Resistance of NICKEL and HIGH NICKEL ALLOYS to corrosion by HYDROCHLORIC ACID, HYDROGEN CHLORIDE and CHLORINE

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NiDI

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Nickel-clad steel jacketed reactor used for organic chlorinations. It was built in accordance with the A.P.I. A.S.M.E. code for unfired pressure vessels and operates at a temperature of 650° F, and pressures of 25 lb. per sq. in in the body and 125 Ib per sq. in. in the jacket.

Resistance of Nickel and High Nickel Alloys to Corrosion by Hydrochloric Acid, Hydrogen Chloride and Chlorine†

CONTENTS

Hydrochloric Acid

NICKEL and high nickel alloys are among the few metallic materials having useful resistance to hydrochloric acid solutions. Nominal compositions of the nickel alloys most commonly used in this service are shown in Table 1. Selection of the most useful and economical of these materials usually depends upon the concentration, aeration and temperature of the acid and upon such other factors as velocity, film formation, continuity of exposure, allowable metallic content of the solution and the physical properties of the material.

The performance of all of the high-nickel materials in hydrochloric acid solutions has been determined by service experience and by numerous laboratory and plant corrosion tests which are summarized in the following pages.

TABLE 1

Nominal Compositions of High-Nickel Alloys Commonly Used with Hydrochloric Acid Solutions

Material	Nickel %	Copper %	Iron	Chromium	Molybdenum	Silicon	Manganese	Carbon	Other
Nickel 200°..........	99.0•	0.1	0.15	....	....	0.05	0.25	0.1	….
Nickel 201°..........	99.0	0.1	0.15	....	....	0.05	0.25	0.02 Max.	….
Duranickel* alloy 301.	94.0	0.05	0.35	....	....	0.50	0.30	0.25	A14.5 Ti 0.50
Monel* alloy 400°....	67	30	1.4	....	....	0.1	1	0.15	….
Monel* alloy K-500...	66	29	0.9	....	....	0.25	0.4	0.15	A1 2.75
Monel* alloy 506b....	63	31	2.0	....	....	3.0	0.9	0.1	….
Monel* alloy 505b....	65	28	2.0	....	....	4.0	0.9	0.1	….
Inconel* alloy 600°...	77	0.25	7.0	15.0	....	0.25	0.25	0.08	.....
Inconel * alloy X-750..	73	.05	7.0	15.0	....	0.40	0.50	0.05	Ti 2.50 Al 0.75 Cb & Ta 0.90
Chlorimet# 2b.......	63	....	3.0 Max.		32	1.0	1.0	0.10	….
Chlorimet# 3b......	60		3.0 Max.	18.0	18	1.0	1.0	.07	….
NI-Resist* (Type 1)b..	13.5-17.5	5.5-7.5	Bal.	1.75-2.50	....	1.0-2.5	1.0-1.5	'3.00 Max.	....
Ni-Resist* (Type 2)b..	18.0-22.0	0.5 Max.	Bal.	1.75-3.00	....	1.0-2.5	0.8-1.5	3.00 Max.	....
Ni-Resist* (Type 3)b..	28.0-32.0	0.5 Max.	Bal.	2.5-3.5	. . .	1.0-2.0	.40-.80	2.75 Max.	....
Hastelloy** alloy Ell..	60	....	6	….	32	1	1		….
Hasfelloy** alloy C...	51	....	6	17	19	1	1	....	W 5
Hastelloy** alloy Db..	85	3	....			10	1		Al 1
Hastelloy** alloy F*..	48	....	15	22	6.5	1	1.5	0.05 Max.	....

† Previously published as Technical Bulletin T-29.
*** INCO Registered Trademark.**
**** Haynes Stellite Company, Trademark.**

 # Duriron Co., Inc., Trademark.
a **Including cobalt.**
b **Available only in cast form.**
c **Also available in form of clad steel.**

MONEL alloy 400 and Nickel 200

The results of laboratory corrosion tests of MONEL nickel-copper alloy 400 and Nickel 200 over a wide range of concentrations and temperatures, and a description of the test methods used have been presented by Friend and Knapp.[1] Test specimens were cut from standard cold-rolled commercial sheets. Tests were made in air-saturated and in air-free solutions to give conditions representative of maximum and minimum corrosion rates respectively. Tests in air-saturated solutions were made in the circular path corrosion testing apparatus shown in Figure 1. This apparatus is similar to that described by Fraser, Ackerman and Sands.[2] The methods of supporting the test specimens and of aerating the solutions are shown in Figure 2. Tests in air-free solutions were made by saturating the solutions with nitrogen. These tests were made in the rotating-spindle type apparatus shown in Figure 3. This apparatus was used because it is entirely closed and permits the maintenance of a nitrogen atmosphere over the solution surface as well as in the solution itself. In most cases, the test specimens were moved at a velocity of 15.7 feet per minute in air-saturated tests and 21.6 feet per minute in air-free tests. The two different types of apparatus in which the tests were made could not be adjusted conveniently to give the same speed in each. Test periods were of 24 hours duration in air-saturated and 48 hours in air-free solutions except where the specific effect of duration of test on corrosion rate was being determined. The test methods proved to be under statistical control.

[1] W. Z. Friend and B. B. Knapp, "Behavior of Nickel and High Nickel Alloys in Hydrochloric Acid and Hydrogen Chloride," Trans. Am. Inst. Chem. Engrs. 39, 731 (1943).

[2] O. B. J Fraser, D. E. Ackerman and J. W. Sands, Ind. Eng. Chem. 19, 332 (1927).

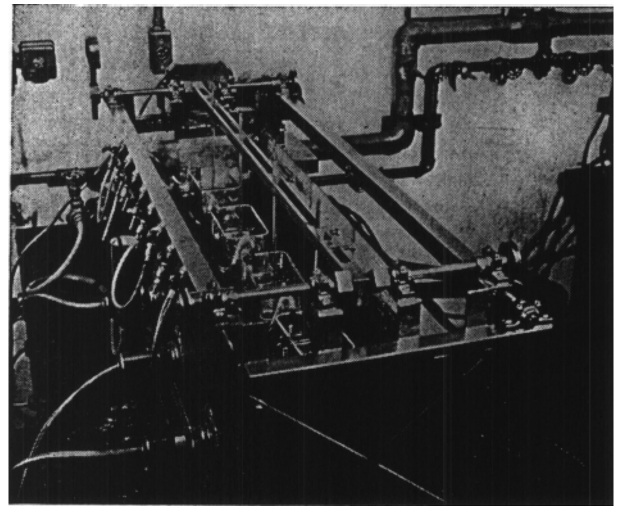

FIG. 1-Circular-path corrosion testing apparatus.

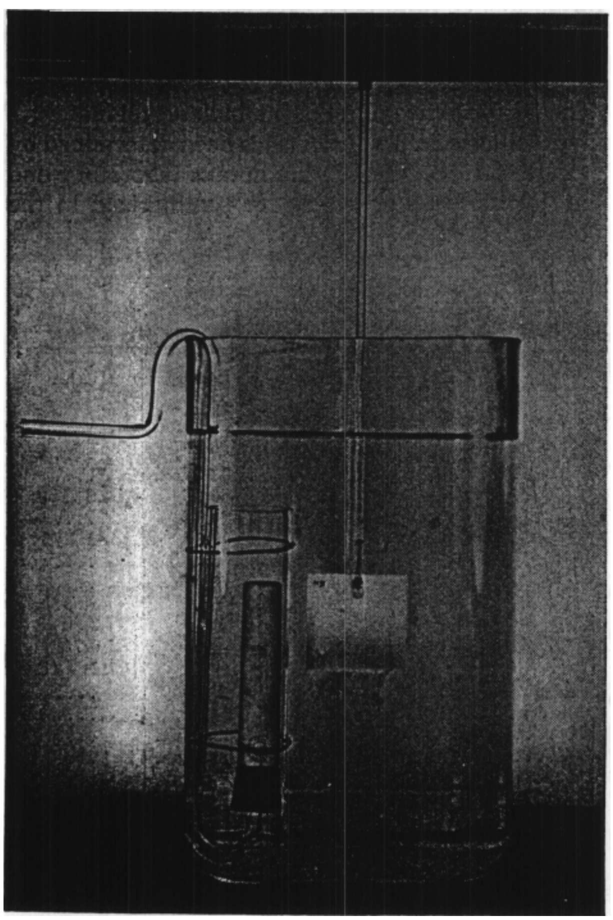

FIG. 2-Method for supporting test specimen and for aerating the test solution.

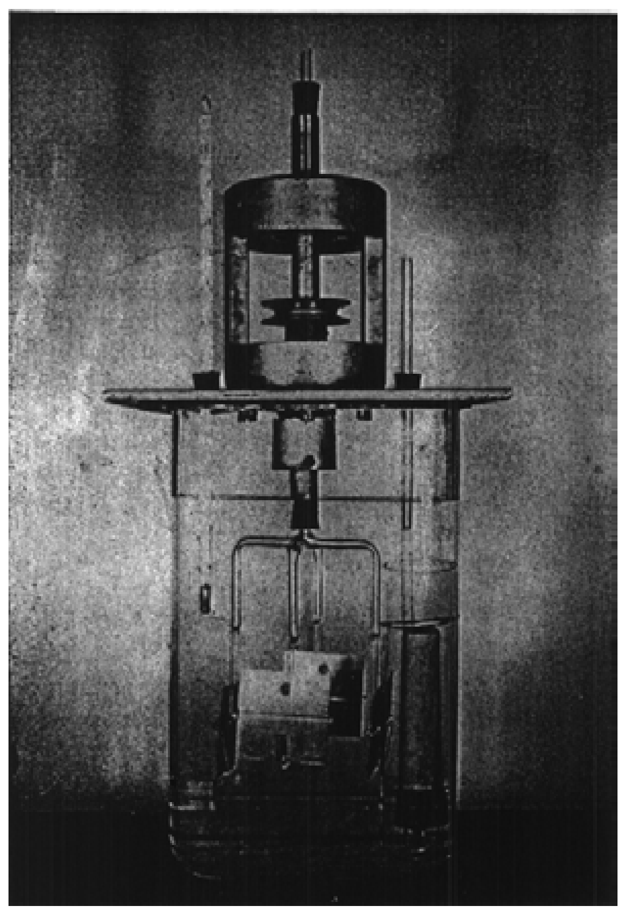

FIG. 3-Rotating-spindle type corrosion testing apparatus.

Acid Concentration

In this bulletin, all acid concentrations are expressed in per cent by weight of HCI. Corrosion rates are shown in milligrams per square decimeter per day (mdd.), and in inches penetration per year (ipy.). The latter unit is based on the assumption of continuous exposure, 24 hours a day and 365 days a year, on one surface of the metal only. Conversion from mdd. to ipy. for any metal or alloy is made by the following equation

$$\text{mdd.} \times \frac{(0.001437)}{d} = \text{ipy.}$$

where d is the density of the metal in gm per cu. cm. Figure 4 shows the effect of hydrochloric acid concentration upon the corrosion rates of MONEL nickel copper alloy 400 and nickel in air-free and air-saturated solutions at 30° C (86° F).

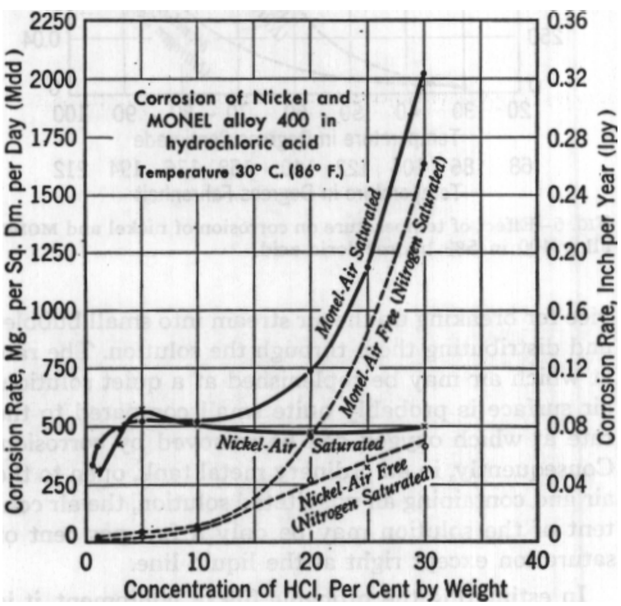

FIG. 4-Corrosion of nickel and MONEL alloy 400 in hydrochloric acid solutions at 30° C (86° F).

It will be noted from Figure 4 that the corrosion rates of MONEL alloy 400 and nickel at room temperature are approximately the same up to 10 per cent acid concentration. In this concentration range, the corrosion rates of both materials in air-free solutions are normally under 0.01 ipy. The rates for both materials are considerably increased by saturating the solutions with air.

Above about 15 per cent acid concentration, the corrosion rates of MONEL alloy 400 begin to increase rather sharply. In practice, applications Of MONEL alloy 400 at room temperature will be, in general, limited to concentrations under about 10 per cent in aerated solutions and under about 20 per cent in air-free solutions.

Nickel is superior to MONEL alloy 400 in resistance to hydrochloric acid concentrations above 20 per cent at room temperature, possibly due to the fact that nickel chloride is less soluble than cuprous or cupric chloride in this range of acid concentrations. The solubilities of these chlorides in hydrochloric acid solutions, as calculated from the data of Seidell[3] are shown in Figure 5. The corrosion data in Figure 4 indicate that occasionally nickel may find suitable applications in acid concentrations up to 30 per cent concentration, either aerated or unaerated, at room temperature. Its performance in air-saturated solutions is of particular interest. As shown in Figure 4, the corrosion rate was a maximum of 574 mdd. at 5 per cent concentration, then fell off to 500 mdd. at 10 per cent and did not exceed this figure at any higher concentration up to and including 30 per cent. At 25 per cent HCl concentration, its corrosion rate took a sharp drop to an average of 304 mdd. Several test specimens, tested in different solutions of this concentration, checked very closely. In drawing the curve for nickel in air-saturated acid in Figure 4, it has been considered prudent to disregard this low point because in commercial practice, it may be difficult to maintain exactly this concentration. The use of nickel with concentrated hydrochloric acid solutions has been very limited and there is little service data to provide confirmation of these test results. If the performance of nickel is due to the relatively low solubility of its corrosion products, caution should be used in applying these test data to service in concentrated acid where high velocities are encountered.

Temperature of the Solution

An increase in temperature increases the corrosion rates of both MONEL alloy 400 and nickel in hydrochloric acid solutions, although nickel is affected more in this respect than MONEL alloy 400. Corrosion rates of both materials in 5 per cent hydrochloric acid, in

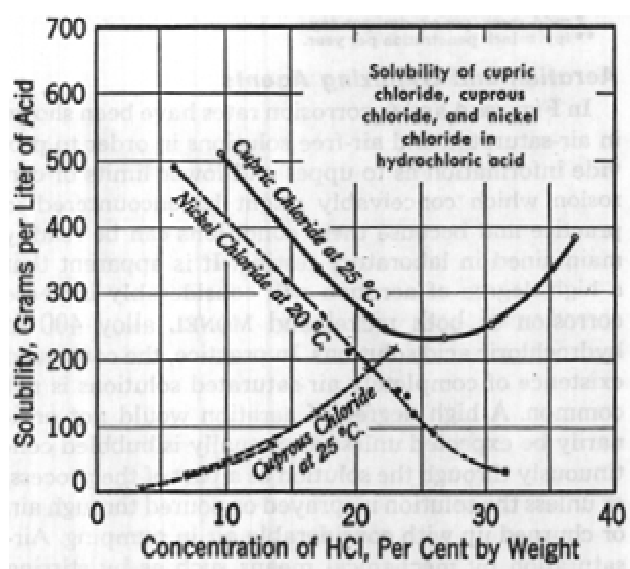

FIG. 5-Solubility of cupric chloride, cuprous chloride, and nickel chloride in hydrochloric acid solutions.

[3] **A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Third Edition, D. Van Nostrand Co. Inc., New York (1940).**

air-free and air-saturated solutions, at temperatures up to 90° C (194° F) are shown in Figure 6. In unaerated 5 per cent acid, MONEL alloy 400 is usefully resistant up to about 75° C (167° F) and nickel up to 55° C (130° F). Applications of both materials, but particularly of MONEL alloy 400, in lower concentrations at higher temperatures are common. In most of the processes in which hydrochloric acid is formed as a result of hydrolysis of chlorides or chlorinated solvents, acid concentrations are less than 0.5 per cent; these are being withstood satisfactorily at temperatures up to 300 to 400° F

Applications of MONEL alloy 400 and nickel in air-saturated hydrochloric acid above room temperature are usually limited to concentrations under 3 or 4 per cent. MONEL nickel-copper alloy 400 is being applied successfully to handling aerated acid of 2 per cent concentration at 120° F and of 1 per cent concentration at 180° F

The results of laboratory corrosion tests of MONEL alloy 400 and nickel in boiling hydrochloric acid solutions are given in Table 2. MONEL alloy 400 can be used often in boiling solutions of 1 per cent or lower concentration 'and in this application is superior to nickel. Under boiling conditions, ebullition sweeps the solution free of air so that aeration is not usually an important factor.

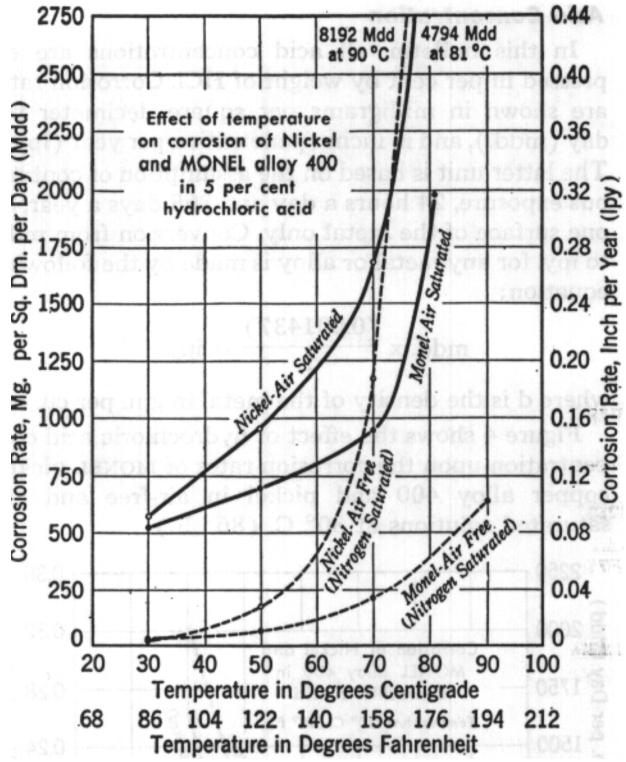

FIG. 6-Effect of temperature on corrosion of nickel and MONEL alloy 400 in 5% hydrochloric acid.

TABLE 2
Corrosion of MONEL alloy 400 and Nickel in Boiling Hydrochloric Acid
Velocity: None
Aeration: None
Duration of tests: 10 days

Add Concentration % HCI by wt.	Corrosion Rate			
	Monel alloy 400		Nickel	
	mdd.*	ipy.**	mdd.	ipy.
0.5	178	0.029	1,875	0.304
1.0	258	0.042	4,200	0.680
5.0	1,500	0.244	35,400	5.74

* mdd.= mg per sq dm per day.
** ipy.= inch penetration per year.

Aeration and Oxidizing Agents

In Figures 4 and 6, corrosion rates have been shown in air-saturated and air-free solutions in order to provide information as to upper and lower limits of corrosion which conceivably might be encountered in practice and because these conditions can be readily maintained in laboratory testing. It is apparent that a high degree of aeration will considerably increase corrosion of both nickel and MONEL alloy 400 in hydrochloric acid solutions. In practice, the continued existence of completely air-saturated solutions is not common. A high degree of aeration would not ordinarily be expected unless air actually is bubbled continuously through the solution as a part of the process, or unless the solution is sprayed or poured through air, or churned up with considerable air in pumping. Air saturation by mechanical means such as by stirring is rather a slow process and requires an efficient device for breaking up the air stream into small bubbles and distributing them through the solution. The rate at which air may be replenished at a quiet solution-air surface is probably quite small compared to the rate at which oxygen can be removed by corrosion. Consequently, in an ordinary metal tank, open to the air and containing an unagitated solution, the air content of the solution may be only a few per cent of saturation except right at the liquid line.

In estimating the probable life of equipment, it is important to have information on the degree of aeration to be expected, and on the presence of any impurities which will affect oxygen availability. Many organic compounds such as foods, fats and sugars will react with dissolved oxygen, removing it from solution. Dyeing and bleaching materials are often oxidizing or reducing. The presence of oxidizing salts in acid solutions may have a very strong effect on corrosion.

Oxidizing Suits in Solution

Oxidizing salts such as cupric and ferric salts, when dissolved in significant amounts in hydrochloric acid solutions, will increase considerably the corrosiveness of the solutions toward MONEL alloy 400 and nickel. To illustrate the corrosive effect of cupric chloride, laboratory tests were made with MONEL alloy 400 in air-saturated hydrochloric acid solutions of various concentrations, at 30° C (86° F) with and without the initial addition of cupric chloride to the solutions. The duration of the tests was 24 hours. The average

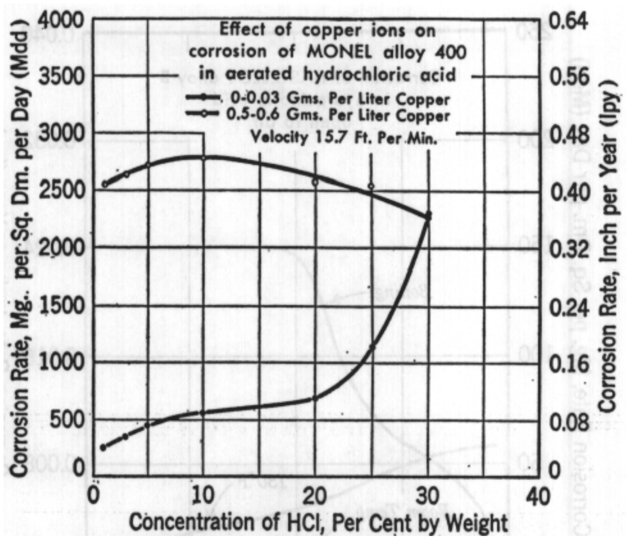

FIG. 7-Effect of copper ions on corrosion of MGNEL alloy 400 in air-saturated hydrochloric solutions at 30° C (86° F).

corrosion rates obtained for both high and low copper content are shown in Figure 7. In one set of tests, no copper was added originally to the test solutions and in the other tests, 0.5 gm per liter were added. The latter amount is high enough that the copper added to the solutions by corrosion of the MONEL alloy 400 specimens was only a small percentage of the total. It will be noted that with a copper content of 0.5 gm per liter the corrosion rate remained at a fairly constant high level regardless of the acid concentration.

In other tests at 80° C (176° F) when the corrosion rate of MONEL alloy 400 in air-saturated 0.5 per cent hydrochloric acid was 98 mdd. (0.016 ipy.), the addition of 0.5 per cent cupric chloride to the air-saturated solution increased the corrosion rate to 1104 mdd. (0.18 ipy.).

Other oxidizing chloride salts, such as ferric chloride and mercuric chloride, are also highly corrosive to nickel and MONEL alloy 400 except in very dilute solutions. In the effluent from ferric chloride coagulation of sewage, where the ferric chloride content of the effluent was only 0.2 to 0.3 per cent, the corrosion rate of nickel was only 55 mdd. (0.009 ipy.) and that of MONEL alloy 400, 86 mdd. (0.014 ipy.). Stannic chloride is apparently not as corrosive to nickel as some of the other oxidizing salts. In three weeks tests in a 26% solution at 24° C (75° F), the corrosion rate of nickel was only 109 mdd. (0.018 ipy.) and that of MONEL alloy 400 was 179 mdd. (0.029 ipy.).

The addition of appreciable amounts of such oxidizing salts as chromates, dichromates, nitrates and peroxides to hydrochloric acid solutions may make them highly corrosive to nickel and MONEL alloy 400.

Cuprous and ferrous chlorides in reducing or air-free hydrochloric acid solutions do not increase the corrosion rates.

Velocity of the Solution

The usual effect of an increase in velocity of relative motion between metal and liquid is to increase the corrosion rate. It brings fresh acid and oxygen, if present, to the corroding surface, removes spent acid, and thins the diffusion film through which soluble reacting substances and corrosion products must pass. If movement is relatively swift, it may prevent the retention of what otherwise might be protective films. Velocities of 15 to 22 feet per minute were used in many of the laboratory tests described in this bulletin because they favor reproducibility of results and represent conditions often found in plant practice.

Film Formation

The formation of films or accumulation of solid products of corrosion upon a metal surface often has a marked effect on corrosion rates. This is particularly true where the deposits are dense and are insoluble in the solution, thus preventing acid and oxygen from reaching the metal surface. The effect of such protective deposits is usually to reduce corrosion to an extent dependent upon the distribution and physical structure of the deposit. In the case of MONEL alloy 400 in pure hydrochloric acid solutions, there is no evidence of such a protective effect from corrosion products. With nickel, as mentioned previously, there is some evidence that the relatively low solubility of nickel chloride may give a certain amount of protection in the more concentrated cold solutions.

In some plant processes in which hydrochloric acid is mixed with other materials, non-metallic films which tend to reduce corrosion may be formed sometimes on a metal surface. This is exemplified by the oily films which may occur in exposure to sewage or in the processing of oily substances.

The addition of protein materials such as milk albumen to dilute, aerated acid solutions is often effective in reducing corrosion as is evident from the results of laboratory corrosion tests given in Table 3.

TABLE 3
Effect of Protein Addition an Corrosion of MGNEL alloy 400 in Hydrochloric Acid Solutions
Temperature: 30° C (86° F)
Duration of Tests: 7 days
Velocity: 16 ft per min.

Solution	Average Corrosion Rate, mdd.*
Air-saturated, 2% HCl........................	1875
Air-saturated, 2 °fo HCl plus 0.5 % milk albumen	745
Air-saturated, 5% HCl........................	2230
Air-saturated, 5 % HCl plus 0.5% milk albumen	1115

*** Corrosion rates are high due to accumulation of cupric chloride in solutions from exposure of MONEL alloy 400 to air-saturated test- solutions for 7 day periods. For normal rate of MONEL alloy 400 in 24 hr tests in air-saturated solutions see Fig. 4.**

It is believed that the inhibiting effect is due to the film-forming characteristics of the protein, together with its reaction with some of the oxygen present.

Effect of Stress

Experience with nickel and MONEL nickel-copper alloy 400 equipment under various conditions of stress has demonstrated that these materials are not subject to stress-corrosion cracking in hydrochloric acid solutions. INCONEL nickel-chromium alloy 600 which is discussed below, also is free from this form of attack.

INCONEL alloy 600

While INCONEL alloy 600 possesses fairly good resistance to dilute hydrochloric acid solutions, its performance, because of its chromium content, will not usually be quite as good as that of MONEL alloy 400 or nickel. It has demonstrated good resistance to cold, aerated acid in concentrations under about 2 per cent. The results of a number of laboratory tests are given in Table 4. Caution should be used in exposing INCONEL alloy 600 to hot hydrochloric acid solutions except where the acid concentrations are very low. It has been applied successfully to such processes as the production of synthetic resins, distillation of coal tar, evaporation of gelatine, distillation of pectin, and handling of glandular compounds where small amounts of residual hydrochloric acid are present from catalytic or acid extraction processes, and particular resistance to organic materials is required.

TABLE 4
Corrosion of INCONEL alloy 600 in Hydrochloric Acid

Arid concen-tration, % HCl by wt.	Tempera-ture		Dura-tion of Test	Aeration	veloc-ity ft. per min.	Corrosion Rate	
	°C	°F				mdd.	ipy.
5	30	86	20 hr	H_2 saturated	16.5	78	0.013
5	30	86	20 hr	Air saturated	16.5	581	0.097
5.9	30	86	5 days	Air saturated	Quiet	267	0.045
5.9	80	176	5 days	Air saturated	Quiet	4,223	0.71
5	85	185	20 hr	H_2 saturated	16.5	9,550	1.59
5	8S	185	20 hr	Air saturated	16.5	11,630	1.95

HASTELLOY Alloys

For handling hydrochloric acid in concentrations and at temperatures above those indicated for the suitable performance of nickel and MONEL alloy 400, the most resistant of the high nickel alloys is the HASTELLOY alloy B. As indicated in the data[4] of Figure 8, HASTELLOY alloy B has unusually high resistance at all concentrations and temperatures, even at the boiling point,

It is recommended particularly for service in hydrochloric acid solutions in the temperature range from 70 to 110° C (158 to 230° F) and for handling wet hydrogen chloride gas. The penetration rate is only 148 mdd. (0.023 ipy.) in a 20 per cent boiling solution, generally considered to be one of the most corrosive conditions.

[4] "Hastellov Corrosion Resistant Atloya," May 1957 Edition. Haynes Stefte Company, Kokomo, Indiana.

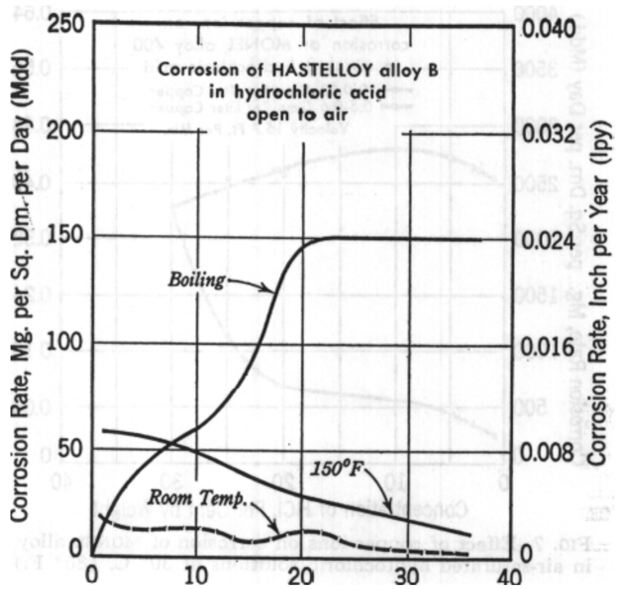

FIG. 8-Corrosion of HASTELLOY alloy B in hydrochloric acid solutions.

HASTELLOY alloy C has useful resistance to all concentrations of hydrochloric acid at room temperature and is used successfully up to 50° C (122° F). Near this limiting temperature, however, HASTELLOY alloy B is the better choice of material, the only exception being when oxidizing salts or traces of free chlorine are present.

HASTELLOY alloy D possesses moderate resistance to hydrochloric acid, although the highest temperature for which it is recommended is about 40° C (105° F).

HASTELLOY alloy F has good resistance to hydrochloric acid of all concentrations at room temperature, and may be used in dilute solutions at temperatures up to 65° C (150° F).

Oxidizing Salts

Ferric chloride, cupric chloride, and other oxidizing salts in solution, considerably increase the corrosion of HASTELLOY alloys B and D in hydrochloric acid solutions and none of these alloys is recommended for handling such solutions except where the concentrations of oxidizing salt is extremely small.

HASTELLOY alloy C, however, is outstanding in its resistance to oxidizing salt solutions and, at moderate temperatures, to hydrochloric acid solutions containing appreciable amounts of oxidizing salts. HASTELLOY alloy C is resistant to ferric chloride solutions at temperatures up to about 70° C (158° F) and to cupric chloride solutions up to about 40° C (105° F).

In Table 5 are given the results of a number of laboratory corrosion tests of HASTELLOY alloy C in quiet ferric chloride solutions and mixtures of hydrochloric acid and ferric chloride.

TABLE 5
Corrosion of HASTELLOY alloy C in Ferric Chloride Solutions and Mixtures of Ferric Chloride and Hydrochloric Acid

Solution	Temperature		Corrosion Rate	
	°C	°F	mdd.	ipy.
5% Ferric Chloride...	Room	...	2.0	0.0003
10% Ferric Chloride...	Room		2.0	0.0003
10% Ferric Chloride ...	65	149	42.0	0.0068
45% Ferric Chloride...	30	86	59.0	0.0095
45% Ferric Chloride...	65	149	294.0	0.047
5% Ferric Chloride plus 1% HCl ...	Room	...	2.0	0.0003
5% Ferric Chloride plus 5% HCl...	Room	...	2.4	0.0004
10% Ferric Chloride plus 1 % HCl ...	Room	...	2.0	0.0003
10% Ferric Chloride plus 5% HCl...	Room	...	2.1	0.0003
10% Ferric Chloride plus 10% HCl..	70	158	1272	0.21

Nickel-Iron Alloys

The addition of nickel to iron increases its resistance to hydrochloric acid solutions at atmospheric temperature. The improvement is roughly in proportion to the nickel content where the nickel addition is above about 12 per cent. So far as nickel steels are concerned, the ones most likely to have practical application in dilute hydrochloric acid applications are the series of nickel-iron alloys containing 25 to 60 per cent nickel used for their special expansion or magnetic characteristics, as for example the INVAR* or ELINVAR* alloys containing about 36 per cent nickel. In Table 6 are given the results of several corrosion tests of high nickel steels in hydrochloric acid solutions at room temperature. Corrosion rates of an ELINVAR alloy in dilute solutions at several temperatures are shown in Table 7.

TABLE 6
Laboratory Corrosion Tests of Nickel Steels in Quiet Hydrochloric Acid Solutions at Room Temperature

Acid Concentration, % HCl by wt.	25% Ni Steel		32% Ni-2% Cr Steel	
	mdd.	ipy.	mdd.	ipy.
1.8	70	0.013	…	…
5	…	…	96	0.017
9	160	0.029	…	…
10	…	…	168	0.036
15	576	0.105	…	…
17.2	...	...	360	0.064

TABLE 7
Laboratory Corrosion Tests of ELINVAR Type Alloy in Quiet Unaerated Hydrochloric Acid Solutions

Acid Concentration, % HCI	Corrosion Rate					
	Room Temp.		52°C (125°F)		74°C (165°F)	
by wt.	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.
1	25	0.005	48	0.009	73	0.013
2	26	0.005	50	0.009	131	0.024
4	27	0.005	54	0.010	291	0.053
8	26	0.005	206	0.038	1260	0.23

* Trademark of Soc. Anon. de Commentry-Fourchambault et Decazivi11e (Aciéries d'Imphy).

The nickel-iron alloys most commonly used with dilute hydrochloric acid at room temperature are the nickel and nickel-copper cast irons of the NI-RESIST cast iron series. Corrosion rates of NI-RESIST Type 1 cast iron (13.5 to 17.5 per cent nickel, 5.5 to 7.5 per cent copper, and 1.75 to 2.5 per cent chromium) in unaerated hydrochloric acid solutions at room temperature are given in Table 8.

TABLE 8
Corrosion of NI-RESIST Type I Cast Iron in Unaerated Hydrochloric Acid Solutions at Room Temperature

Acid Concentration, % HC1 by wt.	Corrosion Rate			
	Ni-Resist Type I Cast Iron		Plain Cast Iron	
	mdd.	ipy.	mdd.	ipy.
1.8	25	0.005	4476	0.9
3.6	74	0.015		
5.0	88	0.018	7440	1.5
10.0	81	0.016	6186	1.2
20.0	230	0.045	....	

NI-RESIST Type 3 (containing 28 to 32 per cent nickel), because of its higher nickel content, will usually have somewhat better resistance to dilute hydrochloric acid solutions than NI-RESIST Type 1 and NI-RESIST Type 2, as indicated by plant tests, the results of which are given in the latter part of this bulletin.

Both aeration and increase in temperature considerably increase the corrosion rates of the NI-RESIST alloys. For example, tests in aerated 2 per cent hydrochloric acid at 49° C (120° F) gave corrosion rates of 520 mdd. (0.10 ipy.) for NI-RESIST Type 1 and 15,000 mdd. (3.0 ipy.) for plain cast iron.

Hydrogen Chloride and Chlorine

All of the nickel alloys considered in this bulletin are resistant to dry chlorine and hydrogen chloride, most of them even at considerably elevated temperatures, as indicated in the following section of the bulletin. MONEL alloy 400 is a standard material for trim on chlorine cylinder and tank car valves, for orifice plates in chlorine pipe lines, and is used frequently for parts of chlorine dispensing equipment.

Wet hydrogen chloride at temperatures below the dew point will usually behave about the same as concentrated hydrochloric acid as discussed in a preceding section of the bulletin. HASTELLOY alloy B is the most resistant nickel alloy.

Wet chlorine at temperatures below the dew point or aqueous solutions containing considerable amounts of free chlorine are highly corrosive to all of these alloys except HASTELLOY alloy C. MONEL alloy 400, nickel and INCONEL alloy 600 frequently can be used with solutions containing 3 gm per liter or less available chlorine in discontinuous operations such as in cyclic textile bleaching with hypochlorite solutions where the bleaching cycle is followed by rinsing and acid “souring” operations in the same vessel. In higher concentrations attack is likely to be severe and accompanied by pitting.

Short-time tests of MONEL alloy 400 in sodium hypochlorite solutions of 3 gm per liter available chlorine have shown average rates of corrosion of about 0.001 ipy. in contact with the solutions for 8 hours daily over a one-year period in cyclic textile bleaching. Lower or higher rates have been found to apply for shorter or longer periods of daily contact with the solutions. Nickel behaves similarly to MONEL alloy 400 in weak hypochlorite solutions, but is generally inferior to MONEL alloy 400 in concentrations where the available chlorine content is over 3 gm per liter. Tests with INCONEL alloy 600 have indicated that it is somewhat more resistant than either MONEL alloy 400 or nickel to corrosion by hypochlorites, especially where the concentration of available chlorine is over 3 gm per liter.

MONEL alloy 400, nickel, INCONEL alloy 600 are resistant to the very dilute hypochlorite solutions, usually containing less than 500 ppm. available chlorine used for sterilizing purposes. Prucha[5] reported the results of tests in sodium hypochlorite sterilizing solutions shown in Table 9.

[5] **M. J. Prucha, "Corrosive Action of Washing Powders and Chemical Sterilizers on Metals used in Milk Plant Equipment," Proc. International Assn. Milk Dealers, Plant Sect. 22, 54 (1929).**

TABLE 9

Corrosion of MONEL alloy 400 and Nickel in Sodium Hypochlorite Sterilizing Solutions

Temperature: 25° C (77° F)

	Corrosion Rate					
	35 ppm Available Chlorine		100 ppm Available Chlorine		500 ppm Available Chlorine	
	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.
Monel alloy 400.	0	0	1.3	0.0002	5.1	0.0008
Nickel.	0.61	0.0001	2.1	0.0003	5.1	0.0008

Inhibitors, such as sodium silicate (water-glass) or trisodium phosphate, have marked effect in reducing corrosion rates of nickel, MONEL alloy 400 and INCONEL alloy 600 in hypochlorite solutions. The inhibitive effect holds for solutions containing as mucn as 6.5 gm per liter available chlorine. Data illustrating the inhibitive properties of these salts in sodium hypochlorite solutions are given in Table 10.

It is important to note that, in those solutions containing an inhibitor, corrosion is more uniform and less confined to local areas. Specimens in contact with solutions containing 6.5 gm per liter available chlorine show some susceptibility to local corrosion, even with the inhibitor present, though the tendency toward such attack has been reduced by the inhibitor. With an inhibitor present in concentrations of 3.3 gm per liter available chlorine, or less, the corrosion of MONEL alloy 400 and nickel is uniform, with local attack entirely absent.

In laboratory tests, as little as 0.025 cc of sodium silicate solution (1.4 sp gr) per liter of bleaching solution has been found effective in reducing corrosion.

HASTELLOY alloy C is outstanding in its resistance to strong chlorine solutions and to wet chlorine gas, in the latter case being limited to temperatures below about 40° C (105° F). Its maximum corrosion rate in wet chlorine gas at room temperature is 0.001 ipy. In water vapors at 170° C (340° F) containing 1000 ppm chlorine, HASTELLOY alloy C corroded at a rate of 0.0003 ipy. In strong bleaching solutions containing over 10% available chlorine, there has been some indication that HASTELLOY alloy C may have a

TABLE 10

Effect of Inhibitors on Corrosion by Sodium Hypochlorite Solutions

Temperature: 40° C (104° F)
Duration of tests: 16 hrs
Beaker tests-No agitation

Solution Composition gm per liter			MONEL alloy 400			NICKEL			INCONEL alloy 600		
Available Chlorine	Sodium Silicate	Trisodium Phosphate	Corrosion Rate		Max. Depth Pitting, inch	Corrosion Rate		Max. Depth Pitting, inch	Corrosion Rate		Max. Depth Pitting, inch
			mdd.	ipy.		mdd.	ipy.		mdd.	ipy.	
6.5	…	...	692	0.113	.011	321	0.052	.022	69	0.012	.027
6.5	0.5	…	107	0.018	.005	64	0.010	.014	15	0.003	.022
6.5		0.5	51	0.008	.006	122	0.020	.024	15	0.003	.017
6.5	2.0	…	13	0.002	.007	9	0.001	None	6	0.001	.008
6.5	…	2.0	21	0.003	.005	57	0.009	None	7	0.001	.012
3.3	…	…	243	0.040	.007	183	0.030	.014	29	0.005	.032
3.3	0.5		6	0.001	None	22	0.004	None	7	0.001	.008
3.3	…	0.5	26	0.004	.003	40	0.006	None	6	0.001	.007
0.1	…	…	23	0.004	.003	26	0.004	None	12	0.002	.006
0.1	0.5	…	2	0.0003	None	3	0.0005	None	4	0.0007	.003
0.1	…	0.5	8	0.0013	None	4	0.0006	None	4	0.0007	None

Chlorine and Hydrogen Chloride at High Temperatures

Developments in recent years in the chemical process industries have been in the direction of using increasingly higher temperatures in order to accelerate reactions or to accomplish reactions not feasible at lower temperatures. This trend has applied to processes involving chlorine and hydrogen chloride, as in the production of new organic or inorganic chlorides, and the treatment of titanium and zirconium ores. In many cases the successful development of the process has depended upon finding suitable materials of construction to withstand the high temperature halogen gases and salts.

A most commendable corrosion study is that of Brown, DeLong and Auld[6] from whose work much of the following discussion has been abstracted.

The corrosion rates of many metals and alloys in dry chlorine and dry hydrogen chloride increase relatively slowly with increase in temperature up to a critical point, which varies with the individual material. Above this point further increase in temperature rapidly accelerates attack. To some degree the corrosion rate is roughly proportional to the vapor pressure of the particular metallic chloride involved, as in the case of nickel, shown in Figure 9. However,

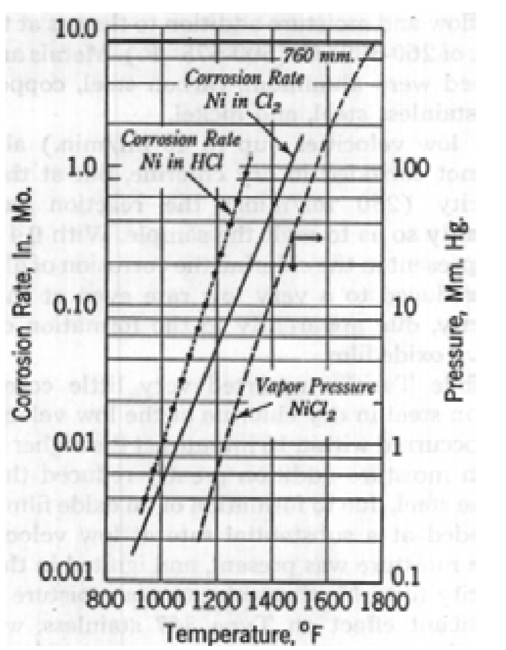

FIG. 9-Corrosion of nickel in dry chlorine and dry hydrogen chloride.

the corrosion resistance may not be predicted solely by this method. Some metal chlorides melt or decompose at temperatures at which the vapor pressure is still low, and the reaction can proceed since the protective effect of the coating is lost. Other materials may be inherently resistant to the formation of surface chloride films. Still others may ignite in chlorine above a certain temperature with evolution of heat, thus raising both the metal temperature and the rate of reaction. Melting points and vapor pressure data for many metal halides have been published by Quill.[7]

The above authors conducted laboratory corrosion tests of a number of materials in dry chlorine and dry hydrogen chloride with test runs of 2 to 6 hours and 10 to 20 hours, using a gas flow rate of 1.3 ft per minute. As indicated in the data for INCONEL nickel-chromium alloy 600 in dry chlorine, Figure 10, the

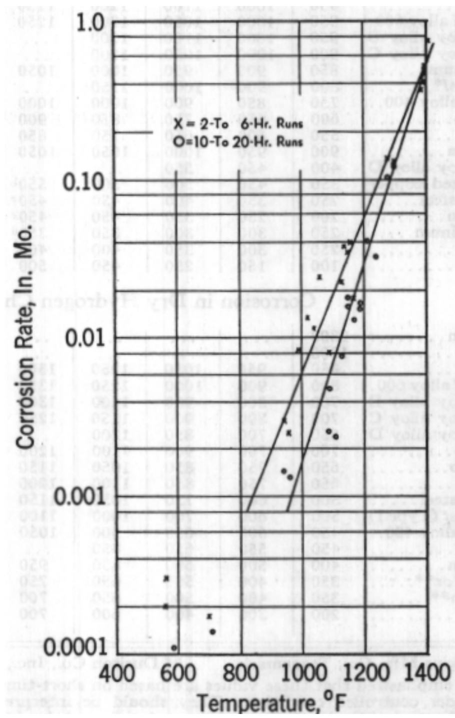

FIG. 10-Corrosion of INCONEL nickel-chromium alloy 600 in dry chlorine gas.

longer test runs yielded somewhat lower corrosion rates, probably due to the effect of time on the formation of protective films. The results of two hour runs with INCONEL alloy 600 in dry hydrogen chloride are given in Figure 11.

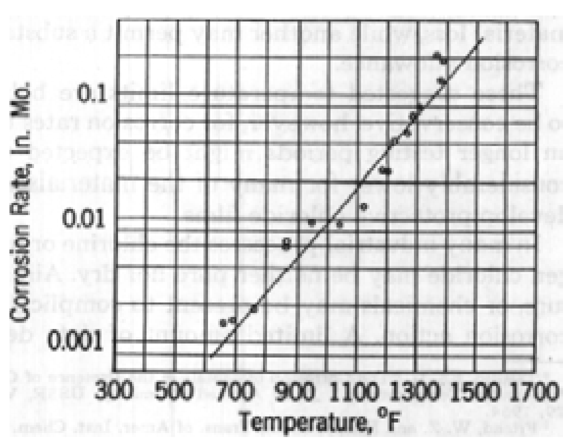

FIG. 11-Corrosion of INCONEL alloy 600 in dry hydrogen chloride gas.

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[6] "Corrosion by Chlorine and by Hydrogen Chloride at High Temperatures," M. H. Brown, W, B. DeLong, and J. R. Auld, Ind. do Eng. Chemistry, Vol. 39, No. 7 pp 839-844.

[7] L. L. Quill, "Chemistry & Metallurgy of Miscellaneous Materials: Thermodynamics," pp 193-206. McGraw-Hill Book Co. 1950.

From this study the authors prepared Table 11 listing temperatures at which various corrosion rates were exceeded, and suggested upper temperature limits for continuous service. These limits are to be interpreted as a rough guide of maximum temperature at which the given materials can be used without serious attack in dry chlorine or dry hydrogen chloride. Such values obviously have limitations, for one service application may call for practically no material loss, while another may permit a substantial corrosion allowance.

TABLE 11
Corrosion of Metals[a]

	Approx. Temp. at Which Given Corrosion Rate Is Exceeded in Short Time Tests in Dry C12, °F					Suggested Upper Temp. Limit for Continuous Service, °F
	0.0025 in/mo	0.005 in/mo	0.01 in/mo	0.05 in/mo	0.1 in/mo	
	Corrosion in Dry Chlorine					
Nickel	950	1000	1100	1200	1250	1000
Inconel alloy 600	950	1000	1050	1200	1250	1000
Hastelloy alloy B	950	1000	1100	1200	...	1000
Hastelloy alloy C	900	1000	1050	1200	...	950
Magnesium	850	900	950	1000	1050	850
Chromel A*	800	900	1000	1150		850
Monel alloy 400	750	850	900	1000	1000	800
18-8-Mo	600	650	750	850	900	650
18-8	550	600	650	750	850	600
Platinum	900	950	1000	1050	1050	500
Hastelloy alloy D	400	450	550	...	...	400
Deoxidized copper	350	450	500	500	5506	400
Carbon steel	250	350	400	450	450-	400
Cast iron	200	250	350	450	450-	350
2S aluminum	250	300	300	350	3504	250
Gold	250	300	350	400	400	...
Silver	100	150	250	450	500	...
	Corrosion in Dry Hydrogen Chloride					
Platinum	2300	...	...	...	...	2200
Gold	1800	...	...	...	...	1600
Nickel	850	950	1050	1250	1300	950
Inconel alloy 600	800	900	1000	1250	1350	900
Hastelloy alloy B	700	800	900	1200	1300	850
Hastelloy alloy C	700	800	900	1150	1250	850
Hastelloy alloy D	550	700	850	1200	...	800
18-8-Mo	700	700	900	1100	1200	800
25-12-Cb	650	750	850	1050	1150	800
18-8	650	750	850	1100	1200	750
Carbon *steel*	500	600	750	1050	1150	500
Ni-Resist (Type 1)	*500*	600	700	1000	1100	*500*
Monel alloy 400	450	500	650	900	1050	450
Silver	450	550	650	850	...	450
Cast iron	400	500	600	850	950	400
*Durichlor***	350	400	500	650	750	350
*Duriron***	350	400	500	650	700	350
Copper	200	300	400	600	700	200

* Hoskins Mfg. Co., Trademark. ** Duriron Co., Inc., Trademark.

[a] It is emphasized that these values are based on short-time laboratory tests under controlled conditions. They should be interpreted only as being indicative of the limitations of the materials and should not be used for estimation of the service life of equipment.

[b] Ignites at about 600° F

[c] Ignites at 450-500° F

[d] Ignites at 400-450° F

These suggested temperature limits are believed to be conservative, however, for corrosion rates based on longer testing periods might be expected to be considerably lower for many of the materials which develop protective chloride films.

In many industrial processes the chlorine or hydrogen chloride may be neither pure nor dry. Air, moisture, or chemicals may be present to complicate the corrosion action. A limited amount of data dealing with the effect of moisture or air dilution which has been reported by Brown et al,[6] Tseitlin,[8] and, Friend and Knapp,[9] will be included in the discussion to follow.

Chlorine

For service temperatures up to 540°C (1000° F), the most resistant alloys are nickel, INCONEL alloy 600 and the high nickel alloy, HASTELLOY alloy B. Closely following these is HASTELLOY alloy C, useable to 480° C (900° F). MONEL alloy 400 appears to be suitable up to 430° C (800° F), and the chromium-nickel stainless steels up to 345° C (650° F). Both platinum and gold form unstable chlorides in hot chlorine, with the result that their usefulness is restricted to the relatively low temperatures shown in Table 11.

Copper, cast iron, and carbon steel should all be restricted to service temperatures of less than 205° C (400° F) in dry chlorine, for they all tend to ignite at somewhat higher temperatures. Tseitlin[8] has reported the ignition of copper at 345° C (650°F) at a low gas flow velocity, and at 260 to 300° C (500 to 575° F) at higher velocities. Brown et al, observed the ignition of steel at 230° C (450° F) towards the end of tests of 16 and 20 hours duration. Heinemann, Garrison and Haber[10] reported the ignition of steel at 250° C (484° F) in tests of 30 minutes or less.

Tseitlin investigated the effect of velocity of chlorine flow and moisture addition to the gas at temperatures of 260-300° C (500-575° F). Metals and alloys studied were aluminum, carbon steel, copper, Type 347 stainless steel, and nickel.

At low velocities (up to 40 ml/min) aluminum was not corroded in dry chlorine, but at the higher velocity (250 ml/min) the reaction proceeded violently so as to melt the sample. With 0.4% moisture present in the chlorine the corrosion of aluminum was reduced to a very low rate even at the higher velocity, due apparently to the formation of a protective oxide film.

While Tseitlin reported very little corrosion of carbon steel in dry chlorine at the low velocity, ignition occurred within 15 minutes at the higher velocity. Again moisture addition greatly reduced the attack on the steel, due to formation of an oxide film. Copper corroded at a substantial rate at low velocity even when moisture was present, and ignited in the higher velocity tests. Neither velocity nor moisture had any significant effect on Type 347 stainless, which exhibited a low corrosion rate, or on nickel which did not react in Tseitlin's tests of 6 hours duration.

Brown et al, included some studies of the effect of 0.4% moisture in chlorine on the corrosion of an 18% chromium-8% nickel stainless steel. At temperatures below 370° C (700° F) the presence of moisture increased the corrosion rate significantly but had no effect at higher temperatures. Tseitlin's work did not show this effect since his tests were conducted in the temperature range found by Brown where the moisture effect began to disappear.

[8] Tseitlin, Kh. L. "The Corrosion of Metals in the Presence of Chlorine at Elevated Temperatures." J1. of Applied Chemistry, USSR, Vol. 27, #9, 1954.

[9] Friend, W. Z. and Knapp, B. B., Trans. of Amer. Inst. Chem. Engrs., Vol. 39, 731-53 (1943).

[10] Heinemann G., Garrison, F. G. as Haber, P. A., Industrial Eng. Chemistry, Vol. 38, 497-9, 1946.

Pershke and Pecherkin[11] reported results of 15 hour laboratory tests in chlorine containing water vapor to approximately 100% of saturation. Included were a number of copper base and iron base alloys. Most of the copper base alloys showed high rates of attack at 300° C (575° F) and were not considered to have useful resistance above 200° C (390° F). Of the iron base alloys, only stainless steels of the 18-8 chromium nickel variety showed useful resistance at 300° C (575° F), none being suitable at 500° C (930° F).

Hydrogen Chloride

The performance of materials in dry hydrogen chloride is somewhat analogous to their behavior in dry chlorine, as can be seen in the tabulation of Brown et al,[6] Table 11. Evidence that these temperature limitations for certain materials may be on the conservative side is supported by the more recent data of Savolainen and Blanco,[12] Table 12. Their tests of

TABLE 12
Laboratory Corrosion Tests in Anhydrous HCl Gas
Temperature: 500° C (930° F)
Test Duration: 500 hrs

Material	Corrosion Rate	
	mdd.	ipy.
Hastelloy alloy B..............................	39	0.0025
Nickel	48	0.003
Inconel alloy 600..............................	51	0.003
Type 304L Stainless	200	0.011

500 hours duration in anhydrous hydrogen chloride at 500° C (930° F) resulted in corrosion rates considerably lower than those observed by Brown.

Notable exceptions in the behavior of materials in hydrogen chloride and chlorine are those of platinum and gold, which exhibit such high resistance to hydrogen chloride attack that the chloride salts are not formed. Platinum appears to be outstanding in its resistance, and useable to temperatures of the order of 1200° C (2200° F).

Nickel and the high nickel alloys such as INCONEL alloy 600 and HASTELLOY alloys B and C appear to be the most practical alloys for service to temperatures of about 540° C (1000° F), and reference to their uses in industrial applications is mentioned below.

While the chromium-nickel family of stainless steels appears to have suitable corrosion resistance at temperatures up to 400 to 425° C (750 to 800° F), one case of stress corrosion cracking of Type 347 stainless steel has been observed in wet mixed gases containing HCl. That certain of the chromium-nickel-iron alloys are suitable is evident by the successful use in muriatic furnace parts of a cast alloy; having a composition of 37% Ni, 27% Cr, 3% Mo, 2% Cu, 0.25% C, balance iron.

[11] Pershke, V. & Pecherkin L., Khimistroi, 6, 140-1 (1934).
[12] "New Developments in Head End Methods for Preparation of Fuels for Aqueous Processing." J. E. Savolainen & R. E. Blanco, Chemical Engineering Progress, Vol. 53, No. 2., February 1957, pp 78-81.

Cast iron and carbon steel appear to be useful in hydrogen chloride to somewhat higher temperatures than in chlorine, and while their corrosion rates increase with temperature of the hydrogen chloride, ignition has not been reported at temperatures up to 760° C (1400° F). Depending upon the corrosion allowance permissible, carbon steel might be useful to temperatures of 260 to 315° C (500 to 600° F).

The effect of moisture in hydrogen chloride at elevated temperatures has been reported for a few materials. Friend and Knapp,[9] whose results are shown in Table 13, found that 0.25% moisture in

TABLE 13
Corrosion of Metals and Alloys in Hydrogen Chloride at High. Temperatures
A. Tests at 205° C (400° F) for 20 hr

Material	Corrosion Rates			
	Wet*		Dry	
	mild.	ipy.	mild.	ipy.
Carbon Steel	5.2	0.0009	5.4	0.0009
Nickel	2.0	0.0003	1.6	0.0003

B. Tests at 538°C (1000°F)

Material	Corrosion Rates, ipy.					Weight Losses, mg/sq dm			
	Wet*				Dry	wet*			
	4 hr	8 hr	20 hr	47 hr	20 hr	4 hr	8 hr	20 hr	47 hr
Carbon Steel ..	0.17	0.21	...	...	0.25-0.42	…	…	…	…
Nickel...........	0.12	0.07	0.028	...	0.037	126	143	140	...
Monel alloy 400 ...	…	…	...	0.049	...	124	165	...	600
Inconel alloy 600 ...	…	…	0.034	...	...	110	105	165	...
Hastelloy alloy B	0.14	0.08	...	...	...				...
Type 316 Stainless (18% Cr, 8% Ni, 3% Mo	0.17	0.14	.	...	...				..
Platinum	Unattacked								

* Moisture content of gas was about 0.25% by weight after bubbling through concentrated hydrochloric acid and before passing over the test specimens.

hydrogen chloride did not significantly alter the corrosion of either carbon steel or nickel in tests conducted at 400° F and 1000° F Pershke and Pecherkin[11] compared several copper base and iron base alloys in wet hydrogen chloride and wet chlorine, finding lower rates to prevail in wet hydrogen chloride. Brown et al, reported that 0.2% moisture in hydrogen chloride did not appreciably alter the corrosion rate of alloys tested at temperatures above the dew point.

The effect of air dilution on the corrosivity of hydrogen chloride is of interest to operators of muriatic acid furnaces, where air leakage is difficult to exclude completely. At temperatures over 370° C (700° F) the corrosion of cast iron has been observed to increase several fold with some air present, while little or no effect was noted at temperatures of

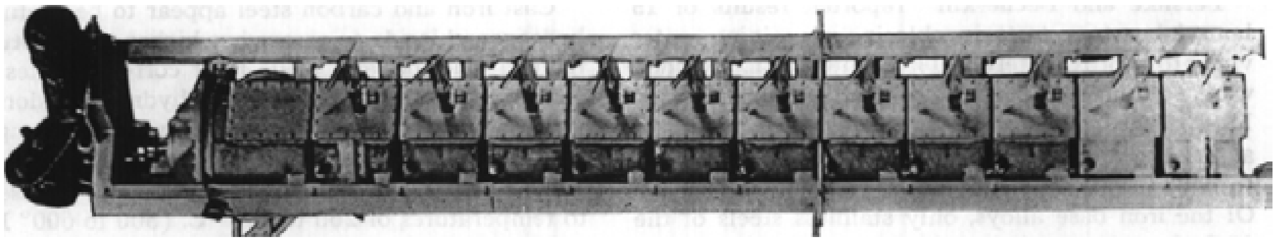

FIG. 12-Specially designed chlorinating furnace used for extraction of precious and semi-precious metals from ores. Built of nickel and nickel-clad steel, it operates at temperatures up to 425° C (800° F).

315 to 340° C (600 to 650° F). Air dilution had little effect on the corrosion resistance of 25% Cr12% Ni (columbium containing), but did lower the temperature at which appreciable attack began on platinum and gold.

Where the major consideration is resistance to corrosion at temperatures below the dew point, but where provision against high-temperature attack is also desired, the indicated order of preference for materials of construction would be platinum, HASTELLOY alloy B, MONEL alloy 400, nickel, INCONEL alloy 600, copper and carbon steel. Nickel 201 and INCONEL alloy 600 would be rated above the HASTELLOY alloys in cases where the major requirement would be resistance to attack at temperatures from 450 to 540° C (850 to 1000° F).

In the synthesis of hydrogen chloride from hydrogen and chlorine, the preferred design of combustion chamber makes use of metal construction with the temperature of the metal being controlled within proper limits by means of water jackets. In this connection, it appears that the danger of corrosion by condensed hydrochloric acid at some temperature near the dew point is greater than by dry hydrogen chloride at some elevated temperature. Maude[13] has pointed out that the allowable temperature range for any metal or alloy may be contracted at its lower end by the hygroscopic nature of the chloride of the metal concerned; for example, iron should not be used at a temperature less than 30° C (54° F) above the HCl-H_2O dew point, while copper may be used so long as the temperature is 5° C (9° F) above the dew point. In view of the hygroscopic nature of nickel chloride, it would be prudent to assume that hydrochloric acid might condense on a nickel surface at a temperature as much above the dew point as in the case of iron, i.e. 30° C (54° F).

Metallurgical Considerations

In the selection of materials for high temperature chlorine or hydrogen chloride service, particularly at temperatures above 370° C (700° F), not only must the corrosion rate of the material be considered, but the effect that the temperature may have on the mechanical properties of the material.

It has been shown above that nickel and high nickel alloys have useful corrosion resistance to temperatures of the order of 540° C (1000° F). In considering the use of commercial nickel at elevated temperatures, it is necessary to consider two of its limitations. Nickel 200, having a nominal content of up to 0.10% C., is subject to embrittlement by intergranularly precipitated carbon or graphite when held at temperatures of 425 to 760° C (800 to 1400° F) for extended periods of time. Nickel 201 (low-carbon nickel), having a maximum carbon content of 0.01 to 0.02%, is not subject to such embrittlement, providing carbonaceous materials are not in contact with it.

Both Nickel 200 and Nickel 201 are subject to intergranular embrittlement by sulfur compounds at temperatures above about 315° C (600° F). In applications where carbon or sulfur compounds are present, or where high temperature strength is required, INCONEL alloy 600 is frequently substituted for Nickel 200 or Nickel 201. At temperatures too high for the suitable performance of metals, use is sometimes made of fused silica, silica brick linings or graphite.

Applications

Nickel and INCONEL nickel-chromium alloy 600 have both been successfully used for chlorination equipment at temperatures up to 540° C (1000° F). The nickel-clad pressure vessel shown in the photograph on page two, operates at 340° C (650° F), and the chlorinating furnace equipment illustrated in Figure 12, consisting of both nickel and nickel-clad steel, operates at 425° C (800° F).

Where arrangements can be made for cooling the metal surface, nickel and INCONEL alloys have been used at even higher gas temperatures. For example, chlorine at 1100° C (2000° F) is being handled in a jacketed nickel tube cooled with high velocity water; chlorine at 760° C (1400° F) is

[12] A. H. Maude, "Anhydrous Hydrogen Chloride Gas", Trans. Amer. Inst. Chem. Engrs., Vol. 38, pp 865-884 (1942).

in the combustion of chlorine and hydrogen to form HCl.

INCONEL nickel-chromium alloy 600 has been employed in the treatment of an organic material with HCl at 700° C (1300° F), and platinum linings are employed in the thermal cracking of a chlorinated organic forming HC1 at a temperature of 750° C (1380° F).

In the Kroll process or similar processes for the production of zirconium and titanium, a first step is the chlorination of the ores to form $ZrC1_4$ or $TiC1_4$, which is subsequently purified and reduced to the metal sponge by reaction with magnesium or sodium. The chlorinating reactor, where temperature may rise to as high as 900° C (1650° F), is usually lined with silica brick. INCONEL alloy 600 or Nickel 201 are used for heating the incoming chlorine to about 400° C (750° F). $ZrC1_4$ or TiC14 vapors are condensed in an initial condenser made of nickel at 95 to 205° C (200 to 400° F), and sometimes an after condenser of steel operating at 150° C (300° F) or lower. Purification of $ZrCl_4$ is carried out by placing the metal salt in INCONEL alloy 600 cans and heating to about 1200° F in a retort made of Type 309 (25 Cr-12 Ni) or Type 310 (25 Cr-20 Ni) stainless steel. The sublimed chloride collects on cooled coils at the top of the retort and is allowed to drop into alloyed steel reduction crucibles frequently located in the same retort.

In corrosion tests of 18 hours in $ZrCl_4$ at 845° C (1550° F), the corrosion rate of INCONEL alloy 600 was 0.0035 inches per month and that of nickel was 0.017 inches per month. Nickel 201 has been used for cylindrical retorts for the sublimation of $ZrCl_4$ at temperatures of 430 to 540° C (800 to 1000° F).

Plant Corrosion Tests

When dealing with straight hydrochloric acid solutions or mixtures where known concentrations of acid are added, the choice of suitably resistant materials often can be based on the laboratory test data in pure solutions. Frequently it is more difficult to predict which will be the most economical material for reactions in which hydrochloric acid is formed by the hydrolysis of chlorides or chlorinated compounds in the presence of water, or by the presence of small amounts of water in reactions involving hydrogen chloride. In such cases it is usually advisable to make corrosion tests in plant or pilot-plant equipment under actual operating conditions.

Numerous plant corrosion tests have been made in such processes and the results of some of the typical tests are presented in the following pages to show the comparison in performance between the various nickel alloys and other materials. The testing device used in most of these tests was the spool-type specimen holder described by Searle and LaQue.[11] This method of testing is substantially in accord with the A.S.T.M. Recommended Practice for Conducting Plant Corrosion Tests, A 224-46[15] Briefly, the assembly consists of previously cleaned and weighed specimens, in duplicate, of the several metals to be tested, mounted on a spool-type holder, with non-metallic parts of bakelite, other organic plastics or porcelain to separate and insulate the specimens from each other, from the metal strengthening members of the device, and from the equipment in which the test is made. Details are shown in Figure 13. The completed

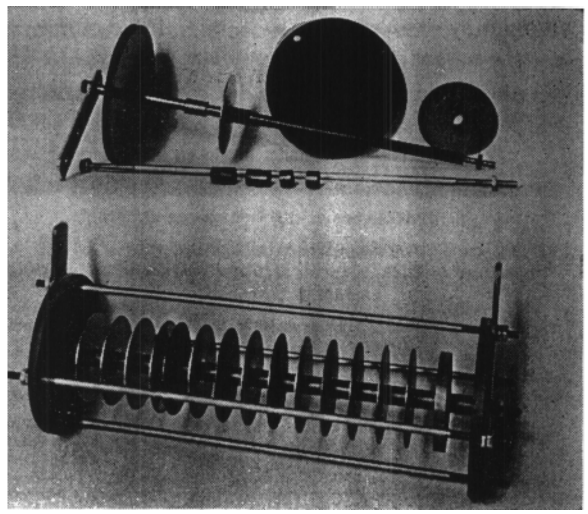

FIG. 13-Spool-type specimen holder.

assemblies are installed in the desired locations, and allowed to remain for a sufficient length of time to give reliable indications of corrosion behavior. Upon completion of a test, the assembly is removed, dismantled, and the specimens examined, cleaned of all adhering corrosion product, and reweighed. From the known weight losses, areas of specimens, and duration of tests, the corrosion rates are calculated. In addition, the specimens are examined for pitting or other local attack.

Chlorinated Solvents

Chlorinated hydrocarbon solvents are used extensively in dry cleaning, metal degreasing, and a wide variety of solvent extraction operations in the process industries. When free from water and at atmospheric temperature, they are not corrosive and steel equipment ordinarily can be used to handle them. However, in the presence of entrained water or a water layer, and, particularly, at elevated temperatures, such as are encountered in the distillation and re-

[14] H. E. Searle and F. L. LaQue, "Corrosion Testing Methods," Proceedings Am. Soc. Testing Mat. 35, 249 (1935).

[15] Am. Soc. Testing Mat. Standards, Part 3, p. 257, (1958).

covery of the solvents, there is appreciable hydrolysis with resulting formation of dilute hydrochloric acid. The development of acidity is accelerated by light and air. Under such conditions, steel frequently is rapidly attacked. Over a period of many years of service MONEL alloy 400 and nickel have shown a high degree of resistance to corrosion under these conditions with a wide variety of chlorinated hydrocarbons. Both materials are used for distillation and recovery equipment in the manufacture and application of the solvents.

Brallier[16] found that the rate of decomposition of carbon tetrachloride by hydrolysis in the presence of water is extremely slow provided that no metal that is attacked by the mixture is present. Carbon tetrachloride was allowed to boil continuously for a week under a layer of water in glass apparatus without the development of any evidence of acidity. A similar test with a sample of steel in the mixture resulted in the decomposition of 1.2 per cent of the carbon tetrachloride to form hydrochloric acid. When nickel was substituted for the steel, and the test repeated, the extent of formation of hydrochloric acid was only 0.0067 per cent of the carbon tetrachloride.

TABLE 14

Effects of Metals on the Decomposition of Boiling Carbon Tetrachloride in the Presence of Water

Experimental Conditions:
Amount of carbon tetrachloride used: 480 to 560 gm
Duration test: 7 days

Metal exposure: 25% of area to liquid carbon tetrachloride 25% of area to liquid water
50% of area to mixed vapors

Material	Total Area, of Specimen, sq cm	Loss of Weight. of Specimen, mg	Weight of Chlorine as Chloride from Hydrolysis, mg
Blank	...	....	31
Blank	...	....	30
Blank	...	....	26
Steel	57.5	3517	3829
Steel	42.8	2117	2237
Steel	42.8	4419	5022
Steel	42.8	4933	5913
Nickel	53.4	42	87
Nickel	54.4	18	54
Nickel	52.0	63	89
Nickel	52.0	443	504
Monel alloy 400 ...	54.4	103	148
Monel alloy 400 ...	53.9	44	95
Monel alloy 400 ...	52.5	62	93
Monel alloy 400 ...	53.5	57	105

Additional tests have been made by Brallier[17] by exposing specimens to carbon tetrachloride-water mixtures boiling under reflux with the results shown in Table 14.

Brallier[17] made a further study of the resistance of metals and alloys to corrosion by several different chlorinated solvents and mixtures of the solvents with water, both at room temperature and boiling. Tests in boiling mixtures of solvent and water exposed to light for prolonged periods constituted exceptionally severe conditions of exposure. Pure nickel was found to be the best of the several materials tested, with MONEL alloy 400 a very good second. The results obtained are reported in Table 15.

In room temperature tests, specimens were exposed to solvent and air, with water absent, and to solvent and air with water present. In both cases, 90 per cent of the area of the specimen was in contact with the solvent.

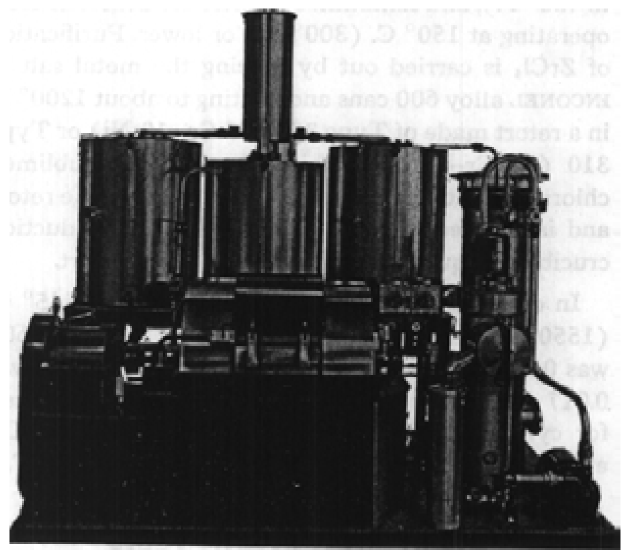

FIG. 14-Dry cleaning system employing chlorinated solvents. All parts in contact with solvent are made of MONEL alloy 400 or nickel.

In tests at the boiling point, where specimens were exposed to solvent and vapor with water absent, about 25 per cent of the area of each specimen was in contact with the solvent and 75 per cent with the vapor. In tests with water present, about 25 per cent of the area of each specimen was exposed to solvent, 25 per cent to the water layer and the remaining 50 per cent to the vapors.

In the rectification of chlorinated solvents during their production, corrosive conditions are usually most severe in the still or reboiler, or in the bottom sections of distilling columns where water tends to accumulate. This is indicated by the results of plant corrosion tests in a continuous process for rectifica-

[16] P. S. Brallier, "Properties of Carbon Tetrachloride," Laundry Age, Sept. 1, 1931, p. 88.
[17] P. S. Brallier, Private Communication (1934).
[18] P. S. Brallier, Private Communication (1934).

tion of crude carbon tetrachloride, given in Table 16 and in a batch process for rectification of crude trichlorethylene, given in Table 17. It will be noted from Table 16 that, in addition to MONEL alloy 400, nickel and INCONEL alloy 600 and NI-RESIST Types 1, 2 and 3 have useful resistance to the corrosive conditions encountered, and these materials are used where a cast material is required for valves, pumps and fittings, and in some cases for cast bubble caps and plates.

Common applications of MONEL alloy 400 and nickel are in the construction of dry cleaning ma-

TABLE 15

Results of Corrosion Tests in Chlorinated Solvents and Their Vapors

Solvent	CORROSION RATE							
	Tests at 25-30°C (77-86°F)				Tests at Boiling Point			
	Water Layer Present		Water Layer Absent		Water Layer Present		Water Layer Absent	
	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.
a. NICKEL								
Carbon Tetrachloride	0.12	0.00002	0.02	0.000003	11.1	0.0018	0.16	0.00003
Chloroform	0.36	0.00006	0.17	0.00003	0.73	0.0001	1.3	0.0002
Ethylene Dichloride	0.08	0.00001	0.04	0.000007	2.2	0.0004	0.20	0.00003
Trichlorethylene	2.3	0.0004	0.94	0.00015	5.9	0.001	0.14	0.00002
Carbon Tetrachloride / Ethylene Dichloride *	0.02	0.000003	0.02	0.000003	1.09	0.0002	0.34	0.00006
b. MONEL alloy 400								
Carbon Tetrachloride	0.66	0.0001	0.06	0.00001	27	0.0044	0.23	0.00004
Chloroform	0.10	0.00002	0.08	0.00001	27.3	0.0045	0.93	0.0002
Ethylene Dichloride	0.15	0.00002	0.06	0.00001	16.5	0.0027	0.17	0.00003
Trichlorethylene	4.1	0.0007	0.45	0.00007	67.1	0.011	0.36	0.00006
Carbon Tetrachloride / Ethylene Dichloride *	0.12	0.00002	0.06	0.00001	6.1	0.0010	0.59	0.0001
c. MILD STEEL								
Carbon Tetrachloride	44.3	0.0082	0.35	0.00006	874	0.16	0.30	0.00006
Chloroform	12.9	0.0024	3.7	0.0007	65.9	0.012	46.8	0.0086
Ethylene Dichloride	7.6	0.0014	0.30	.000006	73.4	0.0135	9.0	0.0016
Trichlorethylene	7.0	0.0013	3.3	.00006	37.8	0.007	...	...
Carbon Tetrachloride / Ethylene Dichloride *	48.4	0.0089	0.04	.0000007	1079	0.20	2.5	0.0005

* Mixture contained 90 per cent carbon tetrachloride and 10 per cent ethylene dichloride by volume.

TABLE 16

Results of Plant Corrosion Tests in a Continuous Process for the Distillation and Rectification of Crude Carbon Tetrachloride

Duration of Tests: 133 days

Test 1-Suspended in vapor stream above top plate of bubble cap rectification column. Approximate analysis of vapor:
Carbon Tetrachloride 99.398%
Sulfur Chloride 0.600%
Carbon Bisulfide 0.002%
Temperature: 78° C (171° F)

Test 2-Suspended from Plate No. 19 of column, which is three plates above feed plate.
Temperature: 80° C. (176° F)

Test 3-Suspended in vapor space immediately below bottom plate of column. Vapor approximately 98% sulfur chloride.
Temperature: 125° C (257° F)

Test 4-Suspended in reboiler for column, completely immersed in liquid with following approximate analysis:
Sulfur Chloride 98.3%
Carbon Tetrachloride 0.13%
Iron as FeCl, 0.01%
Temperature: 138° C (280° F)

Material	CORROSION RATE							
	Test 1		Test 2		Test 3		Test 4	
	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.
Monel alloy 400	1.7	0.0003	1.1	0.0002	1.7	0.0003	5.3	0.0009
Nickel	1.3	0.0002	1.1	0.0002	1.9	0.0003	2.1	0.0003
Inconel alloy 600	1.0	0.0002	0.9	0.0002	2.2	0.0004	3.3	0.0006
Ni-Resist (Type 3)	3.0	0.0005	2.8	0.0005	4.5	0.0009	6.6	0.0013
Ni-Resist (Type 1)	2.8	0.0005	1.9	0.0004	6.8	0.0013	10.7	0.0021
Mild Steel	43.8	0.0081	25.2	0.0046	x		1180	0.217
Cast Iron	36.5	0.0073	25.8	0.0052	800	0.160	640	0.128

x Specimens completely corroded away before end of test. Original thickness of specimens 0.060 inch.

TABLE 17

Results of Plant Corrosion Tests in a Batch Process for the Distillation and Rectification of Crude Trichlorethylene

Duration of Tests: 228 days

Test 1-Suspended in pot still, alternately exposed to trichlorethylene liquid plus water, and trichlorethylene vapor plus steam.
Temperature: 100° C (212° F)

Test 2-Suspended in vapor space above Plate No. 4 of bubble cap rectification column, exposed to vapor and entrained liquid, plus steam.
Temperature: 76 to 93° C (169 to 198° F)

Test 3-Suspended in vapor space above Plate No. 14 of column, exposed to vapor and entrained liquid.
Temperature: 73° C (163° F)

Test 4-Suspended in vapor space above top plate, No. 25, of column. Reflux enters column on this plate.
Temperature: 68 to 70° C (154 to 158° F)

Material	CORROSION RATE							
	Test 1		Test 2		Test 3		Test 4"	
	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.
Nickel	8.7	0.0015	0.6	0.0001	0.7	0.0001	9.9	0.0016
Monel alloy 400	9.2	0.0014	0.7	0.0001	0.7	0.0001	5.7	0.0009
Inconel alloy 600	5.6	0.0009	0.2	<0.0001	0.1	<0.0001	1.9	0.0001
Hastelloy alloy B	6.8	0.0011	0.5	<0.0001	0.4	<0.0001	3.8	0.0006
Hastelloy alloy C	0.5	<0.0001	0.04	<0.0001	0.2	<0.0001	0.3	<0.0001
Copper..................	x	x	x	x	x	x	x	x

< = Less than.

x Specimens completely corroded away before end of test. Original thickness of specimens 0.031 inch.

TABLE 18

Results of Corrosion Tests in Solvent Reclamation Unit of Dry Cleaning Machine Handling Carbon Tetrachloride

Point of Test	Duration of Test, Days	Average Temp.		CORROSION RATE					
				Nickel		MONEL alloy 400		NI-RESIST (Type 1)	
		°C	°F	mdd.	ipy.	mild.	ipy.	mdd.	ipy.
Main Still Liquid..	66	77	170	0.21	0.00003	0.08	0.00001	5.0	0.0011
Main Still Vapor	66	71	160	0.11	0.00002	0.15	0.00003	1.8	0.00035
Auxiliary Condenser Tubes*.........................	96	71	160	9.5	0.0015	8.9	0.0015	. . . .	. . . . .
Auxiliary Condenser Shell (Bottom)**.........	128	66	150	1.6	0.0003	3.1	0.0005	. . . .	. . . . .
Sump Tank...	66	27	80	0.43	0.00007	0.69	0.0001	6.4	0.0012
Main Storage Tank	98	ROOM		1.0	0.00016	1.4	0.0002	11.2	0.0022

*Specimens were in the form of pieces bent so as to clamp over the tubes, from which they were insulated by means of a lacquer on the under side of the specimens.

**These Specimens were circular discs laid at the bottom of the condenser shell underneath the tubes and insulated from the shell by means of a lacquer.

chines, for such parts as solvent recovery stills and condensers, washer cylinders, water separators, lint traps and solvent storage tanks. Such machines use a variety of solvents including carbon tetrachloride, trichlorethylene, perchlorethylene and solvent mixtures. From the clothes, the solvents pick up water, greases, metallic salts and other impurities which frequently tend to cause hydrolysis. The results of corrosion tests in the solvent reclamation unit of a dry cleaning machine using carbon tetrachloride are given in Table 18.

The results of corrosion tests in the liquid and vapor sections of the solvent recovery still of a dry cleaning machine using perchlorethylene as solvent, are given in Table 19.

For metal degreasing applications, a variety of chlorinated solvents are used including trichlorethylene, carbon tetrachloride, perchlorethylene, ethylene dichloride, propylene dichloride, ortho dichlorbenzene, and others. MONEL alloy 400 and nickel are used for degreasing tanks and accessories as well as for solvent recovery equipment.

TABLE 19

Results of Corrosion Tests in Solvent Reclamation Equipmen of Dry Cleaning Unit Handling

Duration of Tests: 64 days
Test 1: In vapors at 127° C (260°F)
Test 2: In liquid at 152°C (305°F)

Material	Corrosion Rate			
	Test 1		Test 2	
	mdd.	ipy.	mild.	ipy.
Monel alloy 400	0.83	0.0001	1.4	0.0002
Nickel	0.64	0.0001	1.3	0.0002
Inconel alloy 600	0.11	<0.0001	0.14	<0.0001
Ni-Resist (Type 1).....	20.1	0.0039	5.7	0.0011
Mild Steel	86.4	0.016	27.2	0.005
Cast Iron	56.1	0.011	18.7	0.004

< = Less than.

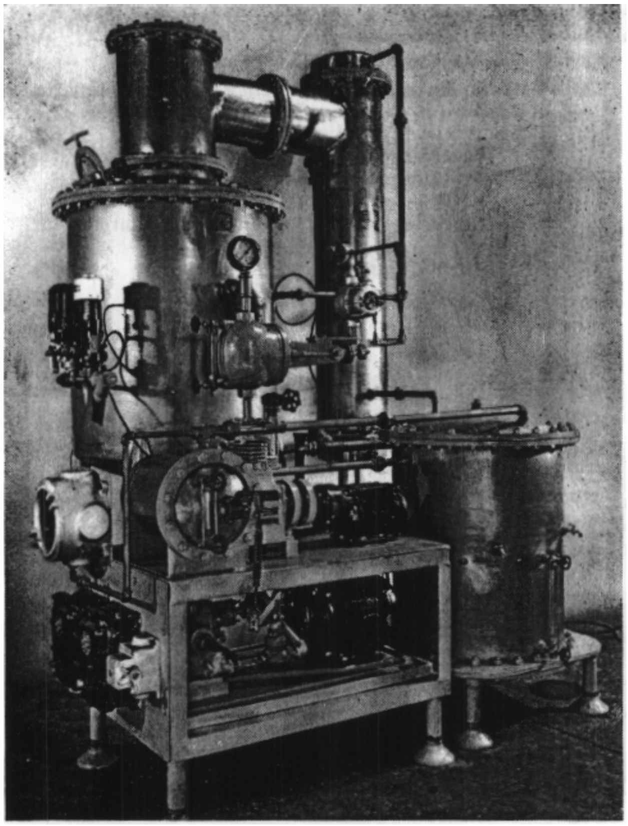

FIG. 15-Completely automatic unit built entirely of MONEL alloy 400 for recovery of chlorinated solvents from the solvent degreasing of metal parts.

In the solvent extraction of animal and vegetable oils, several chlorinated solvents are used. A typical example of the use of MONEL alloy 400 in this service is for solvent recovery apparatus in the production of cod liver extract using ethylene dichloride as solvent.

Organic Chlorinations

In the field of organic chlorinations, a wide range of corrosive conditions is encountered. In some chlorinations, the chlorine as well as all the other reacting materials are charged to the reactor in dry or essentially dry condition. In others the presence of water may be desirable. In some chlorinations, the presence of even small amounts of iron is highly detrimental to the process from the standpoints of undesirable catalytic effect, or effect on color of the product. In others iron is a necessary catalyst in the reaction. Some chlorinations are carried out at room temperature and others at considerably elevated temperatures. In view of the many factors involved, consider- able care must be used in the selection of chlorinators and other process equipment.

A considerable number of organic chlorinations are in the group of those where the raw materials are dry or essentially so, and the presence of iron salts is detrimental to the process or the product. In this class of chlorinations, nickel, nickel-clad steel, MONEL alloy 400 and sometimes 1NCONEL alloy 600 are used for chlorinators. They have suitable resistance to corrosion and the metals have no detrimental catalytic effect on the process or on the color of the product.

Nickel 200 or MONEL alloy 400 reaction vessels, coils and agitators are being used successfully in the chlorination of paraffin and olefine hydrocarbons, benzol, aniline and a number of other organic compounds. In some instances, steel chlorinators have been lined with Nickel 200 or MONEL alloy 400 sheet, thus greatly increasing the useful life of the equipment.

Examples of the corrosion resistance of several materials in dry chlorination reactions at moderate and elevated temperatures are given in Table 20. It will be noted that as the temperature of operation is increased, the corrosivity increases, with the best corrosion resistance being provided by the high nickel alloys.

Experimental work with heptane-chlorine mixtures at temperatures up to 300° C (575° F) and pressures up to 1000 lb per sq in showed that with metals and alloys containing considerable amounts of iron, ferric chloride was formed, which catalyzed the decomposition of the chloro-hydrocarbons with formation of undesirable hydrogen chloride, polychlorides, and gum. A pure nickel reaction tube functioned satisfactorily from the start, and the substitution of MONEL nickel-copper alloy 400 for other ferrous alloy parts of the apparatus proved satisfactory.

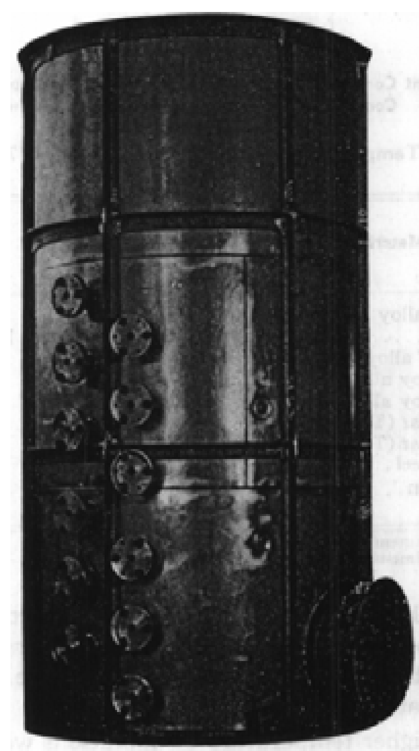

FIG. 16-Nickel 200 vessel used for the chlorination of paraffin.

TABLE 20

Results of Plant Corrosion Tests in Dry Chlorination Processes

Test 1-Plant corrosion test in chlorination of acetylene to make acetylene tetrachloride.
Mixture of crude acetylene tetrachloride with 10 to 21 gm per liter excess chlorine and 0.15 to 1.65 gm per liter dissolved iron. Acidity as HCl, 0.7 to 6.6 gm per liter.
Temperature: 42.3 to 48.9° C (Ave. 46° C) 108 to 120° F (Ave. 115° F)
Duration of test: 282 days.
Velocity: Approx. 0.5 ft per sec.

Test 2-Plant corrosion test in chlorination of phenol. Mixture of phenol, chlorophenol, chlorine and HC1 gas, and ferric chloride. In liquid phase.
Temperature: 50-60° C (123-140° F).
Test duration: 19 days.

Test 3-Same as Test 2. In vapor phase.

Test 4-Plant corrosion test in chlorination of naphthalene. Mixture of chlorine, HCl, and naphthalene chloride. Specimens exposed in splash zone.
Temperature; 165° C (330° F).
Test duration: 52 days.

Test 5-Plant test in chlorination of methane. Specimens exposed in bottom of chlorinator.
Temperature: 230° C (446° F).
Test duration: 9 days.

Material	CORROSION RATE									
	Test 1		Test 2		Test 3		Test 4		Test s	
	mdd.	I ipy.	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.
Monel alloy 400	0.25	<0.0001	43	0.007	12.0	0.002	3.6	0.0006	37	0.006
Nickel	0.27	<0.0001	43	0.007	6.2	0.001	2.0	0.0003	12.4	0.002
Inconel alloy 600........	0.79	0.0001	50	0.009	5.6	0.001	6.3	0.0011	14.8	0.0025
Hastelloy alloy B........	...	...	45	0.007	13	0.002	1.5	0.0002	...	...
Hastelloy alloy C........	3.0	0.0005	4.4	0.0007	6.2	0.001	5.8	0.001	7.5	0.0012
Ni-Resist (Type 3)	3.5	0.0007	...	...	...	. . .	. . .	. . .	222	0.043
Ni-Resist (Type 1)	5.6	0.0011	97	0.019	92	0.018	31.2	0.006	1430	0.283
1% Ni Cast Iron..........	18.6	0.0037	...	...	...	...	...	...	16000	2.92
Cast Iron	...	...	215	0.043	165·	0.033	65.5	0.013	...	...
Mild Steel	...	...	164	0.030	186	0.034	134	0.025	...	...

< - Less than.

In wet chlorinations HASTELLOY alloy C can be used frequently although it is subject to the temperature limitations described on page 10. The production of hexachlorethane by direct chlorination of perchlorethylene in the presence of water is an example of a particularly corrosive condition. In Table 21 are given the results of a plant test in recirculated wet perchlorethylene containing 2 to 16 per cent hexachlorethane and saturated with chlorine gas at approximately 25° C (77° F).

TABLE 21

Plant Corrosion Test in Wet Recirculated Perchlorethylene Containing 2 to 16 Per Cent Hexachlorethane and Saturated with Chlorine

Temperature: Atmospheric to 25°C (77° F)
Duration of test: 50 days

Material	Corrosion Rate		Max. Depth Pitting.
	mdd.	ipy.	inch
Monel alloy 400..........	442	0.072	None
Nickel	216	0.035	Perforated[a]
Inconel alloy 600........	292	0.049	.008
Hastelloy alloy B........	431	0.067	None
Hastelloy alloy C........	205	0.033	None
Ni-Resist (Type 3)	513	0.097	None
Ni-Resist (Type 1)	722	0.140	None
Tank Steel.................	1940	0.36	Perforated
Cast Iron		Completely graphitized[b]	

a Specimens originally 0.031 inch thick.
b Specimens originally 0.188 inch thick.

At higher temperature of operations wet chlorinations may be so extremely corrosive that metallic materials of construction can not be justified, and materials such as glass lined steel become the preferred construction materials. An example of such a condition is shown in Table 22 in a process for the wet chlorination of ethanol at 93° C (200° F).

TABLE 22

Plant Corrosion Test in Wet Chlorination of Ethanol Mixture of ethanol, chlorine, HCl, chlorinated products, and water at 48°Be. Test made in liquid phase.

Temperature: 93°C (200°F) Duration of Test: 20 hrs

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400	12,700	2.07
Nickel	3,100	.50
Inconel alloy 600	13,100	2.22
Hastelloy alloy B...........................	3,500	.54
Hastelloy alloy C...........................	3,600	.58
Mild Steel	25,200	4.8
Ni-Resist (Type 1)	26,400	5.2
Cast Iron	28,500	5.7

In reactions involving wet hydrogen chloride with no free chlorine present HASTELLOY alloy B is usually the most resistant material.

The above corrosion data illustrates the wide range of corrosion conditions which may prevail in chlorination reactions. Prior to the selection of materials for process equipment for a new chlorination process it is advisable to conduct corrosion tests during the laboratory or pilot plant stage of the development.

Synthetic Resins and Rubbers

In the production of phenolic resins, hydrogen chloride is used frequently as a catalyst. A common concentration of HCl is about 0.1 per cent by weight of the charge. The raw materials used are essentially dry, and the temperatures involved are usually high enough that the hydrogen chloride and any moisture present, which tend to concentrate in the vapor phase in the top of the reactor, are in vapor form so that corrosive conditions are often not severe. However, iron salts usually have an objectionable effect in catalysis and upon the color of the resin product, and the possibility that condensed moisture will sometimes be present is such that steel often is not a satisfactory material for reactors. Nickel and nickel-clad steel are used for resin reactors and autoclaves and for condensers, vapor and condensate lines associated therewith, because of the resistance of nickel to the hydrochloric acid conditions which sometimes may occur, its beneficial effect on the color of the product, and its relatively good thermal conductivity. MONEL alloy 400 and INCONEL alloy 600 also are used for reactors in some cases.

Table 23 shows the results of corrosion tests in resin reactors in four different plants. In Test 3, it will be noted that the temperature was low enough and the moisture content high enough for appreciable hydrochloric acid condensation to take place in the vapor space and that MONEL alloy 400 was more resistant than nickel. Test 4 is an example of a case where INCONEL alloy 600 might be preferred because of its resistance to the organic materials at the high temperature used.

†Wrought age-hardeaable high-nickel alloy applicable where higher hardness or strength are required than are available with nickel.

In the production of synthetic resins and rubbers, involving the use of chlorinated hydrocarbon monomers, polymers or reagents, nickel and MONEL alloy 400 are used in applications where processing may involve the formation of dilute hydrochloric acid solutions by hydrolysis or the accumulation of small concentrations of hydrogen chloride in water wash solutions. The following will indicate some of the products or processes in which such applications exist:

Vinyl chloride and vinylidene chloride polymers and copolymers involving vinyl chloride, vinylidene chloride, ethylene dichloride and trichlorethane,

- Chloroprene polymers
- Thio-rubbers involving ethylene dichloride
- Chlorostyrene polymers
- Chlorinated rubber
- Chlorinated paraffins
- Silicone resins involving silicon tetrachloride

DURANICKEL alloy 3011 dies and other parts of nickel are frequently used in the forming of shapes and fabrication of vinylidene and vinyl chloride plastics.

In the production of styrene, nickel and MONEL alloy 400 are sometimes used for covers of alkylation reactors in the synthesis of ethyl benzene using aluminum chloride and hydrogen chloride as catalysts. As a general rule corrosive conditions are less severe in the vapor sections of these reactors than where the metal is in contact with the liquid catalyst complex, which may be corrosive if significant amounts of moisture are present. In this case HASTELLOY alloy B is used.

TABLE 23

Plant Tests in Vapors from Phenol-Formaldehyde Resin Reactors Where Hydrogen Chloride Used as Catalyst

Test 1-In hydrogen chloride vapor plus steam, in vapor line from reactor. Concentration of HCl in vapor varied from 2 to 5 per cent.
Temperature: 149 to 204° C (300 to 400° F)
Duration of test: 46 days

Test 2-In vapor containing dilute HCl and steam, in vapor portion of reactor.
Temperature: 121 to 149° C (250 to 300° F)
Duration of test: 21 days

Test 3- In vapor space of reactor. Hydrogen chloride used as catalyst to extent of 0.1 to 0.175 per cent by weight of charge.
Temperature: 99 to 104° C (210 to 220° F)
Duration of test: 57 days

Test 4-In resin reactor just above HCl gas inlet.
Temperature: Up to 350° C (660° F)
Duration of test: 864 hours

Material	CORROSION RATE							
	Test 1		Test 2		Test 3		Test 4	
	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.
Monel alloy 400	20	0.003.	10	0.002	75	0.012	113	0.018
Nickel	10	0.002	6	0.001	567	0.092	63	0.010
Inconel alloy 600	8	0.001	5	0.001	316	0.048	16	0.003
Hastelloy alloy B	…	0.009	3	0.0005	...	...	15	0.002
Mild Steel	46	...	…	…	...	...	...	…
Ni-Resist (Type 1)	...	...	26	0.005	...	...	44	0.009
Cast Iron	...	…	2161	0.43	...	...	132	0.064

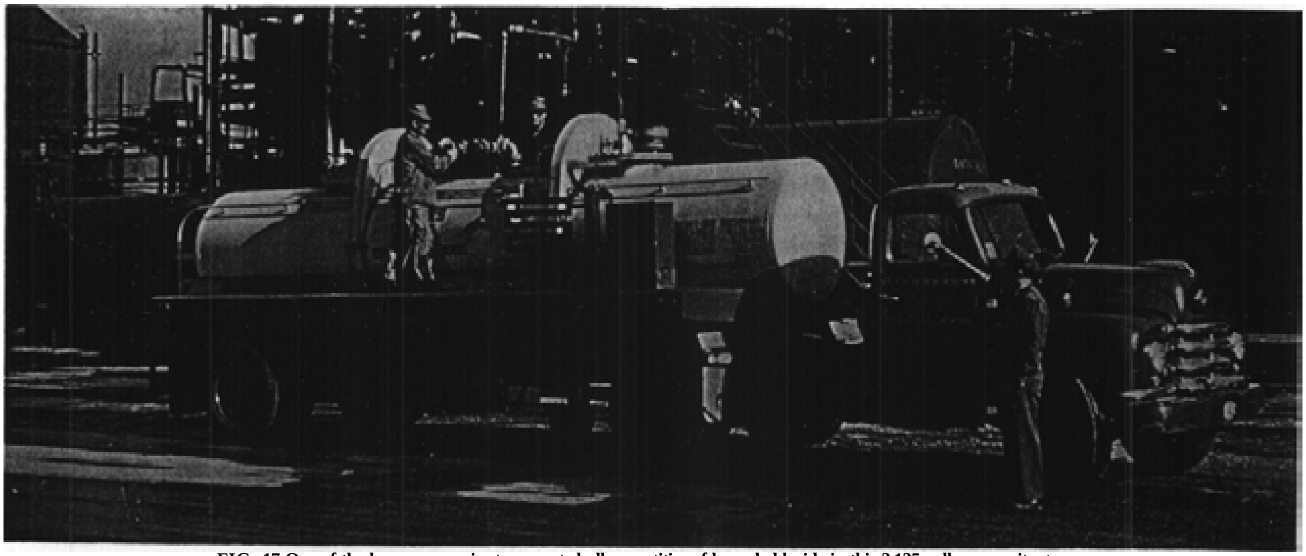

FIG. 17-One of the large companies transports bulk quantities of benzyl chloride in this 2,135-gallon capacity, two-section tank truck. Tanks are constructed from solid Nickel to protect the purity-sensitive chemical from contamination by corrosive attack.

Other Organic Chlorides

Nickel, MONEL alloy 400, INCONEL alloy 600 and NI-RESIST equipment can be used with numerous other non-oxidizing organic chlorides in which some hydrolysis can be expected to occur at elevated temperatures. For example, MONEL alloy 400 and Nickel 200 are used in handling amyl chloride, and Nickel 200 condensers are used for condensing allyl chloride. Nickel 200 shipping drums and tank trucks are employed for transporting both benzyl chloride and benzoyl chloride.

Monochlorobenzene is usually made by treating benzene with chlorine in a steel chlorinator since both constituents are available in the water free condition. However, if traces of water are present in chlorobenzenes, some hydrolysis occurs, with the result that steel or cast iron is attacked at significant rates, as shown in the plant corrosion test data, Table 24. Nickel and MONEL alloy 400 have found uses for handling chlorobenzenes containing moisture.

TABLE 24

Plant Corrosion Test in Monochlorobenzene, Containing Traces of Water and Phenol

Temperature: 60-70°C (140-158°F)
Test Duration: 57 Days
Slight Aeration and Agitation

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400	58	0.009
Nickel	51	0.008
Inconel alloy 600	42	0 007
Copper	116	0.019
Ni-Resist (Type 1)	148	0.029
Cast Iron	721	0.145
Mild Steel	627	0.115

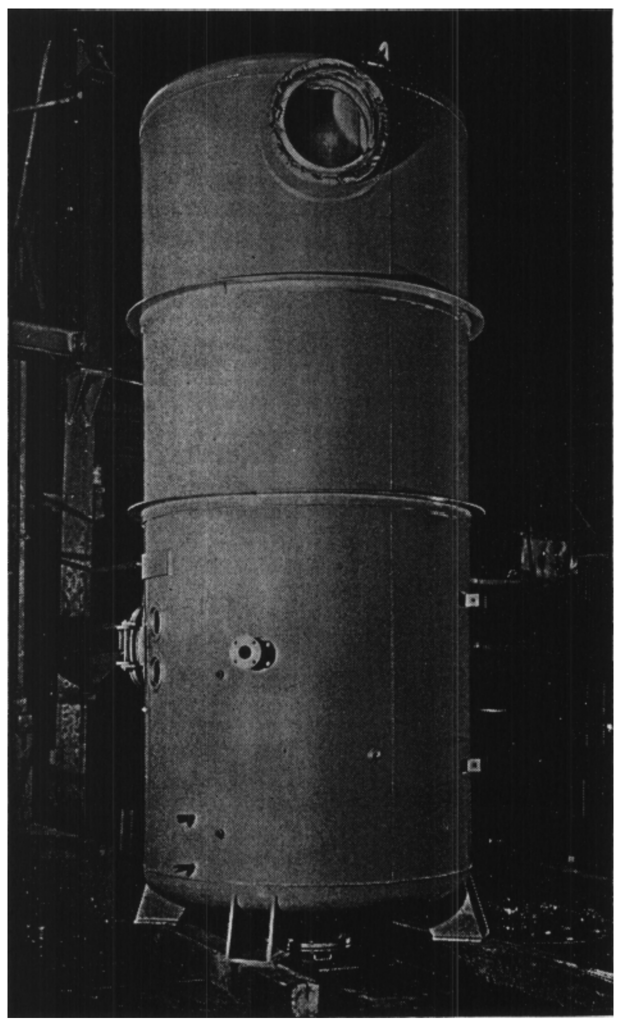

FIG. 18-Evaporator for the concentration of pectin containing a small amount of hydrochloric acid. The evaporator body is built of 15% INCONEL alloy 600-clad steel 5/16 in and 3/8 in thick. Tube sheets and tubes are of solid INCONEL alloy 600.

Chloroacetic acid is frequently a difficult material to handle from a corrosion standpoint. Nickel 200 and MONEL alloy 400 have been found to be suitably resistant under some conditions. Where conditions are too severe for these materials, HASTELLOY alloy C usually will be satisfactory.

Calcott, Whetzel and Whittakerl[19] report the corrosion test data given in Table 25.

TABLE 25
Laboratory Corrosion Tests in Chloroacetic Acid Having Specific Gravity of 1.358 at 50° C
Temperature of tests: 100° C (212° F)

Material	Corrosion Rate	
	mdd.	ipy.
Nickel	142	0.023
Copper	1620	0.262
Lead	5170	0.656
Mild Steel	2030	0.378
Cast Iron	1430	0.286

The results of other laboratory tests in molten 100 per cent chloroacetic acid at 70° C (158° F) and in 90 per cent chloroacetic acid solution at 23° C (73° F) are given in Table 26.

Dilute hydrochloric acid conditions are encountered in the distillation and processing of some foods and other organic materials which have been extracted with hydrochloric acid. MONEL alloy 400, nickel and INCONEL alloy 600 are frequently used in such processes to provide corrosion resistance and protect the purity of the products. As examples, nickel and INCONEL alloy 600 evaporators are used with acidified gelatine, MONEL alloy 400 and INCONEL alloy 600 evaporators are used with acidified pectin, and INCONEL alloy 600 is used for the extraction and concentration of acidified vitamins.

[19] W. S. Calcott, J. C. Whetzel, and H. F. Whittaker, "Corrosion Tests and Materials of Construction for Chemical Engineering Apparatus," D. Van Nostrand Co., New York (1923), p. 118.

Pickling of Iron and Steel

Pickling of steel strip or steel parts, particularly where coatings of enamel, zinc, tin or plated metals are to be applied subsequently, is done often in hydrochloric acid solutions. The most common acid concentrations are from 5 to 10 per cent HCl by weight. Where pickling is done by dipping, the acid is used frequently at room temperature, but higher temperatures are used sometimes for continuous processes where it is desired to speed up the reaction. Frequently organic inhibitors are added to the acid baths. The temperature of the solution has an important bearing on the selection of metals and alloys for pickling equipment.

For room temperature pickling with hydrochloric acid solutions up to 10 per cent HCl concentration, MONEL alloys and nickel have good corrosion resistance. MONEL alloy 402 is used widely for pickling equipment such as baskets, crates, racks, chains, hooks and even for solid metal pickling tanks. It is also used for bolts, nuts, stay-rods, and other parts supporting wooden pickling tanks.

Pickling conditions are particularly favorable because the pickling reactions use up any oxygen that may be dissolved in the acid, and the hydrogen evolved by reaction of the acid with the steel tends to keep the solution in a reducing condition. In addition, MONEL alloy 402 crates, baskets, and chains are protected galvanically by the steel parts with which they are in contact. Consequently, corrosion rates are very low, and it is not unusual to find MONEL alloy 402 pickling crates which show no appreciable corrosion after 10 to 15 years service in room temperature pickling solutions.

Solid MONEL alloy 400 pickling tanks also have shown good performance handling room temperature solutions. At one plant, where range parts are pickled

TABLE 26
Laboratory Corrosion Tests in Chloroacetic Acid

Test 1: Molten pure chloroacetic acid at 70° C (158° F). Test specimens submerged (and half-submerged in the case of nickel) in the liquid in closed Mason jars.

Test 2: Saturated aqueous solution containing 90 parts of chloroacetic acid and 10 parts of water at 23° C (73° F). Test specimens submerged (and half-submerged in the case of nickel) in liquid in closed Mason jars.

Material	CORROSION RATE									
	Test 1						Test 2			
	First 40 hr		Next 64 hr		Next 42 hr		First 97.5 hr		Next 44 hr	
	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.
Monel alloy 400	18	0.003	30	0.005	61	0.010	5.0	0.0008	6.1	0.0010
Nickel										
Totally	111	0.018	93	0.015	111	0.018	5.6	0.0009	5.0	0.0008
Half submerged	130	0.021	111	0.018	148	0.024	22	0.0036	21	0.0034
Inconel alloy 600	30	0.005	137	0.023	131	0.022	5.0	0.0008	5.0	0.0008
Hastelloy alloy B	2.2	0.00034	2.2	0.00035	8	0.0012	2.6	0.0004	4.5	0.0007
Hastelloy alloy C	1.7	0.00028	0.2	0.00003	0	0	0.5	0.00008	0.1	0.00002

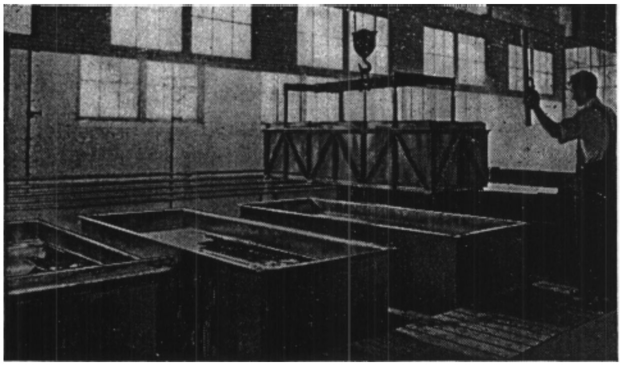

FIG. 19-Solid MONEL alloy 400 pickling tanks of welded construction handling cold 9 to 10 per cent hydrochloric acid. These tanks are in good condition after more than 10 years service. The pickling crates are also of welded MONEL alloy 400 construction.

prior to enamelling, solid MONEL alloy 400 tanks have been in use over 10 years handling 9 per cent hydrochloric acid and show very little evidence of attack.

The relatively low copper content of MONEL alloy 400 is of importance in equipment for the pickling of steel for enamelling or coating since it avoids the development of "copper flash" on the steel surface.

Some alloys are subject, under conditions likely to be encountered in tie-rod service, to a peculiar form of corrosion akin to the well-known "dezincification" of yellow brasses. The net result, in the case of tie-rods of such alloys, is the formation of a mechanically weak outer layer, increasing in thickness as service time goes on, around a correspondingly decreasing core of unaltered material. Ultimately, the cross-sectional area of the unaltered core becomes too small to sustain the loading involved and failure occurs. Fortunately, MONEL alloys 400 and 402 do not corrode in this manner, so that tie-rods of these materials can be depended upon to maintain their high unit strength throughout their useful life.

For pickling acid concentrations higher than 10 to 15 per cent HCl at room temperature, nickel is likely to be more resistant than MONEL alloy 400, as is indicated by the corrosion data in Figure 4. In this higher concentration range, nickel can be used frequently for baskets and crates, although it is not usually recommended for solid metal pickling tanks.

Reports have been received of the satisfactory performance Of MONEL alloy 400 baskets, crates, hooks and chains in acid concentrations under 10 per cent HCl at temperatures up to boiling. Its performance will usually depend upon the amount of galvanic protection received from the steel being pickled, the portion of time it is actually exposed to the acid, and upon whether an inhibitor is used. MONEL alloy 400 would be superior to nickel under such conditions, as is shown in Figure 6. In no case would it be used for a solid pickling tank in elevated temperature acid. For pickling tanks and heating coils used with hot hydrochloric acid solutions HASTELLOY alloy B is usually the most resistant wrought metallic material.

MONEL alloy 400 is used for "nip" or flux rolls and for guide parts carrying steel strip from pickling tanks to flux tanks in continuous galvanizing systems.

Caution should be observed in the use of MONEL alloy 400 or nickel for pickling drums, either of continuous or batch types, which are not completely immersed in the acid bath. In some cases, these drums have only the bottom portion immersed to pick up the acid and in others the entire drum may be suspended above the bath and acid sprayed into it. In such installations, the exposed surfaces of the drum are covered with a thin layer of acid which becomes highly aerated in its travel through the air. Furthermore, the. drums may be only partly loaded, with the load constantly shifting, so that the actual area of contact between the drum and loading may be too small to provide suitable galvanic protection. To provide satisfactory performance, the drum should be immersed completely in the pickling acid, or, if suspended partly or entirely above the acid surface, the pickling tank and drum should be enclosed with a sealed hood which will provide continuously a hydrogen atmosphere around the drum. Where this cannot be done, HASTELLOY alloy B is the preferred material of construction for drums.

If MONEL alloy 400 hoods are installed over continuous hydrochloric acid pickling equipment, they should be installed with the edges of the inlet end immersed in the pickling acid or in a water seal or some other arrangement should be used to keep out air and maintain a reducing atmosphere within the system. *In any hood design, cognizance should be taken of the fact that hydrogen and air may form combustible mixtures.*

The behavior of bare MONEL alloy 400 or nickel in open type hoods above pickling tanks will depend upon their location with respect to the pickling equipment and the acid content of the fumes. They may not be satisfactory if the combination of acid concentration and aeration is too severe. In such cases, a usually satisfactory installation can be made by coating the MONEL alloy 400 or nickel with an acid-resisting paint. If breaks occur in the paint, the underlying alloy will provide suitable resistance until the breaks can be repaired.

Galvanizing and Soldering Fluxes

In the batch processes for galvanizing iron or steel parts it is customary practice to flux the parts after pickling and prior to dipping in the molten zinc bath. The flux bath is usually a water solution of zinc chloride, or a combination of zinc and ammonium chlorides, acidified with a small amount of hydrochloric acid. MONEL alloy 400 baskets, tanks, and heating coils have been used successfully for the fluxing operation providing the bath is not aerated. Laboratory test data for the unaerated conditions are shown in Table 27.

TABLE 27
Laboratory Corrosion Test in Galvanizing Flux
Solution of zinc chloride and ammonium chloride. Specimens half immersed in solution.
No Agitation
Temperature: 15.5°C (60°F)
Test duration: 60 days

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400	10.9	0.002
Nickel................................	9.9	0.002
Inconel alloy 600	*	**

* Based on area of specimen immersed.
** Accelerated attack at liquid level.

In continuous operation procedures employing conveyer mechanisms the flux solution may be sprayed or cascaded over the parts, the solution being recirculated through a system of tanks. Under these conditions of high aeration the flux solution becomes considerably more corrosive, as shown by the plant corrosion test data of Table 28. For such conditions

TABLE 28
Plant Corrosion Test in Galvanizing Flux
25% Zinc chloride solution, acidified to pH 4 with hydrochloric acid.
Specimens immersed in recirculation tank, in aerated solution.
Temperature: 25°C (77°F)
Test Duration: 56 days

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400.........................	348	0.057
Nickel.......................................	378	0.061
Inconel alloy 600	224	.038*
Hastelloy alloy B	102	.016*
Hastelloy alloy C	0.4	.0001
Lead	146	.019

* Severely pitted and perforated.

HASTELLOY alloy C exhibits the best corrosion resistance of the high nickel alloys.

In connection with batch galvanizing operations wherein MONEL nickel-copper alloy 400 or HASTELLOY alloy C baskets may be used to handle the parts through the pickling and fluxing processes, the user should be cautioned against employing the same basket for immersion in the molten zinc bath. These alloys can be intergranularly attacked by molten zinc, leading to premature failure. The usual practice has been to employ steel baskets for the zinc dipping operation. More recently the 20 % Ni, 21 % v1, 20 % Co, 3% Mo alloy, N-155, has been found to be resistant to the molten zinc bath, and baskets fabricated from this alloy are in use for galvanizing of steel nuts and bolts.

Petroleum Refining

In the distillation of crude petroleum containing entrained salt water, corrosion of iron frequently is severe, due to hydrolysis of the brines to form dilute hydrochloric acid. While hydrolysis is likely to be greatest at the higher temperatures, corrosion is likely to be most severe in the top sections of distillation towers because temperatures are lowest in those sections permitting the maximum amount of acid condensation to occur. Acid formation is likely to be greatest when the brines contain considerable proportions of magnesium and calcium chlorides because these hydrolyze more readily than sodium or potassium chlorides. In a case cited by Hamlin and Turner[20], where the entrained brine contained 2.2 per cent $Mg Cl_2$ and 6.5 per cent NaCl, an acidity equal to 8.23 grains of HCl per gallon of water was present after passage through the dephlegmators. Where petroleum contained one per cent brine, HCl was formed in the ratio of 3.39 pounds per 1000 barrels of oil.

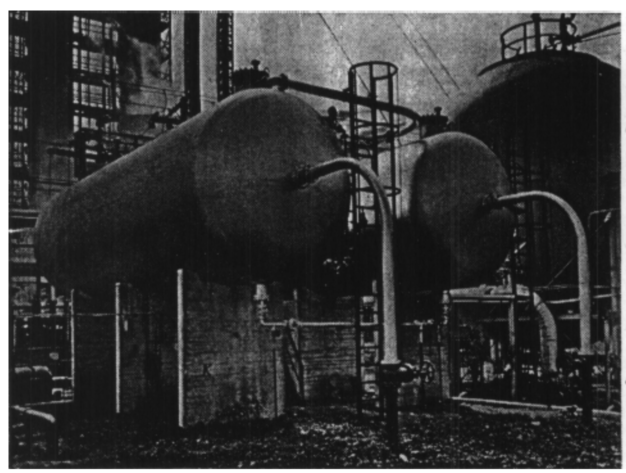

FIG. 20-Refinery accumulator tanks lined with 0.083 in. thick MONEL alloy 400 sheet, plug welded on 4 in. centers, to resist corrosion by naphtha containing dilute hydrochloric acid.

Because of its resistance to this hydrochloric acid condition, MONEL alloy 400 is used to a considerable extent for lining the upper parts of distillation towers and for adjacent equipment such as bubble caps and trays, dephlegmators, condensers and condensate and reflux lines. Some of the new distillation towers have been constructed with MONEL alloy 400 lining for the top section, INCONEL alloy 600 lining for the middle section, and stainless steel lining for the bottom section.

In Table 29 are given the results of plant corrosion tests in the upper sections of distillation towers in three different refineries handling salty crudes. The charging stock in each case had passed through water settling tanks before distillation.

[20] **M. L. Hamlin and F. M. Turner, Jr., "The Chemical Resistance of Engineering Materials." The Chemical Catalog Co., Inc., New York (1923), p. 62.**

TABLE 29
Plant Corrosion Tests in Distillation of Crude Oils Containing Entrained Brine Where Some Hydrochloric Acid Is Formed by Hydrolysis of Brine

Test 1- On top tray of bubble tower of crude topping unit handling Kansas crude. Some hydrogen sulfide also present. Cooled reflux enters top tray.
Temperature: 250 to 260° F (121 to 126° C)
Duration of test: 80 days

Test 2- In top of bubble tower of crude topping unit handling West Texas crude.
Temperature: 250° F (121° C)
Duration of test: 60 days

Test 3- On top tray of bubble tower of crude topping unit handling Michigan crude. Cooled reflux enters top tray.
Temperature: About 200° F (93° C)
Duration of test: 90 days

Material	Corrosion Rate					
	Test 1		Test 2		Test 3	
	mdd.	ipy.	mdd.	ipy.	mdd.	ipy.
Monel alloy 400.....	57	0.0093	18	0.003	46	0.0075
Nickel	28	0.0045	37	0.006[a]	43	0.0069
Inconel alloy 600...	72	0.0120	100	0.017[a]	. . .	. . .
Ni-Resist (Type 1) .	57	0.011	260	0.051		
Mild Steel.............	290	0.054	*	*	263	0.049
Cast Iron	250	0.050	900	0.181	. . .	. . .

a Local attack in form of pitting to maximum depth of 0.016".
* Completely destroyed. Original thickness 0.031".

Several refineries use chlorinated solvents in solvent extraction or dewaxing of lubricating oil. One dewaxing process employs a mixture of carbon tetrachloride and ethylene dichloride. In the recovery of the solvents by steam distillation, the formation of dilute hydrochloric acid by hydrolysis results in corrosive condition in distillation equipment and condensers which can be overcome by the use of MONEL alloy 400 or nickel. The results of corrosion tests in the condenser of the chlorinated solvents recovery unit at one refinery are given in Table 30.

Isomerization processes using aluminum chloride and other metallic chlorides plus hydrogen chloride together as catalysts, provide a corrosive condition

TABLE 30
Plant Corrosion Test in Condenser of Chlorinated Solvents Recovery Unit at Petroleum Refinery
Temperature: 60 to 93° C (140 to 200° F)
Duration of test: 99 days

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400.................	65	0.0106
Nickel	37	0.0061
Inconel alloy 600	28	0.0047
Ni-Resist (Type 1)	65	0.0126
Mild Steel..........................	304	0.0560
Cast Iron	471	0.0943

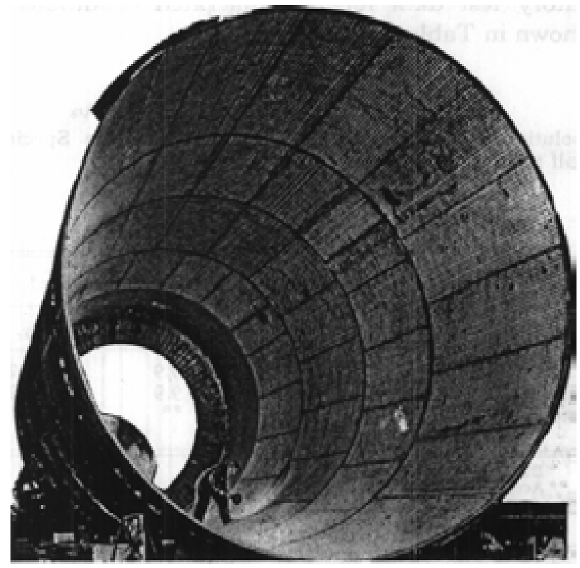

FIG. 21-Section. of a large petroleum fractionating tower. The top part is lined with MONEL alloy 400 sheet to withstand corrosion by dilute HCl formed by hydrolysis of brine in the petroleum.

where there is a certain amount of residual water dissolved or entrained in the charging stocks. The catalyst complex is circulated usually as a viscous tarry mixture of the chlorides and hydrocarbons and where this "tar" contacts the metal surfaces it is likely to be particularly corrosive.

While nickel has been used for isomerization reactors, corrosion rates of the order of 0.036 ipy in the catalyst chamber at 350° F, and 0.025 ipy in the

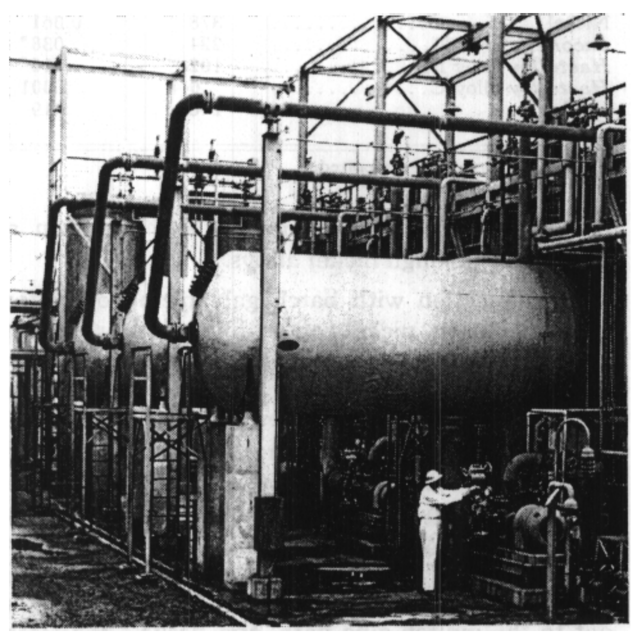

FIG. 22-Piping, pumps, and valves for the isomerization units are made of HASTELLOY alloy B. Chloride catalyst sludge settles out from the tanks and is pumped back through HASTELLOY alloy B equipment.

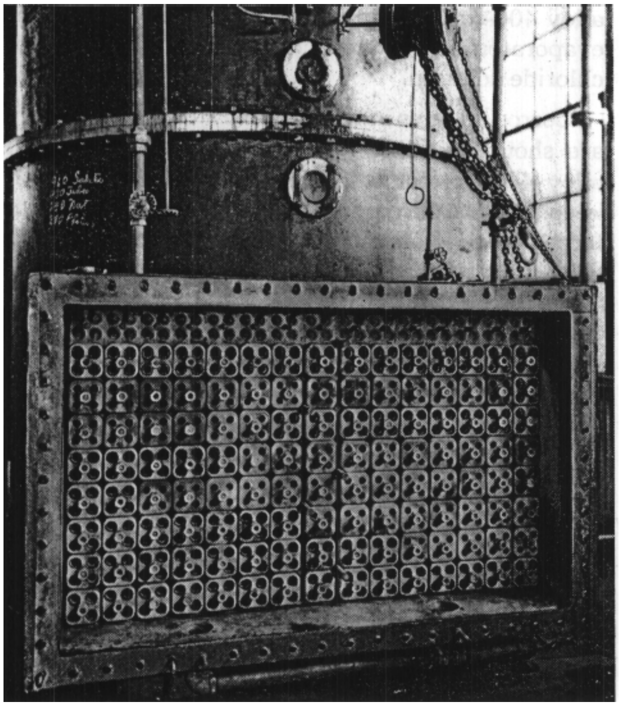

FIG. 23-A vacuum evaporator equipped with MONEL alloy 400 tubes used for the evaporation of zinc chloride.

catalyst removal column have been observed. HASTELLOY alloy B has shown considerably better corrosion resistance and is the preferred material for reactor linings.

The results of plant corrosion tests in the liquid and vapor sections of a "tar" knock-out vessel are shown in Table 31.

In some cases where particular care is taken to dehydrate the charging stocks, nickel may be suitable for parts of isomerization equipment.

Additional information on petroleum refining applications is given in the reprint, "The Selection of Materials for Some Petroleum Refinery Applications".

TABLE 31
Plant Corrosion Tests in "Tar" Knock-Out Vessel of Hydrocarbon Isomerization Unit Employing Aluminum Chloride and Hydrogen Chloride as Catalyst
Temperature: 107 to 121° C (Avg. 116° C)
225 to 250° F (Avg. 240° F)
Duration of tests: 44 days

Material	Corrosion Rate			
	In Liquid		In Vapor	
	mdd.	ipy.	mdd.	ipy.
Monel alloy 400 ...	160	0.026	149	0.024
Nickel	59	0.010	79	0.013
Inconel alloy 600 .	63	0.011	71	0.012
Hastelloy alloy B .	2.5	0.0004	5	0.0008
Ni-Resist (Type 1)	270	0.053	266	0.052
Mild Steel...........	873	0.162	435	0.081
Cast Iron.............	425	0.085	413	0.083

Inorganic Acid Chlorides

Aqueous solutions of most of the inorganic acid chlorides hydrolyze to a certain extent to form dilute hydrochloric acid, particularly at temperatures associated with their evaporation. MONEL nickel-copper alloy 400, nickel, and in some cases INCONEL nickel-chromium alloy 600 have useful resistance to corrosion by many of these salt solutions. As pointed out at the beginning of this bulletin, aeration of hydrochloric acid solutions tends to increase the corrosion rate of MONEL alloy 400 and nickel. Likewise, aeration of the acid chloride salt solutions will also tend to increase the corrosion rate of MONEL alloy 400 and nickel.

Listed below are several of the acid chloride salts with which MONEL alloy 400, nickel or INCONEL alloy 600 have been used, and corrosion data collected from plant and laboratory tests are given in Tables 32 to 40.

Aluminum Chloride-Al Cl_3

Nickel has been used for dissolving tanks, and for isomerization and Friedel Craft reactions wherein aluminum chloride is employed as a catalyst.

Ammonium Chloride-NH_4 Cl

Nickel has been employed as tanks for the mixing of battery pastes containing ammonium chloride, and for evaporator tubes in the concentrating of ammonium chloride solutions to 40%.

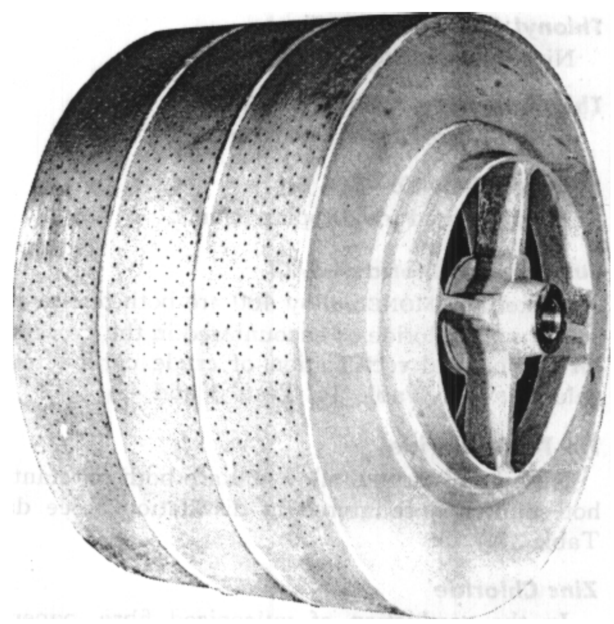

FIG. 24-Welded construction was used for this 40 in. diameter by 24 in. high pure nickel centrifugal basket used with an acid chloride salt. Welded to the 3/8 in. thick shell is a cast nickel hub.

Antimony Chloride-Sb Cl_3

Nickel has been used for condensing of antimony chloride vapors containing moisture.

Magnesium Chloride-Mg Cl_2

In equipment for the evaporation and handling of hot magnesium chloride used in the production of magnesium, INCONEL nickel-chromium alloy 600 has been used satisfactorily. The iron, copper, and nickel content of the finished magnesium must be kept extremely low. INCONEL alloy 600 is used because of its high degree of corrosion resistance and because it (as well as MONEL alloy 400 and nickel) is free from stress-corrosion cracking in boiling magnesium chloride solutions. MONEL alloy 400 and NI-RESIST are used for such equipment as filters, pumps and valves.

Phosphorus Oxychloride-POCl

Nickel is used for both shipping drums and tanks for truck shipment of the commercial product. Nickel and nickel clad steel are employed in the processing equipment for production of tricresyl phosphate wherein phosphorus oxychloride is a reactant.

Phosphorus Trichloride-P Cl_3

Nickel is used for reactors, reflux columns, piping and valves in the manufacture of the product, as well as for shipping drums.

Pyrosulfuryl Chloride-$S_2 0_5 Cl$

Nickel is used for shipping drums.

Nitrosyl Chloride-NOCl

Both nickel and INCONEL alloy 600 are used for piping, and valves in the handling of the dry product following its manufacture. Nickel is standard material for shipping cylinders.

Thlonyl Chloride-SO Cl_2

Nickel is used for shipping drums.

Thlophosphoryl Chloride-PS Cl_3

Nickel is used for shipping drums.

Sulfuryl Chloride-$S0_2$ Cl_2

Nickel is used for shipping drums.

Sulfur Monochloride-S_2 Cl_2

Nickel and MONEL alloy 400 are both resistant to sulfur monochloride as encountered in the process of distillation and rectification of crude carbon tetrachloride. (See Table 16, Tests 3 and 4.)

Tin Tetrachloride

Nickel and MONEL alloy 400 are both resistant to hot solution encountered in distillation. (See data Table 37.)

Zinc Chloride

In the production of vulcanized fibre, paper is treated with 70° Be zinc chloride solution which subsequently is washed from the wet fibre sheet. MONEL alloy equipment is used in the form of MONEL alloy 400-covered drying and processing rolls and in evaporators for recovering and concentrating the zinc chloride solution.

Corrosion rates in the concentration of zinc chloride are shown in Table 38. The resistance of MONEL alloy 400 protects the color of the fibre board and keeps its metallic content at a minimum, so that uniformly good dialetric properties are maintained for electrical insulating uses.

TABLE 32

Plant Corrosion Test in Evaporation of Ammonium Chloride From 28 to 40 Per Cent NHsCl

Test spool immersed in liquor
Temperature: 102º C. (216º F.)
Duration of test: 762 hr

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400	73	0.012
Nickel	52	0.0084
Inconel alloy 600............	3	0.0005*
Ni-Resist (Type 1)	63	0.012
Cast Iron	1780	0.36

* Pitted to maximum depth of 0.006 inch.

TABLE 33

Plant Corrosion Test in Mixture of Arsenic Trichloride and Sulfur Monochloride with Small Amount of Moisture

Arsenic trichloride content varied from 72 to 100%
Sulfur monochloride varied from 0 to 28%
Test spool located in top of first pass of vertical condenser subject to vapor and some condensate.
Temperature: 120 to 130° C (248 to 266° F)
Duration of test: 618 hours

	Corrosion Rate	
Material	mdd.	ipy.
Monel alloy 400	23	0.0038
Nickel	8	0.0013
Inconel alloy 600	10	0.0016
Ni-Resist (Type 1)............	36	0.007
Mild Steel	117	0.022
Cast Iron..........................	148	0.030

TABLE 34

Plant Corrosion Test in Evaporation of 37 Per Cent Manganous Chloride Solution

Test spool half submerged at liquor level in open pan into which atmospheric drum dryer dips.
Temperature: 99 to 107° C (Avg. 104° C)
210 to 225° F (Avg. 220° F)
Duration of test: 19 days

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400..........................	116	0.019
Nickel.......................................	187	0.030
Inconel alloy 600	166	0.028
Ni-Resist (Type 1).......................	204	0.040
Mild Steel	1280	0.236
Cast Iron...................................	1538	0.308

TABLE 35

Laboratory Corrosion Tests in Phosphorus Pentachloride

Test 1: at 76° C (169° F) for 19 days

Test 2 : at 150° C (302° F) for 3 days

Material	Corrosion Rate			
	Test I		Test 2	
	mdd.	ipy.	mdd.	ipy.
Monel alloy 400	2.6	0.0004	. .	. .
Nickel	1.3	0.0002	1.7	0.0003

TABLE 36

Plant Test in Mixture of Phosphoric, Hydrochloric, and Cresylic Acids with Phosphorus Oxychloride

Test spool at liquid line in reaction kettle

Temperature: 82° C (180° F)

Duration of test: 174 hours

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400	459	0.074
Nickel......................	106	0.017
Inconel alloy 600............	588	0.099

TABLE 37

Plant Corrosion Test in Distillation of Crude Tin Tetrachloride

Test spool located in still, above steam coil and below liquid level.

Temperature: 104 to 116° C (220 to 240° F)

Duration of test: 432 hours

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400	20	0.0032
Nickel	24	0.0039
Inconel alloy 600	42	0.0071
Hastelloy alloy C	54	0.0087
Ni-Resist (Type 1)................	118	0.0228
Cast Iron.............................	210	0.0420

TABLE 38

Plant Corrosion Test in Double-Effect Zinc Chloride Evaporato

Test 1:-Weak liquor effect, 7.9 to 21% ZnC12

Temperature: 32 to 38° C (90 to 100° F)

Vacuum: 26 to 28" Hg.

Duration of test: 210 days

Test 2:-Strong liquor effect, 21 to 69% ZnC12

Temperature: 110 to 116° C (230 to 240° F)

Vacuum: 15 to 18" Hg

Duration of test: 90 days

Material	Corrosion Rate			
	Test I		Test 2	
	mdd.	ipy.	mdd.	ipy.
Monel alloy 400	28	0.0045	98	0.016
Nickel...........................	29	0.0046	245	0.040

TABLE 39

Laboratory Corrosion Test in Mixture of Zinc Chloride, Ammonium Chloride and Water

Composition of solution:

66% $ZnCl_2$

20% NH4Cl

14% Water

Specimens immersed in open jars

Temperature: 83 to 95° C (182 to 204° F)

Duration of test: 2 hours

Material	Corrosion Rate	
	mdd.	ipy.
Ni-Resist (Type 1)..............	95	0.0184
Ni-Resist (Type 2)..............	116	0.0225
Cast Iron...........................	3420	0.684

TABLE 40

Plant Corrosion Test in Evaporator Concentrating a Mixture of Magnesium and Calcium Chloride Brines to 50 Per Cent Chlorides

Temperature: Boiling under vacuum

Duration of test: 26 days

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400	12	0.002
Nickel	17	0.003
Inconel alloy 600...............	0.6	0.0001
Ni-Resist (Type 1...............	19	0.004
Mild Steel.........................	410	0.076
Cast Iron	150	0.030

Pulp and Paper

Wood pulp is bleached with either a hypochlorite solution (in some cases sodium chlorite), or by direct chlorination using chlorine water or chlorine gas. Bleaching is done by either single-stage or multi-stage processes. Single-stage bleaching usually is done with hypochlorite solutions, the bleaching being followed by washing on vacuum filters.

In multi-stage bleaching, direct chlorination frequently is used in the first stage and hypochlorite treatment in subsequent stages. It is customary in multi-stage bleaching to wash the pulp on vacuum filters after each stage. The direct chlorination, or acid bleaching, frequently is followed by a caustic neutralizing treatment before washing.

In the preparation of strong hypochlorite bleach solutions or in the bleaching processes themselves, either with hypochlorite or chlorine, corrosive conditions usually are so severe that HASTELLOY alloy C is the only highly resistant wrought metallic material. The results of corrosion tests in the preparation of strong calcium hypochlorite bleach liquor are given in Table 41.

MONEL alloy 400 has satisfactory resistance in the washing of hypochlorite bleached pulps and is used for wire covers on vacuum washers and for lining the vats and repulper sections of these washers. Table 42 gives the results of corrosion tests in the filtrate from a vacuum washer handling hypochlorite bleached

TABLE 41

Plant Test in Preparation of Calcium Hypochlorite Bleach Liquor in Paper Mill

Available chlorine content approximately 40 gm per liter plus small amounts of calcium chloride, calcium chlorate, calcium carbonate, and free lime.
Fresh solution made up twice a week
Temperature: 16 to 38° C (60 to 100° F)
Duration of test: 30 days

Material	Corrosion Rate		Remarks
	mdd.	ipy.	
Monel alloy 400. . . .	455	0.074	Perforated by pitting*
Nickel.	958	0.155	Perforated by pitting*
Inconel alloy 600. . .	276	0.047	Perforated by pitting*
18-8 Mo Stainless. . (Type 316).	21	0.004	Perforated by pitting*
Hastelloy alloy C. . .	0.75	0.0001	. .
Silicon Cast Iron. . . (14.5% Si).	2.1	0.0004	. .
Ni-Resist.	155	0.030	. .

* Specimens originally 0.032 inch thick.

pulp. At one mill the following services were obtained from MONEL nickel-copper alloy 400 wire cloth covers on washers and thickeners:

Thickener handling hypochlorite bleached soda pulp
1st Monel alloy 400 cover..... Gave 26 months service
2nd Monel alloy 400 cover.... Gave 61 months service
3rd Monel alloy 400 cover .... In good condition after 21 months service

Thickener handling hypochlorite bleached sulfite pulp
1st Monel alloy 400 cover ..... Gave 45 months service
2nd Monel alloy 400 cover .... In satisfactory condition after 63 months service

Washer handling hypochlorite bleached soda pulp
1st Monel alloy 400 cover ..... Gave 14 months service
2nd Monel alloy 400 cover .... Gave 6½ years service

In a multi-stage bleach system, MONEL alloy 400 covers on washers handling soda pulp from the caustic extraction stage and the hypochlorite stage, gave the following services:

Caustic extraction stage washer - MONEL alloy 400 covers averaged 12 months.

Hypochlorite stage washers (high and low density)-MONEL alloy 400 covers averaged 2 years:

TABLE 42

Plant Corrosion Test in Filtrate From Washer Handling Hypochlorite Bleached Soda Pulp

Test specimens immersed in filtrate sump
Chlorine content of filtrate, 0.009 gm per liter pH 6.0
Temperature: 21 to 25° C (70 to 78° F)
Duration of test: 72 days
Rate of filtrate flow: 1050 gal per min

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400	0.45	<0.0001
Nickel...................................	0.26	<0.0001
Inconel alloy 600....................	0.69	0.0001
Hastelloy alloy C....................	0.17	<0.0001
Ni-Resist...............................	10.	0.002
Cast Iron...............................	20.	0.004

< = Less than.

The pulp from direct chlorine bleaching usually is too corrosive for the use of MONEL alloy 400 washer covers. For this purpose, Type 316 stainless steel is usually a satisfactory material as indicated by Table 43 giving the results of tests in chlorine bleached sulfite pulp containing 0.02 gm of free chlorine and 0.15 gm of hydrochloric acid per liter. In the filtrate from these washers, the chlorine content frequently is reduced to the point where MONEL alloy 400 and NI-RESIST can be used for such applications as filtrate piping. The results of corrosion tests in the filtrate from the washing of chlorine bleached pulp are given in Table 44.

TABLE 43

Plant Corrosion Test in Chlorine Bleached Paper Stock

Stock contains 0.15 gm per liter of HCl and 0.02 gm per liter of free chlorine.
Test spool attached to cylinder mold of pulp thickener.
Duration of test: 90 days

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400......................	262	0.0425
18-8 Mo Stainless (Type 316)..	0.07	<0.0001
Hastelloy alloy C....................	0.03	<0.0001
Ni-Resist (Type 1)	120	0.0232
Cast Iron................................	886	0.177

< = Less than.

TABLE 44

Plant Corrosion Test in Filtrate from Washer Handling Chlorine Bleached Soda Pulp

Test specimens immersed in filtrate sump Chlorine content of filtrate, 0.011 gm per liter, pH 3.5.
Temperature: 23 to 33° C (74 to 92° F)
Duration of test: 72 days Rate of filtrate flow: 720 gal per min

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400	9	0.0014
Nickel................................	11	0.0018
Inconel alloy 600.................	0.22	<0.0001
Hastelloy alloy C.................	0.13	<0.0001
Ni-Resist	39.	0.0075
Cast Iron	78.	0.016

< = Less than.

In recent years the chlorine dioxide pulp bleaching process has grown considerably, to supply the demand for high brightness, high strength pulps. The generation of chlorine dioxide involves reactions wherein mixtures of methanol, sulfurous or sulfuric acid, chlorine and chlorine dioxide are present at temperatures up to 150° F The corrosive conditions associated with the process are rather severe for most of the corrosion resisting alloys usually employed in pulp handling, and non-metallics are employed wherever possible. A corrosion test study at one plant using chlorine dioxide bleaching has been reported by

Teeple and Adams[21] in which the corrosion test data shown in Tables 45 to 48 were obtained.

One equipment manufacturer has found cast HASTELLOY alloy C to be suitable for the chlorine dioxide

TABLE 45

Plant Test in Top of Chlorine Dioxide Reaction Tower

Media consists of concentrated sulfuric acid, 32% sodium chlorate, methanol, and chlorine dioxide gas.

Temperature: 57°C (135°F) Test Duration: 351 hours

Material	Corrosion rate, ipy.•	Remarks
Tantalum	0.0001	No attack
*LaBour** R-55	0.002	No pitting
Durichlor..........................	0.003	Incipient pits
Chemical lead	0.006	Etched
Duriron............................	0.007	Etched
Hastelloy alloy C (cast).	0.013	No pitting
Chlorimet 3............................	0.020	No pitting
*Durimet*** 20	0.027	0.059 max. pitting[b]
Type 316 stainless steel.....	0.15	Perforated 0.031 in.[c]
Inconel alloy 600....................	> 0.37	Spec. corroded away[d]
Type 430 stainless steel.....	> 0.46	Spec. corroded away[d]
Monel alloy 400................	> 0.48	Spec. corroded away[d]
Nickel..............................	> 0.48	Spec. corroded away[d]
Type 304 stainless steel.....	> 0.55	Spec. corroded away[d]
88/10/2 Bronze	> 1.8	Spec. corroded away[d]

* The LaBour Co., Inc., Trademark. > = More than.
** Duriron Co., Inc., Trademark.
a Corrosion rate expressed in terms *of* inch penetration per year based upon the continuous exposure *of* one surface.
b One of the two duplicate specimens showed no pitting on the surface but was perforated (0.189 in in 351 hr) under the spacer, i.e., in a crevice. The other duplicate specimen showed the max. pitting as indicated.
c Both duplicate specimens were perforated (0.031 in in 351 hr) and there was gross subsurface corrosion up to Y4 in. back from the specimen edges.
d Specimen corroded away during exposure period. Minimum corrosion rate is shown.

TABLE 46

Plant Test in Chlorine Dioxide Gas Line to the Absorber

8 to 10% chlorine dioxide gas plus some condensed chlorine dioxide solution.

Flow rate: 250 cu ft per min
Temperature: 66°C (150°F)
Test Duration: 350 hours

Material	Corrosion rate, ipy.	Remarks
Tantalum..............................	0.0001	No attack
Durichlor	0.003	No pitting
Chlorimet 3	0.015	No pitting
Chemical lead..................	0.030	No pitting
Hastelloy alloy C (cast)......	0.046	No pitting[a]
Durimet 20.............................	0.19	Perforated[b]
Type 316 stainless steel	0.29	Perforated[c]
Inconel alloy 600	0.30	Perforated[d]
Type 304 stainless steel	0.33	Perforated[e]
Nickel	0.35	Etchhd[f]
Monel alloy 400	0.36	Etchhd[f]
Type 430 stainless steel	0.40	Perforated[e]
LaBour R-55	0.46	0.095 in. max. pitting
Duriron	0.62	Gross attacks[g]
88/10/2 Bronze................	0.68	Heavy etch

a Subsurface corrosion on one of duplicate spec.
b Specimen perforated (0.189 in.) during exposure period.
c Specimen perforated (0.031 in.) during exposure period-two thirds of specimen missing.
d Specimen perforated (0.031 in.) during exposure period-specimen looks like filigree.
e Specimen perforated (0.031 in.) during exposure period-one third of specimen missing.
f One half of specimen missing.
g Also deep pitting.

[21] H. O. Teeple & R. L. Adams, Jr. "A Corrosion Study in a Chlorine Dioxide Pulp Bleaching Plant". TAPPI Vol. 38, #1, January 1955.

TABLE 47

Plant Test in Chlorine Dioxide Solution Receiver

Chlorine dioxide concentration 4 to 5 grams per liter, pH 2 to 3.5.
Temperature: 2°C (36° F)
Test Duration: 351 hrs

Material	Corrosion rate, ipy.	Remarks
Tantalum...................	0.0001	No attack
Duriron.....................	0.0001	No pitting
Durichlor..................	0.0001	No pitting
Type 316 stainless steel	0.0001	No pitting
Durimet 20	0.0007	No pitting
LaBour R-55..............	0.0036	No pitting
Hastelloy alloy C (cast)	0.0050	No pitting
Type 304 stainless steel	0.0051	Incipient pitting[a]
Chlorimet 3	0.014	Macro etch
Type 430 stainless steel	0.025	Perforated[b]
Inconel alloy 600	0.11	Perforated[c]
Chemical lead............	0.21	No pitting
Nickel.......................	0.32	Etched[d]
88/10/2 Bronze	0.34	Heavy etch
Monel alloy 400..........	0.48	Specimen almost gone

a Specimen pitted 0.018 in under spacer (crevice), during exposure period.
b Specimen perforated 0.031 in. in line *of* rolling direction during expo sure period.
c Specimen perforated 0.031 in. during exposure period.
d Severe intergranular corrosion.

TABLE 48

Plant Test in Vent Line from Top of Bleach Tower

Spent chlorine dioxide gas
Temperature: 68°C (155°F) Test
Duration: 338 hrs

Material	Corrosion rate, ipy.	Remarks
Tantalum	0.0001	No attack
Durichlor.........................	0.0001	Incipient pitting
Hastelloy alloy C (cast).	0.0002	No attack
Durimet 20.............................	0.0002	No attack
Chlorimet 3............................	0.0003	No attack
Duriron...........................	0.0004	Incipient pitting
Type 316 stainless steel....	0.0005	Pitted[a]
Type 304 stainless steel....	0.0006	Pitted[a]
Monel alloy 400	0.0006	Incipient pitting
Nickel	0.0007	Slightly etched
Inconel alloy 600	0.0007	Perforated[b]
Type 430 stainless steel....	0.0009	Pitted[c]
88/10/2 Bronze................	0.0052	Localized etching
Chemical lead	0.014	Pitted 0.035 in max.[d]

a Two severely pitted areas on each specimen, otherwise surface is good
b Only one perforation on each specimen, otherwise surface is good.
c Only one severely pitted area on each specimen, otherwise surface is good.
d Average pit depth 0.025 in.

mixer at the bottom of the pulp bleaching tower, but cast Type 317 stainless suffered a high corrosion rate. Where corrosive conditions are too severe for the use Of HASTELLOY alloy C, titanium or tantalum may be used.

Other Applications

Corrosion test data and service experience are available for nickel alloys in numerous other industries and processes involving hydrochloric acid or chlorine which, for lack of space, cannot be included in this bulletin. Such information relating to specific processes or corrosion problems will be furnished upon request made to INCO's Development and Research Department.