Materials of Construction for Salt Mine and Plant

by
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In the mining of rock salt, corrosion of mining machinery is generally not considered to be a serious matter, at least in the mines of the North and West, where humidities are relatively low and temperatures rather constant. For example, in the Retsof Mine of International Salt Company, Inc., the mine is dry, at a uniform temperature of about 61° F. the year around, and the relative humidity is 58 per cent. Vernon (1) and other investigators have shown that atmospheric corrosion of iron is much less where humidities are less than 70 per cent than in higher humidities. Wilkinson and Patterson (2) studied the effect of atmospheric humidity on the corrosion of iron coated with a thin layer of salt at a temperature of 70° F. The results of these tests are shown in Figure 1. It will be noted that at 60 per cent humidity the corrosion rate is very low after the first few days, and at 50 per cent humidity there is practically no corrosion.

It is reported that in some of the southern salt mines, higher humidities may exist and, if so, more corrosion of steel mining equipment might be expected. Under such conditions it might be necessary to resort to more use of alloy steels or possibly stainless steels for equipment such as scale buckets or parts of running machinery, where accumulation of rust might interfere with the operation.

The addition of even small amounts of certain alloying metals such as copper, nickel and chromium to steel can have a very significant effect upon the atmospheric corrosion resistance of steel, as indicated by atmospheric corrosion tests made in marine environment near the ocean at Kure Beach, N.C. (3). When all three of these elements are added, atmospheric corrosion resistance is very much improved as indicated by the low alloy, high strength steel in Figure 2 which contains approximately 0.5 per cent each of copper, nickel and chromium.

The effect of these small additions apparently is to form a denser more uniform rust film and to reduce the solubility of this rust film (4). It should be pointed out that these helpful effects of small alloy additions are not so pronounced where the metal is continuously washed with water so that a protective rust film does not get a chance to form, or if the rust film is continuously removed by abrasion or wear. Under such conditions it generally requires much higher alloy additions such as 10 per cent or more of chromium or 14 per cent or more of nickel to provide significant improvements in corrosion resistance.

Going back to the tests in marine atmospheres, it is apparent from Figure 3 that small alloy additions also have a significant effect in prolonging the life of paint coatings on steel where humid chloride-containing atmospheres exist (5).

In the above-ground processing of rock salt such as crushing and screening operations, corrosion of plant machinery often is controlled by control of humidity and temperature in the

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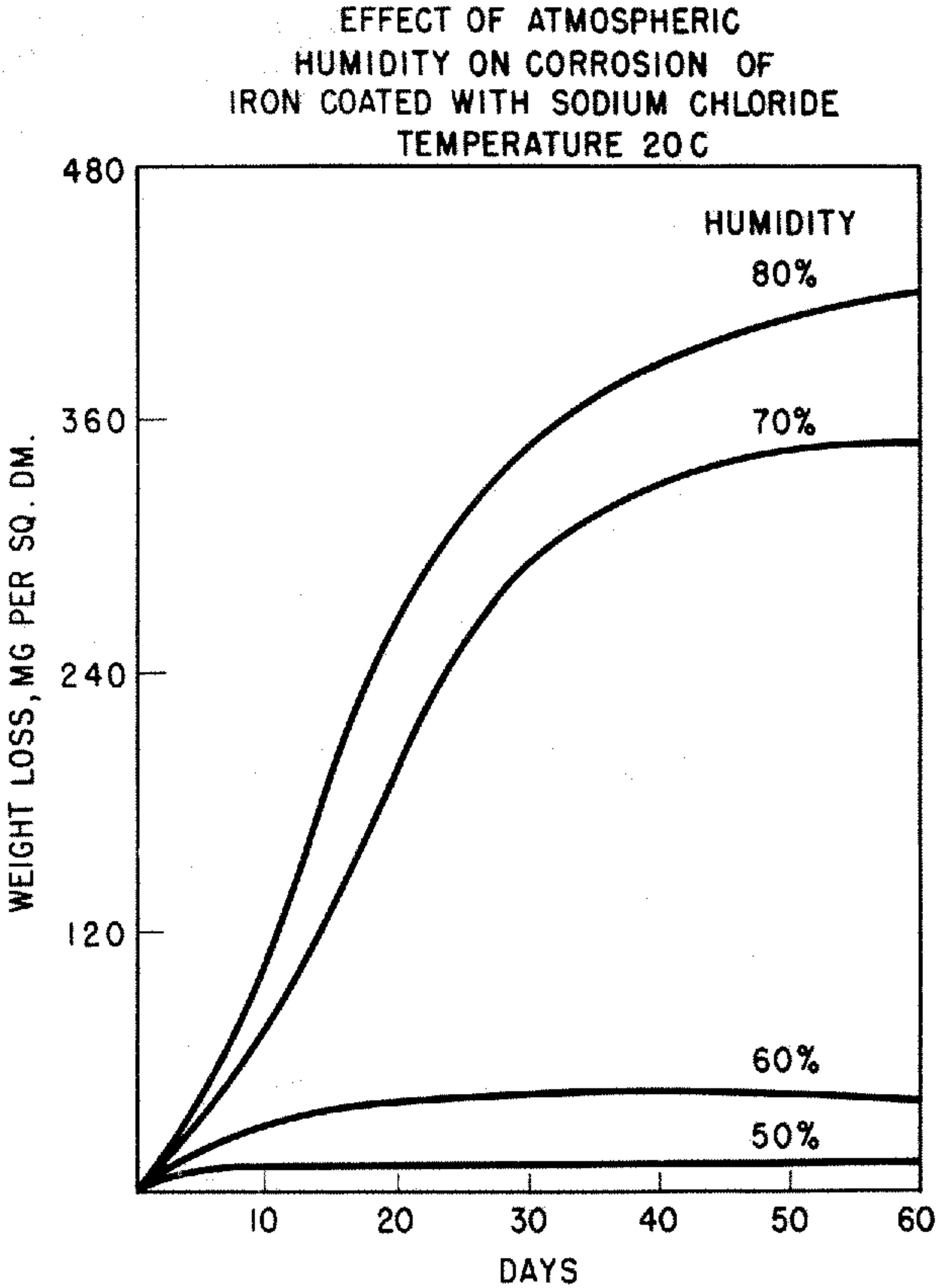
EFFECT OF ATMOSPHERIC
HUMIDITY ON CORROSION OF
IRON COATED WITH SODIUM CHLORIDE
TEMPERATURE 20C
WEIGHT LOSS, MG PER SQ. DM.
480
360
240
120
HUMIDITY
80%
70%
60%
50%
10
20
30
40
50
60
DAYS

Figure 1.

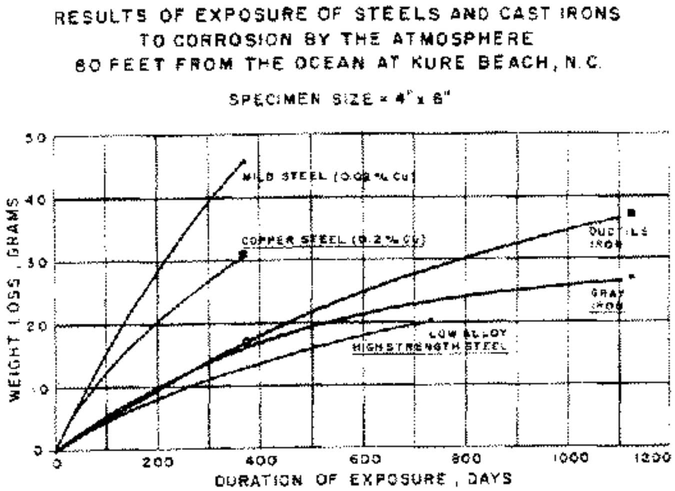

Figure 2.

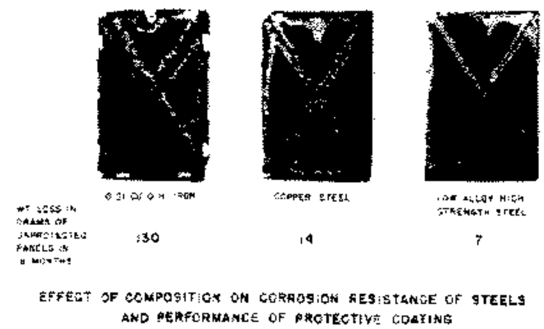

Figure 3.

buildings, sometimes by use of infra red heaters. Crusher rolls sometimes are made of Ni-Hard[2], a nickel-chromium white cast iron with outstanding abrasion resistance.

In water solutions of salt, the amount of corrosion will depend largely upon the salt concentration, degree of aeration, temperature, and hydrogen sulfide content if any. Corrosion by concentrated salt solutions is usually less than by more dilute solutions such as sea water since the latter are more highly ionized. This is indicated by Figure 4. All salt concentrations are good electrical conductors and can readily support all types of electrolytic corrosion including galvanic corrosion, crevice corrosion and pitting where other conditions are favorable for these types of attack to occur.

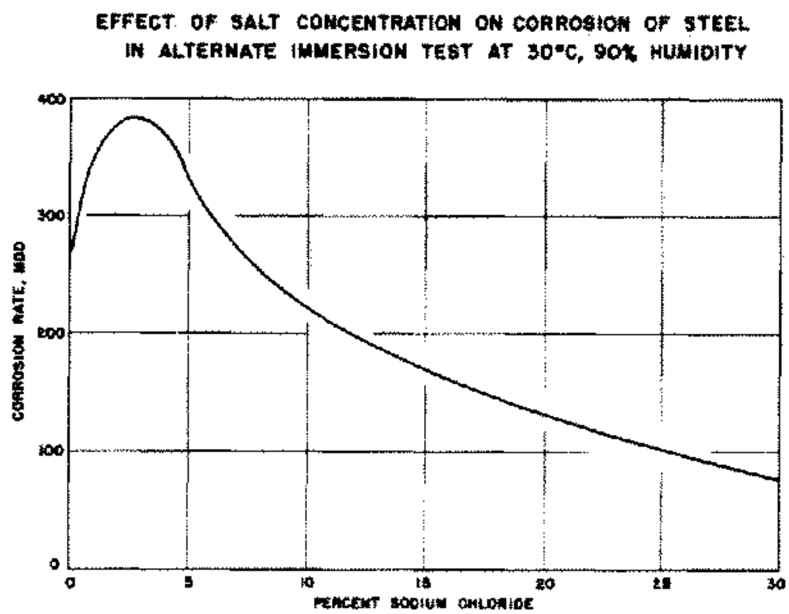

Figure 4.

[2]Trade Mark of The International Nickel Company, Inc.

Aeration usually tends to increase the corrosion of iron and copper alloys but often may be beneficial to the performance of stainless steels. The presence of hydrogen sulfide in neutral or alkaline brines may sometimes be beneficial to the performance of iron in that it may form an adherent iron sulfide coating which gives some protection. However, if there are breaks in this coating, pitting of the iron may occur since the iron sulfide is cathodic to uncoated iron. These various factors may affect the performance of steel pipe and tubing used in brine wells.

Cast iron generally has useful resistance to salt brines at moderate velocities and in the absence of aeration. Plain cast iron frequently is subject to graphitization (6). Cast iron evaporator bodies have been in use for many years. They have been subject to some maintenance trouble, especially with tube sheets and the tops of the pans which have to be renewed periodically because of corrosion. The product of this corrosion is iron oxide or carbon particles which may appear in the salt and affect its salability. With new equipment there is a trend to the use of nonferrous metals such as Monel[3] alloy 400 for evaporator bodies and tube sheets, and for brine heaters (7) (8).

Type 1 Ni-Resist[3], an alloy cast iron containing 14 per cent nickel and 6 per cent copper is considerably more resistant than plain cast iron to hot and cold brines at higher velocities and is used to a considerable extent for pump casings and impellers and for filter bodies and grids. The superior performance of Ni-Resist alloy in the latter application is illustrated in Figure 5. Ni-Resist is less subject to graphitization than cast iron, and from a galvanic standpoint is more compatible with materials such as nickel-copper alloys, bronzes, and stainless steels sometimes used for pump, valve and filter parts. The D-2 Ni-Resist ductile cast iron, containing 20 per cent nickel and treated with magnesium to give strength and ductility of steel is now available in pumps, valves and other cast parts.

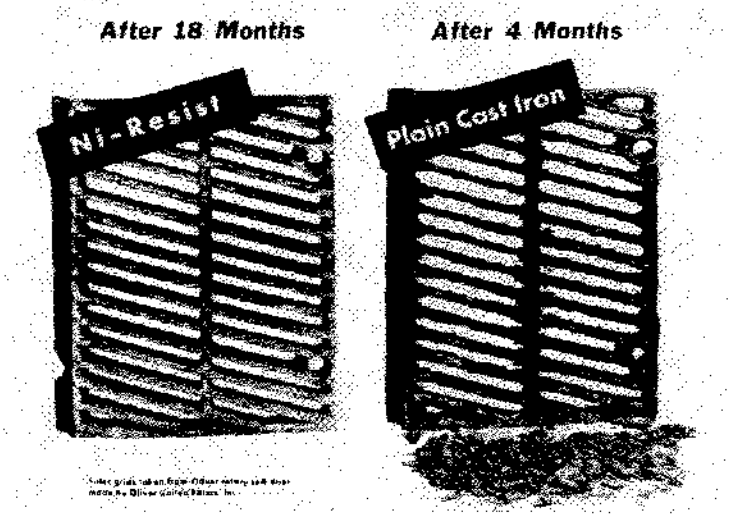

Figure 5. Comparison of Performance of Ni-Resist Alloy Type 1 and Plain Cast Iron Filter Grids on Salt Filter.

Copper has good resistance to hot and cold brines at moderately low velocities. Copper tubes have in the past been commonly used for evaporator tubes in calandria type evaporators. However, copper is subject to wear by high velocity brines, particularly where there is turbulence at tube inlets and especially where entrained salt crystals are present. Consequently, there has been considerable variation in performance from one plant to the other. Copper tubes could

[3] Trade Mark of the International Nickel Company, Inc

not be used for the newer type forced circulation evaporators and is gradually being replaced with the copper-nickel alloys. Silicon bronze, sometimes used for brine piping is subject to somewhat the same erosion effects at high velocities.

The 90-10 copper-nickel alloy is considerably more resistant to velocity effects than copper. Evaporator tubes of this alloy are frequently used, but there is an occasional failure due to wear at inlet ends. The 70-30 copper-nickel alloy provides better resistance to these velocity and erosion effects, and is now being used in some evaporator effects.

Monel alloy 400 consisting approximately of 2/3 nickel and 1/3 copper is the strongest and most corrosion and erosion resistant of the nickel-copper series of alloys and is being used in a number of the newer plants for evaporator bodies and tube sheets, heaters, piping, filter bodies, parts of pumps and valves and miscellaneous equipment.

All of the above copper-containing alloys may sometimes be subject to a localized corrosion known as metal-ion concentration cell attack in crevices or under the edges of certain deposits so that crevices should be avoided where possible. An example of this type of attack at the crevice formed by an incompletely rolled tube of brine heater is shown in Figure 6.

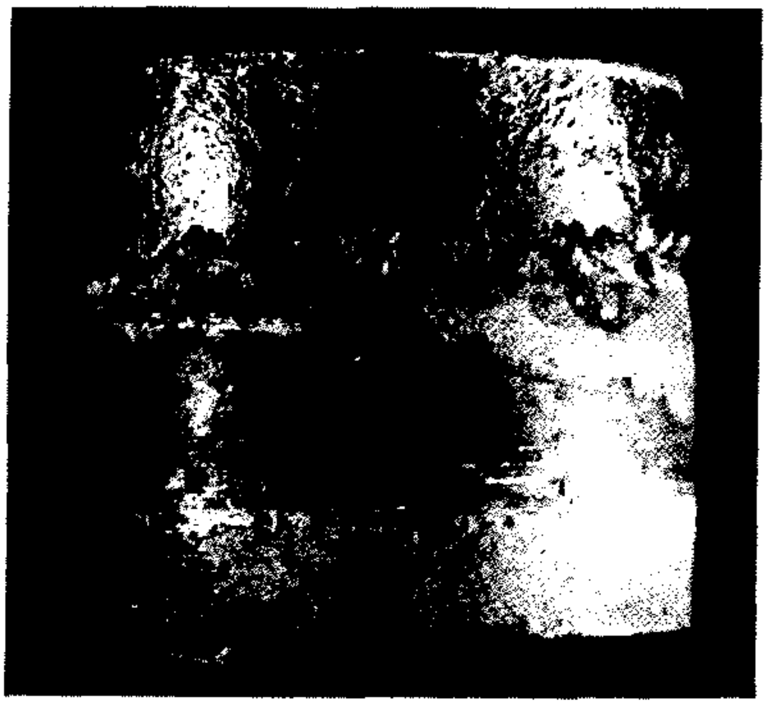

Figure 6. Metal Ion Concentration Cell Attack on Tube where Incompletely Rolled into Tube Sheet of Brine Heater.

The use of austenitic stainless steels in salt production has been increasing considerably due to their high degree of resistance to erosion by brine slurries and generally good corrosion resistance. Types 316 and 316ELC stainless are the varieties most commonly used because in addition to 18 per cent chromium and 10 per cent nickel they contain 3 per cent molybdenum which provides considerably better resistance to pitting attack in brines than Type 304 stainless which contains no molybdenum. However, considerable care must be used in the application of these stainless steels since the wrought alloys are subject to stress corrosion cracking and pitting attack in hot brines at temperatures above about 150° F.

The alloys having probably the best resistance to combinations of corrosion and abrasion in the handling of salt brines and slurries are the more highly alloyed cast materials such as Worthite[4] and the "20" alloys. These are commonly used in the most severe pumping applications.

In a large plant in western New York a modern four-effect forced circulation evaporator system was installed several years ago. At this plant the raw brine from wells is acidified by adding sulfuric acid in a rubber-lined pipe, then sent to rubber-lined packed towers where it is degassified to remove hydrogen sulfide and carbon dioxide, then neutralized with calcium hydroxide in steel tanks and settled. The brine is drawn off and after passing through wash tanks is fed to the four evaporator effects in parallel.

Two grades of salt are made at this refinery: standard evaporated salt and a highly purified salt. Standard evaporated salt is made by evaporation of an almost neutral brine (pH approximately 7.5) which contains calcium chloride, magnesium chloride and sodium chloride in solution. The highly purified salt is produced by evaporation of an alkaline brine (pH over 12) containing sodium carbonate, sodium hydroxide and sodium chloride in solution. Production of the two grades of salt necessitates periodic emptying and refilling of evaporators with the required brine, either standard or alkaline, because the two grades are not produced concurrently.

The evaporator bodies of all four effects are of solid Monel alloy 400 plate with welded construction. External vertical tubular heaters attached to each effect were originally equipped with Monel alloy tube sheets and 90-10 copper-nickel tubes. Design velocity of brine through these tubes is 4 to 5 ft/sec. The original 90-10 copper-nickel tubes in the first effect heater failed in less than two years by corrosion and erosion at the inlet ends. All heater tubes as they fail are being replaced with 70-30 copper-nickel. Performance of 90-10 copper-nickel tubes was much better in the same type of equipment processing only standard brine at another plant of the same company.

Most of the hot brine and slurry circulating lines at one plant are of schedule 10 Monel alloy pipe, which is giving satisfactory performance. Some polyethylene plastic piping used at the other plant is reported to give about six months service.

Evaporator circulating pumps are cast Type 316 stainless steel. The impeller of the circulating pump of the first effect evaporator failed by cracking due to accelerated corrosive attack of delta ferrite stringers and of the austenitic matrix next to sigma particles precipitated in the alloy. It seems apparent that the casting had not received the proper heat treatment.

The main feed brine pumps and slurry pumps are Worthite alloy. Large evaporator dump valves have Ni-Resist alloy bodies and Type 316 stainless plugs.

At this plant the salt is dried in rotary vacuum filters with heated air and discharged at about 200 F. through Monel screws to a rotary cooler. The filter body, originally of Type 316 stainless failed by stress corrosion cracking and by intergranular attack near welds, and was replaced with Monel alloy.

The filter drum is Monel, grids of Ni-Resist and screens of Type 316 stainless.

Turnbull (9) has reported the results of a series of corrosion tests in the evaporation system at this plant handling both standard and alkaline brines, using spool-type specimen holders (ASTM A224-46). Tests were made with two sets of test specimens (mounted on test spools) being exposed in each of the four evaporator effects. One set of specimens in each effect was exposed only during alkaline brine processing, and the other set during processing of standard brine. Total duration of tests was 185 days in standard brine and 125 days in alkaline brine. The results of those tests are shown in Table 1.

It will be noted that the corrosion rates of copper and the copper-base alloys including copper-nickels were higher in the alkaline brine particularly at higher temperatures. The same trend was noted, but to a lesser extent, with Type 316 stainless steel, Inconel[5] alloy 600 and

[4]Trade Mark of Worthington Manufacturing Company.

[5]Trade Mark of the International Nickel Company, Inc.

Table 1

PLANT CORROSION TESTS IN EVAPORATION
OF STANDARD AND ALKALINE BRINES (9)

Corrosion Rate, mils per year

	ALKALINE BRINE				STANDARD BRINE			
	1st Effect	2nd Effect	3rd Effect	4th Effect	1st Effect	2nd Effect	3rd Effect	4th Effect
Temperature, °F.	208	169	135	92	225	185	158	104
Material								
Cast Monel alloy 505	1.1	1.0	1.8	0.2	4.3	2.7	2.2	1.8
Cast Monel alloy 410	0.8	1.0	0.5	0.2	3.8	2.5	1.8	2.0
Monel alloy 400	0.9	0.7	0.6	0.4	3.9	3.0	2.5	2.1
70-30 Copper-nickel	0.9	0.5	0.6	0.4	6.5	4.8	4.6	4.1
90-10 Copper-nickel (0.5% Fe)	111.0	22.0	17.6	6.4	11.5	7.3	8.4	7.0
90-10 Copper-nickel (1.2% Fe)	68.0	13.7	12.4	5.5	10.3	7.2	7.9	6.8
Copper	49.0	27.5	15.0	8.2	18.5	12.9	14.0	11.2
Phosphor Bronze	61.0	26.0	17.0	8.6	16.3	10.6	10.4	8.4
Carpenter 20 alloy	0.4	0.1	0.1	.04	0.4	0.3	0.2	0.1
Type 316 stainless	37.6	2.0	0.7	0.1	0.5	0.3	0.2	0.1
Worthite alloy	2.9	1.1	0.3	.04	0.3	0.2	0.2	0.1
Inconel, alloy 600	5.3	3.4	2.2	0.7	1.1	0.6	1.1	0.5
Ni-Resist, Type 2	10.3	3.4	3.7	2.7	8.0	3.8	3.7	2.5

Worthite alloy. Ni-Resist alloy and Carpenter 20 performed about the same in both brines. Corrosion of Monel alloy was somewhat higher in standard brine than in alkaline brine.

Samples of Type 316 stainless steel in the first effects in both brines showed stress corrosion cracking, pitting attack, and crevice corrosion under insulating spacers. This alloy showed pitting and crevice attack in the second effects with both brines although stress cracking was not apparent. This experience leads to the setting of 150 F. as perhaps the maximum temperature for the use of this alloy in brine service.

Monel samples showed some crevice attack under insulating spacers in alkaline brine in the first effect. This corresponds with plant experience with the Monel first effect evaporator where some crevice attack has occurred under the edges of scale adhering to some rough surfaces such as weld beads. This has been largely overcome by smoothing down the top surface of welds. It has not been apparent in similar plants handling only standard brine.

In another salt plant operating a four effect evaporator system, using standard brine, the first effect, operating at about 220° F., has a Monel-clad steel body with 90-10 copper-nickel evaporator tubes. The other three effects operating at approximately 180 F., 140 F., and 100 F. respectively, have cast iron bodies and copper tubes. The results of corrosion tests in the first effect liquid and vapor and grainer heater are given in Table 2.

This plant makes considerable use of Type 316 stainless steel with apparent success under suitable temperature conditions. This alloy is used for slurry tanks, filter drums, filter screens, salt bins and for the lining of rotary salt dryers.

The materials used in pumps throughout the plant have been gradually upgraded. At the present time pumps having Ni-Resist alloy casings, impellers, seal rings and sleeves, and Monel shafts are used in such services as: brine feed, brine wash, and slurry pumping. Pumps with Ni-Resist alloy casing and sleeves, bronze impellers and Monel alloy shafts are used in evaporator filling and grainer feed. Sludge pumps are of Worthite alloy. Recently a number of cast CF-8M (Type 316 stainless) pumps have been added.

Table 2

PLANT CORROSION TESTS IN SALT EVAPORATION

Standard Brine

	Corrosion Rate, mils per year		
	1st Effect Evaporator		Grainer Heater After 1st Pass
	Liquid	Vapor[a]	
Ave. Temp., °F.	218	190	200
Duration of Test, days	90	90	180
pH	5.8	-	6.5
Material			
Monel alloy 400	3.0	1.0	0.2
70-30 Copper-nickel	5.0	1.0	0.9[d]
Nickel 200	3.0	2.0	0.7
Type 316 stainless	0.5[b]	0.4[c]	3.0[e]
Inconel alloy 600	0.6	0.5	2.0[e]
Ni-o-nel alloy 825	0.4	0.2	1.0[e]

(a) Tests made in steam chest of 2nd effect pan.

(b) Stress corrosion cracking.
Pitted to max. depth of .012" on surface; .007" under spacer.

(c) Stress corrosion cracking.
Pitted to max. depth of .021" on surface; .015" under spacer.

(d) Concentration cell attack to max. depth of .008" at edge of spacer.

(e) Samples .031" thick perforated by pitting.

Teeple, Abbott, and Burdick (10) presented the results of corrosion tests in the triple effect vacuum pan evaporator system of a Michigan salt plant handling a mixture of Marshall and Dundee brines containing approximately 13.9% NaCl, 9.25% $CaCl_2$, 2.54% $MgCl_2$, and 0.14% sulfate ion. The Marshall brine was treated with lime to remove iron and manganese and to raise its pH value. The Dundee brine was aerated to remove all traces of hydrogen sulfide (originally present at approximately 12 ppm) and then limed to raise its pH value. The mixed brine was kept at 6.8 to 7.5 pH. The results of the corrosion tests in liquid, vapor and salt settler of each effect are shown in Table 3.

The vacuum evaporator bodies originally were made of cast iron, but the first effect has since been lined with Monel alloy sheet in the vapor area. External tubular evaporator heaters and brine preheaters were originally equipped with cast iron heads and copper tubes. The design velocity through tubes is about 6 ft/sec. Cast iron heads failed by corrosion and erosion and were lined with a copper base alloy. Copper tubes in brine heaters failed by erosion-corrosion at inlet and outlet ends and were replaced with copper-nickel alloy tubes. Slurry pumps originally had cast iron casings which suffered corrosion-erosion and were replaced with pumps having Ni-Resist alloy casings and Monel alloy impellers, shafts and sleeves. Evaporator circulating pumps have Ni-Resist alloy casings, Type 316 stainless impellers and shafts, and Monel alloy K-500 sleeves.

The cast iron bodies of salt filters lasted about ten years. Ni-Resist alloy filter grids gave over two years' service life compared to about six months for cast iron. Monel alloy backing screens had a life of about 18 months and Type 316 top screens about 12 months.

The above examples, taken from plants operating with a variety of brines and making several grades of salt, will serve to illustrate the present trend toward the use of more corrosion resistant materials of construction. The initially higher cost of these materials usually can be made

Table 3

PLANT CORROSION TESTS IN SALT EVAPORATORS AND SETTLERS (10)

Corrosion Rate, mils per year

	FIRST EFFECT			SECOND EFFECT			THIRD EFFECT		
	Brine Heater	Vapor in Evaporator	Salt Settler	Brine Heater	Vapor in Evaporator	Salt Settler	Brine Heater	Vapor in Evaporator	Salt Settler
Temperature, °F.	205	175	200	160	136	157	125	101	119
Duration of test, days	215	244	215	215	268	215	215	268	215
Material									
Monel alloy 400	0.4	0.3	0.4	0.9	0.3	0.5	1.1	0.2	0.8
Nickel 200	0.5	0.4	0.4[a]	1.2	0.3	0.5	1.1	0.2	0.6
Inconel alloy 600	0.1[a]	0.1[a]	0.1[a]	0.3[a]	0.1[a]	0.1[a]	0.6	0.1	0.4
Type 316 stainless	0.1[b]	0.1[b]	0.1[b]	0.4[d]	0.1[d]	0.1[d]	0.6	0.1	0.4
70-30 Copper-nickel	0.6	0.5	0.3	1.4	0.4	0.8	2.0	0.4	1.2
80-20 Copper-nickel	0.9	0.7	0.5	1.8	0.6	1.2	2.5	0.5	1.5
90-10 Copper-nickel	1.8	0.8	1.0	1.8	0.5	1.1	2.2	0.4	1.5
Silicon bronze	3.1	1.1	1.2	1.9	0.7	2.5	3.3	0.9	1.7
Copper	3.1[c]	0.8	1.1	2.4	0.9	2.0	3.4	0.8	2.6
Type 1 Ni-Resist	1.5	3.1	2.0	3.4	2.0	3.0	3.0	1.7	3.1
1.5% Cu Cast Iron	9.5	21.0	12.0	25.0	20.0	18.0	18.0	14.0	14.0
Plain Cast Iron	11.0	23.0	11.0	26.0	22.0	21.0	17.0	16.0	16.0

(a) Incipient pitting.

(b) Pitting and stress corrosion cracking.

(c) Metal ion concentration cell attack at spacer crevice.

(d) Pitted to depth of .012". Crevice attack under spacer.

up quickly by more continuous production, less down time, maintenance and replacement costs, and by the protection of product purity.

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