Zirconium in Hydrochloric Acid Applications

INTRODUCTION

Hydrochloric acid is a very important industrial chemical, with numerous diverse uses throughout the chemical processing industry. It is a strong reducing acid and is employed as an intermediate reactant in the production of many everyday products. Some of the principal applications for hydrochloric acid use are shown in **Table 1**.

TABLE 1: MAJOR USES OF HYDROCHLORIC ACID

• Acidizing of petroleum wells	• Demineralizers and resin regeneration
• Dye manufacturing	• Cleaning products
• Ore reduction	• Gelatin
• Pickling and metal surface cleaning	• Synthetic Rubber
• Water Treatment	• Pharmaceuticals
• Food Processing	• Manufacture of Chemical Intermediates
• Industrial acidizing	• Plastics and Polymers

The majority of hydrochloric acid is produced as a byproduct of petrochemical production or is co-produced in a variety of chemical reactions involving chlorine or chlorine-compounds with hydrogen containing materials. There are also a few chemical facilities that produce hydrochloric acid by burning chlorine and hydrogen to form gaseous HCl. This gas is then absorbed into water to produce the aqueous solution. Commercially pure hydrochloric acid is available at concentrations up to 37%.

Hydrochloric acid is highly corrosive and attacks most common metals including iron, stainless steel and lead. Stainless steels and high performance alloys can only be used to handle very dilute and/or low temperature HCl solutions. Zirconium has proven to be an outstanding metal for use in hydrochloric acid applications. In fact, zirconium is resistant to corrosion in hydrochloric acid solutions at all concentrations, and at temperatures well in excess of the boiling point. The most advantageous use of zirconium is in hydrochloric acid processes with temperatures above the boiling point and in the absence of oxidizing impurities.

Current types of zirconium equipment in hydrochloric acid service include pumps, valves, piping, condensers, and evaporators. One example can be found in an azo-dye coupling reaction, where zirconium heat exchangers and pumps have been used for over 20 years. This is due to zirconium's superior corrosion resistance in the HCl process solution, and because zirconium does not form undesirable salts that could change the color and stability of the dyes. Since zirconium is resistant to corrosion in caustic solutions, it can also be used in processes that cycle between hydrochloric acid and alkaline conditions.

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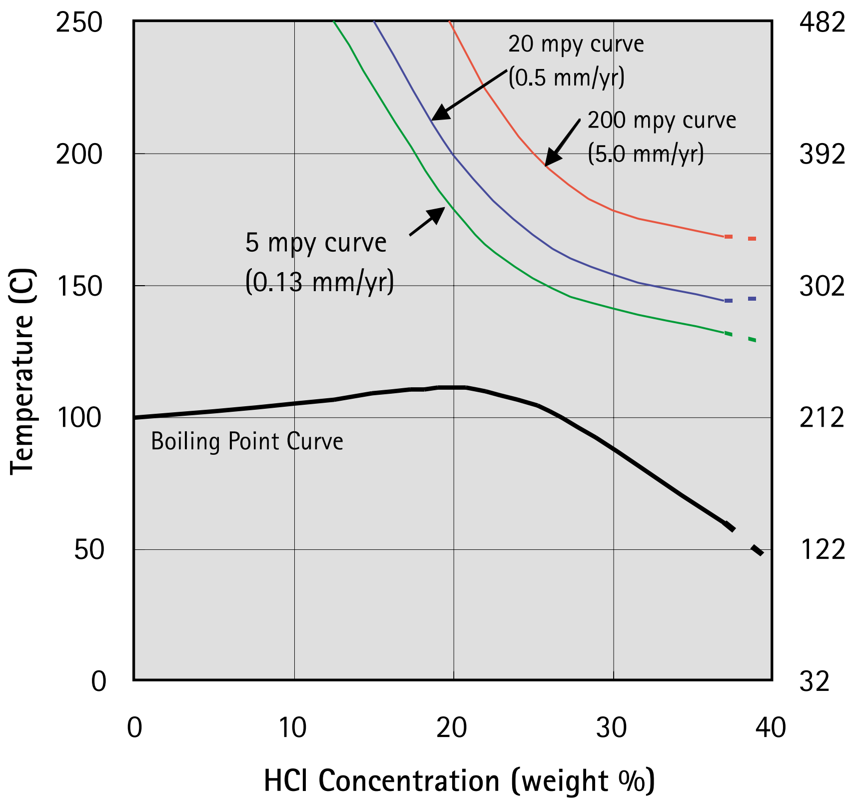
CORROSION DATA

The iso-corrosion curve for zirconium in pure hydrochloric acid is shown in **Figure 1**. The data clearly demonstrates the wide range of zirconium's corrosion resistance in HCl solutions; for example, at 10% acid concentration the temperature limit for zirconium is above 250°C and at 37% the limit is about 130°C.

FIGURE 1: ISO-CORROSION CURVES FOR ZIRCONIUM IN HYDROCHLORIC ACID



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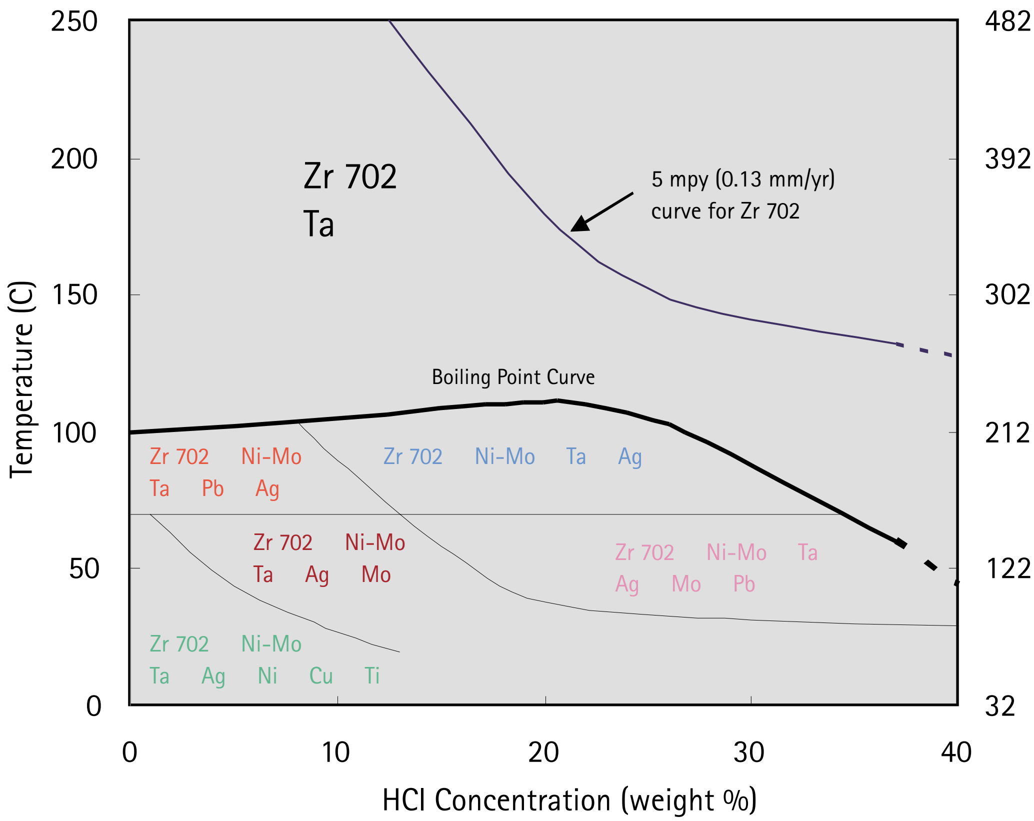
ADVANTAGES OF ZR OVER OTHER MATERIALS

As shown in **Figure 2**, there are several compatible materials that can be used in a hydrochloric acid solution at low concentration and low temperature, but zirconium stands out as the economic choice at higher concentrations and elevated temperatures, where the only alternative is the higher priced tantalum. In addition to lower raw material cost, there are two more advantages for using zirconium instead of tantalum. Zirconium is not as susceptible to hydrogen embrittlement as tantalum and the density of zirconium is approximately one-third the density of tantalum, which can lead to significant cost reductions by decreasing the weight of material necessary to build a piece of process equipment.

FIGURE 2: MATERIAL SELECTION ALTERNATIVES IN HYDROCHLORIC ACID SOLUTIONS



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LIMITATIONS

Although zirconium exhibits excellent corrosion resistance in pure hydrochloric acid solutions, the presence of certain oxidizing impurities can be detrimental. In particular, ferric ion (Fe^{+3}) or cupric ion (Cu^{+2}) contamination can lead to breakdown of the protective zirconium oxide film and initiate localized corrosion, such as pitting, intergranular corrosion and stress-corrosion cracking (SCC). When either of these oxidizing species is present and HCl concentrations are at or below 20%, pitting is the mechanism of attack; at concentrations greater than 20%, the mechanism is intergranular corrosion. These effects can be seen with as little as 50 ppm of Fe^{+3} added in the solution, as shown in **Table 2**.

TABLE 2: EFFECT OF FERRIC ION ON THE CORROSION OF ZIRCONIUM

Corrosive Media	Temperature(C)	Corrosion Rate (mpy)	Corrosion Observations
10% HCl + 50 ppm Fe^{+3}	30	<1	None
	60	<1	None
	100	<1	Pitting
10% HCl + 500 ppm Fe^{+3}	30	<1	Pitting, SCC
	60	<1	Pitting, SCC
	100	<1	Pitting, SCC
20% HCl + 50 ppm Fe^{+3}	30	<1 None	
	60	<1	None
	100	<1	Pitting
20% HCl + 500 ppm Fe^{+3}	30	<1	Pitting, SCC
	60	<1	Pitting, SCC
	100	<1	Pitting, SCC
32% HCl + 50 ppm Fe^{+3}	30	<1	None
	77	<2	Weld Sensitization
32% HCl + 500 ppm Fe^{+3}	30	<1 SCC	
	77	<5	SCC, Weld Sensitization

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The damaging effect of these impurities makes it critically important to prevent the introduction of these oxidizing impurities into the process environment. Corrosion products from upstream equipment can be carried into the zirconium equipment; therefore material selection and process control of upstream equipment are crucial in maintaining the corrosion resistance of the zirconium. Another source of potential problems is iron or copper particles that can be embedded in zirconium equipment during fabrication or maintenance work.

In order to overcome this limitation, it is highly recommended that dedicated tools be used when fabricating zirconium equipment to prevent contamination. Treating the zirconium surface, by pickling, is also recommended to remove any potential contamination and eliminate preferred anodic sites where the protective zirconium oxide film could breakdown. A final preventative measure, electrochemical protection, can also be used to maintain zirconium at a potential below its corrosion potential, although this method is not always practical in a process environment.

One other impurity that always has a negative impact on the corrosion performance of zirconium is the fluoride ion. Fluoride ions present in a hydrochloric acid process solution can dramatically decrease the corrosion resistance of zirconium by forming hydrofluoric acid. Zirconium is rapidly attacked by hydrofluoric acid and fluoride solutions when the pH is less than 3. Corrosion inhibitors, such as zirconium sponge or other zirconium chemicals, may be used to form fluoride complexes and prevent corrosive attack of the zirconium equipment.

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SAFETY

Reactive metals like zirconium can develop pyrophoric films under certain conditions in specific corrosive media. While there is no evidence of pyrophoric films forming on zirconium used in hydrochloric acid solutions, this is a special safety concern when using zirconium.

Normally zirconium corrodes uniformly and all the zirconium is converted to zirconium oxide. If corrosion rates are low, less than 5 mpy, there is time to react all the zirconium uniformly. For very high corrosion rates, above 200 mpy, the reaction rate is so high that all zirconium is also reacted. In certain conditions, it is possible that the corrosive media will attack grain boundaries, trapping small pieces of zirconium 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 in a controlled atmosphere. This is achieved by passing hot air or steam through the equipment to make sure all the zirconium particles in the film are reacted. At 250°C, steam must flow for 30 minutes; at lower temperatures, longer treatment times are required.

SUMMARY

As outlined above, zirconium can be the best alternative for material selection in many hydrochloric acid applications. 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.

Although zirconium has proven its outstanding corrosion resistance performance in a wide variety of HCl environments, 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 Wah Chang for use in on-line process equipment. These tests can show how zirconium will hold up under actual process conditions. Wah Chang also has a fully capable corrosion laboratory for complete testing and detailed analysis for specific hydrochloric acid applications.

For further information or any questions regarding the use of zirconium in hydrochloric acid applications, please contact the Technical Services Division at Wah Chang.

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