acid, stress corrosion cracking and pitting/crevice corrosion was dominant.

The effect of acidified borated chemical spray solutions containing chlorides on 304 stainless is presented in Attachment 6. Increasing chloride concentration and decreasing pH were shown to promote stress corrosion cracking. All stressed samples (U-bend) and samples "sensitized" to cracking by heat treatment showed cracking after exposures to spray containing 200 ppm chloride at a pH of 4.5 for 24 hours at 285°F, 7 days at 212°F, and 2 months storage in the spray solution at 180°F. Two (2) of four (4) welded and ground coupons (more nearly representative of panel retaining bolts at Ginna) exhibited cracking in that environment. At higher pH's, cracking was indicated as much less significant.

Ginna's relatively low temperature and the moderate static stress for the retaining bolts would reduce the probability of failure by stress corrosion cracking of the retaining bolts in slightly to moderately acid environments.

A neutral to slightly alkaline environment is more probable for the retaining bolts and such environment would not result in stress corrosion cracking or significant general corrosion rates.

## 6.0 CONCLUSION

The panels could experience corrosion which could penetrate the panels in 1.4 months. The rate of continued corrosion would be slowed by the neutralization of the HCL by the chemical spray and these penetrations are most likely to occur in areas furthest from the retaining bolts.

6.0 CONCLUSION (CONTINUED)

The time for the panels to fall is most probably a function of the corrosion around the retaining bolts. The corrosion in these areas would progress to the point of penetration of the panels in 7.5 months. In order for a panel to fall, penetrations around retaining bolts would have to be well connected. As a penetration developed, the chemical spray would further neutralize the HCL and retard corrosion.

The time to failure of the retaining bolts is assumed to be the time when the failure shear load is realized. This time is predicted to be 1.9 years.

Thus, the time required after a DBE to cause falling of the panels is between 7.5 months and 1.9 years.

7.0 REFERENCES

1. Bill of Materials for Robert E. Ginna, Unit 1, Containment Insulation, from Gilbert Associates, Inc. (Attachment 1)
2. Taylor, Lyman, Ed., "Properties and Selection of Metals," Metals Handbook, Vol. 1, 8th Edition, American Society for Metals, 1966 (Excerpt - Attachment 2)
3. Contact Report, M. Bruce, Wyle, with Bill Davis, Carboline, and Product Data Sheet on Vinyl Paint (Attachment 3)
4. Anderson, D.B., "Spool Corrosion Tests in Wet Scrubber Systems," Materials Performance, Vol. 20, No. 10, October, 1981 (Attachment 4)
5. Asphahani, A.I., "Effects of Acids on the Stress Corrosion Cracking of Stainless Materials in Dilute Chloride Solutions," Materials Performance, Vol. 19, No. 11, November, 1980 (Excerpt - Attachment 5)
6. Cottrell, W.B., "ORNL Nuclear Safety Research and Development Program Bimonthly Report for November-December, 1970," ORNL-TM-3263, Oak Ridge National Laboratory, March, 1971 (Excerpt - Attachment 6)
7. ASME Boiler & Pressure Vessel Code, Section III, Division 1 - Appendices, July, 1980

**CLIENT:**

Westinghouse Atomic Power Division  
(Rochester Gas & Electric Corporation)  
Thermal Insulation and Refractory  
Robert Emmett Ginna Nuclear Power Plant - Unit No. 1

LOCATION: Pittsburgh, Pa.

GAI W. O. 4155  
CLIENT W. O. RH-33000

ITEM NO.	QUANTITY	DESCRIPTION OF MATERIAL	ISSUE	ORDER NO.
AP-1 REVISION	All	<p><u>Containment Insulation</u>, Herbert Construction Corporation, shall include the furnishing, fabricating, delivering and installation of heat insulation with stainless steel facing, to include 129 penetrations and two hatches required for the interior of the containment vessel to be in accordance with GAI Specification SP-5296.</p> <p>Johns-Manville Vinylcel Insulation shall be applied to the areas specified in the above specification as follows:</p> <p>Insulation to be 1-1/4" th. Vinylcel sheets .019" ga. Type 304 44" x 84". Sheets will have specified design routed edges on face. Sheet face to routed edges shall be finished with #1/24 stainless steel. Sheets to be mounted on stainless steel studs KSM#304 stainless #10-24 x 1-1/2. A 1-1/8 dia. silver colored neoprene and stainless steel combination washer will be placed outside the sheet over the stud and held in place by a self-locking stainless hex head nut. The sheets will have predrilled 5/8" dia. holes and the studs will be welded through same while the sheet is held in position manually. Through these holes Herbert Construction Corporation will spray Carbolene Vinyl paint to coat steel around weld joints. Backs of sheets will be routed to fit over the 1-1/4 x 1/2" channels in the field. Sheets will be erected with 44" dimension vertical and vertical joints will be staggered. All sheets will be spaced approximately 1/16" apart. The joints at base of routed edges will be taped with 3/8" wide tape as specified. The routed area will be covered with heavy Dow forming Sealant #780 applied as recommended by the manufacturer to make a flush finished joint.</p> <p>At penetrations, etc., where sheets must be cut to fit around and butt to same, the edges shall be beveled and caulked as described above.</p> <p>Herbert Construction Corporation will spray on the sheet metal face a 1-1/2" diameter circle indicating location of test plugs.</p> <p>Where plates at penetration areas project into the vessel beyond the normal wall line, Herbert Construction Corporation will work out acceptable details in the field, by either using thinner insulation or developing an approved overlap at the juncture point.</p> <p>(Continued Sheet 2)</p>	A/ 2	216114

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DATE 9-1-68  
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ENGINEER E.D.

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GAI-62 REV.5/4



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GILBERT ASSOCIATES, INC.  
BILL OF MATERIALS

ATTACHMENT 1 (CONTINUED)

BM SYMBOL ARDCK-00D-RP  
SHEET NO. 2

CLIENT:

Westinghouse Atomic Power Division  
(Rochester Gas & Electric Corporation)

FOR:

Thermal Insulation and Refractory  
Robert Emmett Ginna Nuclear Power Plant - Unit No. 1

LOCATION: Pittsburgh, Pa.

GAI W. O. 4155  
CLIENT W. O. RH-33000

ITEM NO.	QUANTITY	DESCRIPTION OF MATERIAL	ISSUE	ORDER NO.
RP-1 cont. REVISION		<p>Herbert Construction Corporation shall use electric swing scaffolds to insulate the area from 16 ft above the spring line where the insulation is indicated to start, to the operating floor. Tubular scaffold shall be used for the balance of the side walls.</p> <p>The metal face shall be laminated, the sheets shall be face routed and drilled before shipment to the job site. Herbert Construction Corporation shall store sheets on job site in area provided. Herbert Construction Corporation shall erect a small fab shop on the job site. Herbert Construction Corporation will keep CO<sub>2</sub> fire extinguishers on the scaffolds and in the areas they are working. Herbert Construction Corporation shall hang a tarp from the bottom of the swing scaffolds as a safety measure.</p> <p>Herbert Construction Corporation will secure from material vendors certificates as specified. Herbert Construction Corporation shall guarantee workmanship for a period of two years after installation.</p> <p>(321.5)</p> <p>Engineering and price to be in accordance with Herbert Construction Corporation Quotation dated January 8, 1968 and telegrams dated January 10, 1968 and January 12, 1968 and letters dated February 6, 1968 and March 7, 1968</p> <p>Delivery and Installation of Material: On approximately March 1, 1968 Herbert Construction Corporation shall start the insulation below the operating floor, working in conjunction with the Bechtel Engineers as to what areas should be done first, etc. The second phase consisting of the area above the operating floor would be done later in the year.</p> <p>Delivery required: February 15, 1968</p>	1/ 2	216114

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# METALS HANDBOOK

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*Properties and Selection of Metals*

*prepared under the direction of the  
METALS HANDBOOK COMMITTEE*

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AMERICAN SOCIETY FOR METALS  
Metals Park, Ohio

Table 12. Corrosion by Spent Solutions of Inorganic Compounds

Compound and % concentration	Steel	Temperature, F	Corrosion, mpy	Compound and % concentration	Steel	Temperature, F	Corrosion, mpy
30 ammonium arsenate .....	304	Boiling	5	30 sodium sulfide .....	304	130	9.1
10 ammonium chloride .....	316	Boiling	<1	30 sodium sulfide .....	316	130	21
0.4 hydrochloric acid .....	304	80	10	40 sodium sulfide .....	304	Boiling	1.5
0.4 hydrochloric acid .....	316	120	5	40 sodium sulfide .....	316	Boiling	2.5
30 manganese chloride .....	304	194	0.7	6 sulfurous acid .....	304	104	0.1
30 manganese chloride .....	347	194	0.7	6 sulfurous acid .....	304	194	18
28 nickel sulfate .....	304	122	0.04	100 sulfur chloride .....	304	Boiling	1.3
40 sodium bisulfide .....	304	Boiling	1.6	100 sulfur chloride .....	410	...	3.1
40 sodium bisulfide .....	316	Boiling	1.1	All steels in the annealed condition. All solutions from CP chemicals. Tests made in the laboratory.			

Table 13. Corrosion by Stannous Fluoride

Solution strength, weight %	Corrosion, mpy		
	304	316	347
2.0 .....	3.92	...	...
15 .....	0.9	None	0.39
30 .....	0.56	None	0.79
50 .....	1.81(a)	...	...

(a) Stained black

Table 14. Corrosion by 78% Sulfuric Acid Mixed with Sulfonation Products

Alloy	Corrosion, mpy	
	80 F	140 F
Type 316 .....	0.2	20
Hastelloy B .....	...	0.6
Hastelloy C .....	...	1.5
No. 20 .....	None	3.0
Inconel .....	None	8.0
Mild steel .....	20	134

Table 15. Corrosion by Spent Sulfuric Acid after Separation of Sulfonation Products

Alloy	Corrosion, mpy	
	80 F	140 F
Type 316 .....	0.21	15.12
No. 20 .....	0.06	3.94
Inconel .....	0.09	19.25
Mild steel .....	18.9	63.6

In repairing equipment that has been in sulfide service, the surface should be cleaned thoroughly by abrasive blasting before welding, to avoid weld cracking.

### Stannic Chloride

Types 304 and 316 have satisfactory resistance to aqueous solutions of stannic chloride at temperatures to 200 F for concentrations not exceeding 1%. Type 316 is more resistant than 304 and has fair resistance to solutions of 10 to 15% at 70 F, but is unsatisfactory at higher temperatures and concentrations.

### Stannous Fluoride

Laboratory tests made at 200 F with aqueous solutions ranging from 2 to 50% by weight indicate that stannous fluoride solutions can be handled in equipment made of the series 300 stainless steels. A maximum rate of 3.9 mpy was obtained in a 2% solution. With allowance for experimental error, all rates either decreased or remained the same with increasing concentrations. No tendency toward pitting could be found, and stressed horse-shoe-type specimens of 304 and 316 tested for stress-corrosion cracking did not fail. Table 13 summarizes these tests.

### Sulfation and Sulfonation Products

The austenitic stainless steels and carbon steels have low corrosion rates in oleum (fuming sulfuric) and sulfuric acid of more than 80% concentration at room temperature. At 100 to 103% there is a distinct rise in the corrosion rate with carbon steel. Above 103%, both stainless and carbon steels have satisfactory corrosion rates. Steels of the 300 series are satisfactory for sulfonation practice at room temperature with 78% sulfuric acid

mixed with sulfonation products. At 140 F corrosion of series 300 steels is excessive. Corrosion rates at these temperatures are reported in Tables 14 and 15.

If accuracy of parts is essential, as in valves and control instruments, or if velocity of liquid is high, as in pumps or mixing operations, corrosion rates are excessive, and steels such as CN-7M and nickel-base alloys are needed. The neutralized products of sulfonation may separate when stagnant, and the series 300 steels can be severely pitted by the resulting diluted acid.

### Sulfuric Acid

The 18-8 varieties of stainless steel are resistant to corrosive attack by sulfuric acid within rather narrow ranges of concentration and temperature.

Although the stainless steels may be used safely in contact with 80 to 100% sulfuric acid at ambient temperature (carbon steel is ordinarily used in this range), they are attacked at slightly higher temperatures. One to 5% sulfuric acid at ambient temperature should not be stored in vessels of molybdenum-free stainless steels. Type 316 may be used for this purpose; 317, with a higher molybdenum content, may be used safely in this range of acid concentration at temperatures as high as 150 F.

Alloys such as No. 20 and CN-7M resist all concentrations of sulfuric acid at temperatures to 140 F, and to the boiling point for concentrations to 10%, but do not resist all concentrations over a wide range of temperatures.

The preceding data pertain to pure sulfuric acid. The addition of oxidizing agents (such as nitric acid, air and copper salts) will widen the range of applicability of all stainless steels; reducing agents (such as hydrogen) will narrow the range of usefulness. If other than pure sulfuric acid is used with stainless steel, corrosion tests must be made under conditions of operation in order to evaluate the usefulness of the alloys.

Only those concentrations of sulfuric acid and temperatures should be used that have given satisfactory results in corrosion tests. Tests should include annealed, sensitized (1200 F for 8 hr), stressed and crevice-type specimens.

Agitation and aeration in stainless steel equipment and the velocities of sulfuric acid solutions in piping should be ade-

quate (5 to 15 fps) to keep all solids suspended. Charring of organic matter or deposition of scale (such as calcium sulfate) may result in pitting and perforation. The surfaces should be kept clean during shutdown periods.

**Corrosion Failures.** Organic acids and traces of inorganic salts contributed to the corrosion failure of welded zones in a steam-jacketed kettle of type 316 used to heat 4% sulfuric acid in methanol. The interior surfaces of the kettle are shown in Fig. 8. This failure could have been avoided or delayed by the use of 316L or by fully annealing the kettle after fabrication.

The corrosion failure of Van Stone ends (type 316) on a continuous converter for sugar solutions is shown in Fig. 9. Crevice-type corrosion in the flanged ends was increased by a carbonaceous deposit at these points. The solution contained sulfuric acid at pH 1.8 and was held between 275 and 325 F. Since the ends had not been annealed after forming, corrosion was increased by the severe stresses developed in the flanged areas. The corrosion could have been curtailed by using ends with a thicker wall and annealing, and by cleaning the deposit.

### Sulfurous Acid and Sulfur Dioxide

Stainless No. 20, types 316, CF-8M, 317 and CN-7M have been used in equipment for sulfur dioxide (wet) and sulfurous acid environments. The molybdenum in these alloys gives the required resistance to reducing environments of sulfurous acid. The wrought type 316 and cast CF-8M alloys are the most widely used.

Complete suspension of any solids present is necessary to avoid crevice-type pitting. Figure 10 shows pitting and perforation of a Van Stone flanged end of 304 stainless welded to a tube of type 316; the latter did not corrode. Crevice pockets, lapped joints, 90° corner intersections, and similar obstructions should be avoided, and the surfaces should be clean and smooth.

Cold and hot working should be limited to minor forming operations that will keep the hardness of the steel below Rockwell B 98. Stress-corrosion cracking can occur in steel exposed to sulfurous acid solutions containing 100 ppm or more of metal chlorides.

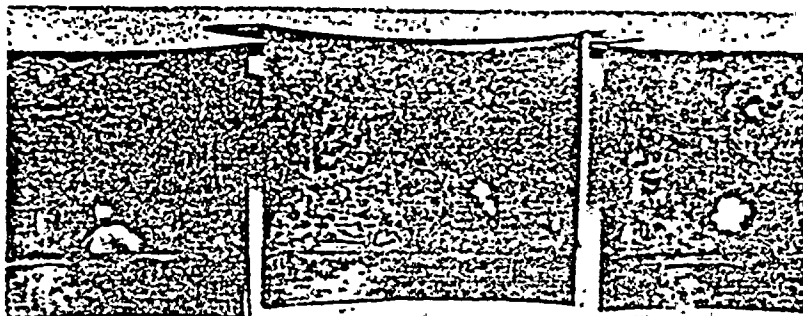


Fig. 10. Van Stone flange of type 304 that was pitted and perforated by sulfurous acid. The type 316 tubing to which it was welded was not corroded.

## 570 SELECTION OF STAINLESS STEEL FOR CORROSION SERVICE IN CHEMICAL PROCESSING

In the process, destroys the passivity of stainless steels. Mixtures of acetic acid with other acids—especially sulfuric, hydrochloric and formic—may produce conditions more corrosive than acetic acid itself, particularly at high temperatures. The data in Table 6 emphasize that slight changes in solution concentrations can have a significant effect on corrosion rates and that suitable corrosion tests must be made whenever any change in operating conditions is contemplated.

Stainless steels are not always satisfactory for contact with hot solutions of acetic acid of concentrations greater than about 25% and containing 2% or more reducing agent (such as formic acid). If oxidizing agents such as sodium dichromate may be added to the acetic acid, the useful life of the stainless steels may be appreciably extended.

In a still handling boiling 99.5% acetic acid liquors and vapors, the service life of the heating coils of 316 varied from ten months to five years. Corrosion tests have also shown that in boiling 75% acetic acid vapors, both 304 and 316 were susceptible to severe pitting corrosion. In some boiling liquors where excessively severe corrosive conditions exist (for example, where acetic acid is contaminated with various chlorides) nickel-base alloys such as Hastelloy C have proved more resistant than stainless steels, and their use is justified economically by the longer life of equipment.

The CF-8M cast alloy is generally used with the 18-8 types of wrought steels because its resistance to pitting attack is greater than that of CF-8. To obtain service comparable with that of the 18-8 molybdenum types of wrought alloys, the chromium content of cast alloys should be on the high side of the composition range. Casting should be fully annealed for best service.

#### Ammonium Sulfate Plus Free Sulfuric Acid

Types 316 and CN-7M are used in this service. Before these steels were available, construction was almost entirely of lead, which was subject to fatigue cracking, and occasionally of silicon iron, which is brittle, thus requiring continuous maintenance. The 18% Cr and 18% Cr-8% Ni steels became pitted and underwent severe corrosion.

Type 316 is useful when properly heat treated after welding; otherwise, heavy intergranular corrosion occurs adjacent to the welds. When extra-low-carbon stainless steel is used (type 316L) heat treatment is unnecessary and large tanks can be fabricated. Such tanks have been in service for several years with no evidence of either general corrosion or intergranular attack. CF-8M and CN-7M castings heat treated after casting are also useful, although if the casting skin is damaged, corrosion may occur. Castings repaired by welding must be heat treated again after welding; otherwise they will corrode intergranularly adjacent to the welds. Pretreatment of the steel by passivation is not required.

Table 6. Corrosion in Formic-Acetic Acid Mixtures

Steel	Temperature, F	Acid content, % Acetic	% Formic	Corrosion, mpy
304, 347	223	30 to 50	2 to 10	(a)
316	223	30 to 50	2 to 10	3 to 20
317	223	30 to 50	2 to 10	2 to 11
316	200 to 230	Glacial	0	<1.5
316	200 to 230	Glacial	4	3.3
316	220	25	1.25	1.5
317	220	25	1.25	<1.0
316	220	25	4	3.0
317	220	25	4	2.0
321, 347	220	25	4	(a)

(a) Completely corroded

#### Bromoform

Type 304 generally is satisfactory for handling bromoform, either wet or dry, at ambient temperatures; however, wet bromoform will discolor slightly. If a water-white product is required, stainless steel is not suitable.

#### Chlorinated Solvents

The halogen derivatives of methane, ethane, ethylene, propane and benzene are widely used in dry cleaning, metal cleaning, vapor degreasing and solvent extraction processes, and as chemical intermediates. The compounds of primary interest are methylene chloride, chloroform, carbon tetrachloride, ethylene dichloride, trichloroethylene, perchloroethylene, methyl chloroform, propylene dichloride, dichloroethyl ether, monochlorobenzene and orthodichlorobenzene. They are used individually as chemically pure or commercial grades, as mixtures, or with other compounds to control boiling point, freezing point, solvency, and flammability of mixtures.

Stainless steels are not corroded by chlorinated solvents when water is absent; but when a water phase is present, the compounds hydrolyze to form hydrochloric acid and sometimes organic acids. Although the presence of metallic materials usually increases the rate of decomposition, stainless steels do not, and their use in equipment for handling chlorinated solvents is generally satisfactory. The corrosion rate of type 304 after 12 days in wet chlorinated solvents at refluxing temperatures is shown in Table 7. These data are from laboratory tests with mixtures of solvent and water, in which one third of the specimen was in the solvent layer, one third in the water layer and one third in the vapor phase.

Consideration should be given to the use of types 316, 317 or No. 20 for applications where pitting is encountered. Intergranular attack occurs sometimes at welded joints; tests should be made. Stress-corrosion cracking may also be encountered in equipment handling chlorinated solvents.

#### Chlorosulfonic Acid

Although carbon steels are satisfactory for chlorosulfonic acid below the liquid level, type 317 or higher alloys are recommended for withstanding the vapors above

and at the liquid level. The products of sulfation, which may retain chlorides, cause stress corrosion and sometimes severe pitting. Pipe welds and vessels of the austenitic steels should be fully annealed whenever this is feasible.

#### Epichlorohydrin

Failure in processing equipment by stress-corrosion cracking was confirmed by laboratory tests with horseshoe specimens at 140 F. Types 304, 316 and 347 cracked in a seven-day test.

#### Fatty Acids

The fatty acids of lower molecular weight, such as acetic and formic, require the use of 18-8 stainless steels (see section on Acetic Acid). The following discussion is concerned with the acids of higher molecular weight, such as lauric, myristic, palmitic, and stearic, which are less corrosive. At temperatures to 150 F, cheaper metals such as carbon steel and aluminum are moderately corroded, but if color and absence of contamination of the product are important, the 18-8 steels should be used.

If the temperature is below 350 F, all standard 18-8 types are satisfactory; above 350 F, type 316 is needed to avoid pitting corrosion.

Corrosion in fatty acid vapors is no greater than in liquid, except at high vapor velocities. Under these conditions corrosion-erosion rates have been lower in type 316 than in types 304, 321 and 347.

Pitting and loss of surface metal are caused by high-temperature plant processes (Fig. 6). There are no reports of straight fatty acids having caused intergranular failures in 18-8 stainless steels.

Cast alloys, including type CN-7M, have been satisfactory. The molybdenum-bearing wrought steels and the newer precipitation-hardening stainless steels have been used for pump and valve parts where galling is a factor or where hardness of parts is desirable. High-nickel cast iron has given satisfactory service in fatty acid at 500 F.

Fatty acids mixed with chlorides cause failures by stress-corrosion cracking (Fig. 7). Acidulation of fatty acids by sulfuric acid produces a wide variation in corrosion rates of stainless steels. Factors that contribute to such variation include unknown dilution of the concentrated sulfuric acid, the moisture inherent in the fatty acids, temperature, and methods of agitation. Corrosion rates encountered with acidulated fatty acids of higher molecular weight with steam agitation are reported in Table 8.

#### Hydrochloric Acid (Dilute)

Although types 316, 317, 329 and No. 20, and the cast alloys CN-7M and CF-8M find some use in very dilute aerated hydrochloric acid environments, stainless steels are not usually recommended for this service.

Solutions containing chloride salts at pH below 7.0 are essentially hydrochloric acid environments. Pitting and stress-corrosion cracking are encountered at acid concentrations less than 1%, depending on the temperature, aeration and agitation. Bimetallic couples between stainless

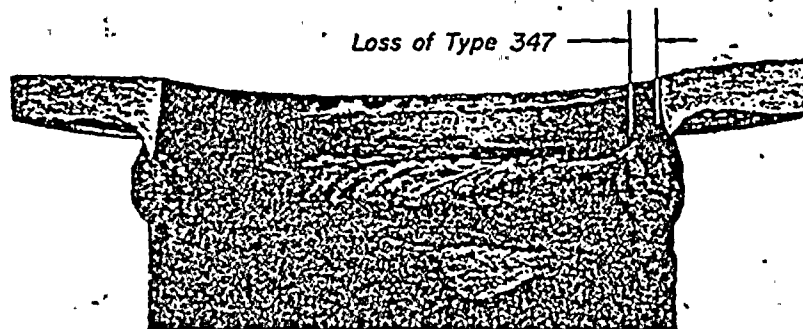


Fig. 6. Weld metal and pipe of type 316 and flange of type 347 corroded by fatty acid at 400 F

and other alloys should be avoided, since corrosion may be accelerated at their junction. In such couples the stainless steel may become the anode in dilute hydrochloric acid, resulting in loss of passivity and rapid corrosion.

**Corrosion Failures.** Hydrochloric acid at pH 2.0 to 4.0 and 120 to 180 F has caused pitting and subsequent failure of heat-exchanger tubing and heating coils. Calcareous scale has induced pitting failures. Activated carbon that settled out has caused pitting of heating coils and tank bottoms (type 316).

**Stress-corrosion cracking** of heat-exchanger tubes has occurred at pH 4.0 and 160 F. Excessive stresses were induced in the tubes when a floating head on the heat exchanger became "fixed". Bending of tubes between baffle supports has induced stress-corrosion cracking of tubes of 316 stainless steel. Excessive rolling of tubes into the tube sheets has induced stress-corrosion cracking of the tubes just adjacent to the sheets.

Weld deposits of type 316 on sheet of similar grade have corroded, weakening the joint. Weld deposits using an electrode of type 317 or 310-Mo have improved the corrosion resistance of these welds. Weld-zone attack has been observed in type 316 linings for steel tanks handling acidified starch slurry at pH 2.0 and 120 F.

Covers and vents from acidified starch slurry tanks usually corrode rapidly. Condensed vapors of dilute hydrochloric acid environments are usually more corrosive than the liquid phase. Stainless steels are usually unsatisfactory for tank covers or vent piping for such tanks.

### Hydrocyanic Acid

Pure hydrocyanic acid is not corrosive to most materials of construction, but when stabilized against polymerization at elevated temperature by the addition of acidic materials, it becomes corrosive to steel, copper and aluminum. The straight-chromium stainless steels are not recommended for use with stabilized hydrocyanic acid solutions.

The austenitic stainless steels resist corrosion by hydrocyanic acid that contains small amounts of sulfur dioxide as a polymerization inhibitor, at all concentrations and temperatures to the boiling point. Types 316 and 317, as well as CN-7M and CF-8M, have greater corrosion resistance than the stainless steels without molybdenum. The unstabilized steels should be fully annealed to prevent intergranular attack in these solutions.

### Lactic Acid

Types 304, 316, 317, No. 20, CN-7M and CF-8M have limited use in lactic acid solutions. The molybdenum-containing varieties generally have greater corrosion resistance than type 304.

Purity, concentration, temperature, aeration and agitation are environmental factors that determine the type of stainless steel for use in process equipment. The presence of chlorides or sulfates in lactic acid solutions increases the severity of corrosion. Impure solutions from which lactic acid is ultimately separated and concentrated are usually more corrosive than the purified solutions. Stainless steels are not suitable for use with lactic acid above 200 F.

Heating coils or heat exchangers for lactic acid should be designed for use with hot water or low-pressure steam. Decomposition of lactic acid with formation of carbonaceous deposit on heating coils can result in pitting and perforation under these deposits.

Temperatures above 200 F, concentrations of lactic acid ranging from 30 to 70%, and the presence of chlorides or inorganic impurities usually increase severity of corrosion. Use of type 304 should be limited to vessels for storing pure solutions at temperatures below 100 F. Distillation of lactic acid causes corrosion



Fig. 7. Stress-corrosion cracking caused in type 304 by citric acid and salt at 212 F

by the vapor phase, and if lactic acid esters and volatile acid impurities are present, pitting attack will result.

**Corrosion Failures.** Pitting failures in heat exchangers for lactic acid solutions have been reported. One failure of this type was limited to surfaces covered by the liquid, particularly in the parts of the tubing where solids have settled out.

Weld-zone attack and corrosion failures have been reported for type 304, but rarely for type 316. The weld-zone failures were in stainless steels that were not of the extra-low-carbon variety and had not been annealed.

### Monoethanolamine

Stainless steels have excellent resistance to corrosion by monoethanolamine and by monoethanolamine saturated with carbon dioxide plus oxygen, at temperatures to 200 F. Stainless steel is used in preference to carbon steel in process steps where carbon dioxide is stripped from monoethanolamine—for example, in reboilers, exchangers and parts of fractionating columns. For heat exchangers, a common practice is to specify stainless steel only for tube bundles having 150-psi steam inside and monoethanolamine that is rich in carbon dioxide outside. Type 304 is adequate.

Experience has been variable with stainless steel in monoethanolamine solutions as used in processes for removing hydrogen sulfide or carbon dioxide from natural and refinery gases. Probably about one fourth of the amine gas treating plants make some use of stainless steel piping and vessels. Remedial process changes can often be devised to avoid the use of stainless.

### Nitric Acid

Stainless steels, first used commercially on a large scale in service involving nitric acid, continue to be used in such installations. These first applications were of 15 to 18% Cr steel (now type 430) and soon thereafter of 18% Cr-8% Ni steel (now type 304). The necessity for proper heat treatment to prevent accelerated corrosion and intergranular attack in nitric acid was demonstrated at once through service failures of improperly heat treated and as-welded equipment. These difficulties were eliminated by post-fabrication heat treatments involving slow cooling from about 1450 F for type 430, and rapid cooling from about 2000 F for type 304. Subsequently, for the austenitic grades, the use of stabilizing elements (particularly columbium in type 347) and, more recently, reduction of carbon content to 0.03% max (type 304L) have been effective in controlling this problem without the necessity for quenching fabricated equipment from a high-temperature heat treatment. In the as-welded condition, 304L and 347 show satisfactory resistance to corrosion by nitric acid and are therefore suitable for field-erected equipment. Where corrosion rates on equipment must be held to less than 5 mpy, types

304L and 347 can be used with nitric acid in concentrations up to about 40%, at the atmospheric boiling point; 40 to 70%, to about 175 F; and 70 to 90%, to about 120 F. For a corrosion rate of 50 mpy max, the corresponding limits are approximately 40 to 70% concentration of nitric acid at the boiling point; 70 to 90% at 160 F, and 90% at 85 F. If the acid is recirculated so that corrosion products accumulate, attack in hot solutions at the higher concentrations is accelerated when the chromium in the acid exceeds a certain level. With boiling 65% nitric acid, the limiting chromium content of the solution is about 0.005%, above which corrosion increases rapidly with further increases of chromium in the nitric acid solution. Under these conditions, corrosion is intergranular, even with the stabilized or extra-low-carbon grades.

Corrosion by nitric acid in storage is slight for concentrations to about 94%, but the acid condensate is of higher concentration, and attack becomes appreciable on the part of the tank exposed to the condensate (Table 3). (Aluminum is commonly used for storing 95 and 98% nitric acid, but its resistance decreases rapidly with decreasing concentration; consequently, exposure to the dilute acid must be avoided.) Corrosion data for specimens of 347 and 430 steels for various concentrations of nitric acid at 72 F are compared in Table 9. In hot concentrated solutions where attack is too severe to be tolerated, high-silicon iron can be used if its mechanical properties are suitable.

In reactions under pressure and at temperatures considerably above the atmospheric boiling point, corrosion rates of all the stainless steels increase rapidly with both temperature and concentration; under these conditions, only very dilute nitric acid solutions can be handled suit-

Table 7. Corrosion of Type 304 After 12 Days in Wet Chlorinated Solvents at Reducing Temperatures

Solvent	Corrosion, mpy
Methylene chloride .....	0.1
Carbon tetrachloride .....	5.0
Methyl chloroform .....	10.0
Trichloroethylene .....	0.2
Ethylene dichloride .....	0.3
Perchloroethylene .....	0.1
Propylene dichloride .....	17.0

One third of specimen was in solvent layer, one third in water layer, and one third in vapor phase.

Table 8. Corrosion in Fatty Acids Acidulated with Sulfuric Acid (Steam agitation)

Sulfuric acid, %	Temp, F	Corrosion, mpy, 304	316
0.01 .....	205	15.4	6.0
0.1 .....	225	7.55	3.8
5.0 .....	200	48.0	19.2
10 .....	215	....	77.5
25 .....	240	....	467

Contact Report Of: W. Bruce

Telephone ☒ Visit ☐

Date Of Contact: 12-14-81

Follow Up Date: \_\_\_\_\_

Agency Or Company and Address	Carboline Company St. Louis, MO Job 17490 R 5 1 E
Phone	314 - 644 - 1000
Person(s) Contacted and Title	Bill Davis - Technical Service
Purpose	Information on Vinyl Paints
Discussion	<p>Our customer has "Carboline Vinyl Paint" around bolt holes through 304 SS. The paint was used about 12 years ago. It asked for which of their products would have been used.</p> <p>Answer - They now have a wide variety of vinyl paints but for that long ago there are about three possibilities: 933-1, 936 and Rustbond 8. The Rustbond 8 is most likely since it does not need a primer coat; the other two usually do. He will send product data sheet on all three.</p> <p>The Rustbond 8 is a modified vinyl alkyl based material with good acid resistance.</p>
Action	
Copies To:	J. G. Leason, R. Thorne

**carboline**

## RUSTBOND 8 HB

350 HANLEY INDUSTRIAL COURT • ST. LOUIS, MO. 63144 • 314-644-1000

### SELECTION DATA

**GENERIC TYPE:** Modified vinyl-alkyd.

**GENERAL PROPERTIES:** Rustbond 8 HB is excellent as a primer for bare steel and a tie coat for the following generic coatings: vinyls, catalyzed epoxies, epoxy esters, chlorinated rubbers, alkyds, acrylics and acrylic latexes. Material dries quickly permitting rapid topcoating. Provides good weathering and corrosion resistance for a single package material.

**RECOMMENDED USES:** Developed specifically for use as a primer and universal tie coat for most generic topcoats. Rustbond 8 HB is an excellent shop primer. For maintenance, Rustbond 8 HB permits topcoating, thereby reducing the possibility of surface contamination. This product will find applications wherever an economical, fast drying primer requiring excellent topcoat compatibility is specified.

**NOT RECOMMENDED FOR:** Heavily rusted or pitted surfaces or immersion service.

**CHEMICAL RESISTANCE GUIDE:** (with suitable topcoat)

Exposure	Splash and Spillage	Fumes
Acids	Good	Good
Alkalies	Fair	Fair
Solvents	Fair	Good
Salt	Very Good	Very Good
Water	Very Good	Very Good

**TEMPERATURE RESISTANCE:**

Continuous: 160°F (71°C)  
Non-continuous: 200°F (93°C)

**FLEXIBILITY:** Excellent      **WEATHERING:** Very Good

**ABRASION RESISTANCE:** Good

**SUBSTRATE:** May be applied over properly prepared steel, aluminum or others as recommended.

**TOPCOAT REQUIRED\*:** May be topcoated with acrylics, chlorinated rubbers, vinyls, catalyzed epoxies, alkyds or others as recommended.

**COMPATIBILITY WITH OTHER COATINGS\*:** May be applied over tightly adhering vinyls, chlorinated rubbers, acrylics, alkyds, catalyzed epoxies or others as recommended. May be used over inorganic zinc primers for non-immersion, atmospheric exposures.

\*NOTE: A test patch is recommended to assure adhesion of Rustbond 8 HB over other coatings or the adhesion of topcoats to Rustbond 8 HB.

### SPECIFICATION DATA

**THEORETICAL SOLIDS CONTENT OF MIXED MATERIAL:**

By Volume

Rustbond 8 HB      42% ± 2%

**RECOMMENDED DRY FILM THICKNESS PER COAT:**  
2-3 mils (50-75 microns).

**THEORETICAL COVERAGE PER MIXED GALLON\*:**  
674 sq. ft. (16.8 sq. m/l @ 25 microns)  
269 sq. ft. at 2½ mils (6.5 sq. m/l @ 65 microns)

\*NOTE: Material losses during mixing and application will vary and must be taken into consideration when estimating job requirements.

**SHELF LIFE:** 12 months minimum.

**COLORS:** Red, Off-White, Gray.

**GLOSS:** Flat.

### ORDERING INFORMATION

Prices may be obtained from Carboline Sales Representative or Main Office. Terms — Net 30 days.

**SHIPPING WEIGHT:**

	1's	5's
Rustbond 8 HB	11 lbs. (5.0 kg)	55 lbs. (25.0 kg)
Polyclad Thinner	9 lbs. (4.1 kg)	45 lbs. (20.4 kg)
Carboline Thinner #25	9 lbs. (4.1 kg)	45 lbs. (20.4 kg)

**FLASH POINT:** (Pensky-Martens Closed Cup)

Rustbond 8 HB	52°F (11°C)
Polyclad Thinner	73°F (23°C)
Carboline Thinner #25	77°F (25°C)

Oct. 80 Replaces Mar. 78-N

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## APPLICATION INSTRUCTIONS

These instructions are not intended to show product recommendations for specific service. They are issued as an aid in determining correct surface preparation, mixing instructions, and application procedure. It is assumed that the proper product recommendations have been made. These instructions should be followed closely to obtain the maximum service from the materials.

**SURFACE PREPARATION:** Remove any oil or grease from surface to be coated with clean rags soaked in Carbo-line Thinner #2 or toluol.

**Uncoated Steel:** Dry abrasive blast to a Commercial Grade Finish in accordance with SSPC-SP6-63 to a degree of cleanliness in accordance with NACE #3 to obtain a 1/2 to 1-1/2 mil (12-40 microns) blast profile. Note: Power Tool Clean per SSPC-SP3-63 is acceptable.

For application over existing coating, the surface must be clean, dry and free of any contaminants.

**MIXING:** Mix to smooth consistency before thinning. Thin up to 25% with Polyclad Thinner if necessary. Use Carbo-line Thinner #25 for brushing or rolling or for temperatures above 85°F (29°C).

### APPLICATION TEMPERATURES:

	Material	Surfaces
Normal	60-90°F (16-32°C)	65-85°F (18-29°C)
Minimum	45°F (7°C)	35°F (2°C)
Maximum	100°F (38°C)	150°F (66°C)

	Ambient	Humidity
Normal	55-100°F (13-38°C)	10-85%
Minimum	40°F (4°C)	0%
Maximum	120°F (49°C)	95%

Special thinning and application techniques may be required above or below normal condition.

**SPRAY:** Use adequate air volume for correct operation.

Use a 50% overlap with each pass of the gun. On irregular surfaces, coat the edges first, making an extra pass later.

**NOTE:** The following equipment has been found suitable; however, equivalent equipment may be substituted.

**Conventional:** Use a 3/8" minimum I.D. material hose. Hold gun 8-10 inches from the surface and at a right angle to the surface.

Mfr. & Gun	Fluid Tip	Air Cap
Binks #18 or #62	66	66PB
DeVilbiss P-MBC or JGA	E	704
approx. 0.07" I.D.		

**Airless:** Use a 3/8" minimum I.D. material hose. Hold gun 12-14 inches from the surface and at a right angle to the surface.

Mfr. & Gun	Pump*
DeVilbiss JGB-507	QFA-514
Graco 205-591	President 30:1 or Bulldog 30:1
Binks Model 500	Mercury 5C

\*Teflon packings are recommended and available from pump manufacturer. Use a .018"-.022" tip with 2000 psi.

**BRUSH OR ROLLER:** Use natural bristle brush. Use full strokes; avoid rebrushing. Thin up to 25% in hot weather.

**DRYING TIMES:** 2-1/2 mils and 50% RH

Temperature	To Handle	To Topcoat
40°F (4°C)	6 hours	24 hours
50°F (10°C)	4 hours	16 hours
60°F (16°C)	2 hours	8 hours
75°F (24°C)	1 hour	4 hours
90°F (32°C)	30 minutes	2 hours

**CLEAN UP:** Use Carboline Thinner #2 or ketone solvent.

### STORAGE CONDITIONS:

Temperature: 40-110°F (4-43°C)  
Humidity: 0-100%

**CAUTION:** CONTAINS FLAMMABLE SOLVENTS. KEEP AWAY FROM SPARKS AND OPEN FLAMES. IN CONFINED AREAS WORKMEN MUST WEAR FRESH AIRLINE RESPIRATORS. HYPERSENSITIVE PERSONS SHOULD WEAR GLOVES OR USE PROTECTIVE CREAM. ALL ELECTRIC EQUIPMENT AND INSTALLATIONS SHOULD BE MADE AND GROUNDED IN ACCORDANCE WITH THE NATIONAL ELECTRICAL CODE. IN AREAS WHERE EXPLOSION HAZARDS EXIST, WORKMEN SHOULD BE REQUIRED TO USE NONFERROUS TOOLS AND TO WEAR CONDUCTIVE AND NONSPARKING SHOES.



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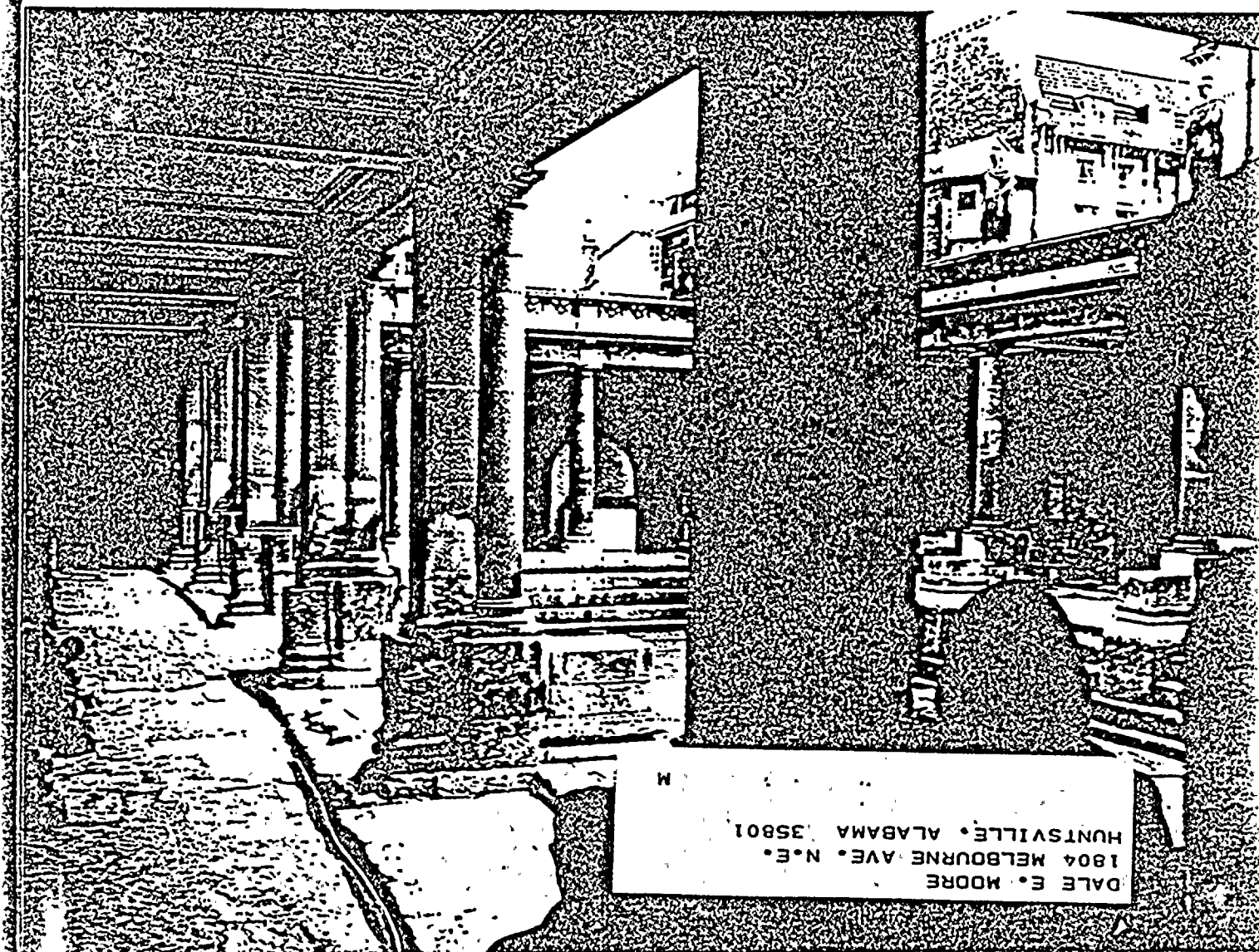
ATTACHMENT 4

# Materials Performance

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DALE E. MOORE  
1804 MELBOURNE AVE. N.E.  
HUNTSVILLE, ALABAMA 35801

## Spool Corrosion Tests in Wet Scrubber Systems\*

DAVID B. ANDERSON\*

*Data from field corrosion studies in seven wet scrubber systems are surveyed to assess environmental effects on alloy performance. Units studied include utility boiler flue gas desulfurization systems utilizing lime, limestone, double alkali and sodium sulfide as absorbents plus water scrubbers on refuse and sewage sludge incinerators. The data illustrate the severity of corrosion problems which can occur in the variety of environments produced by these complex wet chemical processes. Important considerations include pH, temperature, chlorides, absorbent oxidation stage, acid condensation, and alkaline scaling. Unprotected carbon steel consistently shows unacceptable corrosion resistance except in areas restricted to exposure to hot, dry flue gas. Stainless steels and more highly alloyed materials provide useful corrosion resistance but alloy selection must consider specific environmental conditions. Particularly corrosive environments are encountered in inlet prescrubbers and exit ducting subjected to acidic condensates. Corrosivity is often compounded by introduction of high chloride levels from fuel sources or use of closed loop water systems.*

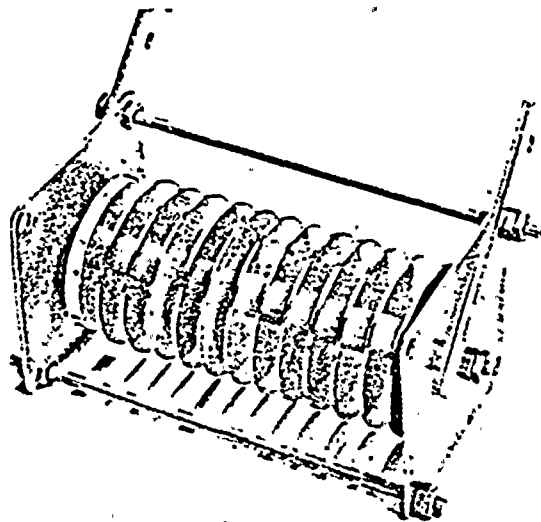


FIGURE 1 — Corrosion test spool.

### Introduction

WITH THE PASSAGE of strict environmental control regulations and concurrent expansion of coal usage, installation of fossil fired power plant FGD scrubber systems increased from essentially zero in 1970 to 55 units with a combined capacity of 18,000 MW by June, 1979. Capacity is expected to expand to at least 70,000 MW over the next decade.

Wet scrubbing processes, commonly utilizing lime or limestone slurries to chemically capture  $SO_2$ , rapidly achieved industry dominance. Materials engineers recognized prospects for severe corrosion problems introduced by a complicated wet chemical process with variable, and often unpredictable complex conditions of pH, temperature, chlorides, oxidation stage, acid condensation, and alkaline scaling. Initial designs were hampered by limited guidelines for selection of materials with assurance of optimum durability.

Extensive field exposures have been conducted over the past six years utilizing the established Inco corrosion test spool program.<sup>1</sup> Results have provided interesting insight into the corrosion characteristics of a wide range of alloys, the important corrosion mechanisms involved, and the effects of specific operating variables.

### Field Corrosion Test Program

A typical corrosion test spool utilized for this program is shown in Figure 1. Spools were assembled and processed

within the guidelines outlined in ASTM Standard Recommended Practices G4-74 and G1-79. Wrought alloy samples were prepared from 1.0 to 1.5 mm thick cold rolled strip while cast alloy samples were machined from 50 mm diameter cast bars. Samples were exposed without applied stresses or welds. Tight crevices were provided, however, by the small Teflon<sup>(1)</sup> insulating spacers.

Ideally, corrosion test specimens should be exposed for three to twelve months under relatively steady state conditions with minimum process upsets. Unfortunately, this ideal is not in harmony with typical pilot plant operation. Most of the case histories cited in this paper meet the exposure period requirements. However, since most of the systems studied were in early development stages, steady state operating conditions were the exception rather than the rule.

### Case Histories

Extensive corrosion test spool exposures were conducted in seven wet scrubber installations to be described. In many cases, multiple spools were exposed, each including samples of a wide range of corrosion resistant alloys plus mild steel. Rather than provide a detailed review of all of the data generated, the results presented are limited to alloys selected to illustrate a range of corrosion resistance and to isolate environmental effects for a wide range of exposure conditions. Alloy compositions are given in Table 1.

#### Case 1—Limestone FGD System

A five month study was conducted in a double loop design limestone scrubber with test spools exposed in the areas

\*Presented during Corrosion/81 (Paper 127), April, 1981, Toronto, Ontario.

\*The International Nickel Company, Inc. New York, New York.

<sup>(1)</sup>Trademark of E. I. Du Pont de Nemours & Co., Inc.

TABLE 1 — Nominal Composition of Test Materials

	Percent							
	Ni	Fe	Cr	Mo	Cu	C	Mn	Other
AISI 1010 steel	—	bal.	—	—	—	0.10	0.40	—
HSLA steel	0.4	bal.	0.9	—	0.4	0.08	0.3	0.05 Si
AISI 304 stainless steel	9.5	bal.	18.5	—	—	0.08 max.	1.5	—
AISI 316 stainless steel	13.0	bal.	17.0	2.25	—	0.08 max.	1.7	—
AISI 317 stainless steel	14.0	bal.	19.0	3.25	—	0.08 max.	2.0	—
Alloy G	45.0	20.0	22.0	6.5	2.0	0.03	1.3	2.1 Cb + Ta
Alloy 625	60.0	5.0	21.5	9.0	—	0.1 max.	—	3.7 Cb + Ta
Alloy C-276	54.0	5.0	15.5	16.0	—	0.02 max.	—	4.0 W

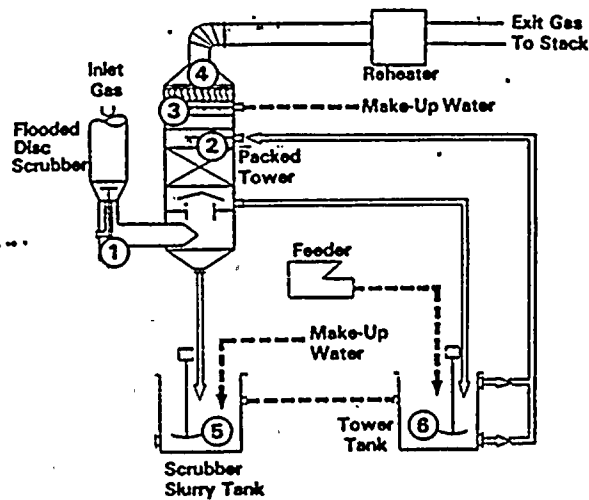


FIGURE 2 — Limestone FGD system.

shown in Figure 2. This design confines the recirculating chloride containing scrubbing solution to the first loop, i.e., the flooded disc scrubber and the absorber area below the packed tower. Corrosion data for AISI 1010 steel and three alloys are given in Table 2.

Average corrosion rates for the carbon steel samples were an unacceptable 0.20 to 0.58 mm/y (8 to 23 mpy). AISI 304 stainless steel also exhibited limited corrosion resistance, particularly in creviced areas. The single exception was the hot gas outlet, which was presumably above the dew point. More highly alloyed AISI 316 stainless steel provided a marked improvement in corrosion resistance in all areas, but only alloy G provided virtual corrosion immunity. It is of significance to note that with the relatively low chloride levels in this unit, the two stainless steel alloys showed little sensitivity to the environmental differences in the scrubber and absorber tower.

#### Case 2—Lime FGD System

A three month test evaluation was conducted in the absorber section in a double marble bed lime system with exposures in the areas indicated in Figure 3. Corrosion data are given in Table 3. As in Case 1, carbon steel and AISI 304 stainless steel exhibited limited corrosion resistance except in the exit gas above the mist eliminator where no condensation was

TABLE 2 — Limestone FGD Scrubber Absorber

158 days, pH = 5-7 chlorides: 2250 in scrubber 100-850 in absorber				
Exposure Area	Max. Pitting/Crevice Corrosion—mm			Average Corrosion Rate For 1010 Steel mm/y
	304 Stainless Steel	316 Stainless Steel	Alloy G	
Base of scrubber (1)	0.66 (26.0 mils)	0.05	0	0.34
Absorber tower —below nozzles (2)	0.79 (31.1 mils)	0.18	0	0.25
Absorber tower —mist eliminators (3)	0.28	0.15	0	0.20
Absorber tower —gas outlet (4)	0	0	0	0.26
Scrubber slurry tank (5)	0.25	0.05	0	0.58
Absorber slurry tank (6)	0.18	0.03	0	0.33

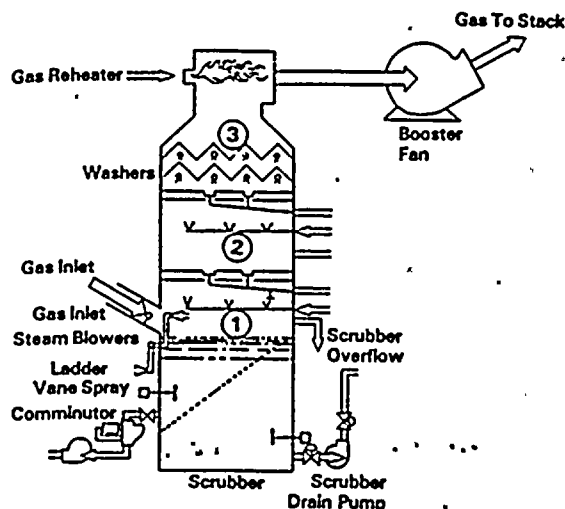


FIGURE 3 — Lime FGD scrubber.

TABLE 3 — Lime FGD Scrubber

93 days, 400-600 ppm Cl, Shower Water pH = 4.9			
Max. Pitting Corrosion—mm			
AISI Alloy	Shower Spray (1)	Above Marble Bed (2)	Above Mist Eliminator (3)
304	0.28	0.18	0
316	<.03	0.13	0
317	0	0	0
Average corrosion rate (mm/y) —1010 steel	1.60	0.74	0.13

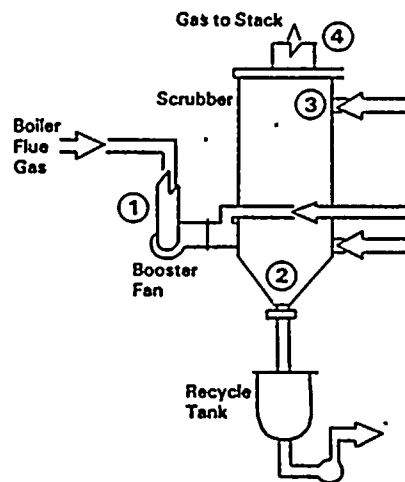


FIGURE 4 — Double alkali FGD system, dilute mode.

evident. AISI 316 stainless steel (2.3% Mo) provided greatly improved corrosion resistance, while AISI 317 stainless steel (3.2% Mo) was unaffected over this relatively short exposure period.

#### Case 3—Dilute Mode Double Alkali System

A typical dilute mode double alkali system recycles highly oxidized regenerated liquor and can be expected to achieve moderate chloride concentrations. Corrosion test locations in a short term exposure program of this type are shown in Figure 4 and corrosion data are given in Table 4. The variable corrosivity of the process conditions in the different areas is evidenced by corrosion rate of carbon steel, ranging from 0.35 mm/y (14 mpy) in the dry inlet gas to 3.3 mm/y (130 mpy) in the moist outlet gas. AISI 304 stainless steel again exhibited limited corrosion resistance in wet sections. AISI 316 stainless provided some improvement except in the aggressive quench area where maximum chloride concentrations are expected.

#### Case 4—Concentrated Mode Double Alkali System

Exposures in a concentrated mode system were limited to two areas shown in Figure 5. Corrosion data in Table 5 show

TABLE 4 — Double Alkali FGD System—Dilute Mode

31 Days, Slurry pH = 10-13, 1000 ppm Cl				
Max. Pitting Corrosion—mm				
Alloy	Flue Gas Inlet (1)	Quench Section (2)	Absorber Tray (3)	Discharge Duct (4)
AISI 304	0	0.10	0.20	0.28
AISI 316	0	0.10	0	0.05
Alloy G	0	0	0	0
Average corrosion rate (mm/y) AISI—1010 steel	0.35	0.53	0.39	3.31

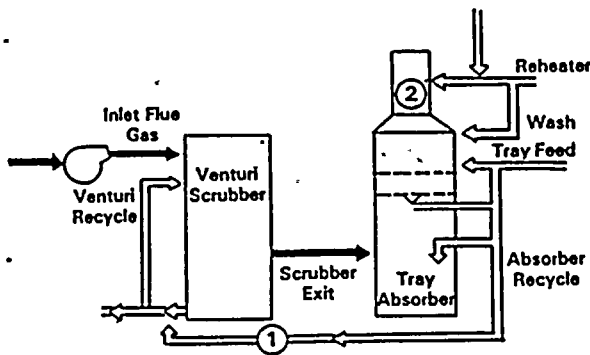


FIGURE 5 — Double alkali FGD system, concentrated mode.

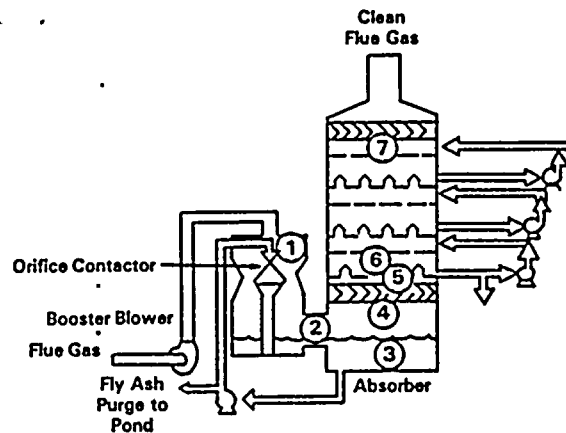


FIGURE 6 — Sodium sulfite SO<sub>2</sub> recovery process.

TABLE 5 — Double Alkali FGD System—Concentrated Mode

4 months, pH = 4-5, 1400 ppm Chlorides		
Max. Pitting/Crevice Corrosion—mm		
Alloy	Absorber Overflow (1)	Above Mist Eliminator (2)
AISI 304	0.20	1.2
AISI 316	0	0.9
AISI 317	0	0.6
Alloy 825	0	0.7
Alloy G	0	0.8
Alloy 625	0	0
Alloy C-276	0	0

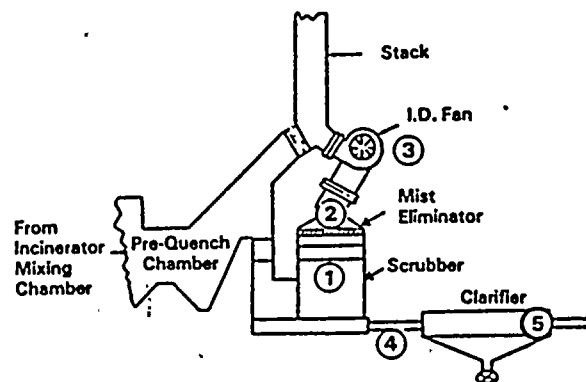


FIGURE 7 — Refuse incinerator scrubber.

minimal attack in the absorber overflow piping system. However, the exposure in the outlet duct above the mist eliminator provides an example of the severity of corrosion which can occur in sulfurous and sulfuric acid condensates. Only nickel base alloys 625 and C-276 were resistant to attack in this area.

#### Case 5—Sodium Sulfite SO<sub>2</sub> Recovery Process

An extensive exposure program in the scrubber/absorber areas of a sodium sulfite SO<sub>2</sub> recovery system is outlined in Figure 6 with corrosion data summarized in Table 6. The com-

bination of high temperature, uncontrolled pH, abrasive flyash, and heavy solids buildup in the venturi scrubber entrance resulted in severe corrosion of all of the alloys evaluated. Reduction in temperature and flyash abrasion significantly reduced corrosion at the venturi exit and absorber tower bottom although clearly, high alloys are required to cope with the low pH environment containing 1200 ppm chloride. Condensate conditions above the mist eliminator again provided aggressive conditions while exposure to scrubber solution sprays and the scrubbed flue gas caused minimal corrosion.

TABLE 6 — Sodium Sulfite SO<sub>2</sub> Recovery Process

3 Months, 1200 ppm Cl, pH = 1.5-2							
Max. Pitting/Crevice Corrosion—mm							
Alloy	Venturi Entrance (1)	Venturi Exit (2)	Tower Bottom (3)	Mist Eliminator Below (4)	Mist Eliminator Above (5)	Absorber Solution (6)	Scrubber Flue Gas (7)
AISI 316	0.94(p)	0.20	0.46	0.18	0.94(p)	0	0
AISI 317	0.36	0.20	0.33	0.20	0.38	0	0
Alloy G	0.18	0.10	0	0	0	<0.03	0
Alloy 625	0.30	0	0	0	<0.03	0	0

TABLE 7 — Refuse Incinerator Scrubber

161 Day Exposure					
Max. Pitting/Crevice Attack—mm					
Alloy	Scrubber Inlet (1)	Scrubber Roof (2)	Induced Draft Fan (3)	Flume (4)	Clarifier (5)
AISI 304	0.43	1.40(p) (5.5 mils)	0.51	0.25	0.10
AISI 316	0.13	0.69	0.20	0.15	0.10
Alloy G	0	0.33	0.30	0	0
Alloy 625	0	0.28	0.15	0	0
Average Corrosion rate—mm/yr					
AISI 1010 steel	>1.3	0.9	1.0	>1.3	0.4
HSLA steel	>1.4	0.8	0.9	>1.4	0.2

(p) = perforated

TABLE 8 — Sewage Incinerator Scrubber

15 Month Exposure				
Max. Pitting/Crevice Attack—mm				
Alloy	Gas Inlet Baffle (1)	Scrubber Liquid (2)	Impingement Plate (3)	Exhaust Stack (4)
AISI 304	0	0.30	0.28	0.08
AISI 316	0	0.03	0.46	0
AISI 317	0	2	0.51	0
Alloy G	0	0	0	0
Average corrosion rate—mm/yr —1010 steel	0.07	—	0.02	0.13

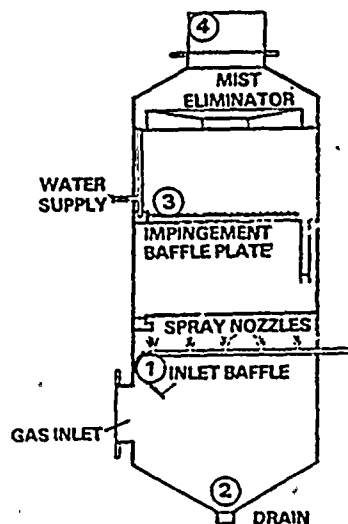


FIGURE 8 — Sewage Incinerator scrubber.

#### Case 6—Refuse Incinerator Scrubber

Day-to-day variations in refuse create equally variable environmental conditions in refuse incinerator off-gas scrubbers. Typically, the gases contain significant levels of chlorides from the burning of chlorinated plastics. Use of fresh water as a scrubbing medium produces unbuffered HCl. Corrosion test locations in a municipal system are identified in Figure 7 and corrosion data are given in Table 7. Carbon and low alloy steels are clearly inadequate for this application with the possible exception of the clarifier tank. Condensate carryover from the mist eliminator created a severe environment at the scrubber roof and the induced fan area with localized corrosion developing to some extent with all of the alloys evaluated. The corrosivity is, in part, aggravated by the use of a recirculating water system in this plant which does not allow for dilution of neutralization of the acid chlorides. The importance of this is evidenced by the significantly reduced level of corrosion observed in a comparison incinerator operated with a once through water system.

#### Case 7—Sewage Sludge Incinerator

Chlorides in sewage sludge incinerators are introduced by the scrubbing water and generally do not reach the high levels developed in refuse incinerator systems. The corrosion

data in Table 8 developed from the exposures detailed in Figure 8 illustrate the reduced severity of corrosion in contrast to Case 6. Heavy deposits accumulated on the samples exposed in the impingement baffle plate area, the one area where the stainless steels developed significant pitting. These deposits, in turn, provided a mechanism for crevice formation with further chloride concentration. The deleterious effect of the deposits on the stainless steels is in contrast to the apparent protective effect on carbon steel.

### Summary

The exposure of corrosion test spools in operating wet scrubber systems has proven to be a useful method for evalu-

ating environmental effects and for assessing relative corrosion resistance of candidate materials of construction. The results of exposures in systems utilizing alkaline slurries and water as scrubbing media demonstrate the limited usefulness of unprotected carbon steel. Corrosion problems associated with deposit formation, wet flyash abrasion, unbuffered acidic condensates, and excessive chloride concentration are common to most systems and must be considered when selecting materials of construction with promise of optimum durability.

### References

1. L. W. Gleekman. ASTM STP 534, p. 167-169 (1973).

### CORROSION/81 Symposia Proceedings Available

For the first time proceedings of symposia presented at a NACE Annual Conference will be made available in bound form. The 36 symposia will be grouped by subject interest in 12 volumes. Each volume will contain an introduction by the sponsoring Technical

Group Committee. The volumes will be bound in soft cover form and vary in size depending on the number of symposia on the subject. They may be ordered as follows:

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## Effect of Acids on the Stress Corrosion Cracking of Stainless Materials in Dilute Chloride Solutions\*

A. I. ASPHAHANI

Stellite Division, Cabot Corporation, Kokomo, Indiana

The chloride stress cracking of stainless steels (304, 304L, 316, 316L) is shown to occur in dilute 0.8 to 4% sodium chloride solutions containing 0.2 to 1%  $H_3PO_4$  or 0.5%  $CH_3COOH$ . While more localized attacks (pitting-crevice corrosion) are observed in the chloride solution containing acetic acid, the 0.2% phosphoric acid addition to 0.8% NaCl is sufficient to induce stress cracking of the austenitic stainless steels within less than 10 days of exposure at 141 C. The higher nickel content austenitic stainless alloys (20Cb-3, 825, 20-Mod) are more resistant to the chloride stress cracking. However, some pitting and crevice corrosion attack is observed on these alloys, except for 20-Mod. The high performance nickel base alloys (G, C-276) show excellent resistance to chloride stress cracking and to localized corrosive attack. The susceptibility of the stainless steels to the observed stress cracking is related to the acidity of the dilute chloride solutions, and is explained using the concept of the critical potential for stress corrosion cracking.

data have been reported from SCC tests in dilute chloride environments at 300 C,<sup>12</sup> in chloride solutions containing  $H_2S$ ,<sup>13</sup> in brines simulating geothermal environments,<sup>14</sup> in pure or inhibited hydrochloric acid at room temperature,<sup>15,16</sup> and in refrigerated HCl solution.<sup>17</sup>

Still, almost no data exist on the chloride stress cracking of austenitic stainless steels in dilute chloride environments containing traces of acids, specifically less than 2% phosphoric acid. These environments appear of interest in some CPI applications dealing with phosphate chemicals and to the food processing industries using phosphate compounds as preservatives or mixtures containing table salt and weak organic acids, where AISI 304 and 316L stainless steels have already experienced SCC in field service.<sup>7,18,19</sup>

It is the purpose of this study to present data on the SCC of several stainless materials in dilute chloride solutions containing small amounts of different acids. The effects of temperature, acid additions, and galvanic coupling are shown. Also, the resistance and/or susceptibility of various alloys are established and discussed.

TABLE 1 — Nominal Composition of Alloys Tested (Wt%)

Alloys	Fe	Ni	Cr	Mo	Mn	Si	Cu	C
AISI 304	Bal	9	19	—	2 <sup>(1)</sup>	1 <sup>(1)</sup>	—	0.05
AISI 304L	Bal	9	19	—	2 <sup>(1)</sup>	1 <sup>(1)</sup>	—	0.03 <sup>(1)</sup>
AISI 316	Bal	12	17	2.5	2 <sup>(1)</sup>	1 <sup>(1)</sup>	—	0.05
AISI 316L	Bal	12	17	2.5	2 <sup>(1)</sup>	1 <sup>(1)</sup>	—	0.03 <sup>(1)</sup>
Carpenter 20Cb-3 <sup>(2)</sup>	Bal	33	20	2.5	2 <sup>(1)</sup>	1 <sup>(1)</sup>	3	0.04
Incoloy 825 <sup>(3)</sup>	30	Bal	21	3	1 <sup>(1)</sup>	0.5 <sup>(1)</sup>	2	0.04
Haynes alloy No. 20-Mod <sup>(4)</sup>	Bal	26	22	5	2.5 <sup>(1)</sup>	1 <sup>(1)</sup>	—	0.05 <sup>(1)</sup>
Hastelloy alloy G <sup>(4)</sup>	20	Bal	22	7	1.5	1 <sup>(1)</sup>	2	0.05 <sup>(1)</sup>
Hastelloy alloy C-276 <sup>(4)</sup>	5	Bal	16	16	1 <sup>(1)</sup>	0.8 <sup>(1)</sup>	—	0.02 <sup>(1)</sup>

(1) Maximum.

(2) Registered trademark of Carpenter Technology Corporation.

(3) Registered trademark of International Nickel Company, Inc.

(4) Registered trademark of Cabot Corporation.

### Introduction

CHLORIDE STRESS CRACKING of austenitic stainless steels has always been a problem limiting the safe use of these alloys in the various chemical processing industries (CPI). This subject of stress corrosion cracking (SCC) in chloride environments is by no means a neglected one for researchers. However, most of the studies have been limited to tests in hot, concentrated chloride solutions, specifically the boiling 42 to 45%  $MgCl_2$  solutions.

A limited amount of data exists on the SCC of stainless steels in other aqueous solutions. The stress cracking in sulfuric acid containing chloride ions has been observed,<sup>1</sup> investigated,<sup>2,3</sup> and commented on.<sup>4</sup> Also, the effects of various cations (e.g.,  $Ba^{++}$ ,  $Ca^{++}$ ,  $Cr^{+++}$ ,  $Fe^{+++}$ ,  $Hg^{++}$ ,  $Li^+$ ,  $Mg^{++}$ ,  $Ni^{++}$ ,  $Zn^{++}$ ) have been mentioned,<sup>5</sup> examined,<sup>6,7</sup> and summarized.<sup>10,11</sup> Furthermore,

\*Presented during Corrosion/79 (Paper 42), March, 1979, Atlanta, Georgia.

### Experimental Procedure

#### Materials

The alloys examined included several stainless steels and high performance nickel base alloys. The nominal chemical compositions and the registered trademarks are presented in Table 1.

#### Specimens

The SCC tests were conducted on U-bend specimens  $\approx 133 \times 13 \times 3$  mm (5.25 x 0.5 x 0.125 inch). Each specimen was deformed around a 25 mm (1 inch) mandrel. The specimen's ends were maintained in a parallel position with a bolt and a nut made out of Hastelloy alloy C-276. Teflon inserts were used to insulate the bolt/nut from the specimen. The specimen was further stressed by straining its ends (tightening the nut) to a final span of 12 mm (1/2 inch). The imposed stress depended on the yield strength of the material, and no effort was made to calculate the exact value of the



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**SELECTION DATA****GENERIC TYPE:** Modified vinyl-alkyd.

**GENERAL PROPERTIES:** Rustbond 8 HB is excellent as a primer for bare steel and a tie coat for the following generic coatings: vinyls, catalyzed epoxies, epoxy esters, chlorinated rubbers, alkyds, acrylics and acrylic latexes. Material dries quickly permitting rapid topcoating. Provides good weathering and corrosion resistance for a single package material.

**RECOMMENDED USES:** Developed specifically for use as a primer and universal tie coat for most generic topcoats. Rustbond 8 HB is an excellent shop primer. For maintenance, Rustbond 8 HB permits topcoating, thereby reducing the possibility of surface contamination. This product will find applications wherever an economical, fast drying primer requiring excellent topcoat compatibility is specified.

**NOT RECOMMENDED FOR:** Heavily rusted or pitted surfaces or immersion service.

**CHEMICAL RESISTANCE GUIDE:** (with suitable topcoat)

Exposure	Splash and Spillage	Fumes
Acids	Good	Good
Alkalies	Fair	Fair
Solvents	Fair	Good
Salt	Very Good	Very Good
Water	Very Good	Very Good

**TEMPERATURE RESISTANCE:**

Continuous: 160°F (71°C)

Non-continuous: 200°F (93°C)

**FLEXIBILITY:** Excellent**WEATHERING:** Very Good**ABRASION RESISTANCE:** Good

**SUBSTRATE:** May be applied over properly prepared steel, aluminum or others as recommended.

**TOPCOAT REQUIRED\*:** May be topcoated with acrylics, chlorinated rubbers, vinyls, catalyzed epoxies, alkyds or others as recommended.

**COMPATIBILITY WITH OTHER COATINGS\*:** May be applied over tightly adhering vinyls, chlorinated rubbers, acrylics, alkyds, catalyzed epoxies or others as recommended. May be used over inorganic zinc primers for non-immersion, atmospheric exposures.

\*NOTE: A test patch is recommended to assure adhesion of Rustbond 8 HB over other coatings or the adhesion of topcoats to Rustbond 8 HB.

**SPECIFICATION DATA****THEORETICAL SOLIDS CONTENT OF MIXED MATERIAL:**By Volume

Rustbond 8 HB

42% ± 2%

**RECOMMENDED DRY FILM THICKNESS PER COAT:**  
2-3 mils (50-75 microns).

**THEORETICAL COVERAGE PER MIXED GALLON\*:**  
674 sq. ft. (16.8 sq. m/l @ 25 microns)  
269 sq. ft. at 2½ mils (6.5 sq. m/l @ 65 microns)

\*NOTE: Material losses during mixing and application will vary and must be taken into consideration when estimating job requirements.

**SHELF LIFE:** 12 months minimum.**COLORS:** Red, Off-White, Gray.**GLOSS:** Flat.**ORDERING INFORMATION**

Prices may be obtained from Carboline Sales Representative or Main Office. Terms — Net 30 days.

**SHIPPING WEIGHT:**

	1's	5's
Rustbond 8 HB	11 lbs. (5.0 kg)	55 lbs. (25.0 kg)
Polyclad Thinner	9 lbs. (4.1 kg)	45 lbs. (20.4 kg)
Carboline Thinner #25	9 lbs. (4.1 kg)	45 lbs. (20.4 kg)

**FLASH POINT:** (Pensky-Martens Closed Cup)

Rustbond 8 HB 52°F (11°C)

Polyclad Thinner 73°F (23°C)

Carboline Thinner #25 77°F (25°C)

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## APPLICATION INSTRUCTIONS

These instructions are not intended to show product recommendations for specific service. They are issued as an aid in determining correct surface preparation, mixing instructions, and application procedure. It is assumed that the proper product recommendations have been made. These instructions should be followed closely to obtain the maximum service from the materials.

**SURFACE PREPARATION:** Remove any oil or grease from surface to be coated with clean rags soaked in Carbo-line Thinner #2 or toluol.

**Uncoated Steel:** Dry abrasive blast to a Commercial Grade Finish in accordance with SSPC-SP6-63 to a degree of cleanliness in accordance with NACE #3 to obtain a 1/2 to 1-1/2 mil (12-40 microns) blast profile. Note: Power Tool Clean per SSPC-SP3-63 is acceptable.

For application over existing coating, the surface must be clean, dry and free of any contaminants.

**MIXING:** Mix to smooth consistency before thinning. Thin up to 25% with Polyclad Thinner if necessary. Use Carbo-line Thinner #25 for brushing or rolling or for temperatures above 85°F (29°C).

### APPLICATION TEMPERATURES:

	Material	Surfaces
Normal	60-90°F (16-32°C)	65-85°F (18-29°C)
Minimum	45°F (7°C)	35°F (2°C)
Maximum	100°F (38°C)	150°F (66°C)
	Ambient	Humidity
Normal	55-100°F (13-38°C)	10-85%
Minimum	40°F (4°C)	0%
Maximum	120°F (49°C)	95%

Special thinning and application techniques may be required above or below normal condition.

**SPRAY:** Use adequate air volume for correct operation.

Use a 50% overlap with each pass of the gun. On irregular surfaces, coat the edges first, making an extra pass later.

**NOTE:** The following equipment has been found suitable; however, equivalent equipment may be substituted.

**Conventional:** Use a 3/8" minimum I.D. material hose. Hold gun 8-10 inches from the surface and at a right angle to the surface.

Mfr. & Gun	Fluid Tip	Air Cap
Binks #18 or #62	66	66PB
DeVilbiss P-MBC or JGA	E	704
approx. 0.07" I.D.		

**Airless:** Use a 3/8" minimum I.D. material hose. Hold gun 12-14 inches from the surface and at a right angle to the surface.

Mfr. & Gun	Pump*
DeVilbiss JGB-507	QFA-514
Graco 205-591	President 30:1 or Bulldog 30:1
Binks Model 500	Mercury 5C

\*Teflon packings are recommended and available from pump manufacturer. Use a .018"-.022" tip with 2000 psi.

**BRUSH OR ROLLER:** Use natural bristle brush. Use full strokes; avoid rebrushing. Thin up to 25% in hot weather.

**DRYING TIMES:** 2-1/2 mils and 50% RH

Temperature	To Handle	To Topcoat
40°F (4°C)	6 hours	24 hours
50°F (10°C)	4 hours	16 hours
60°F (16°C)	2 hours	8 hours
75°F (24°C)	1 hour	4 hours
90°F (32°C)	30 minutes	2 hours

**CLEAN UP:** Use Carbo-line Thinner #2 or ketone solvent.

### STORAGE CONDITIONS:

Temperature: 40-110°F (4-43°C)  
Humidity: 0-100%

**CAUTION: CONTAINS FLAMMABLE SOLVENTS. KEEP AWAY FROM SPARKS AND OPEN FLAMES. IN CONFINED AREAS WORKMEN MUST WEAR FRESH AIRLINE RESPIRATORS. HYPERSENSITIVE PERSONS SHOULD WEAR GLOVES OR USE PROTECTIVE CREAM. ALL ELECTRIC EQUIPMENT AND INSTALLATIONS SHOULD BE MADE AND GROUNDED IN ACCORDANCE WITH THE NATIONAL ELECTRICAL CODE. IN AREAS WHERE EXPLOSION HAZARDS EXIST, WORKMEN SHOULD BE REQUIRED TO USE NONFERROUS TOOLS AND TO WEAR CONDUCTIVE AND NONSPARKING SHOES.**

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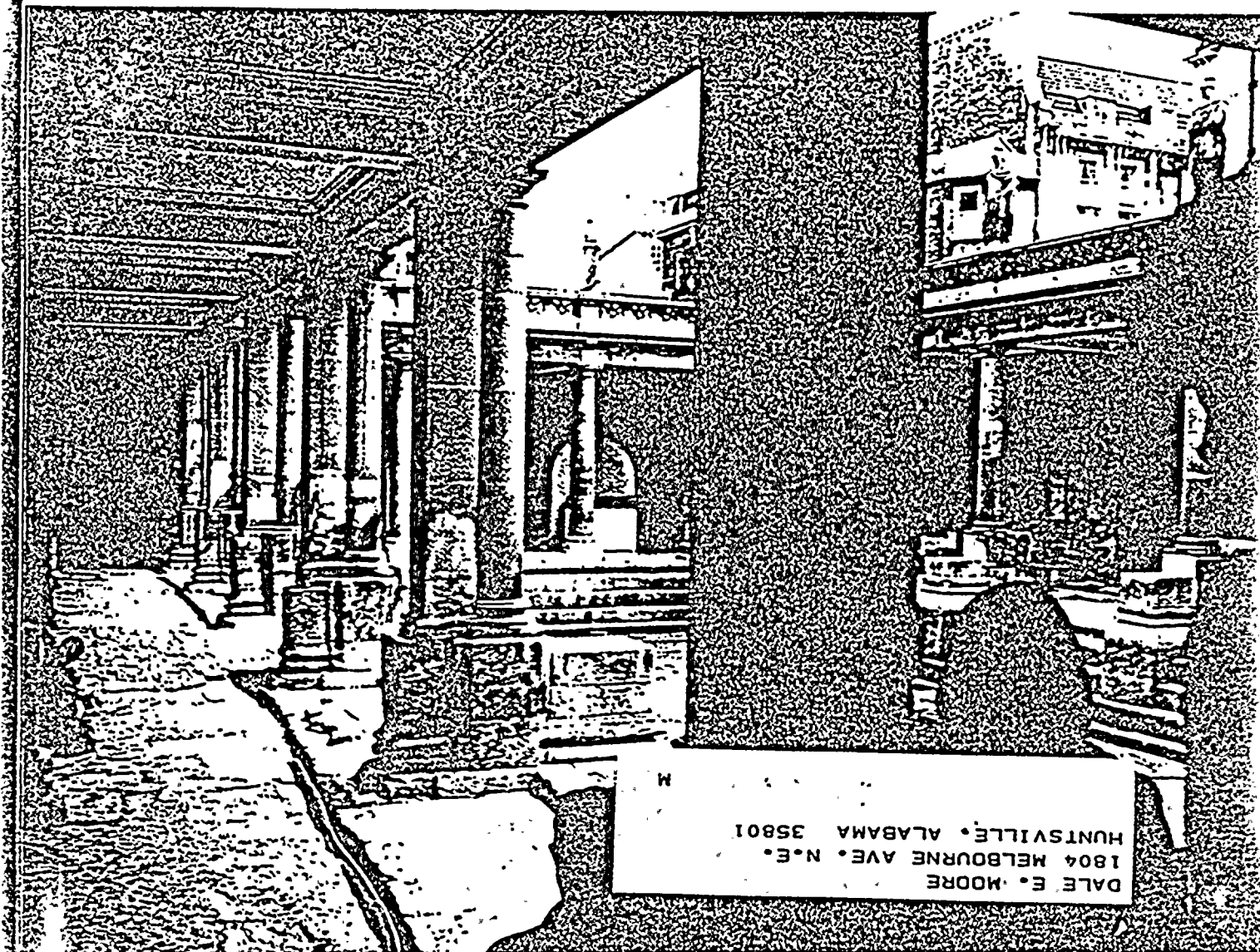


# Materials Performance

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DALE E. MOORE  
1804 MELBOURNE AVE. N.E.  
HUNTSVILLE, ALABAMA 35801

## Spool Corrosion Tests in Wet Scrubber Systems\*

DAVID B. ANDERSON\*

*Data from field corrosion studies in seven wet scrubber systems are surveyed to assess environmental effects on alloy performance. Units studied include utility boiler flue gas desulfurization systems utilizing lime, limestone, double alkali and sodium sulfide as absorbents plus water scrubbers on refuse and sewage sludge incinerators. The data illustrate the severity of corrosion problems which can occur in the variety of environments produced by these complex wet chemical processes. Important considerations include pH, temperature, chlorides, absorbent oxidation stage, acid condensation, and alkaline scaling. Unprotected carbon steel consistently shows unacceptable corrosion resistance except in areas restricted to exposure to hot, dry flue gas. Stainless steels and more highly alloyed materials provide useful corrosion resistance but alloy selection must consider specific environmental conditions. Particularly corrosive environments are encountered in inlet pre-scrubbers and exit ducting subjected to acidic condensates. Corrosivity is often compounded by introduction of high chloride levels from fuel sources or use of closed loop water systems.*

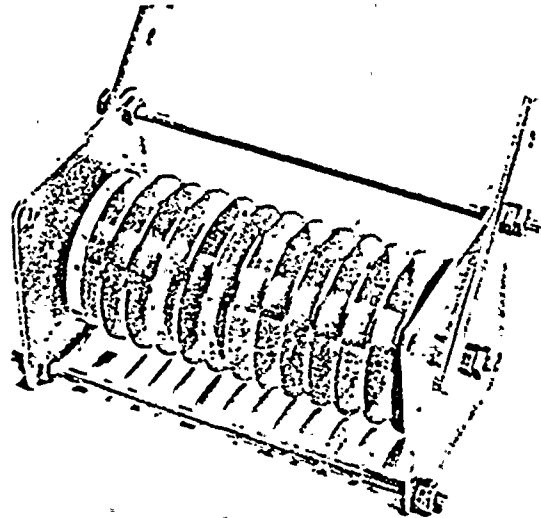


FIGURE 1 — Corrosion test spool.

### Introduction

WITH THE PASSAGE of strict environmental control regulations and concurrent expansion of coal usage, installation of fossil fired power plant FGD scrubber systems increased from essentially zero in 1970 to 55 units with a combined capacity of 18,000 MW by June, 1979. Capacity is expected to expand to at least 70,000 MW over the next decade.

Wet scrubbing processes, commonly utilizing lime or limestone slurries to chemically capture  $\text{SO}_2$ , rapidly achieved industry dominance. Materials engineers recognized prospects for severe corrosion problems introduced by a complicated wet chemical process with variable, and often unpredictable complex conditions of pH, temperature, chlorides, oxidation stage, acid condensation, and alkaline scaling. Initial designs were hampered by limited guidelines for selection of materials with assurance of optimum durability.

Extensive field exposures have been conducted over the past six years utilizing the established Inco corrosion test spool program.<sup>1</sup> Results have provided interesting insight into the corrosion characteristics of a wide range of alloys, the important corrosion mechanisms involved, and the effects of specific operating variables.

### Field Corrosion Test Program

A typical corrosion test spool utilized for this program is shown in Figure 1. Spools were assembled and processed

within the guidelines outlined in ASTM Standard Recommended Practices G4-74 and G1-79. Wrought alloy samples were prepared from 1.0 to 1.5 mm thick cold rolled strip while cast alloy samples were machined from 50 mm diameter cast bars. Samples were exposed without applied stresses or welds. Tight crevices were provided, however, by the small Teflon<sup>(1)</sup> insulating spacers.

Ideally, corrosion test specimens should be exposed for three to twelve months under relatively steady state conditions with minimum process upsets. Unfortunately, this ideal is not in harmony with typical pilot plant operation. Most of the case histories cited in this paper meet the exposure period requirements. However, since most of the systems studied were in early development stages, steady state operating conditions were the exception rather than the rule.

### Case Histories

Extensive corrosion test spool exposures were conducted in seven wet scrubber installations to be described. In many cases, multiple spools were exposed, each including samples of a wide range of corrosion resistant alloys plus mild steel. Rather than provide a detailed review of all of the data generated, the results presented are limited to alloys selected to illustrate a range of corrosion resistance and to isolate environmental effects for a wide range of exposure conditions. Alloy compositions are given in Table 1.

### Case 1—Limestone FGD System

A live month study was conducted in a double loop design limestone scrubber with test spools exposed in the areas

\*Presented during Corrosion/81 (Paper 127), April, 1981, Toronto, Ontario.

\*The International Nickel Company, Inc. New York, New York.

<sup>(1)</sup>Trademark of E. I. Du Pont de Nemours & Co., Inc.

TABLE 1 — Nominal Composition of Test Materials

	Percent							
	Ni	Fe	Cr	Mo	Cu	C	Mn	Other
AISI 1010 steel	—	bal.	—	—	—	0.10	0.40	—
HSLA steel	0.4	bal.	0.9	—	0.4	0.08	0.3	0.05 Si
AISI 304 stainless steel	9.5	bal.	18.5	—	—	0.08 max.	1.5	—
AISI 316 stainless steel	13.0	bal.	17.0	2.25	—	0.08 max.	1.7	—
AISI 317 stainless steel	14.0	bal.	19.0	3.25	—	0.08 max.	2.0	—
Alloy G	45.0	20.0	22.0	6.5	2.0	0.03	1.3	2.1 Cb + Ta
Alloy 625	60.0	5.0	21.5	9.0	—	0.1 max.	—	3.7 Cb + Ta
Alloy C-276	54.0	5.0	15.5	16.0	—	0.02 max.	—	4.0 W

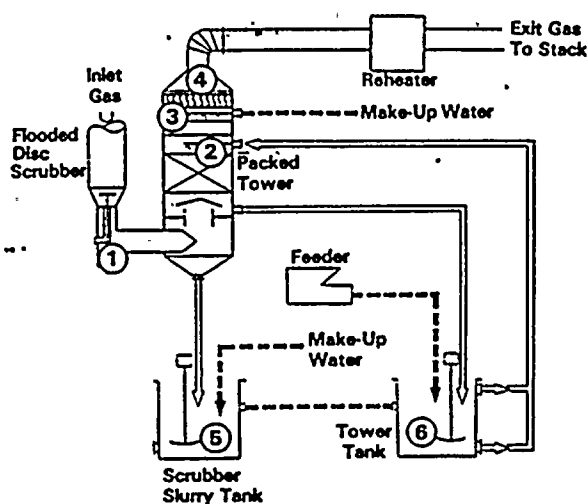


FIGURE 2 — Limestone FGD system.

shown in Figure 2. This design confines the recirculating chloride containing scrubbing solution to the first loop, i.e., the flooded disc scrubber and the absorber area below the packed tower. Corrosion data for AISI 1010 steel and three alloys are given in Table 2.

Average corrosion rates for the carbon steel samples were an unacceptable 0.20 to 0.58 mm/y (8 to 23 mpy). AISI 304 stainless steel also exhibited limited corrosion resistance, particularly in creviced areas. The single exception was the hot gas outlet, which was presumably above the dew point. More highly alloyed AISI 316 stainless steel provided a marked improvement in corrosion resistance in all areas, but only alloy G provided virtual corrosion immunity. It is of significance to note that with the relatively low chloride levels in this unit, the two stainless steel alloys showed little sensitivity to the environmental differences in the scrubber and absorber tower.

#### Case 2—Lime FGD System

A three month test evaluation was conducted in the absorber section in a double marble bed lime system with exposures in the areas indicated in Figure 3. Corrosion data are given in Table 3. As in Case 1, carbon steel and AISI 304 stainless steel exhibited limited corrosion resistance except in the exit gas above the mist eliminator where no condensation was

TABLE 2 — Limestone FGD Scrubber Absorber

158 days, pH = 5.7 chlorides: 2250 in scrubber 100-850 in absorber				
Exposure Area	Max. Pitting/Crevice Corrosion—mm			Average Corrosion Rate For 1010 Steel mm/y
	304 Stainless Steel	316 Stainless Steel	Alloy G	
Base of scrubber (1)	0.66 (26.0 mils)	0.05	0	0.34
Absorber tower —below nozzles (2)	0.79 (31.1 mils)	0.18	0	0.25
Absorber tower —mist eliminators (3)	0.28	0.15	0	0.20
Absorber tower —gas outlet (4)	0	0	0	0.26
Scrubber slurry tank (5)	0.25	0.05	0	0.58
Absorber slurry tank (6)	0.18	0.03	0	0.33

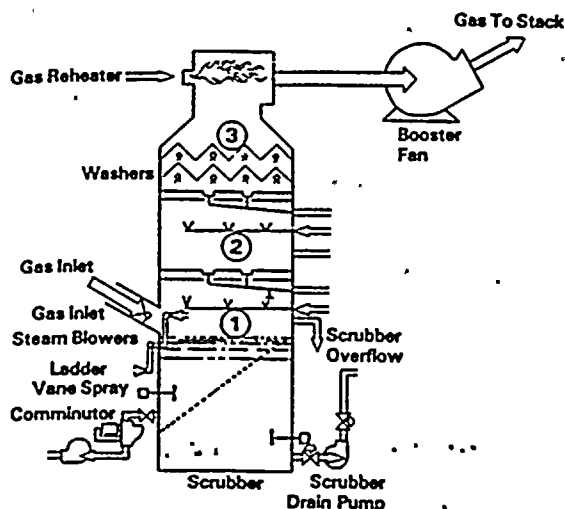


FIGURE 3 — Lime FGD scrubber.

TABLE 3 — Lime FGD Scrubber

93 days, 400-600 ppm Cl, Shower Water pH = 4.9			
Max. Pitting/Crevice Corrosion—mm			
AISI Alloy	Shower Spray (1)	Above Marble Bed (2)	Above Mist Eliminator (3)
304	0.28 (1.0 mm)	0.18	0
316	<.03	0.13	0
317	0	0	0
Average corrosion rate (mm/y) —1010 steel	1.60	0.74	0.13

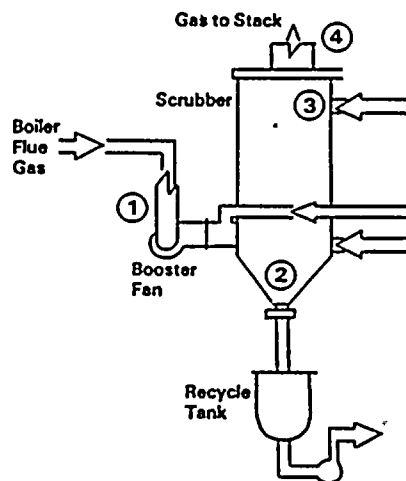


FIGURE 4 — Double alkali FGD system, dilute mode.

evident. AISI 316 stainless steel (2.3% Mo) provided greatly improved corrosion resistance, while AISI 317 stainless steel (3.2% Mo) was unaffected over this relatively short exposure period.

#### Case 3—Dilute Mode Double Alkali System

A typical dilute mode double alkali system recycles highly oxidized regenerated liquor and can be expected to achieve moderate chloride concentrations. Corrosion test locations in a short term exposure program of this type are shown in Figure 4 and corrosion data are given in Table 4. The variable corrosivity of the process conditions in the different areas is evidenced by corrosion rate of carbon steel, ranging from 0.35 mm/y (14 mpy) in the dry inlet gas to 3.3 mm/y (130 mpy) in the moist outlet gas. AISI 304 stainless steel again exhibited limited corrosion resistance in wet sections. AISI 316 stainless provided some improvement except in the aggressive quench area where maximum chloride concentrations are expected.

#### Case 4—Concentrated Mode Double Alkali System

Exposures in a concentrated mode system were limited to two areas shown in Figure 5. Corrosion data in Table 5 show

TABLE 4 — Double Alkali FGD System—Dilute Mode

31 Days, Slurry pH = 10-13, 1000 ppm Cl				
Max. Pitting/Crevice Corrosion—mm				
Alloy	Flue Gas Inlet (1)	Quench Section (2)	Absorber Tray (3)	Discharge Duct (4)
AISI 304	0	0.10	0.20	0.28
AISI 316	0	0.10	0	0.05
Alloy G	0	0	0	0
Average corrosion rate (mm/y) AISI—1010 steel	0.35	0.53	0.39	3.31

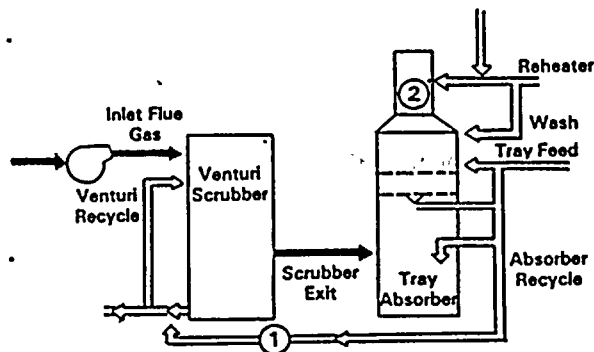


FIGURE 5 — Double alkali FGD system, concentrated mode.

TABLE 5 — Double Alkali FGD System—Concentrated Mode

4 months, pH = 4-5, 1400 ppm Chlorides		
Max. Pitting/Crevice Corrosion—mm		
Alloy	Absorber Overflow (1)	Above Mist Eliminator (2)
AISI 304	0.20	1.2
AISI 316	0	0.9
AISI 317	0	0.6
Alloy 825	0	0.7
Alloy G	0	0.8
Alloy 625	0	0
Alloy C-276	0	0

minimal attack in the absorber overflow piping system. However, the exposure in the outlet duct above the mist eliminator provides an example of the severity of corrosion which can occur in sulfurous and sulfuric acid condensates. Only nickel base alloys 625 and C-276 were resistant to attack in this area.

#### Case 5—Sodium Sulfite SO<sub>2</sub> Recovery Process

An extensive exposure program in the scrubber/absorber areas of a sodium sulfite SO<sub>2</sub> recovery system is outlined in Figure 6 with corrosion data summarized in Table 6. The com-

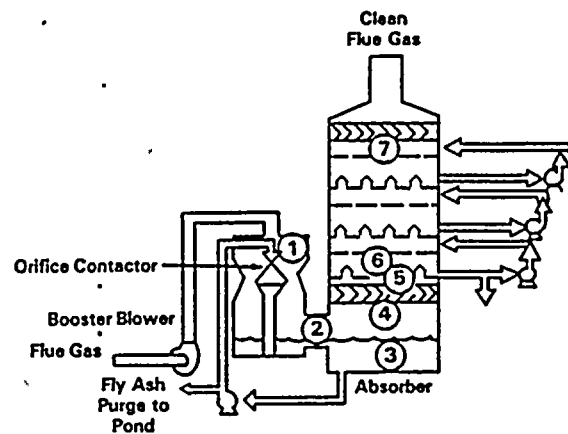


FIGURE 6 — Sodium sulfite SO<sub>2</sub> recovery process.

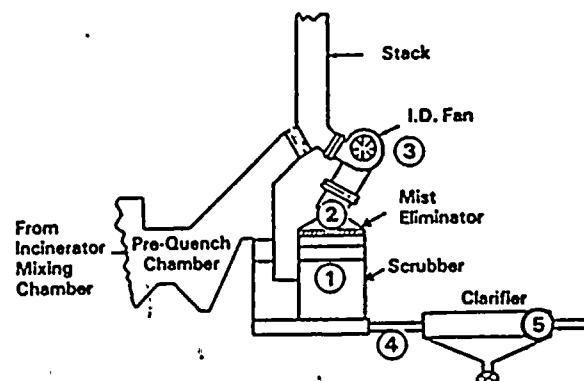


FIGURE 7 — Refuse Incinerator scrubber.

bination of high temperature, uncontrolled pH, abrasive flyash, and heavy solids buildup in the venturi scrubber entrance resulted in severe corrosion of all of the alloys evaluated. Reduction in temperature and flyash abrasion significantly reduced corrosion at the venturi exit and absorber tower bottom although clearly, high alloys are required to cope with the low pH environment containing 1200 ppm chloride. Condensate conditions above the mist eliminator again provided aggressive conditions while exposure to scrubber solution sprays and the scrubbed flue gas caused minimal corrosion.

TABLE 6 — Sodium Sulfite SO<sub>2</sub> Recovery Process

3 Months, 1200 ppm Cl, pH = 1.5-2							
Max. Pitting/Crevice Corrosion—mm							
Alloy	Venturi Entrance (1)	Exit (2)	Tower Bottom (3)	Mist Eliminator Below (4)	Mist Eliminator Above (5)	Absorber Solution (6)	Scrubber Flue Gas (7)
AISI 316	0.94(p)	0.20	0.46	0.18	0.94(p)	0	0
AISI 317	0.36	0.20	0.33	0.20	0.38	0	0
Alloy G	0.18	0.10	0	0	0	<0.03	0
Alloy 625	0.30	0	0	0	<0.03	0	0

TABLE 7 — Refuse Incinerator Scrubber

161 Day Exposure					
Max. Pitting/Crevice Attack—mm					
Alloy	Scrubber Inlet (1)	Scrubber Roof (2)	Induced Draft Fan (3)	Flume (4)	Clarifier (5)
AISI 304	0.43	1.40(p) (55.1 mils)	0.51	0.25	0.10
AISI 316	0.13	0.69	0.20	0.15	0.10
Alloy G	0	0.33	0.30	0	0
Alloy 625	0	0.28	0.15	0	0
Average Corrosion rate—mm/yr					
AISI 1010 steel	> 1.3	0.9	1.0	> 1.3	0.4
HSLA steel	> 1.4	0.8	0.9	> 1.4	0.2

(p) = perforated

TABLE 8 — Sewage Incinerator Scrubber

15 Month Exposure				
Max. Pitting/Crevice Attack—mm				
Alloy	Gas Inlet Baffle (1)	Scrubber Liquid (2)	Impingement Plate (3)	Exhaust Stack (4)
AISI 304	0	0.30	0.28	0.08
AISI 316	0	0.03	0.46	0
AISI 317	0	2	0.51	0
Alloy G	0	0	0	0
Average corrosion rate—mm/yr —1010 steel	0.07	—	0.02	0.13

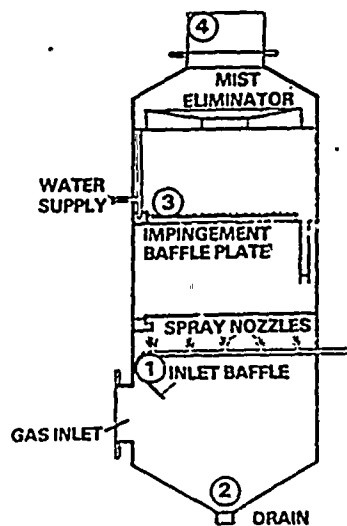


FIGURE 8 — Sewage Incinerator scrubber.

#### Case 6—Refuse Incinerator Scrubber

Day-to-day variations in refuse create equally variable environmental conditions in refuse incinerator off-gas scrubbers. Typically, the gases contain significant levels of chlorides from the burning of chlorinated plastics. Use of fresh water as a scrubbing medium produces unbuffered HCl. Corrosion test locations in a municipal system are identified in Figure 7 and corrosion data are given in Table 7. Carbon and low alloy steels are clearly inadequate for this application with the possible exception of the clarifier tank. Condensate carryover from the mist eliminator created a severe environment at the scrubber roof and the induced fan area with localized corrosion developing to some extent with all of the alloys evaluated. The corrosivity is, in part, aggravated by the use of a recirculating water system in this plant which does not allow for dilution of neutralization of the acid chlorides. The importance of this is evidenced by the significantly reduced level of corrosion observed in a comparison incinerator operated with a once through water system.

#### Case 7—Sewage Sludge Incinerator

Chlorides in sewage sludge incinerators are introduced by the scrubbing water and generally do not reach the high levels developed in refuse incinerator systems. The corrosion



data in Table 8 developed from the exposures detailed in Figure 8 illustrate the reduced severity of corrosion in contrast to Case 6. Heavy deposits accumulated on the samples exposed in the impingement baffle plate area, the one area where the stainless steels developed significant pitting. These deposits, in turn, provided a mechanism for crevice formation with further chloride concentration. The deleterious effect of the deposits on the stainless steels is in contrast to the apparent protective effect on carbon steel.

### Summary

The exposure of corrosion test spools in operating wet scrubber systems has proven to be a useful method for evalu-

ating environmental effects and for assessing relative corrosion resistance of candidate materials of construction. The results of exposures in systems utilizing alkaline slurries and water as scrubbing media demonstrate the limited usefulness of unprotected carbon steel. Corrosion problems associated with deposit formation, wet flyash abrasion, unbuffered acidic condensates, and excessive chloride concentration are common to most systems and must be considered when selecting materials of construction with promise of optimum durability.

### References

1. L. W. Gleekman. ASTM STP 534, p. 167-169 (1973).

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For the first time proceedings of symposia presented at a NACE Annual Conference will be made available in bound form. The 36 symposia will be grouped by subject interest in 12 volumes. Each volume will contain an introduction by the sponsoring Technical

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## Effect of Acids on the Stress Corrosion Cracking of Stainless Materials in Dilute Chloride Solutions\*

A. I. ASPHAHANI

Stellite Division, Cabot Corporation, Kokomo, Indiana

The chloride stress cracking of stainless steels (304, 304L, 316, 316L) is shown to occur in dilute 0.8 to 4% sodium chloride solutions containing 0.2 to 1%  $H_3PO_4$  or 0.5%  $CH_3COOH$ . While more localized attacks (pitting, crevice corrosion) are observed in the chloride solution containing acetic acid, the 0.2% phosphoric acid addition to 0.8% NaCl is sufficient to induce stress cracking of the austenitic stainless steels within less than 10 days of exposure at 141 C. The higher nickel content austenitic stainless alloys (20Cb-3, 825, 20-Mod) are more resistant to the chloride stress cracking. However, some pitting and crevice corrosion attack is observed on these alloys, except for 20-Mod. The high performance nickel base alloys (G, C-276) show excellent resistance to chloride stress cracking and to localized corrosive attack. The susceptibility of the stainless steels to the observed stress cracking is related to the acidity of the dilute chloride solutions, and is explained using the concept of the critical potential for stress corrosion cracking.

data have been reported from SCC tests in dilute chloride environments at 300 C,<sup>12</sup> in chloride solutions containing  $H_2S$ ,<sup>13</sup> in brines simulating geothermal environments,<sup>14</sup> in pure or inhibited hydrochloric acid at room temperature,<sup>15,16</sup> and in refrigerated HCl solution.<sup>17</sup>

Still, almost no data exist on the chloride stress cracking of austenitic stainless steels in dilute chloride environments containing traces of acids, specifically less than 2% phosphoric acid. These environments appear of interest in some CPI applications dealing with phosphate chemicals and to the food processing industries using phosphate compounds as preservatives or mixtures containing table salt and weak organic acids, where AISI 304 and 316L stainless steels have already experienced SCC in field-service.<sup>7,18,19</sup>

It is the purpose of this study to present data on the SCC of several stainless materials in dilute chloride solutions containing small amounts of different acids. The effects of temperature, acid additions, and galvanic coupling are shown. Also, the resistance and/or susceptibility of various alloys are established and discussed.

TABLE 1 - Nominal Composition of Alloys Tested (Wt%)

Alloys	Fe	Ni	Cr	Mo	Mn	Si	Cu	C
AISI 304	Bal	9	19	—	2 <sup>(1)</sup>	1 <sup>(1)</sup>	—	0.05
AISI 304L	Bal	9	19	—	2 <sup>(1)</sup>	1 <sup>(1)</sup>	—	0.03 <sup>(1)</sup>
AISI 316	Bal	12	17	2.5	2 <sup>(1)</sup>	1 <sup>(1)</sup>	—	0.05
AISI 316L	Bal	12	17	2.5	2 <sup>(1)</sup>	1 <sup>(1)</sup>	—	0.03 <sup>(1)</sup>
Carpenter 20Cb-3 <sup>(2)</sup>	Bal	33	20	2.5	2 <sup>(1)</sup>	1 <sup>(1)</sup>	3	0.04
Incoloy 825 <sup>(3)</sup>	30	Bal	21	3	1 <sup>(1)</sup>	0.5 <sup>(1)</sup>	2	0.04
Haynes alloy No. 20-Mod <sup>(4)</sup>	Bal	26	22	5	2.5 <sup>(1)</sup>	1 <sup>(1)</sup>	—	0.05 <sup>(1)</sup>
Hastelloy alloy G <sup>(4)</sup>	20	Bal	22	7	1.5	1 <sup>(1)</sup>	2	0.05 <sup>(1)</sup>
Hastelloy alloy C-276 <sup>(4)</sup>	5	Bal	16	16	1 <sup>(1)</sup>	0.8 <sup>(1)</sup>	—	0.02 <sup>(1)</sup>

(1)Maximum.

(2)Registered trademark of Carpenter Technology Corporation.

(3)Registered trademark of International Nickel Company, Inc.

(4)Registered trademark of Cabot Corporation.

### Introduction

CHLORIDE STRESS CRACKING of austenitic stainless steels has always been a problem limiting the safe use of these alloys in the various chemical processing industries (CPI). This subject of stress corrosion cracking (SCC) in chloride environments is by no means a neglected one for researchers. However, most of the studies have been limited to tests in hot, concentrated chloride solutions, specifically the boiling 42 to 45%  $MgCl_2$  solutions.

A limited amount of data exists on the SCC of stainless steels in other aqueous solutions. The stress cracking in sulfuric acid containing chloride ions has been observed,<sup>1</sup> investigated,<sup>2,3</sup> and commented on.<sup>4</sup> Also, the effects of various cations (e.g.,  $Ba^{++}$ ,  $Ca^{++}$ ,  $Cr^{+++}$ ,  $Fe^{+++}$ ,  $Hg^{++}$ ,  $Li^+$ ,  $Mg^{++}$ ,  $Ni^{++}$ ,  $Zn^{++}$ ) have been mentioned,<sup>5</sup> examined,<sup>6,7</sup> and summarized.<sup>10,11</sup> Furthermore,

### Experimental Procedure

#### Materials

The alloys examined included several stainless steels and high performance nickel base alloys. The nominal chemical compositions and the registered trademarks are presented in Table 1.

#### Specimens

The SCC tests were conducted on U-bend specimens  $\approx 133 \times 13 \times 3$  mm (5.25 x 0.5 x 0.125 inch). Each specimen was deformed around a 25 mm (1 inch) mandrel. The specimen's ends were maintained in a parallel position with a bolt and a nut made out of Hastelloy alloy C-276. Teflon inserts were used to insulate the bolt/nut from the specimen. The specimen was further stressed by straining its ends (tightening the nut) to a final span of 12 mm (1/2 inch). The imposed stress depended on the yield strength of the material, and no effort was made to calculate the exact value of the

\*Presented during Corrosion/79 (Paper 42), March, 1979, Atlanta, Georgia.

applied stress. However, all specimens were stressed the same way, i.e., the same straining of 12 mm (1/2 inch) final span was imposed on every specimen.

When studying the effects of galvanic coupling, small strip specimens having  $\approx 45 \times 5 \times 1$  mm ( $1.75 \times 0.19 \times 0.04$  inch) dimensions were used. They were strained by bending into a C-shape and fitting into a slotted holder with a 39 mm (1.50 inch) opening, and held at a constant plastic strain ( $\epsilon \approx 7\%$ ). Galvanic couples were achieved through making the holders out of various dissimilar materials. This type of specimen/holder has been found practical in studying the environmental stress cracking of high performance and stainless alloys.<sup>20,21</sup>

#### Containers and Solutions

The SCC tests at 82 C (180 F) and the tests at boiling temperature were conducted in glass vessels. The tests at 141 C (285 F) were conducted in sealed Hastelloy alloy C-276 autoclaves. The test solutions were prepared from distilled water and reagent grade chemicals. The specimens were checked after 7 to 10 days of exposure. The failed specimens were then removed, and the tests were resumed on the remaining specimens. The tests were finally stopped after a total of 30 days of exposure. Visual examination at 30X was used to determine the presence/absence of stress corrosion cracks. Occasionally, specimens were polished and examined metallographically at 100X.

#### Results

##### Effect of Phosphoric Acid Addition

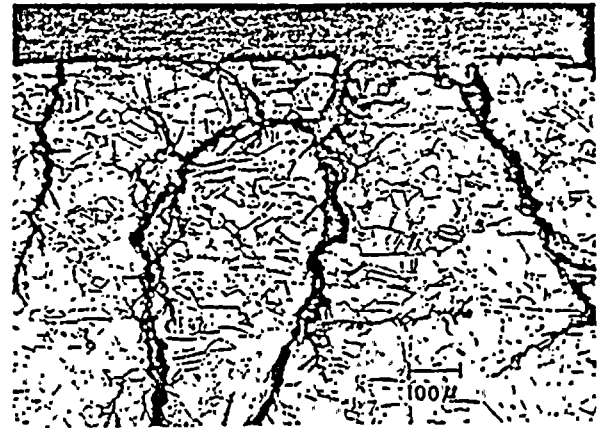
The data on stress cracking tests conducted in 4% NaCl + 1%  $H_3PO_4$  solution at 141 C (285 F) are summarized in Table 2 and

TABLE 2 — U-Bend Specimens (Two of Each Alloy)  
One Month Exposure: 4% NaCl + 1%  $H_3PO_4$  at 141 C (285 F)

Alloys	Corrosion Rate mm/y	mpy	Localized Corrosion	Stress Corrosion Cracking
304	0.15	6.1	Crevice Corrosion	Yes
304L	0.13	5.4	Crevice Corrosion	Yes
316	0.11	4.4	Crevice Corrosion	Yes
316L	0.04	1.8	Slight Attack	Yes
20Cb-3	0.07	3	Pitting-Severe	No
825	<0.01	<0.1	Crevice Corrosion	No
20-Mod	<0.01	<0.1	Slight Attack	No
G	<0.01	<0.1	No Attack	No
C-276	<0.01	0.3	No Attack	No

indicate that weight losses as well as localized crevice corrosion attack (the areas beneath the bolt/nut) occurred on the 304, 304L, 316, and 316L specimens. Also, all these stainless steels suffered SCC. The cracks were of the "branching-transgranular" type (Figure 1), which is similar to the classical chloride stress cracking of these steels encountered in the boiling magnesium chloride test. No SCC was observed on the rest of the alloys tested. However, alloy 20Cb-3 suffered severe localized attack (pitting-crevice corrosion) after the 30 day exposure in the 4% NaCl + 1%  $H_3PO_4$  solution, while alloy 20-Mod showed much better resistance (Figure 2). Slight crevice corrosion attack was observed on alloy 825; however, alloys G and C-276 showed no attack at all.

It should be noted that SCC of the stainless steels was observed at 141 C (285 F) only in the chloride solution containing the phosphoric acid. No SCC occurred in the sodium chloride solution (without  $H_3PO_4$ ) nor in the boiling phosphoric acid (without NaCl), as indicated by the data summarized in Tables 3 and 4. It is appreciated that the test reported in Table 2 was in 4% NaCl + 1%  $H_3PO_4$  at 141 C, while in Table 3, the medium was 2% (not 4%) NaCl at 141 C, and in Table 4 it was 2% (not 1%)  $H_3PO_4$  at 102 C (not 141 C). These variations were dictated by a customer problem being worked on. However, I believe the conclusions are valid since



a



b

FIGURE 1 — Stress corrosion cracks; 4% NaCl + 1%  $H_3PO_4$  at 141 C (285 F). (a) AISI 304 stainless steel; 50X, and (b) AISI 316L stainless steel; 50X.

Table 5 shows SCC of the 300 series stainless steels in 0.8% NaCl + 0.2%  $H_3PO_4$  at 141 C. Pitting attack was observed on the 304 and 304L specimens in the hot sodium chloride solution.

The SCC of the stainless steels in the  $Cl^-$  or  $PO_4^{3-}$  solution did not appear to be dependent on the  $Cl^-$  or the  $PO_4^{3-}$  concentrations, within the dilute concentration range of 0.1 to 5 weight percent. Tests conducted in 0.8% NaCl + 0.2%  $H_3PO_4$  solution at 141 C (285 F) showed that 304, 304L, 316, and 316L specimens failed by SCC within 10 days of exposure. The data, summarized in Table 5, indicated that alloys 20Cb-3 and 825 suffered localized attack while alloys 20-Mod, G, and C-276 showed no attack.

#### Effect of Temperature

Tests were also conducted in the 4% NaCl + 1%  $H_3PO_4$  solution at 82 C (180 F). Even at this lower temperature, the stainless steel specimens failed by SCC, as indicated in Table 6. Again, no attack was observed on alloys 20-Mod, G, or C-276.

#### Effects of Acetic Acid and Hydrochloric Acid

The results from similar tests conducted in an 0.8% NaCl + 0.5%  $CH_3COOH$  solution (data summarized in Table 7) indicated that SCC of the 304, 304L, 316, and 316L stainless steels was not limited only to the chloride solutions containing phosphoric acid. The typical "branching-transgranular" stress corrosion cracks were observed on the stainless steel specimens (Figure 3). However, pitting associated with the cracks was more evident on the specimens tested in the 0.8% NaCl solution containing the acetic

TABLE 8 — U-Bend Specimens  
(Two of Each Alloy)  
0.8% NaCl + HCl (pH ≈ 2.2) at 141 C (285 F)

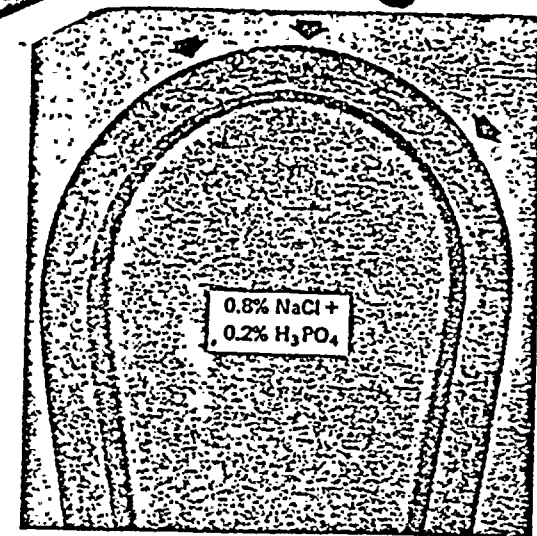
Alloys	10 Day Exposure	30 Day Exposure (1)
304	No Cracking (2)	Cracking
304L	No Cracking (2)	Cracking
316	No Cracking (2)	Cracking
316L	No Cracking (2)	Cracking
20Cb-3	No Cracking	No Cracking
825	No Cracking (2)	No Cracking
20-Mod	No Cracking	No Cracking
G	No Cracking	No Cracking
C-276	No Cracking	No Cracking

(1) All specimens with no cracking after the 10 day exposure were further tested for an additional 20 day exposure. The container developed a leak at the seal and the test solution evaporated some time during the testing period. The temperature of the container was maintained at 285 F.

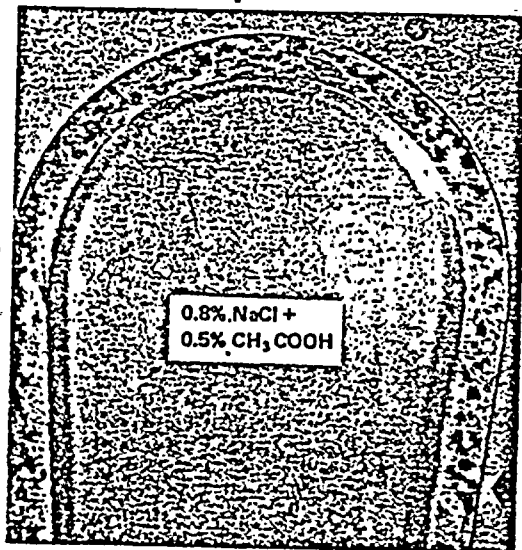
(2) General dissolution, uniform thinning.

TABLE 9 — C-Shape Specimens of  
AISI 316L Stainless Steel —  
Ten Day Exposure:  
0.8% NaCl + 0.2% H<sub>3</sub>PO<sub>4</sub> at 141 C (285 F)

The Dissimilar Alloy of the Galvanic Couple	Stress Corrosion Cracking
Copper	No
Carbon Steel	No
200 (99 Ni)	No
400 (70 Ni-30 Cu)	No
304	No
304L	Yes
316	Yes
316L	Yes
20Cb-3	Yes
G	Yes
25 (52 Co-20 Cr-15 W-10 Ni)	Yes



a



b

FIGURE 4 — Overall appearance of AISI 304L stainless steel specimens after exposure to the dilute chloride solutions at 141 C (285 F). (a) Fine stress corrosion cracks (arrows), no obvious pitting, and (b) stress corrosion cracks (arrow), severe pitting.

solution.<sup>23</sup> However, it should be noted that the observed SCC of the stainless steels is not solely due to the tests being conducted at relatively high temperature, i.e., 141 C (285 F). The present data indicate that SCC of the 304, 304L, 316, and 316L specimens persisted in 4% NaCl + 1% H<sub>3</sub>PO<sub>4</sub> at the moderate temperature of 82 C (180 F). The relatively short time involved in producing SCC at 80 C (less than 10 days, Table 6) tends to indicate that in the dilute acidic chloride solutions, temperature is not the critical single feature for causing SCC of the tested stainless steels. Stress cracking of 304 tubulars has occurred within less than two years of service<sup>16</sup> in complex mixtures of weak organic acids (juice at pH = 4.8) operating at temperatures close to 80 C (176 F). It appears that the presence of acids in the chloride solution plays a role as important as that of temperature.

The present data, delineating the special effects of acids in inducing SCC of austenitic stainless steels, are in agreement with

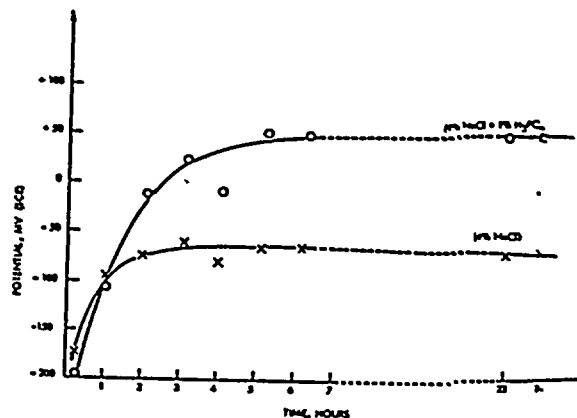


FIGURE 5 — Corrosion potential of AISI 316 stainless steel as a function of time; T ≈ 82 C (180 F).

reports on the chloride stress cracking of AISI 316 stainless steel tubes.<sup>18</sup> These tubes are reported to suffer SCC, within less than three months of service, in an environment containing 1 to 2% NaCl and about 7% CH<sub>3</sub>COOH. Furthermore, the present data

that addition of any of the acids investigated (phosphoric, acetic, and hydrochloric) causes SCC of the stainless steels in sodium chloride solutions. However, some differences between the overall effects of these acids should be mentioned. The features of the corrosive attack vary from one acid addition to another. Acetic acid was more severe in inducing pitting corrosion of the stainless steels than phosphoric (Figure 4) or hydrochloric acids, within the same pH range of 1.7 to 2.2. However, the phosphoric acid addition was much more severe than acetic acid addition in causing pitting-crevice corrosion type attack on alloys 20Cb-3 and 825 (Tables 5 and 7).

As to the special effect of the hydrochloric acid addition, general dissolution with uniform thinning was the predominant form of corrosive attack observed during the first 10 days of testing. (Contrary to the localized attack and SCC observed on the stainless steels within the same period of testing in the NaCl solutions containing phosphoric acid or acetic acid.) Furthermore, due to solution evaporation, it is not definite that the observed SCC is representative of an aqueous 0.8% NaCl + HCl solution at 141 C (285 F).

Still, it is most interesting that phosphoric or acetic acids cause localized corrosion and SCC of stainless steels in dilute chloride solutions. Phosphates or acetates have been known to inhibit corrosion and SCC. For example, 1%  $\text{NaH}_2\text{PO}_4$  addition to boiling 3% NaCl solution (pH adjusted to 6.4) is reported to inhibit the SCC of high strength low alloy steel.<sup>24</sup> Similarly, 2%  $\text{CH}_3\text{COONa}$  addition to boiling  $\text{MgCl}_2$  solution has been proven effective in inhibiting the SCC of 18-8 stainless steel.<sup>25</sup> Yet, the data presented herein clearly indicate that the presence of " $\text{PO}_4$ " or " $\text{CH}_3\text{COO}$ " compounds in acidic dilute chloride solutions was the cause of the stress cracking of the 304, 304L, 316, and 316L specimens. The role of the " $\text{PO}_4$ " or " $\text{CH}_3\text{COO}$ " compounds in inhibiting or causing SCC can be explained through their effects on the critical potential for SCC, i.e.,  $\phi$  [critical, SCC] as defined by Uhlig.<sup>26,27</sup> The small phosphoric acid addition (as well as the small acetic acid addition) shifted the free corrosion potential to more noble values, presumably above the  $\phi$  [critical, SCC] and within the potential range where SCC occurred in the hot, dilute chloride solutions. Therefore, alloys susceptible to chloride SCC (304, 304L, 316, and 316L stainless steels) may not fail by SCC in the dilute NaCl solution where the free corrosion potential lies below  $\phi$  [critical, SCC]. However, these stainless steels do fail by SCC upon the addition of compounds that alter the relative position of the corrosion potential "vis-a-vis" the critical potential for SCC. On the other hand, and as expected, the SCC resistance of the high performance nickel base alloys (with very noble or nonexistent  $\phi$  [critical, SCC], e.g., alloys G or C-276) will not be affected by any addition of " $\text{PO}_4$ " or " $\text{CH}_3\text{COO}$ " compounds to the chloride environment.

In this respect, the effects of the various galvanic couples can be explained. Coupling 316L to less noble metals (carbon steel, copper, alloys 200, 400, and 304) polarizes them to a more active potential, presumably below the  $\phi$  [critical, SCC] and away from the SCC potential range. However, coupling 316L to alloys close in performance or more noble (304L, 316, 20Cb-3, G, and 25) shifts their free corrosion potential to more noble values above the  $\phi$  [critical, SCC] and within the susceptible potential range for cracking.

Finally, as expected, no degradation of any kind was observed on the high performance nickel base alloys. These materials, due to their high nickel and high molybdenum contents (alloys G and C-276), are not susceptible to chloride SCC in the classical  $\text{MgCl}_2$  test. They remain resistant to SCC through the various tests summarized above. However, one point of interest is the behavior of the highly alloyed stainless materials, i.e., alloys 20Cb-3, 825, and 20-Mod. While carbon content and molybdenum addition do not improve the performance of the "300" series of stainless steels, increasing the molybdenum content of the high chromium, high nickel stainless alloys (20Cb-3, 825, and 20-Mod) plays a definite role in improving their resistance to localized attack. Alloy 20-Mod (5% Mo) showed no pitting attack and consistently outperformed alloy 20Cb-3 (2.5% Mo) and alloy 825 (3% Mo) which suffered pitting and crevice corrosion in hot dilute NaCl solutions containing a small amount of  $\text{H}_3\text{PO}_4$ .

## Conclusion

1. The presence of less than 1% acid induces stress corrosion cracking of austenitic stainless steels in dilute chloride solutions at temperatures as low as 82 C (180 F).
2. AISI 304, 304L, 316, and 316L stainless steels readily fail by chloride stress cracking in 0.8% NaCl solution containing 0.2%  $\text{H}_3\text{PO}_4$  or 0.5%  $\text{CH}_3\text{COOH}$  or traces of HCl at pH  $\approx$  2.2.
3. Carpenter 20Cb-3 and Incoloy 825 are not susceptible to SCC in the aforementioned environments. However, these two alloys suffer severe pitting and crevice corrosion attack.
4. Under the same testing conditions, Haynes alloy No. 20-Mod is resistant to SCC. Also, presumably due to its high molybdenum content, this alloy shows excellent resistance to pitting and crevice corrosion.
5. Hastelloy alloys G and C-276 do not suffer corrosion of any type under the conditions of the tests conducted.

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Wm. B. Cottrell

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Table 3.3. Effect of  $\text{NaVO}_3$  on Radiolytic  $\text{H}_2$  in Distilled  $\text{H}_2\text{O}$

Test solutions: A — distilled  $\text{H}_2\text{O}$ ,  
B —  $2 \times 10^{-3} M \text{NaVO}_3$ ,  
Gas-to-liquid ratio: 0.5  
Cover gas: air  
Total dose:  $5 \times 10^8$  rad  
Test mode: radiation loop  
Pumping speed: that required for average residence time in radiation capsule of 1 to 2 min

Test Solution	Temperature ( $^{\circ}\text{C}$ )	$\text{H}_2$ (vol. %) <sup>a</sup>
A	65	32
A	95	23
B	65	3.7
B	95	2.6

<sup>a</sup>Established by gas chromatograph after system reached steady state, as evidenced by constant pressure.

### 3.5 CORROSION STUDIES IN SPRAY SOLUTIONS

(AEC Activity 04 60 80 01 1)

J. C. Griess      G. E. Creek

A program to investigate the corrosive effects of low-pH (4.5 to 7.5) spray solutions on materials of construction was initiated, and six sets of types 304 and 316 stainless steel specimens have been treated in the spray loop.<sup>1</sup> A set of specimens usually consisted of metal coupons described as follows:

1. mill-annealed U-bend coupons,
2. sensitized U-bend coupons,
3. sensitized and pickled U-bend coupons,
4. mill-annealed double U-bend coupons,
5. welded and ground straight coupons,

6. welded and ground U-bend coupons,
7. welded and ground pickled U-bend coupons,
8. welded and ground double U-bend coupons,
9. C-shaped specimens formed from tubing,
10. welded pipe.

The U-bend specimens were formed by bending thin rectangular (3 by 5/8-in.) strips having a 1/4-in. hole in each end into the form of a U and then drawing the legs of the U parallel by means of a bolt through the 1/4-in. holes. Welded specimens were formed by butt welding two sheets of the same metal with a seam welder in an inert gas atmosphere and cutting coupons from the welded sheet so that the weld bisected the major axis of the specimens in the middle. C-shaped specimens were formed by cutting a slot from a short (1/2-in.) piece of tubing to form a C. The edges of the C were then pulled together by means of a penetrating bolt until the tubing was stressed to two-thirds its yield strength. Pipe specimens were made by butt welding two pieces of pipe together.

In each loop cycle, four samples from each of the first eight types listed were in the spray and four in the solution; also two C shaped specimens and two butt-welded pipe samples were in each region. The loop was operated at 285°F for 24 hr and then at 212°F for 168 hr. At the end of the 168-hr period, all samples were transferred to another container and submerged in a solution (same composition as that in the loop) for an additional two months at 180°F.

The solution composition and pH for each of the loop runs are listed in Table 3.4.

Specimens from the first four experiments have completed the total exposure. A preliminary examination of these specimens indicates that the two months at 180°F apparently did not add to the corrosion damage. The specimens from the first four experiments were examined visually, and in some instances additional dye-penetrant examinations were employed. The results of the examinations are given in Tables 3.5 and 3.6.

Table 3.5 pertains to those samples that were in the spray region during the loop cycle. The percentage of those samples in which cracks detected is listed with the chloride concentration of the solution.



Table 3.4. Solution Composition and pH  
for Corrosion Experiments

Experiment No.	pH	Boron as H <sub>3</sub> BO <sub>3</sub> (ppm)	Chloride as NaCl (ppm)
1	4.5	3000	200
2	4.5	3000	5
3	4.5	3000	50
4	4.5	3000	20
5	7.5	3000	200
6 <sup>a</sup>	6.5	3000	20

<sup>a</sup>2 ppm of iodine added to the solution.

Table 3.6 contains similar information to that in Table 3.5, except that it concerns those samples that were immersed in the solution during the loop cycle.

The data presented in Tables 3.5 and 3.6 indicates that sensitizing (1250°F for 1 hr) increases stress-corrosion cracking, with the type 304 stainless steel evincing greater damage than the type 316 stainless steel, and stress-corrosion cracking increases with chloride concentration. The type 316 stainless steel C specimens from the first four experiments were free from cracking. In experiment 3 (50 ppm Cl), one of the type 304 stainless steel C specimens cracked. In experiment 1 (200 ppm Cl), all the type 304 stainless steel C specimens cracked.

In the butt-welded pipe samples, cracking was found in only one specimen. The cracked specimen was type 304 stainless steel and was part of the set of experiment 3 (50 ppm Cl).

The specimens in the fifth and sixth runs were visually examined after their removal from the loop and prior to the two-month storage at 180°F. Assuming that the storage does not significantly add to the corrosion damage, the stress cracking in experiments 5 and 6 will be about the same as that in the second experiment (5 ppm Cl, 3000 ppm B, pH of 4.5) with the sensitized type 304 stainless steel U-bend samples being the only samples that showed cracking.

Table 3.5. The Effect of Chloride Concentration on Stress-Corrosion Cracking of Stainless Steel Specimens Exposed to a Spray Solution at a pH of 4.5 Containing 3000 ppm B

Specimen <sup>a</sup>	Type of Stainless Steel	Percentage of Four Samples That Cracked			
		5 ppm Cl <sup>-</sup>	20 ppm Cl <sup>-</sup>	50 ppm Cl <sup>-</sup>	200 ppm Cl <sup>-</sup>
U-bend	304	0	50	100	100
	316	0	0	0	0
Sensitized U-bend	304	100	100	100	100
	316	0	100	100	100
Sensitized and pickled U-bend	304	0	50	100	75
	316	0	0	0	0
Double U-bend	304	0	25	100	75
	316	0	0	0	0
Welded and ground straight coupon	304	0	0	0	50
	316	0	0	0	50
Welded and ground U-bend	304	0	100	100	100
	316	0	100	100	75
Welded and ground pickled U-bend	304	0	0	25	75
	316	0	0	50	0
Welded and ground double U-bend	304	0	50	100	100
	316	0	50	50	75

<sup>a</sup>Specimen treatment: 24 hr at 285°F and 7 days at 212°F in loop; 2 months at 180°F in storage.

Table 3.6. The Effect of Chloride Concentration on Stress-Corrosion Cracking of Stainless Steel Specimens Exposed in a Solution at a pH of 4.5 Containing 3000 ppm B

Specimen <sup>a</sup>	Type of Stainless Steel	Percentage of Four Samples That Cracked			
		5 ppm Cl <sup>-</sup>	20 ppm Cl <sup>-</sup>	50 ppm Cl <sup>-</sup>	200 ppm Cl <sup>-</sup>
U-bend	304	0	50	50	25
	316	0	0	0	0
Sensitized U-bend	304	100	100	100	100
	316	0	100	100	75
Sensitized and pickled U-bend	304	0	0	75	75
	316	0	0	0	0
Double U-bend	304	0	0	25	0
	316	0	0	0	0
Welded and ground straight coupon	304	0	0	0	0
	316	0	0	0	25
Welded and ground U-bend	304	0	75	0	25
	316	0	25	0	0
Welded and ground pickled U-bend	304	0	0	0	0
	316	0	0	0	0
Welded and ground double U-bend	304	25	25	25	100
	316	0	0	25	0

<sup>a</sup>Specimen treatment: 24 hr at 285°F and 7 days at 212°F in loop; 2 months at 180°F in storage.

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