Zirconium passes the acid test

Zirconium has proven its outstanding corrosion resistance performance in a wide variety of sulphuric acid steel pickling conditions. **Steve Sparkowich**, Corrosion Laboratory Manager at ATI Wah Chang, discusses the advantages of zirconium over other metals and reports on the successful use of zirconium heat exchangers in acid recovery systems.

Pickling is an economical method of using acid to remove impurities and scale from metals for etching surfaces in preparation for galvanising, painting, etc. (*see Fig. 1*). Wide variations are possible in the type, strength, and temperature of the acid solutions used. Sulphuric acid in the 5 to 40 % concentration range is a common pickling acid for iron and steel. Sulphuric acid pickling tanks are typically heated to a temperature between 60 °C (140 °F) and 93 °C (200 °F) using steam or hot water circulating through a heat exchanger.

Compared with non-metallic alternatives, metal heat exchangers, sometimes referred to as steam coils, are generally preferred for heating sulphuric acid pickling solutions because they are:

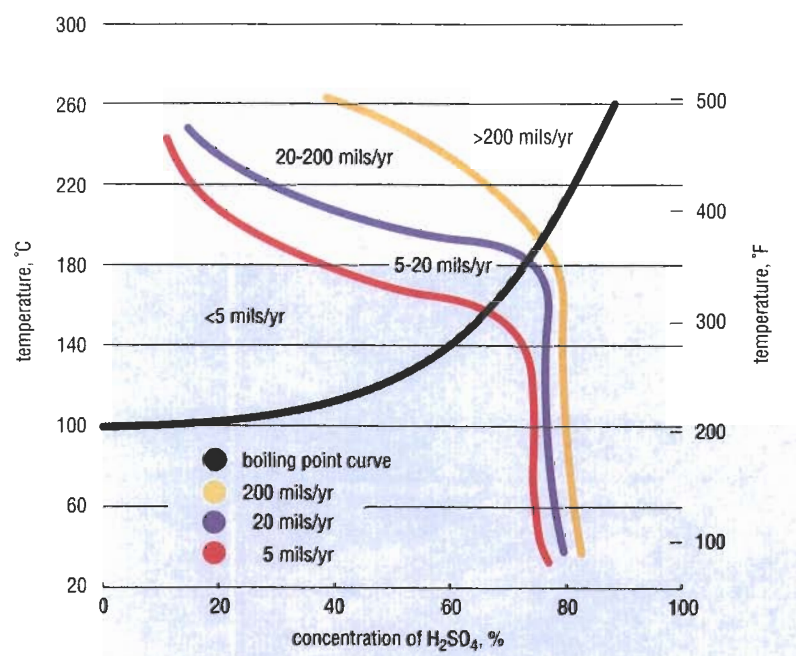
- **more compact:** For the equivalent heat transfer capability, a metallic immersion heat exchanger will typically be 3-4 times smaller than a thermoplastic (e.g. PTFE) heat exchanger. The smaller size results in more room in the tank for pickling and helps to minimise the potential for damage due to mishandled work. Due to their high efficiency, metallic heat exchangers are usually small enough to be placed on the narrow end of the pickling tank where they will not interfere with the work.
- **easier to clean:** Metal heat exchangers are much more rigid than flouropolymer or graphite units and are more easily cleaned when ferrous sulphate salts build up.
- **more durable:** Metallic heat exchangers have inherently higher strength and toughness than non-metallic materials, such as graphite and thermoplastics, and are less prone to damage during handling and in the harsh conditions of a pickling tank.
- **easier to work with:** Metallic heat exchangers are generally easier to fabricate or repair than alternative materials such as graphite or thermoplastics. Good ductility and workability allow for standard methods and equipment to be used in fabrication and repair.
- **compatible with pressurised steam:** Metallic heat exchangers are the most practical choice for use with pressured steam.

Figure 1. *Sulphuric acid pickling bath.*

Table 1: **Corrosion rate (mils/yr) of zirconium vs other alloys in sulphuric acid solutions**

Concentration	Temp	Zr702	310LSS	316L SS	Alloy B-2	Alloy C276
10%	216°F/102°C	<0.1	45	574	<1	7.0
20% + 8% Fe^{3+}	176°F/80°C	<0.1	–	–	–	>20
30%	226°F/108°C	<0.1	1137	>500	2	55
40%	176°F/80°C	<0.1	>28,000	–	–	–
55%	270°F/132°C	0.1	>100,000	>10,000	1.89	295

Fig. 2: **Corrosion rate Zr 702 in sulphuric acid** mils/yr



Thermoplastic heat exchangers are generally not rated for higher than 35 psi (2.4 bar) steam pressure.

It should be noted that at a steam pressure of 100 psi (6.9 bar), the surface temperature on the heat exchanger can be nearly 170 °C (338 °F). A common error is to select heat exchanger materials based on the solution temperature, which can be as much as 93 °C (200 °F) lower than the skin temperature on the heat exchanger. We recommend that material selection decisions for heat exchangers be based on the maximum temperature of the heating medium.

Advantages of zirconium

The conditions in sulphuric acid pickling tanks can be very corrosive to most available metallic heat exchanger materials. Stainless steels and other heat exchanger metals generally do not have adequate corrosion resistance in the sulphuric acid ranges used in steel pickling (*see Table 1*). Zirconium, however, shows superior corrosion resistance in these concentrations and temperatures. The presence of oxidising ferric ion in the pickling solution does not significantly diminish the corrosion resistance of zirconium when the sulphuric acid concentration is less than 50 %. For example, when zirconium was tested

Fig. 3: **Examples of Zr 702 gridcoil heat exchangers**

Photo courtesy of: *Vulcanium*

in 20 % H_2SO_4 contaminated with 8 % ferric ion (Fe^{3+}) ferric ion at 80°C, the results showed nil corrosion of the zirconium samples.

Zirconium 702 exhibits excellent corrosion resistance in 5 to 65 % sulphuric acid up to boiling temperature and beyond as shown on the iso-corrosion curve in *Fig. 2*. Zirconium heat transfer coils, similar to the one in *Fig. 3*, have become widely accepted among metal finishers for over 30 years because they provide an efficient and economical means to heat sulphuric acid. Zirconium heat exchangers can be fabricated in virtually any size or configuration, depending upon space limitations and the amount of heat transfer required.

Zirconium heat exchangers in acid recovery systems

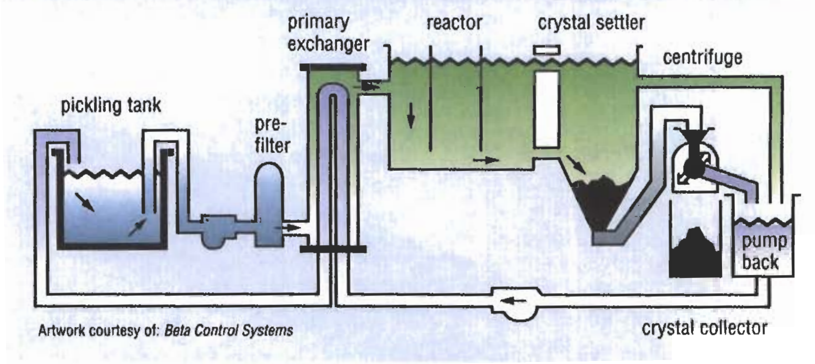
While zirconium does exhibit superior corrosion resistance in most sulphuric acid steel pickling environments, there are a few factors that can limit its effectiveness. The use of sulphuric acid recovery systems (ARS), also known as crystallisers, in metal finishing processes (*Fig. 4*) has required some precautions be taken when using zirconium heat exchangers. When using an acid recovery system, spent pickle acid is recycled rather than being discharged, which can cause a build-up of chloride, fluoride, and other solution contaminants.

The presence of chlorides may have a detrimental effect on the corrosion resistance of zirconium, particularly when ferric ions are also present. The effect of chlorides on zirconium corrosion in sulphuric acid is seen in *Fig. 5*. For example, in 15 wt-% acid, chlorides should be maintained below 4500 ppm with <1800 ppm being preferred.

Figure 6 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 10 ppm when using zirconium with levels below 5 ppm being preferred.

High chloride and fluoride levels are known to cause corrosion, not only to zirconium, but also to metallic components in contact with the pickle solution, especially the sulphuric acid

Fig. 4: **Example of sulphuric acid recovery system**



Artwork courtesy of: *Beta Control Systems*

Fig. 5: **Effect of chloride level on Zr 702 in sulphuric acid**

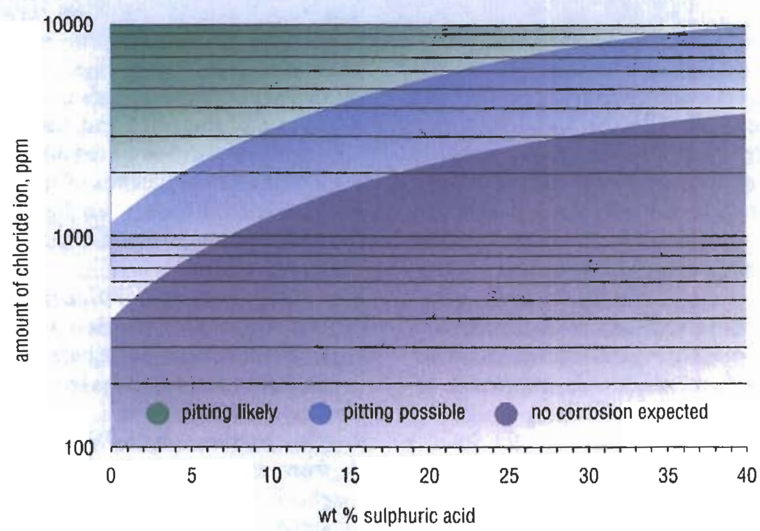


Fig. 6: **Effect of fluoride level on Zr 702 in sulphuric acid**

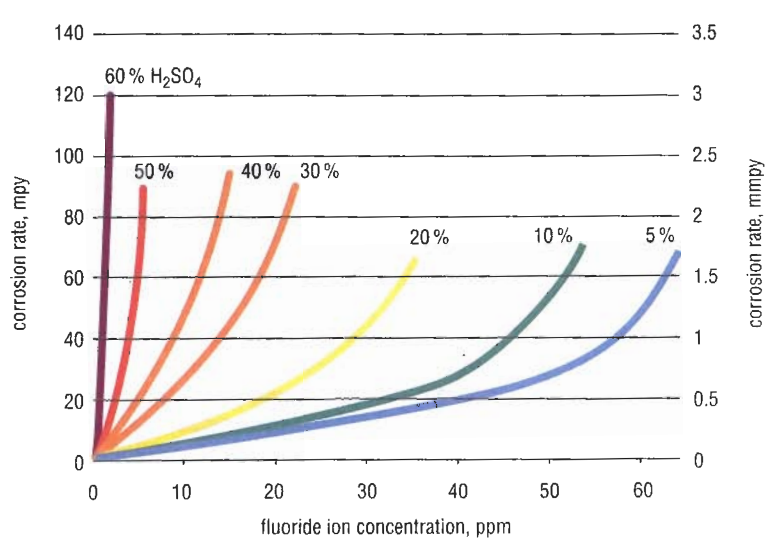


Fig. 7: "Sacrificial" solution level protector exhibiting pitting corrosion

recovery systems centrifuge parts (e.g. screens, scrolls, baskets, clamping rings, etc.). Elevated chloride levels can cause localised pitting. Elevated fluoride levels cause general surface corrosion, which may cause a gradual thinning of tube diameters. In extreme cases, elevated fluoride levels may cause both general corrosion and pitting. Keeping chloride and fluoride concentrations low is important to avoid costly replacements.

Sources for chlorides and fluorides

There are several major sources for chlorides and fluorides:

- **caustic:** The most commonly used caustic, diaphragm cell grade, can have up to 10,500 ppm chloride. These chlorides are dragged into the pickle tank with caustic residues.
- **containment pit water:** The choice to pump containment pit water into the acid tank causes high-chloride spillage from the flux and caustic tanks to be put into the acid tanks. The pit must be divided so that the caustic and the caustic rinse will drain into one section, acids and acid rinses into another section, and flux into yet another section. Thus, drainage from these tanks is pumped directly back into the tanks from which it came.
- **chemicals added to the pickling bath:** Inhibitors, accelerators, or fume-control agents may be a source of fluorides and chlorides as well as corrosive bromides and iodides. Some batches of raw sulphuric acid have been found to contain elevated levels of chlorides and fluorides.
- **chlorinated and/or fluorinated tap water:** Evaporation of water from the heated pickle bath causes chlorides and fluorides to concentrate over time.
- **'freshening up':** When work from the flux tank is placed in the pickle tank to be 'freshened up', large amounts of chloride are dragged in to the sulphuric acid. In some shops, this has proven to be the major source of chlorides in the pickling tank.

Ten tips for success

To reduce the potential for corrosion on zirconium heat exchangers or on other metallic components when using an acid recovery system, the following ten preventative measures should be considered:

1. Use a low chloride grade of caustic: The low cost chloride or low salt membrane grade may be about 10 cents/pound higher than diaphragm grade caustic but should have chloride levels that are ~175 times lower (i.e. 60 ppm vs.10,500 ppm typical chloride levels).
2. Maintain low chloride and fluoride levels in the sulphuric acid pickling bath: Because sulphuric acid recovery systems allow for re-use of sulphuric acid, chlorides and fluorides have been found to accumulate in the pickling solution. Chlorides and fluorides are known to corrode zirconium and most other metals. Elevated chlorides can cause a localised pitting and elevated fluorides can result in general surface corrosion. Refer to *Figure 5* for maximum recommended chloride levels for sulphuric acid pickling solutions. Fluoride concentration should be maintained below 10 ppm with levels below 5 ppm being preferred (*Fig. 6*). This data is based on laboratory analysis using reagent grade chemicals. It should be noted that zirconium heat exchangers in pickling solutions with elevated chloride levels do not always exhibit pitting corrosion. Some organics and other contaminants that build up in pickling solutions over time may have an inhibiting effect on corrosion and reduce the corrosion rate or reduce the potential for the onset of localised pitting corrosion. The limits in *Fig. 5*, however, are considered to be a conservative approach. For existing zirconium heat exchanger installations where chloride levels are high and no corrosion is evident, chloride levels should at least be stabilised. Preferably, they should be reduced to levels below the limits in *Fig. 5*. If chloride levels are allowed to rise,

localised pitting corrosion may eventually occur.

3. Check chloride and fluoride levels in the acid tanks, rinse tanks, and caustic tank on a routine basis: Representative acid samples may be properly packaged and sent to a laboratory for analysis. The ATI Wah Chang Analytical Laboratory provides chloride, fluoride, and other inorganic chemical analysis services. If the chloride and fluoride levels are known, corrective measures can be instituted before corrosion problems occur.
4. Understand chloride and fluoride levels of all additives prior to use in pickling baths: This includes sulphuric acid, inhibitors, accelerators, fume control agents, caustic, and even water. Softened water can have high levels of chlorides. Municipal water may have chlorides and/or fluorides. If any additives are found to have high chloride or fluoride, reasonable alternatives should be considered.
5. Consider chemical cleaning of zirconium heat exchangers: As a precaution, consider chemical cleaning of newly fabricated zirconium heat exchangers in a mixture of nitric acid-hydrofluoric acid. Chemical cleaning will remove embedded particles or surface contaminants rendering the zirconium more resistant to corrosion. Chemical cleaning also improves the surface finish, which may reduce the crystallisation of ferrous sulphate monohydrate salts. Chemical cleaning of zirconium should be performed in at least a 10:1 ratio of nitric acid to hydrofluoric acid to minimise the potential for hydrogen absorption. Because of the hazardous nature of hydrofluoric acid, a properly equipped facility should be used to perform the chemical cleaning.
6. The heat exchangers must include a second concentric zirconium tube of larger diameter at the acid/air interface of the riser pipes: This outer tube section is known as a solution level protector, air cover, or air baffle as shown on the inlet and outlet pipes of *Fig. 3C*. Solution level protectors are especially important when high-pressure steam (e.g. 100 psi) is used as the heating medium. Acid residues on the pipe just above the solution level will concentrate to very corrosive levels due to evaporation of water. Solution level protectors provide an extra layer of protection to this vulnerable area of the heat exchanger as well as give a visual indication of corrosion as shown in *Fig. 7*. Solution level protectors should be as long as possible, perhaps 20-30 cm or more, to account for the evaporative cycle of the tank. Solution level protectors should be inspected periodically to prevent heat exchanger leakage.
7. Mount heat exchangers so that the coils are always immersed: Evaporation of the pickling solution during off-shift and other down-times may cause the solution to drop to a level that exposes the heating coils to air. Acid residues on the exposed coils will then concentrate to very corrosive levels as they dry, similar to the phenomenon described in Tip 6.
8. Insulate heat exchangers from stray currents: Stray electrical currents can reach a heat exchanger via piping, tanks walls, hangers, or other metal objects. Because corrosion is an electrochemical process, metallic heat exchangers need to be electrically isolated from contact with other metals. To eliminate the potential of stray currents, a piece of pressure hose or a dielectric union should be placed between the heat exchanger fittings and the water/steam line. Consider using a PTFE insulator as shown in *Fig. 8*. Also, insulate metal hangers that support the heat exchanger from contact with other metal objects.
9. Avoid grey coloured "monohydrate" crystal build-up on the coils: Build-up of ferrous sulphate monohydrate crystals is usually lower when using hot water heating versus high pressure steam heating. Techniques that have been used to minimise crystal build-up on the heat exchanger include:
   a) Maintaining a smooth surface on the heat exchanger,
   b) Bubbling or sparging of air beneath the heat exchanger
   c) Keeping the bath at a temperature where ferrous sulphate monohydrate is most soluble (i.e. 140-150 °F)

   If crystal build-up occurs, do not damage the surface of the zirconium by scraping, scratching, or marring when trying to remove the salts. These actions may embed iron particles or other contaminants that reduce the corrosion resistance of zirconium. Non-contact techniques such as soaking in hot water, pressure washing, or steam cleaning may be employed. Do not sandblast zirconium heat exchangers to remove crystal build-up or for any other reason. Sandblasting media may embed foreign particles in the surface that increase the potential for corrosion.
10. Protect the heat exchanger from damage using a barrier or shield: The heat exchanger should be protected to prevent it from being damaged. Consider having zirconium angle welded to the side of the unit as a shield. Other possible shielding materials include plastisol-coated steel, some grades of fibreglass, thermally stable plastics, or even hardwood.

Fig. 8: **PTFE insulating couples**

Photo courtesy of: *Process Technology*

These ten tips will greatly increase the likelihood of success in using zirconium heat exchangers, especially when using an acid recovery system. ■

Reference

Sparkowich, S.: "Tips for success: Zirconium heat exchangers in sulphuric acid pickling processes", OUTLOOK (A Wah Chang/ATI publication), Vol. 25, No. 2, Second Quarter 2004.