

Corrosin-Resistant Aluminum for the Salt Industry

by
Thomas A. Lowe
Kaiser Aluminum & Chemical Co.
Spokane, Washington

ABSTRACT

Choose the proper alloy, and aluminum will serve well in the salt industry. Case histories confirm satisfactory service in many salt mining and solution handling applications. Aluminum-magnesium alloys are best for bulk salt or saline solutions. Service temperatures will dictate the proper alloy. Avoid alloys with copper zinc as principal alloying elements. Aggressiveness of salt solutions toward aluminum increases with concentration up to approximately 5% (by weight), then decreases with more concentrated solutions. Equipment should be designed and fabricated in a manner that will eliminate dissimilar metal contacts. Faying surfaces should be sealed.

INTRODUCTION

Aluminum has found its place in the family of metals because of its light weight and generally good resistance to corrosion. This resistance is directly attributable to, (1) the very thin, but continuous and protective oxide film, and (2) the protective nature of corrosion products which form at discontinuities in this air-formed film. This discussion will touch upon the factors which affect the corrosion resistance of aluminum, primarily the effects of alloying and of design. Some attention will be given to methods by which we can control corrosion, and finally, we will consider the influence of salt upon aluminum and how aluminum might be used in the salt industry.

CORROSION PHENOMENA

The processes of corrosion of aluminum are not unlike those of other metals and alloys. In a broad sense, corrosion represents those reactions by which a metal tends to revert to a lower energy state, such as its ore. This tendency was not recognized in the early years of the metal age, when the metals used were either found in the virgin state or were easily extracted from their ores. As metals technology improved and use of the more difficultly-extracted metals increased, the problems of corrosion and its prevention arose. These problems were overlooked, or accepted as inevitable, for many years. Only recently, as our understanding of the corrosion processes has expanded, have we learned that there are ways of eliminating or alleviating the effects of corrosion in equipment design, fabrication and maintenance.

When corrosion of aluminum or certain other metals occurs in the atmosphere or in an environment containing air, oxygen will promote healing of any weak points in the oxide film. If the nature of the corrosive medium is such that film repair is difficult, corrosion will start at discontinuities and thin points in the film. At these points, aluminum passes into solution and is usually precipitated as hydrated alumina. The precipitated corrosion products offer a barrier to further diffusion of aluminum ions into solution -- a more effective barrier than corrosion products formed on many other metals. It is this combination of protective air-formed oxide film and relatively protective corrosion products that enables aluminum alloys to offer good resistance to most corrosive environments.

EFFECTS OF ALLOYING ON CORROSION RESISTANCE

If aluminum were available only as high purity metal, it would receive little consideration as a material of construction. The pure metal has relatively low mechanical properties. Improvement of these properties is the primary purpose of alloying.

The alloy designation system adopted by the Aluminum Association is based on the principal additions to aluminum alloys, as shown in Table I. These alloying additions influence the corrosion performance of aluminum. Only a few of them, however, have major significance.

TABLE I

ALUMINUM ASSOCIATION DESIGNATIONS FOR ALLOY GROUPS

Aluminum - 99.00% minimum and greater		1xxx
Major Alloying Element		
Aluminum	(Copper)	2xxx
Alloys	(Manganese)	3xxx
grouped	(Silicon)	4xxx
by major	(Magnesium)	5xxx
Alloying	(Magnesium and Silicon)	6xxx
Elements	(Zinc)	7xxx
	(Other Elements)	8xxx
Unused Series		9xxx

Copper

It has been established that additions of copper (2000 series alloys) to the aluminum solid solution decrease the corrosion resistance of the alloy. This is due in part to the fact that the aluminum oxide film is not consistent over the surface. It now contains oxides of copper which decrease its protective qualities. Furthermore, redeposition of copper passing into solution as a result of corrosion sets up galvanic cells on the aluminum surface, markedly increasing the corrosion rate. These deleterious effects are multiplied if the copper is out of solution at grain boundaries.

Manganese

Manganese additions (3000 series alloys) improve work hardenability but have little effect upon resistance to corrosion. The most common alloys of this group, 3003 and 3004, have found use in many applications involving salt solutions -- indicative of their generally good corrosion resistance.

Silicon

Silicon alloys (4000 series alloys) are used primarily in castings and find little use in wrought products. Aluminum-silicon alloys have good corrosion resistance.

Magnesium

The 5000 series contains more alloys of interest to the salt industry than any other series. Addition of magnesium increases strength, not only in the annealed condition, but also in the cold-worked tempers. Small additions of manganese to the Al-Mg group provide further improvement in strength.

All alloys of this series have application potential in the salt industry for two reasons:

1. they have excellent resistance to corrosion by salt or saline solutions, and
2. they are readily weldable and retain high strength in the "as-welded" condition.

The good corrosion resistance of the Al-Mg series is attributed to the ease of formation of an oxide film over magnesium-rich aluminum of the type $\text{Al}_2\text{O}_3 \cdot \text{MgO}$ (spinel). The protective properties of such a film are similar to those of the oxide formed on high purity aluminum.

Magnesium and Silicon

Another family of alloys which has found extensive service in salt environment is the 6000 series. These alloys, containing magnesium and silicon, are commonly referred to as the magnesium silicide type. Until the advent of the Al-Mg and Al-Mg-Mn series, they represented the most corrosion resistant of the high strength aluminum alloys. Alloys 6061 and 6063 of this group are readily weldable but have lower welded strengths than most of the 5000 series unless properties are restored by post-weld heat treatment.

Zinc

The 7000 series, with zinc as the principal alloying element, have the highest strength of the many aluminum compositions. Al-Zn-Mg-Cu alloys make up the most widely used members of this group. Unfortunately, in higher concentrations, these strengthening elements can form constituents detrimental to corrosion resistance, as evidenced by the exfoliation attack shown in Figure 1. Zinc, as the sole additive, provides an alloy, 7072, which is anodic to most other

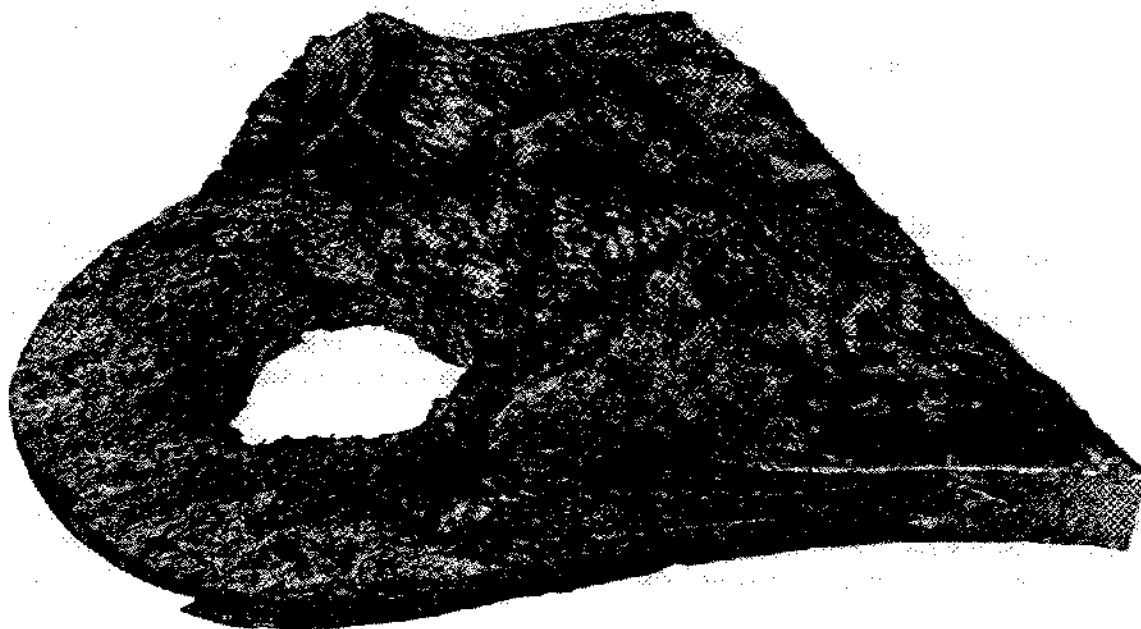


Figure 1. A 7000 series aluminum part which failed in a severe marine atmosphere as a result of exfoliation corrosion.

aluminum alloys. Alloy 7072 is therefore used extensively as cladding for wrought products where it provides longer service life of the base alloy by means of cathodic protection.

It is well established that copper and zinc-magnesium-copper additions detract from the overall corrosion resistance of aluminum. This applies to major alloying additions of these elements rather than to impurities in minor amounts. We do not know the exact relationship of these other elements, when present as impurities, upon the formation of surface films and subsequently upon corrosion resistance. It is believed that their role relates to defect structures in the oxide film. Such defects are weak points or flaws, vulnerable to penetration and subsequent attack of the metal surface by aggressive ions.

It can be readily shown that by decreasing the levels of impurity content, corrosion performance is improved. Alloys 6061 and 6063 show this relationship, perhaps as a result of their difference in copper content. The exact influence of each individual element becomes a matter of the specific alloying system under consideration, as well as the presence of other impurity elements. Not only copper, but iron and silicon are suspected of being detrimental. For example, the amount of copper impurity may be influential on corrosion performance in the 6000 series alloys; however, silicon impurity may exert a more significant effect than copper on the corrosion resistance of the 5000 series alloys.

Both 5052 and 6063 have low impurity contents. This fact definitely contributes to their improved corrosion resistance. There are other alloys which have low impurity contents and which should, therefore, be of service in the salt industry. Some of these are shown in Table II. You will note in Table III that these alloys have attractive mechanical properties which, as mentioned earlier, remain high in the as-welded condition.

TABLE II
NOMINAL CHEMICAL COMPOSITIONS

Alloy	%Mg	%Mn	%Cu	%Si	%Fe	%Cr
2014	0.5	0.8	4.3	0.85		
2024	1.6	0.6	4.3			
3003		1.2	0.20 ⁽¹⁾		0.7 ⁽¹⁾	
3004	1.0	1.2	0.25 ⁽¹⁾		0.7 ⁽¹⁾	
5050	1.4		0.2 ⁽¹⁾	0.4 ⁽¹⁾	0.7 ⁽¹⁾	
5052	2.5		0.1 ⁽¹⁾	0.45 Si + Fe		0.25
5154	3.4		0.1 ⁽¹⁾	0.45 Si + Fe		0.25
5454	2.7	0.8	0.1 ⁽¹⁾	0.40 Si + Fe		0.15
5086	4.0	0.4	0.1 ⁽¹⁾	0.4 ⁽¹⁾	0.5 ⁽¹⁾	0.10
5083	4.5	0.7	0.1 ⁽¹⁾	0.4 ⁽¹⁾	0.4 ⁽¹⁾	0.10
5456	5.2	0.7	0.2 ⁽¹⁾	0.40 Si + Fe		0.10

(1) Maximum per cent

TABLE III

TYPICAL STRENGTH OF ALLOYS COMMONLY USED
IN MARINE ENVIRONMENT SERVICE

<u>Alloy & Temper</u>	<u>TS, ksi</u>	<u>YS, ksi</u>	<u>% El</u>
1100-H14	18	17	9
3003-H14	22	21	8
Alclad 3004-H18	29	27	4
5052-H34	38	31	10
5454-H34	44	35	10
5154-H34	42	33	13
5086-H34	47	37	10
5083-H113	46	35	16
5083-H34	54	44	10
5456-H321	50	36	16
5456-H343	55	45	10
6061-T4	35	21	22
6061-T6	45	40	12
Alclad 2024-T3	65	45	18
Alclad 7075-T6	76	67	11

EFFECTS OF DESIGN ON CORROSION RESISTANCE

There are, of course, other factors besides alloying, which can influence the corrosion performance of aluminum. These would include design and fabrication. A distinction is made in these factors since what the designer specifies is often far from what is built. One should similarly add maintenance to the term fabrication, since what is originally constructed might be changed significantly during repair.

The most serious problems thus encountered are dissimilar metal contacts, particularly between aluminum and copper or copper-base alloys, but also with mild steel. Table IV indicates the effect on aluminum of direct contact with different metals in several environments. As the table shows, the weight loss in aluminum-to-aluminum contacts is insignificant. Contacts with dissimilar metals result in accelerated attack of the more anodic aluminum member in the aggressive environments common to the salt industry. Such dissimilar metal contacts may be eliminated by substitution of copper or mild steel with a material more compatible with aluminum such as an aluminum alloy, plastic, stainless steel, galvanized or aluminized steel. They may be alleviated, if substitution is impossible, by use of non-metallic insulators which separate the dissimilar metals, by painting or by cathodic protection. Since paint coatings cannot be relied upon to be completely free from holidays, it is best to paint both members of the galvanic couple. If only one member can be painted, it should be the cathode, or more noble metal. Holidays in the paint coating will then allow only small areas of cathodic material to be exposed, thereby reducing the corrosion currents which would flow and the amount of attack. Less severe, though probably more frequent, are problems involving crevices. Despite the use of compatible materials for mating surfaces, crevices are harmful due to their susceptibility to moisture entrapment with

TABLE IV

PERCENTAGE WEIGHT LOSS OF ALUMINUM COUPLED DIRECTLY TO DIFFERENT METALS

Dissimilar Metal	Environment		
	Marine	Industrial	Rural
Aluminum	1	0	0
Copper	10	3	1
Iron	4	3	1
Lead	7	1	0
Nickel	3	1	0
Tin	4	1	0
Zinc	0	0	0

subsequent concentration cell attack, as shown in Figure 2. If crevices cannot be eliminated by such means as the use of welded butt joints, then they can be mitigated by sealing them and preventing entry of moisture or solutions.

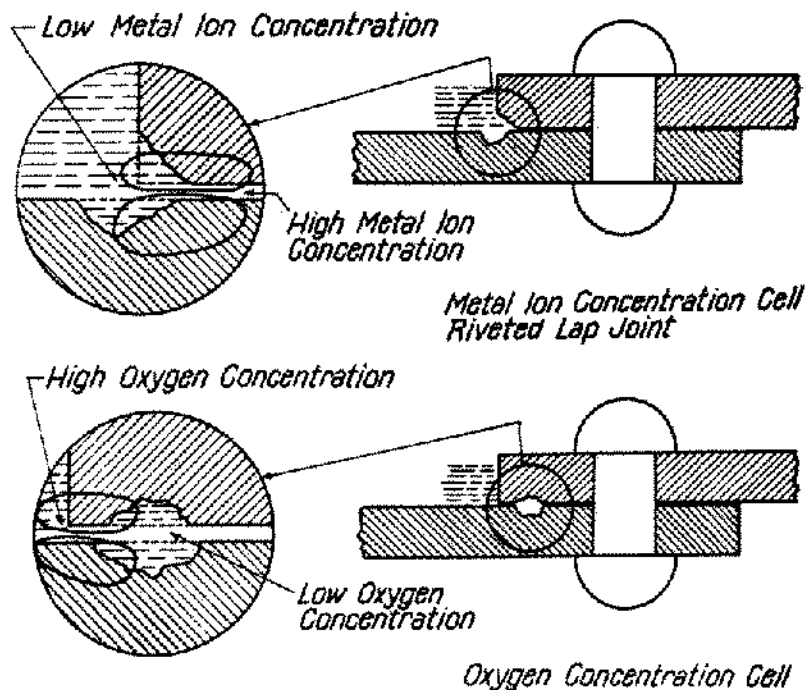


Figure 2. Schematic illustration of the types of concentration cells which can occur in crevices.

PROTECTIVE MEASURES FOR ALUMINUM

When the performance of bare aluminum proves unsatisfactory, protection of the surface may offer improvement. Such protection may take the form of cladding, cathodic protection, coating, or inhibiting.

Cladding is frequently used for the less corrosion-resistant alloys, such as 2024 and 7075. It is also used on such common alloys as 3003, 3004, and 6061. As indicated in Figure 3, clad coatings work on the principle of cathodic protection. They are designed to be more electronegative than the core alloy which they are to protect. Should the core become exposed at a break in the cladding, the more electronegative layer will corrode sacrificially to protect the core.

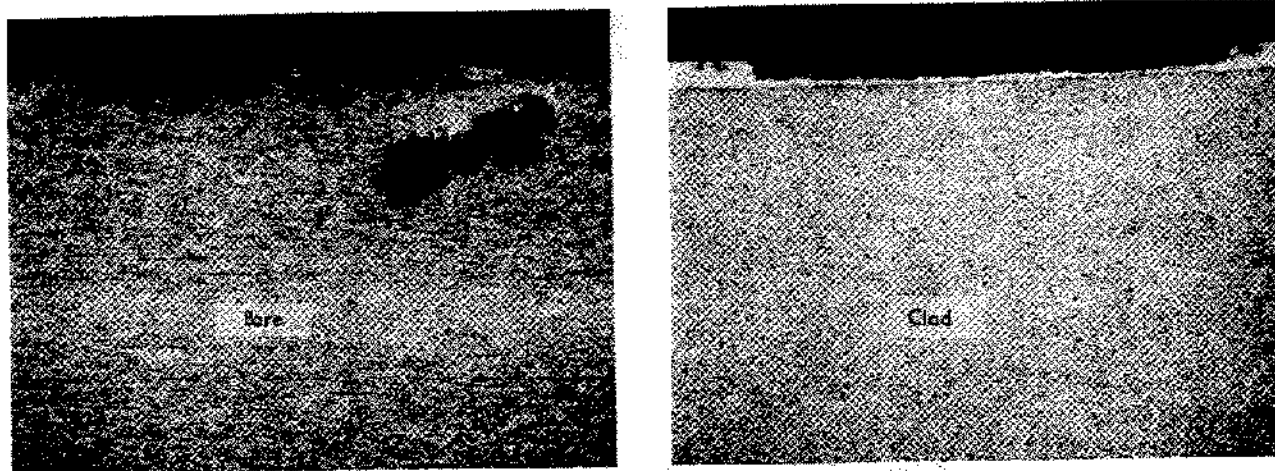


Figure 3. Pitting of bare aluminum in aggressive environments might result in perforation. Cladding alleviates this type of attack by spreading it laterally.

Cathodic protection of a different nature is possible through the use of magnesium, zinc, or aluminum alloy anodes or by means of impressed current. Such protection is afforded aluminum-hulled boats in the vicinity of bronze propellers. Caution must be used in the design of cathodic systems for aluminum to insure against over-protection with resulting formation of an alkaline environment at the aluminum cathode which would itself cause corrosion.

Protective coatings are popular and can be used to great advantage. Proper surface pre-treatment is imperative for successful coating performance. Major suppliers of coatings may be consulted about proper techniques.

Inhibitors offer a valuable method for controlling or preventing corrosion. Chromates, silicates, and phosphates have been found to inhibit attack of aluminum in saline solutions (Ref. 1, 2, 3).

INFLUENCE OF SALT ON ALUMINUM

There is little need to remind the salt industry of the aggressiveness of chlorides. The solubility of chloride compounds and the size of the chloride ion contribute to the active role that they play in the corrosion of metals. For aluminum, the chloride ion is believed to penetrate the oxide film at defect points. The resulting exposure and oxidation of the active aluminum surface results in the formation of corrosion products which may, or may not, be protective depending upon the conditions of exposure.

In natural atmospheric environments, where an electrolyte is not always present, the localized points of attack are readily healed. Aluminum will display a surface with tiny mounds of white corrosion products after exposure to a saline environment. With increasing exposure, the

areas susceptible to attack become progressively fewer. The surface reaches a condition which is little changed with time. The effects of exposure on certain alloys in a marine atmosphere are given in Table V (Ref. 4).

TABLE V

CORROSION RESISTANCE OF ALUMINUM ALLOYS IN A MARINE ATMOSPHERE
80 FOOT SITE - Kure Beach, North Carolina

Alloy & Temper	Maximum Pit Depth, mils				Per Cent Change in 10 Years		
	1 Year	2 Years	5 Years	10 Years	TS	YS	% EI
1100-H18	3	2	Lost	6	0	-2	-12
3003-H14	3	4	5	6	0	0	-12
5050-H34	2	2	3	5	-1	-2	-12
5052-H34	2	2	Lost	4	-1	-4	0
Alclad 2024-T3	1	1.5	1.5	2	0	0	0
Alclad 7075-T6	2	3	3	3	0	0	0

There is not much difference in the performance of aluminum in saline solutions if a wet-dry cycle is part of the process routine. Film repair can be accomplished during the dry stage.

The experience with aluminum, constantly immersed in saline solution, has not been significantly different from its performance in marine atmospheres. Film repair is effected and the rate of attack decreases with time. Table VI indicates the performance of unprotected aluminum alloys in seawater (Ref. 4).

TABLE VI

CORROSION RESISTANCE OF UNPROTECTED ALUMINUM ALLOYS IN SEAWATER
Daytona Beach, Florida

Alloy & Temper	Exposure Period, Yrs	Maximum Measured Pit Depth, mils	Per Cent Change in TS
3003-H14	8	7.0	-1
Alclad 3004-H18	8	2.5 ^x	0
5050-H34	8	12.0	-3
5052-H34	8	10.5	-2
5052-H36	6	23.0	-2
5086-H34	6	34.0	0
6061-T4	8	14.0	-8

^x Depth of pitting confined to the cladding.

Although none of the losses in strength is considered significant, it is of interest to observe the probable reason for the difference in performance of 6061 and 5052. The frequency of pitting on the 6061 was markedly greater than on 5052. A previous study (Ref. 5) has shown the relation of pitting frequency for these two alloys when exposed for two years in seawater. The pit data from that study, Table VII, indicate that alloy 6061 had approximately fifteen times more pits than alloy 5052.

TABLE VII	
PIT COUNT DATA OF ALUMINUM IN SEAWATER	
<u>Alloy and Exposure Period</u>	<u>Pit Count</u>
5052-H34	
6 months	326
12 months	463
24 months	455
6061-T4	
6 months	6963
12 months	3583
24 months	7503

These data also provide evidence of the decrease in rate of attack with time -- often referred to as the "self-arresting" nature of attack on aluminum alloys.

Laboratory tests have confirmed the resistance of aluminum to attack by salt solutions. Results of an evaluation of the comparative performance of aluminum alloys in several solutions are shown in Table VIII. The rate of attack decreased with increasing sodium chloride concentration above 5%. The maximum attack occurred at approximately 5% (by weight) solution concentration. This estimate of most aggressive concentration is in agreement with the work of Best and McGraw (Ref. 6). The results of their investigations are shown in Table IX. Included are corrosion rates which they determined for 1020 steel and magnesium alloy AZ91. The aluminum alloy which they tested, 7075, would not be recommended for use in aggressive environments. It is interesting, however, to compare their results with those given previously for alloy 5052.

ALLOYS FOR SALT SERVICE

Again referring to Table V, you will note that there is no great difference in the overall corrosion performance of many of the common aluminum alloys. However, small specific differences, such as in frequency of attack or effect on tensile strength, are often important enough to dictate the use of one alloy over another. A thorough appraisal of the major types of aluminum alloys with sodium chloride has been made by Bryan (Ref. 7). Our laboratory and field experience with saline solutions and with seawater, and the experience in the salt industry tend to confirm Bryan's general observations. A rating of these alloy systems for salt service would be as follows:

Best resistance

Al-Mg-Mn
Al-Mg
Al-Mn

Moderate resistance

Al-Mg-Si
Commercial purity Al
Al-Si

Poor resistance

Al-Cu
Al-Zn-Mg-Cu

TABLE VIII

CORROSION RATE OF ALUMINUM ALLOYS
MILS PER YEAR⁽¹⁾

	<u>99.5% Al</u>	<u>3003</u>	<u>5052</u>	<u>6061</u>
0.5% Acetic Acid	4.1	5.0	4.7	5.5
99.5% Acetic Acid	0.0	0.1	0.6	0.2
1% NaCl	1.7	1.3	1.4	1.6
5% NaCl	1.9	1.0	1.5	1.4
10% NaCl	1.0	0.7	0.8	0.7
20% NaCl	0.7	0.5	0.9	0.5
1% Na ₂ SO ₄	0.0	0.1	0.2	0.1
20% Na ₂ SO ₄	0.3 ⁽²⁾	0.1	0.4	0.3
1% Na ₂ CO ₃	4.0 ⁽²⁾	4.3	17.6	12.0 ⁽²⁾
20% Na ₂ CO ₃	128.4 ⁽³⁾	91.5 ⁽³⁾	47.7	77.8 ⁽²⁾

(1) Exposure for 30 days at 95F (2) Varying degrees of pitting noted on samples. (3) Pitting attack resulting in panel perforation.

TABLE IX

CORROSION RATES IN SODIUM CHLORIDE SOLUTIONS
Mils per Year (Best and McGraw)

	<u>Solution Concentrations</u>		
	<u>5%</u>	<u>10%</u>	<u>20%</u>
Steel 1020	33.90	30.25	19.24
Aluminum 7075	6.71	4.13	1.03
Magnesium AZ91	16.52	20.65	24.78

The end application would most often determine the particular alloy choice, since requirements for strength, weldability, appearance, and corrosion resistance must be considered.

SUCCESSFUL APPLICATIONS OF ALUMINUM

The applications of aluminum in saline environments have been many and varied. They range from hypodermic needle hubs to ferry boats. The great bulk of this usage is in marine atmospheres, as roofing, siding, and other structural forms. A recent examination of aluminum roofing and siding, exposed for ten years on a dockside warehouse, Terminal Island, California, showed that the maximum depth of attack was 5.0 mils (0.005 inch). An increasing amount of aluminum is being used in seawater for boats, barges, superstructures, and underwater pipelines. One excellent example is the Cabrillo, shown in Figure 4. Other examples include pilot boats, commercial fishing boats and pleasure craft.

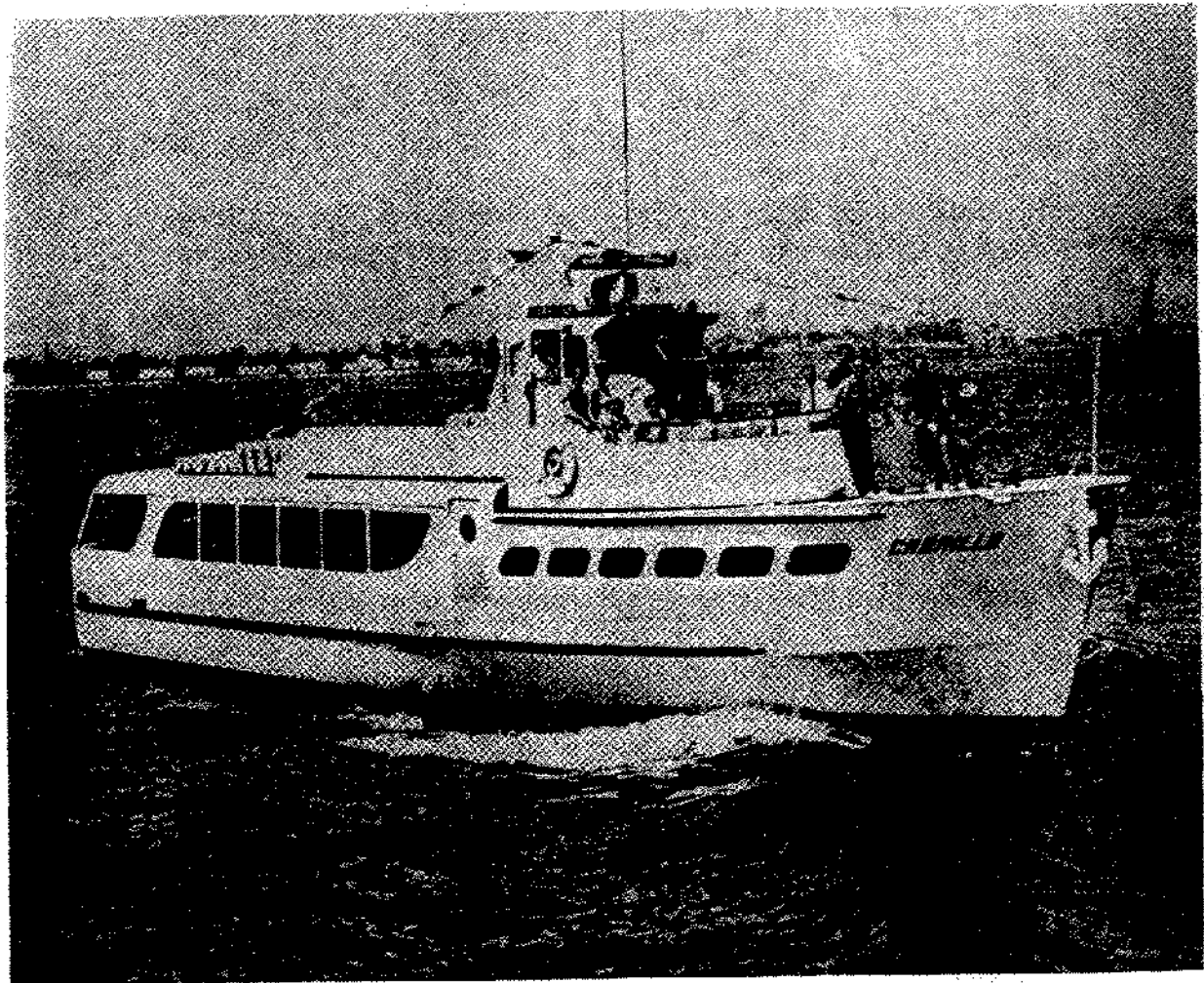


Figure 4. The 65-foot ferry boat, Cabrillo, operates between Wilmington, California, and Catalina Island.

Present interest in desalting seawater for drinking purposes has resulted in new uses for aluminum. The most prominent of these is in a portable desalting unit designed for use by the U. S. Army and described by Gainey (Ref. 8). During the development of this unit, the deleterious effects of dissimilar metal contacts on the performance of aluminum was well demonstrated.

Testing which has accompanied the use of aluminum hubs for hypodermic needles has pointed out not only a resistance to the normal saline solutions used in the medical field, but also the non-toxic nature of any corrosion products which might result. Considerably more weight has been given these attributes by the successful use of aluminum cooking ware over the years. Weak saline solutions are constantly encountered in this latter application.

The salt industry has used aluminum primarily in the mining and handling of bulk salt and in buildings which house salt-processing equipment. The use of aluminum conduit in salt mines (Ref. 9) is described in another paper of this Symposium. Aluminum's application in mine skips, mine cars, and for walkways and platform gratings has been successful (Refs. 10, 11). Resistance to attack by bulk salt and by salt dust has enabled aluminum to serve in storage bins, bulk handling equipment (as in the all-welded aluminum hopper car shown in Figure 5) and for roofing and siding in areas where salt is handled.



Figure 5. Modern hopper car for bulk materials. This design, incorporating aluminum alloy body, provides maximum material handling versatility.

Continued successful use of aluminum in the salt industry can be assured if care is taken in the choice of alloy, and in the design and fabrication of the particular installation. The 5000 series of aluminum alloys is to be preferred (Ref. 12). Elimination of dissimilar metal contacts and of crevice-forming joints should be a goal for the designer and fabricator. If these contacts and joints cannot be avoided, then they should be properly insulated and sealed. With these precautions, aluminum will perform well in the salt industry.

REFERENCES

1. R. B. Mears and G. G. Eldredge, Transactions Electrochemical Society, 83, 403-17 (1943).
2. Marc Darrin, Industrial & Engineering Chemistry, 37, 741-49 (1945).
3. G. G. Eldredge and R. B. Mears, Industrial & Engineering Chemistry, 37, 736-741 (1945).
4. T. J. Summerson, Corrosion Resistant Aluminum Structural Alloys for Marine Environments, Presented at the 18th NACE Conference, March 19-23, 1962.
5. T. J. Summerson, et al., Pit Depth Measurements as a Means of Evaluating the Corrosion Resistance of Aluminum in Sea Water, METALS, Special Technical Publication No. 196, American Society for Testing Materials.
6. George E. Best and John W. McGraw, Corrosion, 12, 286t-92t (1956).
7. J. M. Bryan, Aluminium and Aluminium Alloys in the Food Industry, Special Report No. 50, Department of Scientific and Industrial Research, 1948, His Majesty's Stationery Office, London.
8. Richard J. Gainey, Use of Aluminum for Portable Sea Water Distillation Equipment, Corrosion, 17, 526t-528t, November, 1961.
9. Electrical World, 154, 46, August 1, 1960.
10. Engineer (London), 211, 1962-163, February 3, 1961.
11. Private Correspondence, R. G. Ganong.
12. S. E. Pavlov and V. A. Soboleva, Causes of Pitting Corrosion of Aluminum in Tap Water, Korrozlia i. Zashita Metallov Sbornik, 236-259, (1957).