The performance of stainless steels in concentrated sulphuric acid

Sulphuric acid is one of the most commonly used chemicals in the world and, at concentrations greater than 90wt%, it is also very corrosive. This paper discusses the choice of materials for handling concentrated sulphuric acid, particularly at the elevated temperatures (up to 200°C) that occur during its manufacture. Some of the modern austenitic and duplex stainless steels are reviewed and their limitations and advantages are discussed.

By Roger Francis, RA® Materials, United Kingdom

Sulphuric acid is a chemical that is used in numerous industrial processes as well as in the leaching of many metals from their ores. It is produced from sulphur dioxide, which may be generated by burning sulphur, it may be a by-product of a metallurgical smelting process, or it may be produced by thermal decomposition (regeneration) of spent acid. The sulphur dioxide is reacted with oxygen over a catalyst at ~420° to 625°C to form sulphur trioxide. The latter gas then reacts with water in the absorbing towers to form sulphuric acid. This process is exothermic and the acid can reach temperatures as high as 180° to 200°C. Most of this energy is recovered by a range of means to minimise energy consumption. Usually the acid is then cooled from around 100°C to close to ambient for storage.

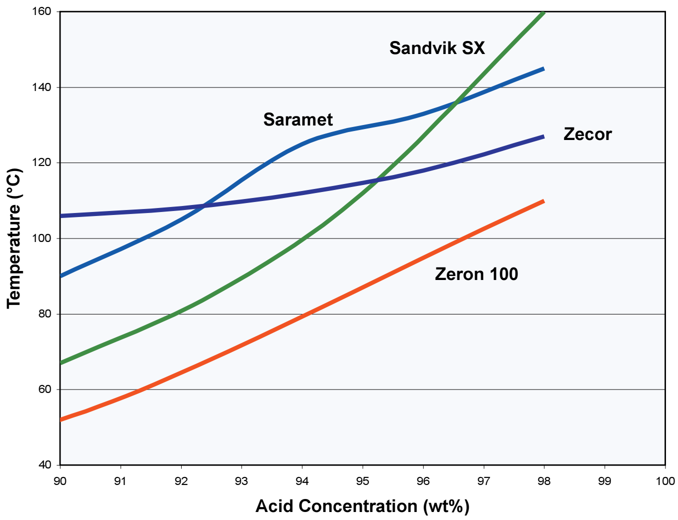
Materials

Traditionally materials such as acid-brick lined steel were used for vessels, and ductile irons, such as Mondi® or low alloy austenitic stainless steels such as 316 for piping, within a limited temperature and acid concentration range. However, the development of modern, high alloy stainless steels, with improved resistance to hot concentrated acid has changed the materials selection options. Table 1 shows the composition of some stainless steels that are used with sulphuric acid. 304 and 316 are the common austenitic grades that are widely used by the chemical and process industry. Alloy 310 is a high chromium, nickel austenitic alloy that has superior acid corrosion resistance compared with 304 and 316. ZERON®100 and 2507 are

NAME	UNS No.	NOMINAL COMPOSITION (wt%)							
		Fe	Cr	Ni	Mo	N	Cu	W	Si
304	S30403	Bal	18	8	-	-	-	-	-
316	S31603	Bal	17	10	2	-	-	-	-
310	S31008	Bal	25	20	-	-	-	-	-
Alloy 20	N08020	Bal	20	28	2.5	-	3.5	-	-
ZERON 100	S32760	Bal	25	7	3.5	0.25	0.7	0.7	0.6
2507	S32750	Bal	25	7	3.5	0.25	-	-	0.6
Saramet 23	S30601	Bal	18	18	-	-	-	-	5
Saramet 35	S32615	Bal	18	18	1	-	2	-	5
Sandvik SX	S32615	Bal	18	18	1	-	2	-	5
ZeCor	*	No Composition defined							

Table 1: Nominal composition of some stainless steels used in strong sulphuric acid.
* No UNS No. Bal = Balance

FIGURE 2 Iso-corrosion curves (0.1mm/y) in strong sulphuric acid



superduplex stainless steels with an approximate 50/50 austenite/ferrite phase balance. This structure gives a much higher strength (~2½ times) than that of the austenitic alloys and offers the possibility of wall thickness savings for applications involving high pressures and/or temperatures.
Saramet®, Sandvik SX® and ZeCor® are all proprietary austenitic stainless steels containing ~ 5% silicon, which improves the corrosion resistance in hot strong acid. Saramet comes in two variants, with slightly different compositions. ZeCor has no UNS number and the composition of ZeCor has not been published, although it is believed to be similar to that of Saramet and SX.

Corrosion

Figure 1 shows the iso-corrosion curves for some common alloys in sulphuric acid. It can be seen that the superduplex alloys are superior to 316L. ZERON 100 is also superior to 2507, which is believed to be due to the deliberate additions of tungsten and copper to ZERON 100. Alloy 20 is commonly used in sulphuric acid and from about 50% to 90% acid it is superior to ZERON 100. However, in strong acid (>90%) ZERON 100 shows a marked increase in corrosion resistance compared with 2507 and alloy 20. Figure 2 compares the iso-corrosion curves for the three proprietary alloys containing silicon and ZERON 100. There are clearly differences between the alloys, with the silicon-containing alloys showing improved corrosion resistance in more dilute acid. When researching this paper, the author was unable to find any published data for 310 stainless steel over this acid concentration range. This is probably because the manufacturers of acid plants regard this as commercially sensitive data. However, it is known that the corrosion resistance of 310 stainless decreases markedly when the acid concentration drops below 96%.
Figure 3 shows the iso-corrosion curves for 304, 310 and Saramet 23 in very strong acid [1,2]. It can be seen that, at higher temperatures, the corrosion resistance at lower acid concentrations increases (regions to the right of the line corrode at <0.05mm/y) for both Saramet 23 and alloy 310. It is assumed that SX and ZeCor show similar behaviour. This means that these alloys can be used in the higher temperature parts of acid plants. There is no data for ZERON 100 over the complete temperature range of Figure 3 and it is not known if superduplex stainless

FIGURE 1 Iso-corrosion curves (0.1mm/y) for some common alloys in pure sulphuric acid

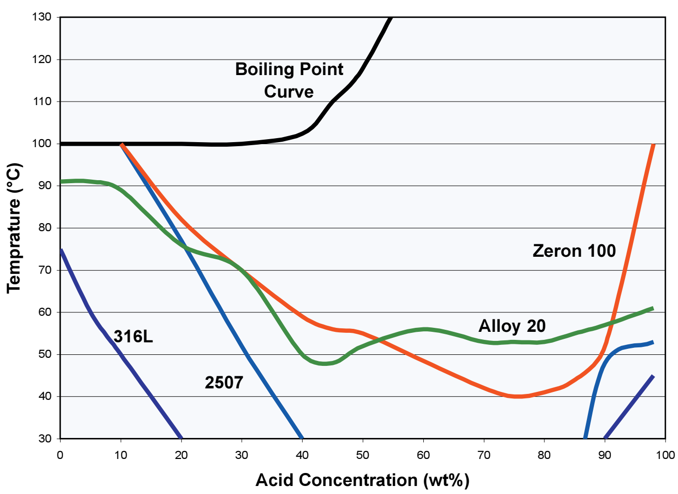


FIGURE 3 Iso-corrosion curves (0.05mm/y) for some austenitic stainless steels in sulphuric acid

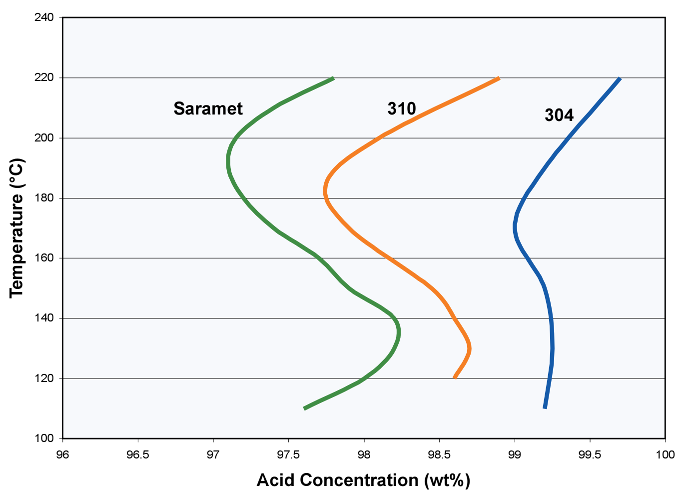


FIGURE 4 Corrosion rate of some stainless steels in strong sulphuric acid at 110°C

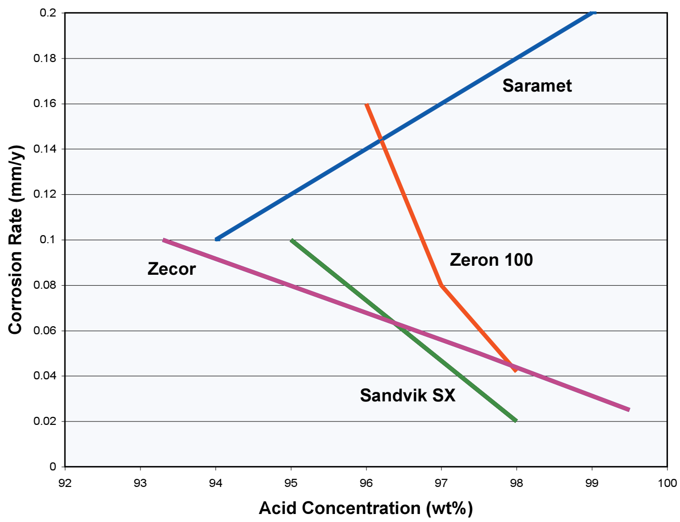
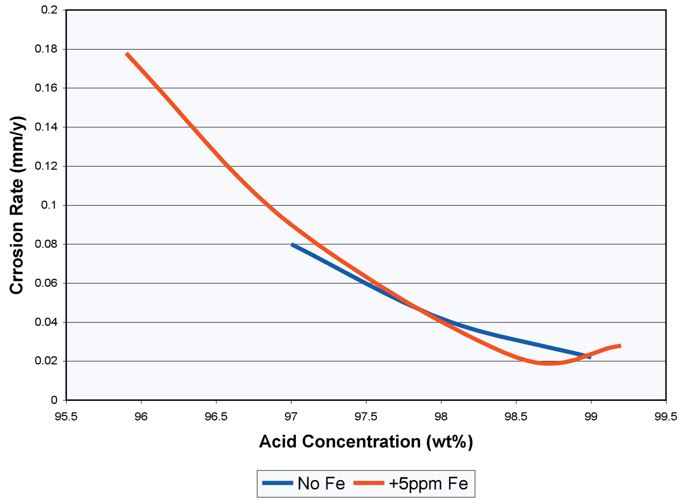


FIGURE 5 The effect of iron on the corrosion of Zeron 100 in concentrated sulphuric acid at 110°C



steels also show this feature.

Figure 4 shows the corrosion rate of some stainless steels in strong sulphuric acid at 110°C taken from the manufacturers' published data. It can be seen that the corrosion resistance of Saramet 23 decreases with increasing acid concentration unlike the other alloys. At acid concentrations greater than 100% there is excess sulphur trioxide and the mixture is then known as oleum. This is known to be more corrosive to alloys like Saramet than to ZERON 100 and alloy 310.

Although there is no publicly available data on 310 stainless in very strong acid, there is a single data point. At an acid concentration of 99%, the corrosion rate of 310 was 0.1mm/y[1]. The data in Figure 4 show the superior resistance of Zeron 100 over alloy 310 at this temperature. ZERON 100 also has similar corrosion resistance to ZeCor and Sandvik SX in stronger acid, >97 wt%.

In commercial acid plants there is usually a small quantity of iron present (typically 5ppm) and this can affect the corrosion rate of some alloys. Figure 5 shows the effect of 5ppm of iron on the corrosion rate of ZERON 100 at 110°C. It can be seen that, within experimental error, there was no significant effect of iron on corrosion. At 200°C (Figure 6) in 98.5% acid, iron caused a small increase in the corrosion rate, but nothing of engineering significance.

The effect of velocity

Because stainless steels are often active (as opposed to passive) in hot, concentrated sulphuric acid, the corrosion rate is a function of velocity. It is commonly recommended that alloys such as 316 and 310 be restricted to a maximum flow velocity of 1.5m/sec [2]. Velocity tests have been conducted in aerated 95 wt% sulphuric acid at 70°C using rotating cylindrical samples. Using the analysis of Silverman[3] the rotational flow was calculated to be equivalent to 2.5m/sec in an NPS 4 pipe. The corrosion rate of ZERON 100 was high for the first two or three days. Thereafter the corrosion rate was less than 0.1mm/year. The high initial rate of corrosion was associated with the formation of a thin black film on the metal surface. The film appears to confer corrosion resistance as shown by the subsequent low metal loss rate. These results show that ZERON 100 can be used at higher temperatures and velocities than 316L in strong sulphuric acid. Tests in stronger acid showed even lower corrosion rates.

Silicon additions tend to remove the velocity sensitivity of stainless steels to corrosion in hot, strong sulphuric acid. Sandvik report extremely low corrosion rates (<0.01mm/y) for SX in 96% acid at 70°C and 25m/sec in the alloy data sheet. They obtained a similar corrosion rate in 98.5% acid at 115°C and 10m/sec flow velocity. Saramet 35 showed similar very low corrosion rates in 98.5% acid at 120°C at 9 and 25 m/s velocity[4]. Although there is no data published for ZeCor at high velocities, it is presumed that it is also superior to the 304 and 316 grades.

Applications

The data in Figure 3 shows that alloy 310 can be very suitable for the heat recovery section provided that the acid concentration is running at 98% or greater. However, in some plants excursions to low acid concentrations are common and then the proprietary silicon-containing alloys are more reliable, within their limits of use. All three silicon-containing alloys have been used for towers,

FIGURE 6 Effect of iron on the corrosion of Zeron 100 in 98.5% sulphuric acid at 200°C

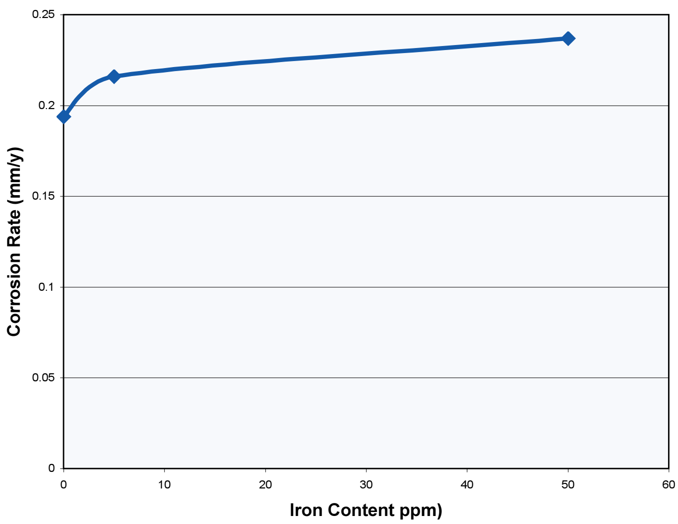


Figure 7 ZERON 100 orifice plates being prepared for shipping.

tanks, pipes, fittings, strainers, trough distributors, heat exchangers and mist eliminators where the conditions have been too onerous for 310[5,6]. Alloy 310 is still widely used in strong acid, particularly where oleum can be produced. In heat exchangers, 316L (often with Mo≥2.5%) tubes are frequently used with anodic protection to keep them passive.

The data above clearly show the good corrosion resistance of ZERON 100 in concentrated sulphuric acid at temperatures up to 200°C. It can be particularly effective in the high temperature heat recovery section of sulphuric acid plants. PCS Phosphates in the USA exposed an NPS1 spool of ZERON 100 for 18 months in concentrated acid at 200°C. The corrosion rate was <0.2mm/y. PCS have also fitted a ZERON 100 filter upstream of a sulphuric acid pump operating at high temperatures (~200°C). After 18 months in service the filter was in excellent condition. This was a substantial improvement over the 310 stainless steel filter used previously.

ZERON 100 has also been used by one of the major sulphuric acid plant design companies for orifice plates (Figure 7). These are used to control flow in such applications as trough distributors. This exploits the good erosion corrosion resistance of ZERON 100. ZERON 100 is also available as seam welded heat exchanger tubing. This makes it ideally suited for acid coolers where the cooling water is brackish or seawater, as ZERON 100 has a proven history of excellent resistance to this environment[7].

Availability

The use of these alloys for new projects is generally not a problem as a mill run quantity is usually required. However, for late add-ons, repairs or plant modifications, smaller quantities are generally required. The proprietary silicon-containing alloys are not held by stainless steel stockholders in significant quantities for such applications. The major OEM's hold limited stocks in some product forms to support their customers. Alloy 310 is widely available as plate, but is not so readily available as pipes, fittings and flanges.

ZERON 100 is stocked in a wide range of product forms including pipes, fittings, flanges, plate, wire, bar etc and is thus a useful alloy for applications where rapid delivery is important or small quantities are needed.

ZERON 100 is fully weldable by all the common arc welding techniques and the alloy's wide use by the oil and gas industry means that there are many qualified fabricators. Alloy 310 is weldable provided that the carbon is reasonably low; 0.04% is a reasonable maximum. This needs to be specially specified as UNS S31000 has a carbon maximum of 0.08% and the low carbon version (UNS S31002) is not readily available. The high silicon austenitic alloys are also relatively easy to fabricate and all come with carbon levels of 0.03% maximum to ensure no carbides form on welding.

Conclusions

1. Alloy 310 has good resistance to concentrated sulphuric acid at elevated temperatures, but it is not so resistant as the acid concentration decreases from 98%. The alloy is not readily available in other than plate form.
2. The high silicon austenitic stainless steels have good corrosion resistance in hot concentrated sulphuric acid and are better than 310 in weaker acid. The silicon gives these alloys good resistance to sulphuric acid at high flow velocities. These alloys are less resistant in oleum compared with alloy 310.
3. ZERON 100 has useful resistance to hot concentrated sulphuric acid, intermediate between that of alloy 310 and the high silicon austenitic alloys. Its ready availability in a wide range of product forms makes it suitable for both new plant and up-grades.

References

1. C. M. Schillmoller, Nickel Institute Technical Report No. 10 057.
2. D. K. Louie, Handbook of Sulphuric Acid Manufacturing, 2nd Edition, 2008, published by DKL Engineering.
3. D. G. Silverman, Corrosion 44, 1 (1988) 42.
4. S. Clarke, "Saramet Alloys – Applications in Demanding Sulphuric Acid Applications", AIChE Convention, Florida, USA, June 2003.
5. "Saramet Austentic Stainless Steel", Aker Solutions Publication, 2009.
6. S Richardson, M Spence and J Horne, "Engineered ZeCor Equipment for Sulphuric Acid Service", AIChE Convention, Florida, USA, June, 2007.
7. R. Francis and G. Byrne, "Experiences with Superduplex Stainless Steel in Seawater" Stainless Steel World, Vol 16, June, 2004, KCI, page 53.

® Registered Trademarks