

# Sulfuric Acid

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Spring/Summer 2010



## PCS Phosphate Co. Inc.'s Aurora facility brings North America's largest sulfuric acid plant on-line

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Aerial photo provided by The Roberts Company



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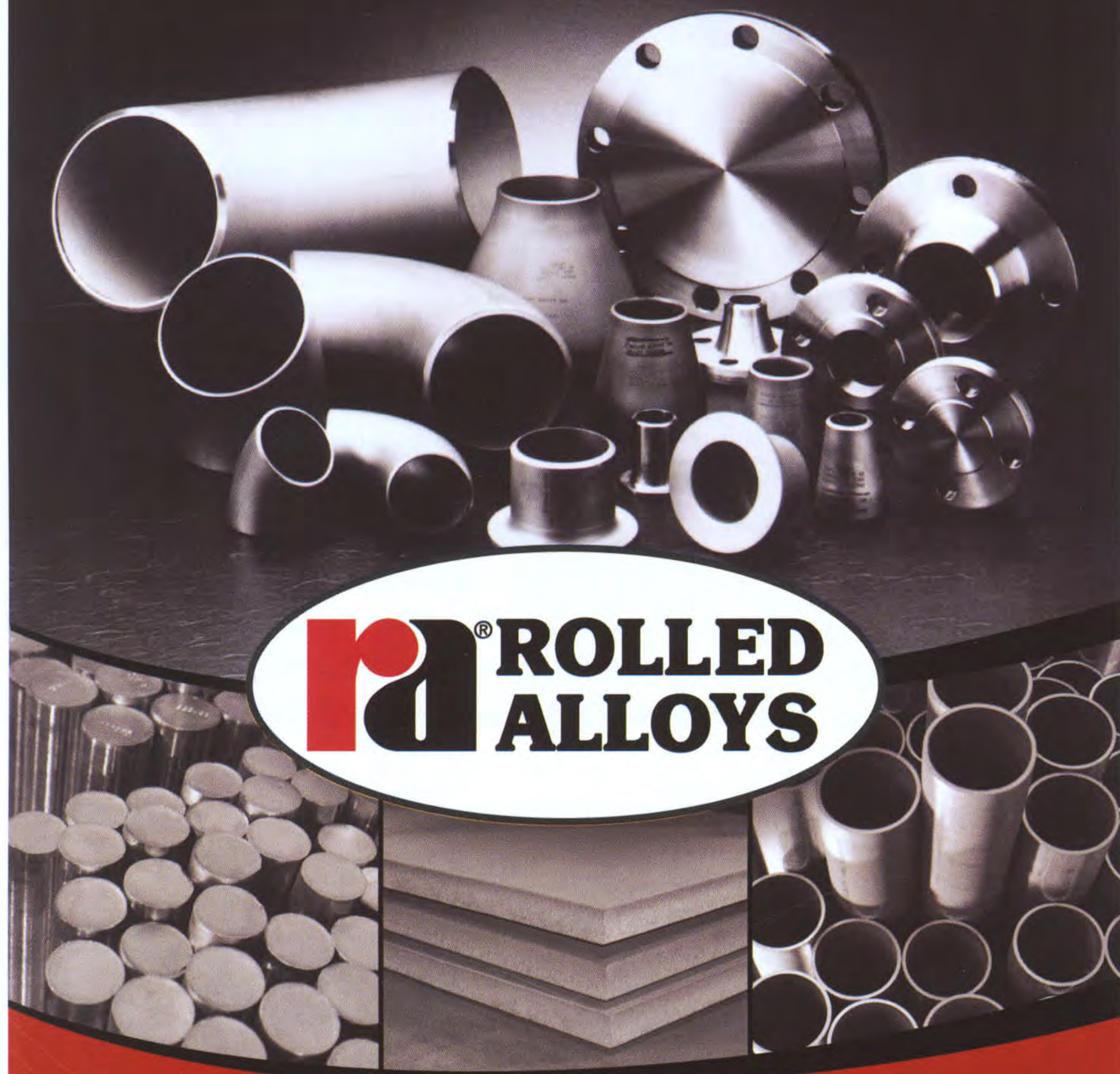


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## Morocco's OCP to have new sulfuric acid plants

CASABLANCA, Morocco — Morocco's Office Cherifien des Phosphates (OCP), the world's leading phosphate exporter, is building two sulfuric acid production plants worth \$200 million.

The new units, much more efficient than the old ones, will each have a capacity of 3,410 tons per day. They will use the double absorption process and heat recovery ventilation to discharge steam which will be later turned into clean energy.

This operation costs 630 million dirhams and requires an installed power capacity of 32 MW. The produced volume of energy will help meet the chemical demands of the city of Safi (300 km south of Rabat).

## Outotec to deliver copper plant for Codelco in Chile

ESPOO, Finland — Outotec has signed a contract with Codelco for the design and delivery of a copper concentrate roasting plant, gas cleaning system and sulfuric acid plant for Codelco's new Mina Ministro Hales mine close to Calama, Northern Chile. The contract price is approximately EUR 116 million.

Outotec's turnkey plant delivery includes basic and detail engineering, proprietary and process equipment, installation and start up services. Outotec and Codelco also signed a Memorandum of Understanding for two years' operation and maintenance of the new plant.

The new plant will annually treat up to 550,000 tons of copper concentrate and it will produce approximately 250,000 tons of sulfuric acid. The plant is scheduled to be commissioned in early 2012.

"Codelco, the world's largest copper producer, has been our business partner for decades. The company has high standards for operational safety and environmental requirements. This significant order demonstrates their confidence in the sustainability of our technologies and project execution competence," Pertti Korhonen, president and chief executive officer for Outotec, said.

## Topsøe signs refining contract with PetroPeru

LYNGBY, Denmark — Haldor Topsøe has signed a contract supplying technologies for three new plants with oil refiner PetroPeru. The contract includes license and basic engineering of process design for the Talara refinery in Peru.

The Topsøe technologies are part of a modernization project of the Talara refinery located in northern Peru. The refinery will be upgraded to produce more environmentally friendly products with lower sulfur content. The plants are

planned to be on-stream in 2015.

In addition, Topsøe will supply license, engineering, catalyst and proprietary equipment for:

- a hydrogen plant of 30 million standard cubic feet per day
- an ultra low sulfur diesel hydrotreating plant for 41,000 standard barrels per day
- a WSA plant for reduction of sulfur emissions producing 460 tons sulfuric acid per day

The contract is expected to total about \$40 million.

"We look forward to collaborating with PetroPeru," Sales Manager Ernst Hansen said. "We are very proud that we have been awarded the contracts, especially as they include three licensing contracts to the same supplier."

## SNC-Lavalin awarded contract for fertilizer plant in South Africa

TORONTO, Ontario — SNC-Lavalin is pleased to announce that it has been awarded a contract by Sasol Nitro to provide engineering, procurement and construction management (EPCM) services for a new 400,000 Mtpy calcium ammonium nitrate (CAN) production plant in an existing chemical complex in Secunda, South Africa.

SNC-Lavalin's involvement with this project started in 2008 with a conceptual study, followed by the basic engineering in 2009, and finally this EPCM contract. The plant is scheduled to be completed in 2011.

"This contract is a significant achievement for our Fertilizer Division, and for the presence of SNC-Lavalin in Southern Africa," said Georges Sontag, Vice-President, Operations, Industrial Processes and Power, SNC-Lavalin Europe.

CAN is a specific concentrated fertilizer that is delivered in solid granules. It is formed by mixing pure melted ammonium nitrate with an appropriate dolomite and then granulated. The granulation will take place in a fluidized bed granulator designed by SNC-Lavalin's Fertilizer Division in Brussels.

"The technology we will be using on this project yields a high-quality product and achieves energy-efficient operations," said Jean Claude Pingat, Executive Vice-President SNC-Lavalin Group Inc. "Sasol selected SNC-Lavalin after a thorough investigation of the proposed technology and its successful application on other projects."

The total project cost is approximately CA\$96 million.

SNC-Lavalin (TSX:SNC) is one of the leading engineering and construction groups in the world and a major player in the ownership of infrastructure, and in the provision of operations and maintenance



# The corrosion resistance of stainless steels in sulfuric acid plants

By: Roger Francis, RA® Materials and Jason Wilson, Rolled Alloys

## Introduction

Sulfuric 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 sulfur dioxide, which may be generated by burning sulfur, it may be a byproduct of a metallurgical smelting process, or it may be produced by thermal decomposition (regeneration) of spent acid. The sulfur dioxide is reacted with oxygen over a catalyst at ~420° to 625°C to form sulfur trioxide. The latter gas then reacts with water in the absorbing towers to form sulfuric acid. This process is exothermic and the acid can reach temperatures as high as 180 degrees Celsius (C) to 200 degrees C. Most of this energy is recovered by a range of means to minimize energy consumption. Usually the acid is then cooled from around 100 degrees 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 sulfuric acid. Stainless lines 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 improved acid corrosion resistance compared with 304 and 316. ZERON®100 and 2507 are super-duplex stainless steels with an approximate 50/50 austenite/ferrite phase balance. This structure gives a much higher strength (approximately 2 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 approximately 5-percent 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.

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							

\* No UNS No. Bal = Balance

TABLE 1 Nominal composition of some stainless steels used in strong sulfuric acid.

## Corrosion

Figure 1 shows the iso-corrosion curves (0.1mm/y) for some common alloys in sulfuric acid. It can be seen that the super-duplex 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 sulfuric acid and from about 50-percent to 90-percent acid it is superior to ZERON 100. However, in strong acid (greater than 90 percent) ZERON 100 shows a marked increase in corrosion resistance compared with 2507 and alloy 20.

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

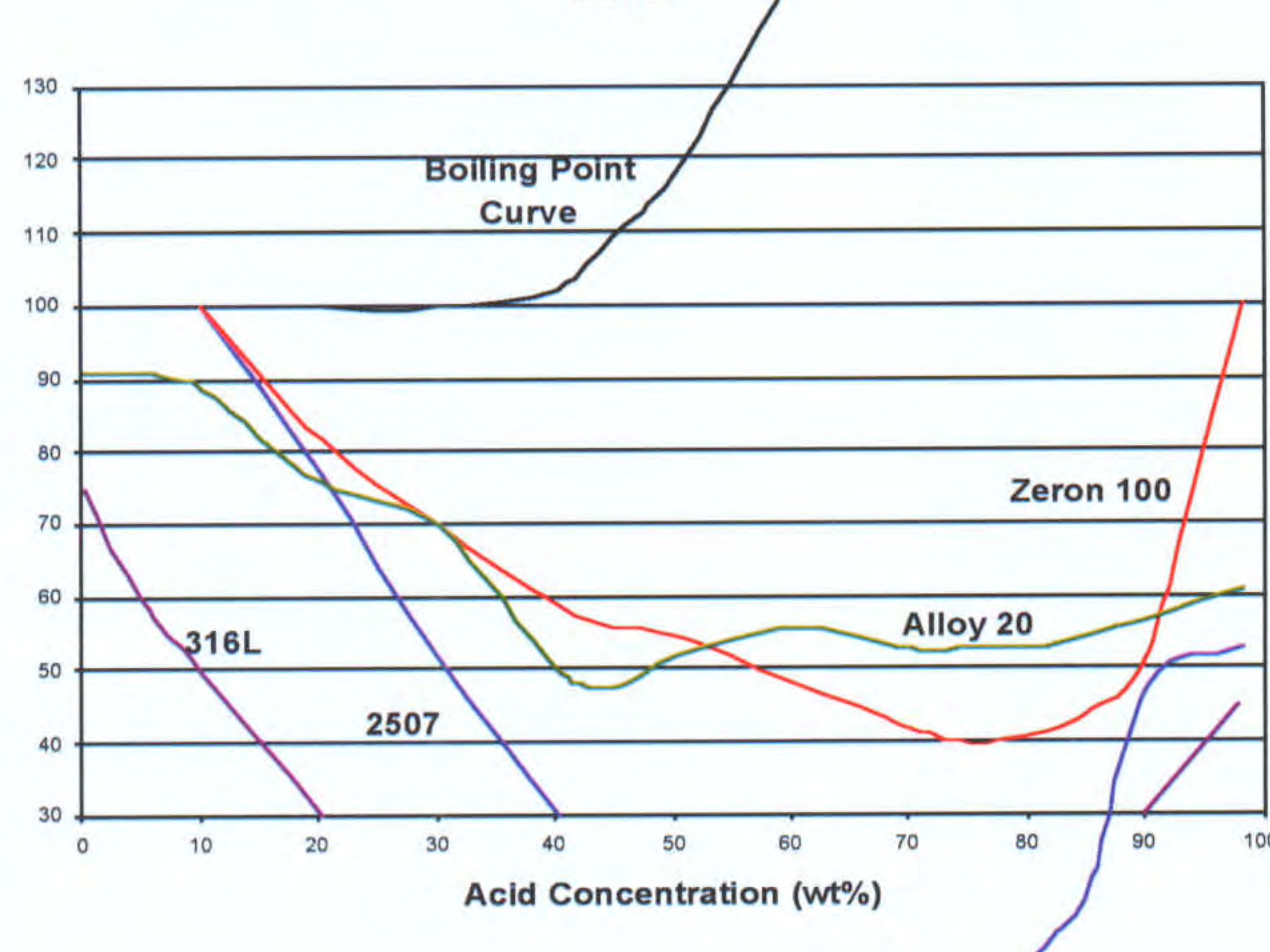


Figure 2 compares the iso-corrosion curves (0.1mm/y) for the three proprietary alloys containing silicon and ZERON 100, taken from the manufacturers' data sheets. There are clearly differences between the alloys, with the silicon-containing alloys showing improved corrosion resistance in more dilute 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 percent.

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

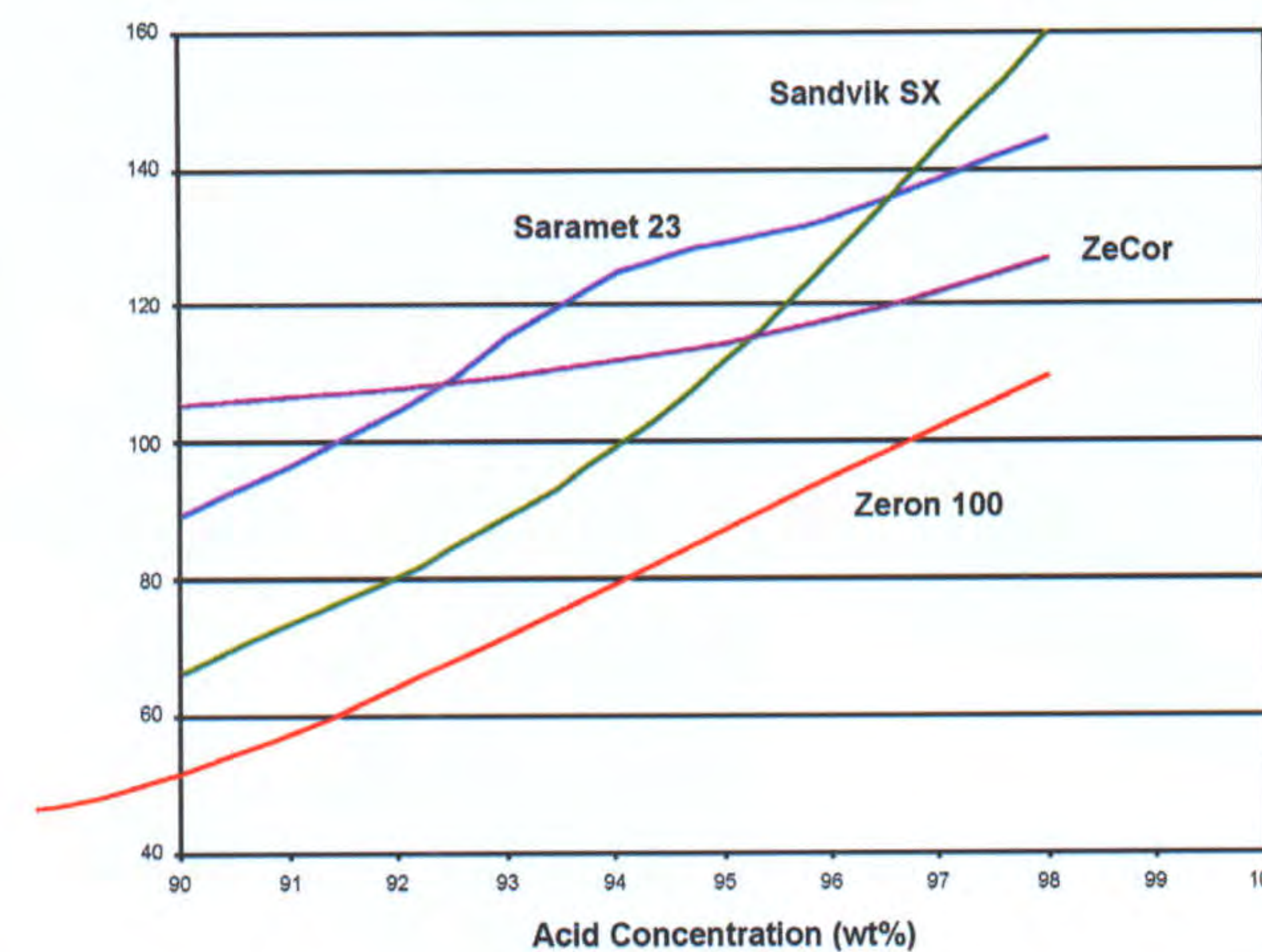
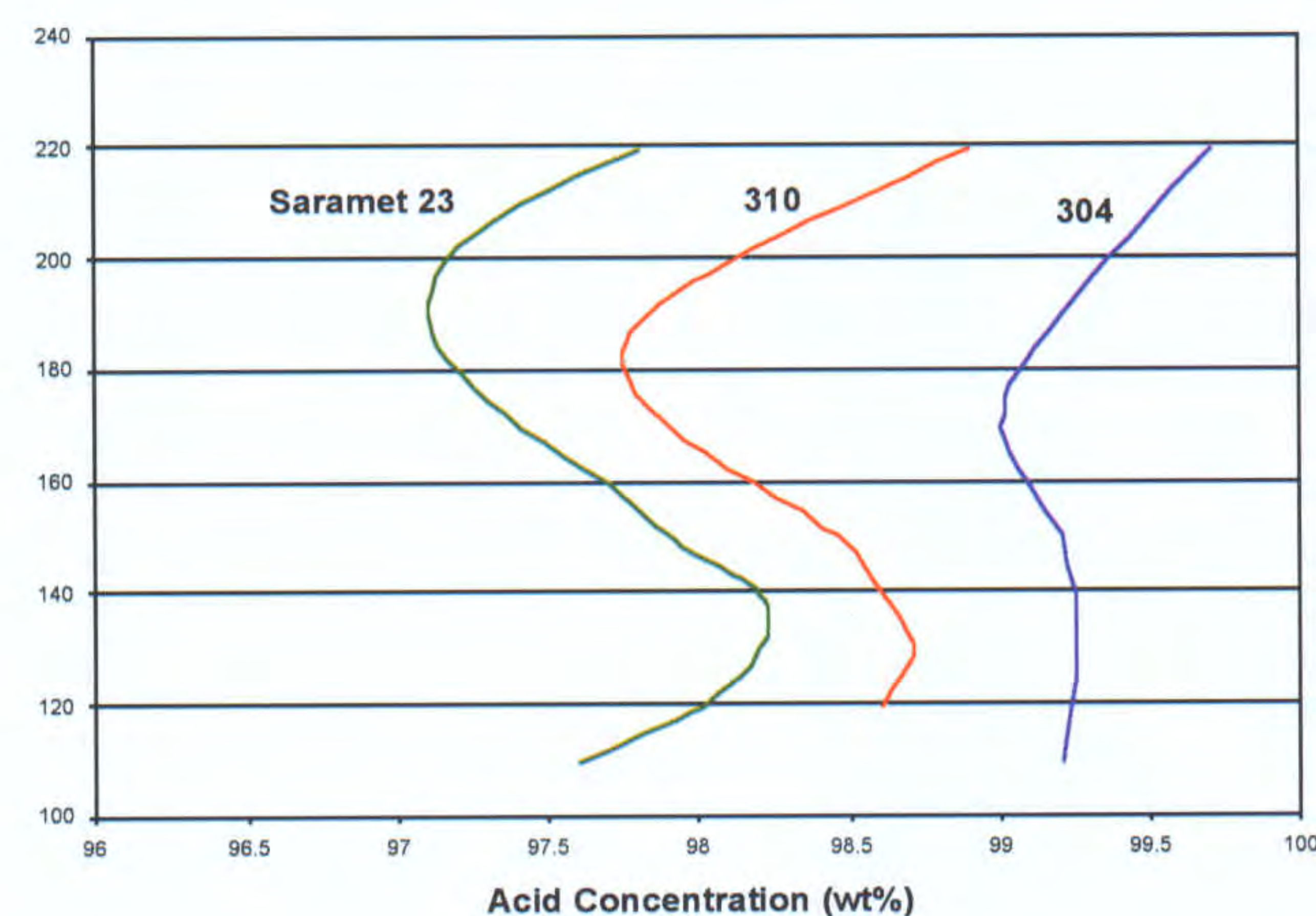


Figure 3 shows the iso-corrosion curves (0.05mm/y) for 304, 310 and Saramet 23 in very strong acid 1,2. It can be seen that there is an increase in the corrosion resistance of both 310 and Saramet in the temperature range 180 degrees C to 200 degrees C. It is assumed that SX and ZeCor show similar behavior. 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 super-duplex stainless steels also show this feature.

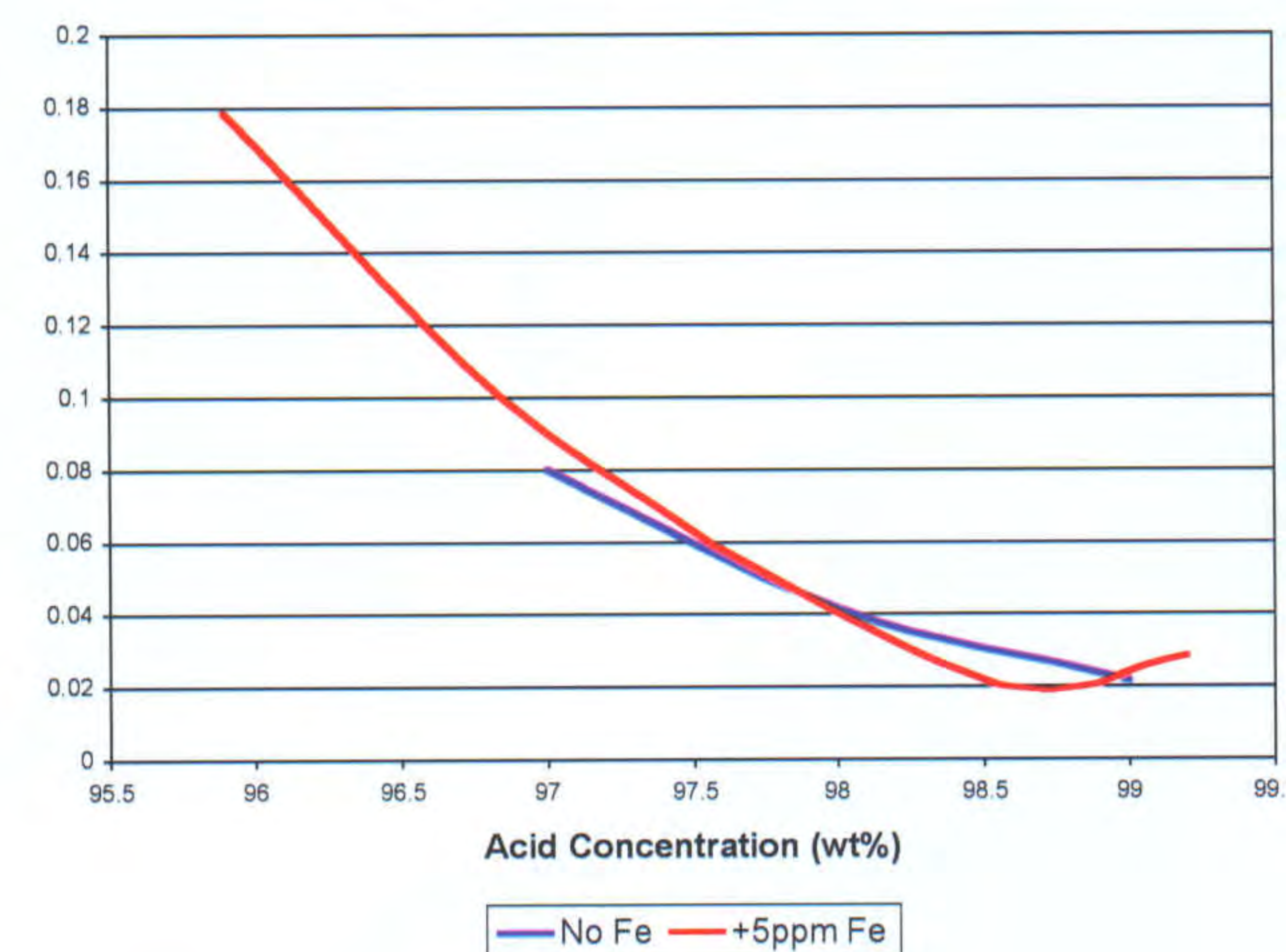
FIGURE 3 Iso-corrosion curves (0.05mm/y) for some austenitic stainless steels in sulphuric acid



At acid concentrations greater than 100 percent there is excess sulfur 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.

In commercial acid plants there is usually a small quantity of iron present (typically 5 parts per million (ppm)) and this can affect the corrosion rate of some alloys. Figure 4 shows the effect of 5 ppm of iron on the corrosion rate of ZERON 100 at 110 degrees C. It can be seen that, within experimental error, there was no significant effect of iron on corrosion. At 200 degrees C in 98.5-percent acid, iron caused a small increase in the corrosion rate, but nothing of engineering significance (0.20 to 0.23mm/y)3.

FIGURE 4 The effect of iron on the corrosion of Zeron 100 in concentrated sulphuric acid at 110°C



## The effect of velocity

Because stainless steels are often actively corroding (as opposed to passive) in hot, concentrated sulfuric 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/sec2.

Velocity tests have been conducted in aerated 95-percent sulfuric acid at 70 degrees C using rotating cylindrical samples. Using the analysis of Silverman 4 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 sulfuric 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 sulfuric acid. Sandvik reported extremely low corrosion rates (<0.01mm/y) for SX in 96-percent acid at 70 degrees C and 25m/sec in the alloy data sheet. They obtained a similar corrosion rate in 98.5-percent acid at 115 degrees C and 10m/sec flow velocity. Saramet 35 showed similar very low corrosion rates in 98.5-percent acid at 120 degrees C at 9 and 25 m/s velocity<sup>5</sup>. 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-percent 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, tanks, pipes, fittings, strainers, trough distributors, heat exchangers and mist eliminators where the conditions have been too onerous for 3106,7. Alloy 310 is still widely used in strong acid, particularly where oleum can be produced. In heat exchangers, 316L (often with Mo greater than or equal to 2.5 percent) 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 sulfuric acid at temperatures up to 200 degrees C. It can be particularly effective in the high temperature heat recovery section of sulfuric acid plants. PCS Phosphates exposed an NPS1 spool of ZERON 100 for 18 months in concentrated acid at 200 degrees C. The corrosion rate was less than 0.2mm/y. PCS has also fitted a ZERON 100 filter in front of a sulfuric acid pump operating at high temperatures (approximately 200 degrees 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 sulfuric acid plant design com-

panies for orifice plates (Figure 5). 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<sup>8</sup>.

## 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



Figure 5 ZERON 100 orifice plates being prepared for shipping.

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 percent is a reasonable maximum. This needs to be specially specified as UNS S31000 has a carbon maximum of 0.08 percent 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 percent maximum to ensure no carbides form on welding.

For more information, please contact Rolled Alloys by phone at (800) 521-0332 or visit the company's Web site at [www.rolledalloys.com](http://www.rolledalloys.com). □

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