Zirconium in Sulfuric Acid Applications

INTRODUTION

Sulfuric Acid is undoubtedly the most important raw material in the chemical and pharmaceutical industry today.This fact is not unique to the United States,but is true on a worldwide basis. One can often look to the production and/or use of sulfuric acid as an indication of the industrial activity of a nation. Few chemicals are manufactured without sulfuric acid being involved. It is a strong dibasic acid and can be a reducing acid,an oxidizing acid, and/or a dehydrating agent.

In the chemical industry, sulfuric acid has many diverse applications. The largest quantities are used in the manufacture of phosphate and nitrogen based fertilizers. The petrochemical sector utilizes sulfuric acid in alkylation and paraffin refining. The inorganic branch of the chemical industry uses sulfuric acid in the production of chromic and hydrofluoric acids, aluminum sulfate and sodium sulfate.The organic arm employs sulfuric acid in the manufacture of explosives, soaps, detergents, dyes, isocyanates, plastics, pharmaceuticals, etc.Everywhere one turns in today's world we encounter products which use sulfuric acid in their manufacturing process.

Many chemical plants use sulfuric acid in one or more process steps and this generally results in severe corrosion problems. Each process has unique minor constituents that can change the way metals corrode. Zirconium has been used very successfully in many sulfuric acid applications. The advantage of zirconium is that corrosion rate will be very small if properly applied and equipment life of over 20 years is expected. Since there is no corrosion maintenance repair, downtime and replacement costs do not exist and will quickly pay back for the slightly higher initial cost.

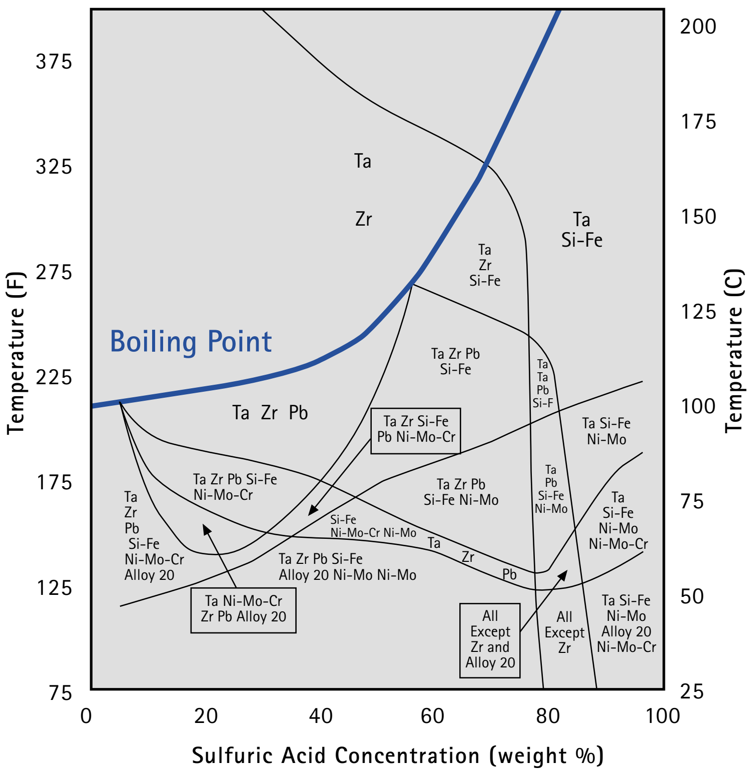
Zirconium is one of the most suitable metals for the containment of sulfuric acid. It is cost-effective, reliable and non-contaminating to the environment. The information that follows gives the reader sulfuric acid corrosion information in a nutshell.

CORROSION DATA

Corrosion of metals by sulfuric acid is very complex, as there are oxidizing and reducing conditions depending on concentration. The graph in **Figure 1** gives approximate conditions where different metals can be used successfully. Warning this chart is not intended to be used for metal selection especially at the boundaries of the ranges marked. There are several alternatives if the temperature is low, from ambient to 150 °F. Once the process temperature requires operation at boiling point or above,very few construction materials are available. At high concentrations,above 95%, the environment is oxidizing,while at low concentrations the conditions are reducing. This requires different metals to be used depending on the conditions.

PO Box 460 • 1600 Old Salem Road NE • Albany, Oregon 97321 • (888) 926-4211 ext. 6977 • Fax (541) 967-6994
Custserv@wahchang.com • www.alleghenytechnologies.com/wahchang

FIGURE 1: SUITABILITY OF MATERIALS IN SULFURIC ACID (MATERIALS IN EACH REGION EXHIBIT A CORROSION RATE OF 5 MPY OR LESS)



In the extreme conditions,the primary alternative to zirconium is tantalum, and zirconium is significantly less expensive than tantalum. There are two regions that zirconium and tantalum are the primary options:

1.Temperatures above the boiling point and concentrations up to 50%
2.Temperatures below boiling and concentration from 50 to 70%

Figure 2 shows the iso-corrosion curve for zirconium in sulfuric acid.It is important to keep corrosion rate of zirconium below 5 mpy. Reactive metals work because of the passive oxide coating. When corrosion is above 5 mpy, the coating is being removed and corrosion rate can increase very quickly with process upsets. Proper selection of zirconium usually means the application will not corrode and give useful equipment life of 20 to 30 years. The best results will be obtained if corrosion coupons are placed in the process or process conditions are duplicated in a corrosion lab. The Wah Chang corrosion lab is capable of testing most conditions with sulfuric acid and verifying what corrosion rates to expect.

PO Box 460 • 1600 Old Salem Road NE • Albany, Oregon 97321 • (888) 926-4211 ext. 6977 • Fax (541) 967-6994
Custserv@wahchang.com • www.alleghenytechnologies.com/wahchang

FIGURE 2: ISO-CORROSION DIAGRAM FOR Zr 702 IN SULFURIC ACID

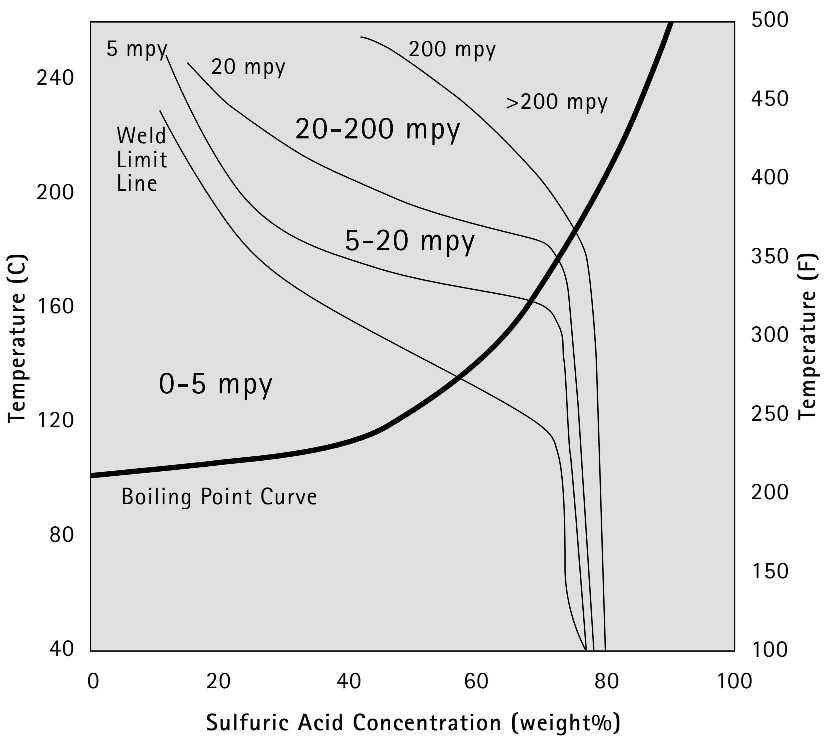
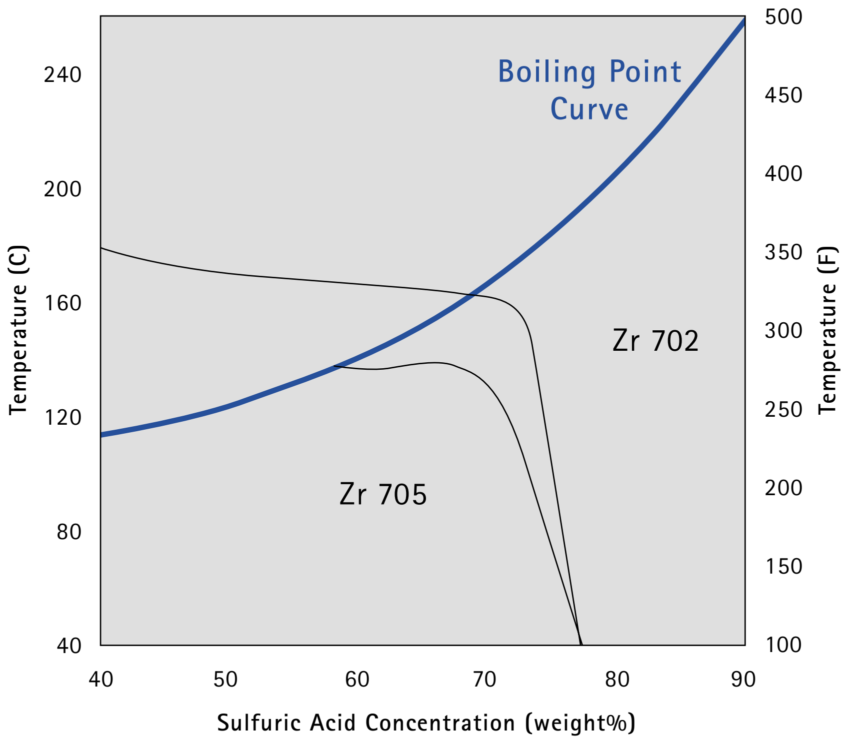


Figure 2 also shows that Zirconium resists attack up to 70%. At low concentrations, <20%, Zirconium resists attack to temperatures well above boiling >200°C. The prime advantage of Zirconium over other metals is in the low concentration/high temperature region and the 40 to 65% concentration. Weld areas exhibit higher corrosion rates as shown by the Weld Limit Line. Heat treatment of the weld will eliminate the weld affect and corrosion of the weld area will be the same as the unwelded surface. Heat treatment should be at 775 15 °C for one hour per inch (25.4 mm) of thickness.

Zirconium is produced as two major alloys for chemical processing applications; grade 702 is “pure ” zirconium, while grade 705 is zirconium alloyed with 2.0 – 3.0% niobium. **Figure 3** compares the iso-corrosion curves of the two different grades. While Zr 702 has better corrosion resistance than Zr 705, Zr 705 has better strength properties due to the addition of niobium.

PO Box 460 • 1600 Old Salem Road NE • Albany, Oregon 97321 • (888) 926-4211 ext. 6977 • Fax (541) 967-6994
Custserv@wahchang.com • www.alleghenytechnologies.com/wahchang

FIGURE 3: COMPARISON OF Zr 702 AND Zr 705 ISO-CORROSION CURVES (5MPY)



PO Box 460 • 1600 Old Salem Road NE • Albany, Oregon 97321 • (888) 926-4211 ext. 6977 • Fax (541) 967-6994
Custserv@wahchang.com • www.alleghenytechnologies.com/wahchang

ADVANTAGES OF ZR OVER OTHER MATERIALS

As shown previously in **Figure 1**, zirconium 's corrosion superiority under certain operating conditions makes it the best choice as a construction material for use in sulfuric acid environments. **Table 1** below compares the corrosion resistance of zirconium with titanium in sulfuric acid. While the corrosion of titanium is lower with aeration and the presence of oxidizers, the corrosion of zirconium is very low in all these conditions.

In **Table 2**, zirconium is compared with other alloys for corrosion resistance in sulfuric acid; this table shows why zirconium is used in low concentration/high temperature and high concentration conditions.

TABLE 1: CORROSION OF ZIRCONIUM VS. TITANIUM IN SULFURIC ACID

Concentration (weight %)	Gas	Temperature F	Corrosion Rate (mpy)	
			Ti	Zr
3	Nitrogen	212	830	nil
3	Air	140	0.5	nil
5	Nitrogen	212	1060	nil
5	Air	140	190	nil
20		210	>2400	nil
20	*Boiling		5	nil

addition 16 g/L of Fe^{3+} (oxidizer)

TABLE 2: CORROSION OF ZIRCONIUM VS. OTHER ALLOYS IN SULFURIC ACID

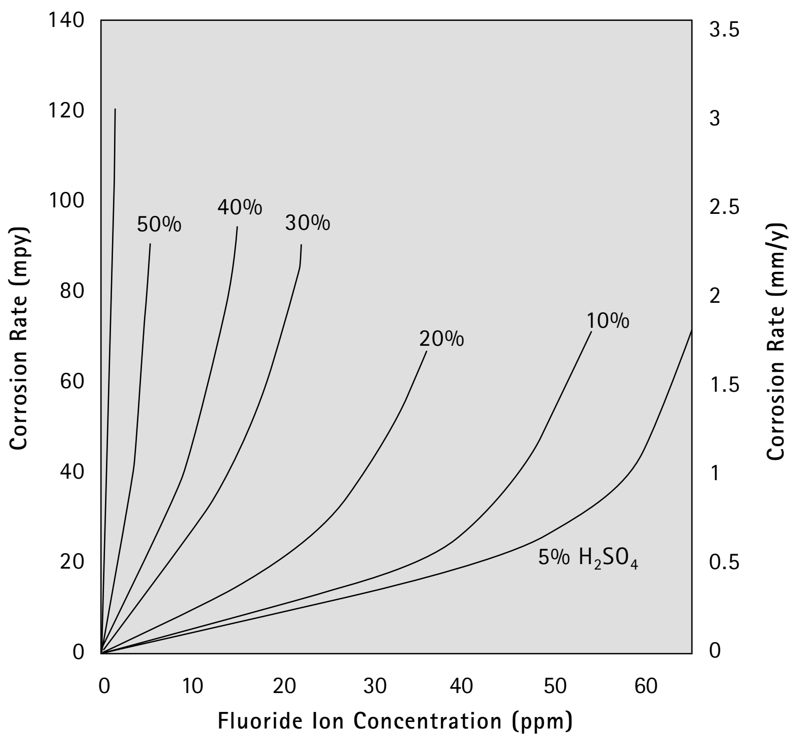
		Corrosion Rate (mpy)				
Concentration (%)	**Temperature (C)**	**Zr 702**	**310L SS**	**316L SS**	**AlloyB-2**	**AlloyC-276**
10	102*	<0.1	45	574	<1	7.0
30	108*	<0.1	1,137	>5000	2	55
55	132*	0.1	<350,000	>10,000	1.89	295
55	168	19.6	-	-	37	212
2	225	<0.1	-	-	14.9	39.7
5	232	0.1	-	-	110	153
10	225	0.1	-	-	1,023	661

PO Box 460 • 1600 Old Salem Road NE • Albany, Oregon 97321 • (888) 926-4211 ext. 6977 • Fax (541) 967-6994
Custserv@wahchang.com • www.alleghenytechnologies.com/wahchang

LIMITATIONS

While zirconium does exhibit superior corrosion resistance in most sulfuric acid environments, there are a few factors that limit zirconium's effectiveness. The presence of small amounts of fluoride ion can dramatically increase the corrosion rate of reactive metals like zirconium. **Figure 4** shows the impact.

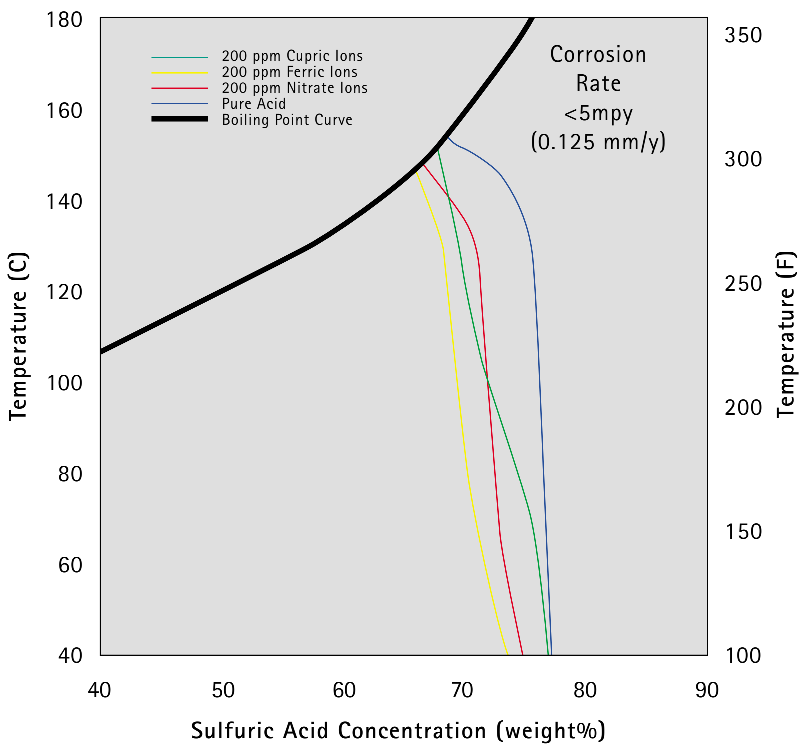
FIGURE 4: EFFECT OF FLUORIDE IONS ON THE CORROSION OF Zr 702 IN BOILING SULFURIC ACID



Fluoride is not the only impurity that must be controlled. The presence of oxidizing impurities will increase the corrosion rate of zirconium in sulfuric acid as shown in **Figure 5.**

PO Box 460 • 1600 Old Salem Road NE • Albany, Oregon 97321 • (888) 926-4211 ext. 6977 • Fax (541) 967-6994
Custserv@wahchang.com • www.alleghenytechnologies.com/wahchang

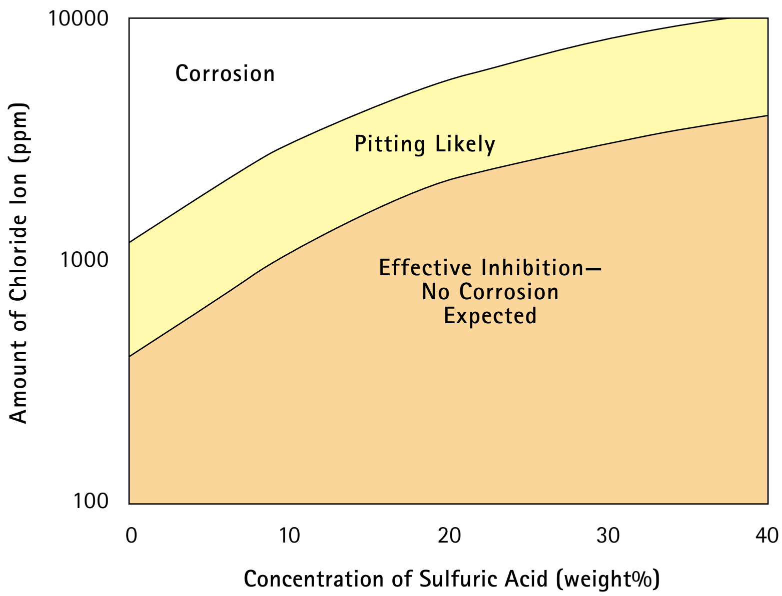
FIGURE 5: EFFECT OF IMPURITIES ON CORROSION OF ZIRCONIUM (5 MPY ISO-CORROSION CURVES)



Generally, the presence of non-oxidizing chlorides will not have an effect on corrosion rate of zirconium. Sulfate ions will inhibit pitting of zirconium when oxidizing halides are present. For example, if the ratio of sulfate to iron chloride is 100:1, the iron chloride will not cause pit corrosion. **Figure 6** shows the affect of chloride ions in sulfuric acid on the corrosion rate of zirconium. It is excess of sulfate to chloride ion.

PO Box 460 • 1600 Old Salem Road NE • Albany, Oregon 97321 • (888) 926-4211 ext. 6977 • Fax (541) 967-6994
Custserv@wahchang.com • www.alleghenytechnologies.com/wahchang

FIGURE 6: EFFECT OF CHLORIDE IONS ON CORROSION OF ZIRCONIUM



Finally, the amount of tin present in zirconium is also a factor in sulfuric acid applications. While tin is not usually a problem in most environments, it should be controlled when zirconium is to be used in sulfuric acid. The ASTM specification for Zr 702 allows tin at a level of 500 – 5000 ppm. When the zirconium is to be used in concentrations of sulfuric acid above 40%, the amount of the tin in the ingot should be 1500 – 2500 ppm; Wah Chang makes a special alloy, Zircadyne 702-S, for this purpose.

PO Box 460 • 1600 Old Salem Road NE • Albany, Oregon 97321 • (888) 926-4211 ext. 6977 • Fax (541) 967-6994
Custserv@wahchang.com • www.alleghenytechnologies.com/wahchang

SAFETY

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 steam or hot air at 240 °C for 20 minutes or 120 °C for 3 days through the equipment to make sure all the zirconium in the oxide film is reacted before opening to air.

SUMMARY / CORROSION LAB AND OTHER WAH CHANG RESOURCES

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

For further information or any questions regarding the use of zirconium in sulfuric acid applications, please contact Technical Services at Wah Chang, phone 541-917-6777 fax 541-967-6987.

PO Box 460 • 1600 Old Salem Road NE • Albany, Oregon 97321 • (888) 926-4211 ext. 6977 • Fax (541) 967-6994
Custserv@wahchang.com • www.alleghenytechnologies.com/wahchang