Zircadyne® 702/705 - in Chloride Solutions

INTRODUCTION

Chloride salt solutions, such as seawater, present a challenging environment for selecting materials with acceptable corrosion resistance. When exposed to these solutions, most metals are susceptible to localized forms of corrosion such as pitting, crevice corrosion and stress corrosion cracking. Zirconium is one of the few metals that can withstand corrosion attack from chloride salts, even at high temperatures. This makes zirconium an ideal material for the construction of heat exchanger equipment where seawater is used as the cooling medium, and also in chemical processes where hot, concentrated chloride salt solutions are used as catalysts.

CORROSION RESISTANCE

While seawater can severely corrode most metals, zirconium is resistant to attack. Tests performed on zirconium samples in ocean water, at temperatures up to 200C and durations up to 275 days, all show little or no corrosion (Table 1).

TABLE 1: CORROSION OF ZIRCONIUM IN SEAWATER

Temperature(C)	Exposure Time (days)	Corrosion Rate (mpy)	Pitting or Crevice Corrosion
10 –15 (ambient)	129	nil	No
Boiling	275	nil	No
200	29	nil	No

In addition to its performance in seawater, zirconium has shown outstanding corrosion resistance in a wide range of chloride salt solutions (Table 2). In most cases, this capability extends to high concentrations and elevated temperatures of 100C and above. Zirconium can handle these conditions without undergoing localized or general corrosion attack, except in the most oxidizing media such as ferric chloride and cupric chloride. Effective use of preventative measures will allow zirconium to be used in these oxidizing solutions as well (see Section IV: Limitations).

TABLE 2: ZIRCONIUM CORROSION RESISTANCE IN VARIOUS CHLORIDE SALT SOLUTIONS

Chloride in Solution	Concentration (%)	Temperature (C)	Corrosion Rate (mpy)
Aluminum	5, 10 and 25	35 – 100	< 1
Ammonium	1, 10 and Saturated	35 – 100	< 1
Barium	5, 20	35 – 100	< 1
Calcium	5, 10, 25	35 – 100	< 1
Calcium	70	Boiling	< 1
Cupric		35 – Boiling	> 50

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Ferric		35 – Boiling	> 50
Magnesium	5, 40	35 – 100	< 2
Magnesium	47	Boiling	< 1
Manganese	5, 20	35 – 100	< 1
Mercuric	1,5,10 and Saturated	35 – 100	< 1
Nickel	5, 20	35 – 100	< 1
Nickel	30	Boiling	Weight Gain
Potassium	Saturated	60	< 1
Sodium	3 – Saturated	35 – Boiling	< 1
Stannic	5	100	< 1
Stannic	24	Boiling	< 1
Tin	5, 24	35 – 100	< 1
Zinc	5, 20	35 – Boiling	< 1
Zinc	70	Boiling	Weight Gain

COMPARISON OF ZIRCONIUM AND TITANIUM

The corrosion resistance capabilities of titanium and zirconium in chloride salts complement each other well. As shown above, zirconium performs well in most solutions, but is limited in the presence of the highly oxidizing ferric and cupric chlorides. Titanium, on the other hand, shows excellent corrosion resistance in oxidizing conditions, but is less effective in reducing salt solutions containing aluminum or zinc chlorides. Table 3 compares the corrosion data for the two metals.

TABLE 3: CORROSION RATES OF TI AND ZR IN CHLORIDE SALT SOLUTIONS

Chloride Salt	Concentration (%)	Temperature (C)	Zirconium Corrosion (mpy)	Titanium Corrosion (mpy)
Aluminum	5, 10, 25 10 40	35 – 100 150 Boiling	< 1 --- ---	--- 1.3 4300
Ammonium	1, 10, Saturated Saturated	35 – 100 100	< 1 ---	--- nil
Calcium	5, 10, 25 70 80	35 – 100 Boiling 200	< 1 < 1 ---	--- nil 0.2

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Cupric	55	35 – Boiling Boiling	> 50 ---	--- 0.1
Ferric	6 10 10 50 50	50 25 50 Boiling 150	1.9 9.0 16 --- ---	--- --- --- 0.7 0.1
Magnesium	47 42	Boiling Boiling	< 1 ---	--- nil
Mercuric	5, 10, Saturated 55	35 – 100 Boiling	< 1 ---	--- nil
Potassium	Saturated 29	60 Boiling	< 1 ---	--- 0.1
Stannic	5 24 20	100 Boiling Boiling	< 1 < 1 ---	--- --- 0.3
Zinc	5, 20 70 20 75	35 – Boiling Boiling 150 Boiling	< 1 nil --- ---	--- --- 0.2 2.4

In neutral chloride salt solutions, zirconium and titanium are almost equally corrosion resistant. This is true for sodium chloride, potassium chloride, and seawater; however, there is one notable exception. Titanium is more susceptible to crevice corrosion, as seen by test results of the metals exposed to boiling seawater (Table 4). This phenomenon may be explained by realizing that the local environment within a crevice becomes more reducing over time; therefore, since zirconium's corrosion resistance is better in a reducing chloride salt solution, it will not be affected as the titanium is by crevice corrosion.

TABLE 4: CORROSION OF TI AND ZR IN

Metal	Artificial Crevice	Corrosion Rate (mpy)	Pitting or Crevice Corrosion
Zr 702	No	nil	No
Ti Grade 2	No	nil	No
Zr 702 (welded)	No	nil	No
Ti Grade 2 (welded)	No	nil	No
Zr 702	Yes	nil	No
Ti Grade 2	Yes	nil	Crevice Corrosion

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LIMITATIONS

Despite the superiority of its corrosion resistance in most chloride salts, zirconium will undergo localized corrosion in oxidizing solutions. The presence of oxidizers, such as ferric or cupric ions, will polarize the metal surface, allowing the breakdown of the passive oxide layer at preferred sites. This can lead to pitting, intergranular corrosion, and/or stress corrosion cracking of zirconium.

There are several ways to improve the corrosion resistance of zirconium in oxidizing chloride salts. The zirconium metal can be pickled to give a well-conditioned surface, free from embedded particles such as silicon carbide and aluminum oxide. Since zirconium is much more susceptible to pitting in low pH solutions, maintaining pH in the neutral region can also have a significant impact on its corrosion resistance in solutions containing oxidizing ions (see Table 5). Adding corrosion inhibitors to the chloride salt solutions is another effective means of altering the environment to make it suitable for using zirconium; possible inhibitors include sulfate, nitrate and stannous ions. Finally, electrochemical protection can be used to prevent the breakdown of the passive zirconium oxide film, and thus maintain its favorable corrosion resistance.

TABLE 5: EFFECT OF PH CONTROL ON THE CORROSION OF ZIRCONIUM (NACL SOLUTIONS CONTAINING 500 PPM CU+2)

pH	Corrosion Rate (mm/yr) 3.5 % NaCl		Corrosion Rate (mm/yr) 25% NaCl	
	Non-welded	Welded	Non-welded	Welded
1.0	0.05*	0.59*	0.04*	0.55*
4.0	0.01*	0.60*	0.03*	0.56*
5.0	0.02	0.64*	nil	nil
6.0	nil	nil	nil	nil
7.5	nil	nil	nil	nil

* = pitting

SPECIAL PRECAUTIONS

There is a special safety concern when using zirconium. Reactive metals like zirconium can develop pyrophoric films. Normally zirconium corrodes uniformly and all the zirconium is converted to zirconium oxide. If corrosion rates are low, <5 mpy, there is time to react all the zirconium uniformly. For very high corrosion rates, >200 mpy, the reaction rate is so high that all zirconium is also reacted.

At certain conditions, it is possible that the corrosion rate will attack grain boundaries and continue attacking the boundaries, trapping small pieces of Zr grains in the oxide and not completing the oxidation. Under these conditions, the oxide film may be pyrophoric. To passify the zirconium, the trapped zirconium pieces need to be completely oxidized before opening the equipment to air. This is achieved by passing hot air or steam through the equipment to make sure all the zirconium in the oxide film is reacted before opening to air. At 250C, air must flow for 20 minutes or steam for 30 minutes; at lower temperatures, several days of treatment are required.

SUMMARY

As demonstrated above, zirconium can be the best alternative for material selection in chloride salt solutions, including seawater systems. Longer equipment life, reduced maintenance downtime, and higher purity product streams are all possible with the proper application of zirconium, making it the most cost-effective option when compared with other alloys.

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Although, zirconium has proven its outstanding corrosion resistance performance in a wide variety of chloride salt solutions and seawater applications, the best way to determine zirconium's suitability for a particular environment is to perform a corrosion test. Zirconium corrosion test kits are available from ATI for use in on-line process equipment. These tests can show how zirconium will hold up under actual process conditions. ATI also has a fully capable corrosion laboratory for complete testing and detailed analysis for specific chloride salt solutions or seawater applications. For further information or any questions regarding the use of zirconium in chloride salt solutions or seawater applications, please contact the Technical Services Division at ATI, phone 541-917-6777 fax 541-967-6987.

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