

## Zirconium in Sulfuric Acid Pickling Applications

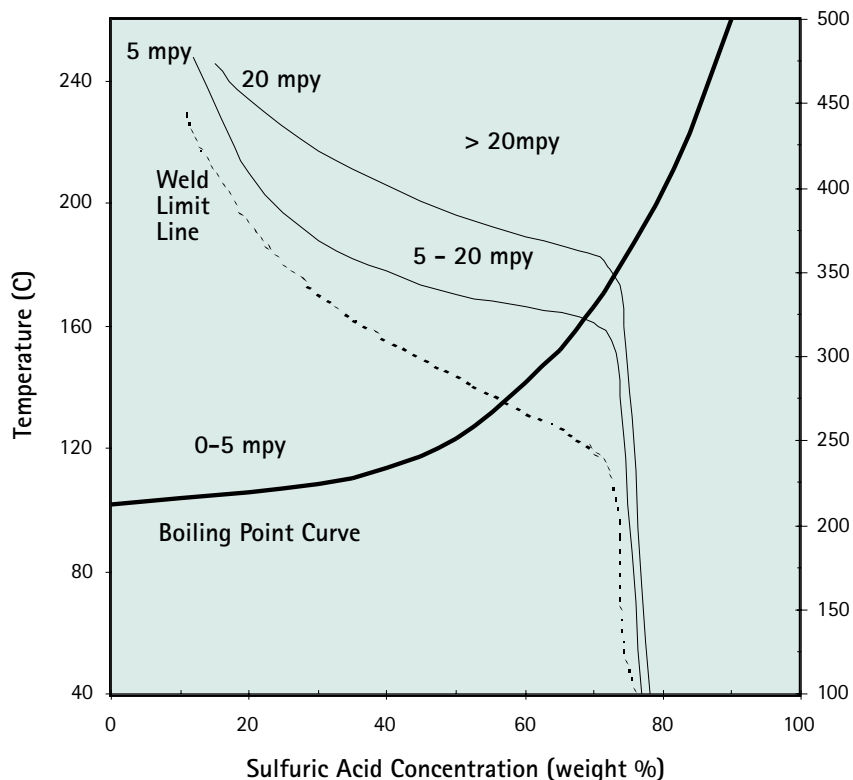
### INTRODUCTION

For more than 30 years, zirconium has been successfully used in hot sulfuric acid tanks for pickling steel. Zirconium is uniquely suited for constructing the heating coils for maintaining the optimum operating temperature of the sulfuric acid pickling solution. The unique physical properties and superior corrosion resistance of zirconium in these sulfuric acid conditions give it a tremendous advantage; the corrosion rate of zirconium will be nil if properly applied, and it is easier to work with than other resistant alternatives such as graphite or plastics. When there is little or no required corrosion repair, maintenance downtime is minimized and a longer equipment life with fewer replacements is expected. In the severe environment of sulfuric acid steel pickling tanks, zirconium stands out as a cost-effective material selection.

### CORROSION DATA

Corrosion of metals by sulfuric acid is very complex, as there are oxidizing and reducing conditions depending on concentration. At high concentrations, generally above 70%, the environment is oxidizing, while at low concentrations the conditions are reducing. Chemical impurities and temperature are also critical factors affecting corrosion levels. In a typical steel pickling application, lower concentrations of sulfuric acid from 5%–40% are employed with elevated operating temperatures of 60°C–100°C to achieve optimum performance.

**Figure 1** shows the iso-corrosion curve for zirconium in sulfuric acid. Reactive metals like zirconium work because of their passive oxide coating; when corrosion is above 5 mpy, this coating is being removed and the corrosion rate can increase very quickly with process upsets. The weld areas exhibit higher corrosion rates as shown by the Weld Limit Line. Heat treatment of the weld will improve the weld affected zone and corrosion of the weld area will be similar to the unwelded surface. For concentrations above 50%, heat treatment should be at  $775 \pm 15^\circ\text{C}$  for one hour per inch (25.4 mm) of thickness; at lower concentrations, heat treatment is not normally required.

**FIGURE 1: ISO-CORROSION DIAGRAM FOR Zr 702 IN SULFURIC ACID**


The conditions that favor zirconium over other metals are temperatures above approximately 80C (175F), with sulfuric acid concentrations of 10% to 65%. At concentrations below 40%, zirconium will resist attack at temperatures well above boiling. While there are several alternatives if the temperatures and concentrations are low, once the process conditions involve higher concentrations and elevated temperatures, very few construction materials are available. In the high temperature region used for steel pickling, the primary alternatives to zirconium are plastics or graphite, and zirconium is less vulnerable to the higher maintenance requirements of these materials.

The presence of oxidizing chemical impurities in the pickling solution does not significantly diminish the corrosion resistance of zirconium when the sulfuric acid concentration is less than 50%. For example, zirconium has been tested in 20%  $H_2SO_4$  contaminated with 8%  $Fe^{+3}$  at 80°C (175°F); the results showed no corrosion of the zirconium samples. Above the 50% sulfuric acid concentration limit, however, the corrosion resistance of zirconium is adversely affected by oxidizing species such as ferric, cupric, and nitrate ions. Effects of other impurities will be discussed in the Limitations section.

## 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 the extreme sulfuric acid environments of steel pickling tanks. In **Table 1**, zirconium is compared with other alloys for corrosion resistance in sulfuric acid; this table demonstrates why zirconium is ideal in low concentration/high temperature conditions.

**Table 1** Corrosion of zirconium vs. other alloys in sulfuric

Concentration (%)	Temperature (°C)	Zr 702	310L SS	316L SS	Alloy B-2	Alloy C-276
10	102*	< 0.1	45	574	< 1	7.0
20 + 8% Fe <sup>+3</sup>	80	< 0.1	---	---	---	> 20
30	108*	< 0.1	1,137	> 5000	2	55
40	80	< 0.1	> 28,000	---	---	---
55	132*	0.1	>100,000	>10,000	1.89	295

\*Boiling Point

In comparison to the few other materials that are corrosion resistant in the steel pickling environment, zirconium has several other advantages:

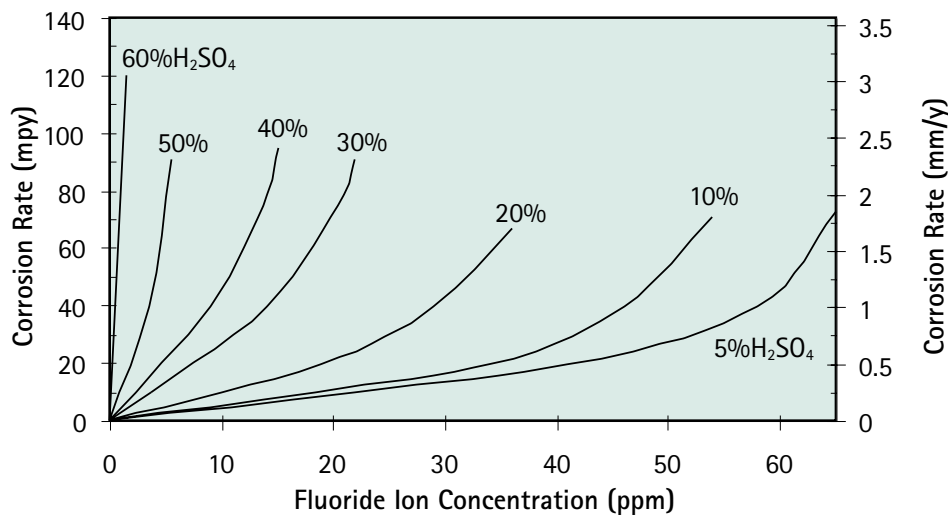
1. Excellent heat transfer characteristics
2. Adequate strength
3. Good ductility and workability, which allows standard machining and forming methods and equipment to be used in fabrication.

The combination of zirconium's superior physical, mechanical, and chemical properties has led to its outstanding reputation of dependable service in steel pickling applications.

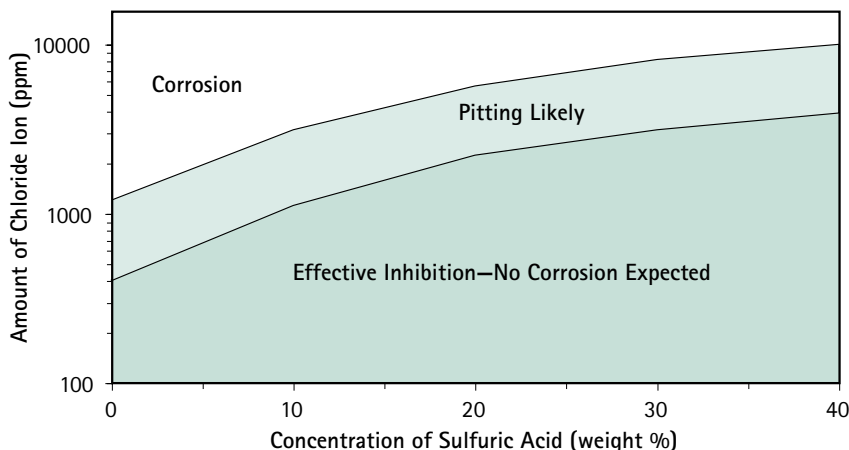
## LIMITATIONS

While zirconium does exhibit superior corrosion resistance in most sulfuric acid steel pickling environments, there are a few factors that can limit zirconium's effectiveness. **Figure 2** shows how the presence of small amounts of fluoride ion can dramatically increase the corrosion rate of zirconium. For this reason, it is recommended that the fluoride concentration level be maintained below 1 ppm when using zirconium.

**FIGURE 2: EFFECT OF FLUORIDE IONS ON THE CORROSION OF Zr 702 IN BOILING SULFURIC ACID**



**FIGURE 3: EFFECT OF CHLORIDE IONS ON CORROSION OF ZIRCONIUM**



The presence of chlorides can also have a detrimental effect on the corrosion resistance of zirconium, particularly when ferric or cupric ions are also present. Sulfate ions inhibit pitting of zirconium when oxidizing chlorides are present, if the molar ratio of sulfate ion to chloride ion is held above 54. The effect of chlorides on zirconium corrosion in sulfuric acid is seen in **Figure 3**.

## 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.

In certain conditions, it is possible that the corrosive media will attack grain 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 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 / CORROSION LAB AND OTHER WAH CHANG RESOURCES

As demonstrated above, zirconium can be the best material for fabricating equipment used in sulfuric acid steel pickling applications. Zirconium's corrosion resistance leads to the long equipment life and elimination of maintenance downtime that make it the most cost-effective option when compared with other alloys. By keeping the sulfuric acid concentration and chemical impurity levels below the recommended limits, zirconium can provide unbeatable service in steel pickling operations.

Although zirconium has proven its outstanding corrosion resistance performance in a wide variety of sulfuric acid steel pickling conditions, 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 and other corrosive environments.

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