A New Nickel Alloy For Semi-Welded Plate Heat Exchangers

A unique solution for your thermal problems in "superoxidizing" environments like hot concentrated sulfuric acid.

B. ORNBERG
Alfa Laval Thermal Inc., Richmond, USA

P. CROOK
Haynes International, USA

ABSTRACT

As the title of this paper says, it is the development of a new Nickel-Chromium-Silicon Alloy commercially known as Hastelloy D205 from Haynes that has given the opportunity to create a unique solution for "superoxidizing" environments, but it is the combination of a semi-welded plate heat exchanger and this new material that really is the unique solution.

INTRODUCTION

The plate heat exchanger is not very well known in the North American sulfuric acid industry thus to understand the statement in the title of this paper, a short explanation is necessary of how and why the plate heat exchanger in Hastelloy D205 is the solution to your thermal problems in the sulfuric acid industry.

The plate heat exchanger (PHE) was introduced to the sulfuric acid industry at the end of the sixties and is today a well known solution to this industry in most parts of the world. There are several reasons for the PHE not being a so well accepted solution here, of which the most important ones are:

- Energy conservation has not been so important here as in the rest of the world
- Plant size and thus flowrates of acid have been larger here than the rest of the world
- Two of the worlds largest process licensees are based in North America and they have their own anodically protected acid coolers (S&T's).
- Cooling source is more often sea water, brackish water, or other corrosive cooling source in the rest of the world than here in North America.

To explain why these factors have delayed the introduction of the PHE into the North American sulfuric acid industry and why the development of Hastelloy D205 will change this, I have to explain the construction, features and benefits of a PHE.

- The plates in a PHE can be pressed from any pressable material. Table 1 shows some examples of materials used in the PHE.

- The corrugation of the plates (Fig.1) creates the high turbulence that gives the PHE its main characteristics of about 4 - 5 times higher overall heat transfer coefficients than the traditional S&T.

- The high turbulence also means that a PHE has much lower fouling tendency than any other heat exchanger types. The turbulence creates such high wall stresses (friction) that at traditional operating conditions in a PHE and an S&T results in about 8 times higher wall shear stress in a PHE than in an S&T. Thus, any fouling problem in an S&T due to bad cooling water probably is non-existing in a PHE. This is something that European plant operators are very grateful for as cooling water (river, lake, CTW, etc.) are very often of bad quality. Plant operators having scrubber acid coolers also really appreciate the low fouling tendency that you can create in a PHE by proper selection of such parameters as plate gap and length.

- It is thus highly important that it is allowed to design a PHE properly and not design a PHE on a typical S&T specification as it will then not work as well as the S&T. This is a <u>very</u>, <u>very</u> common mistake.

- The gasket in the periphery has both a sealing function and function to direct the fluids so that one fluid flows on one side of the plate and the other fluid flows on the other side of the plate in true counter-current (Fig. 2). A lot of people have the opinion that having a gasket in contact with an aggressive fluid at fairly high temperature is just not possible. It is true that the gasket is very often the limiting factor, but if we particularly look on sulfuric acid, there has been quite a dramatic development in gasket technology. A gasket today has much better chemical resistance and temperature resistance as well as much lower absorption tendency (of acid) than yesterdays gasket. The Viton-G, today's best acid quality, has both the highest fluorine content of all Viton's which gives you the good chemical resistance, and it is peroxide cured, which gives you the lowest temperature relaxation and the lowest acid absorption of the gasket. However, even with yesterday's Viton-B quality, that was the best available quality when PHE's were introduced to sulfuric acid plants; you get an acceptable lifetime at moderate temperatures. E.G., one of the first PHE's introduced to an acid plant, was a product cooler delivered to Electrolytic Zinc, Risdon Works, Tasmania, Australia, and 16 years after start-up, it has never been touched. Even if the temperature was moderate (about 170°F), it still gives you an idea that a gasket must not be a problem even with aggressive concentrated sulfuric acid.

  Today's Viton-G gaskets can operate up to about 240° - 250° F and give a good gasket lifetime. However to reduce gasket exposure to high temperature acid, a semi-welded PHE (Fig. 3) is used in anodically protected PHE's and PHE's using the new Hastelloy

D205 to reduce the gasket exposure to just an o-ring, that can be of inert material (e.g. PTFE). We have had such PHE's in operation since 1980, when the first anodically protected PHE was introduced.

- The true counter-current flow and the high overall heat transfer coefficient means that a PHE can very well work at very small temperature approaches and crossing temperatures (Fig. 4). A traditional acid duty (Fig. 5) can be performed well in a S&T, but if you want to recover more of the exothermic heat from the acid process, and use it either for preheating boiler feed water, for district heating, for cogeneration, or in other parts of the plant, a PHE can easily perform such a duty (Fig. 3), while a S&T cannot do it either economically or without many units in series.

- The main thing that previously has been preventing the success of the PHE here in North America has been the temperature. Normally, the absorption acid comes out from the tower around 200^0 - 240^0F, and the maximum temperature of the best metal for concentrated sulfuric acid (Hastelloy C276) is around 195^0F, if you do not want to be dependent on an anodic protection system. To bring the acid temperature down to an acceptable level, recirculation of some kind had to be used. Recirculation means an extra pump, valve's, piping, etc., thus more failure sources than when using anodic protected S&T's. Furthermore, the two big licensee's based here in North America both have their own anodically protected S&T's they were pushing for.

The development of Hastelloy D205 has created quite a dramatically new situation. Combined with the semi-welded PHE, you now have a solution that not only is more economical, but also both has eliminated the dependence of maintaining an anodic protection system, and has the possibility to economically recover the exothermic heat from the acid process.

ALLOY DESIGN

Let us look at Hastelloy D205, how it was developed, and how it has been adopted to be used in semi-welded PHE's for high temperature concentrated sulfuric acid. The composition of Hastelloy D205 is as follows: Ni, bal; Cr, 19.5-20.5; Fe, 5.5-6.5; Si, 4.5-5.5; Mo, 2.0-3.0; Cu, 1.7-2.3.

History

The use of high Silicon contents in Iron- and Nickel-based alloys is well known to improve resistance in hot sulfuric acid. Several Fe-Si and Ni-Si compositions were developed in the early part of the century. The problem with these alloys was their lack of ductility. Haynes has long been conducting research work on silicon alloys and actually had some Fe-Si alloys developed in the beginning of the eighties, when also such high silicon materials like SX and Saramet were introduced. However, in their research work, they found that none of those materials exhibit sufficient thermal stability or formability to be considered ideal for heat exchanger plates. Haynes found that the use of nickel, rather than iron as an alloy base, overcame those disadvantages.

Research Work

In the search for the optimum composition, 45 experimental alloys of varying silicon, chromium, molybdenum, copper and iron contents were melted and processed into wrought products and tested.

The upper and lower limits of silicon were determined from formability, stability, and resistance to highly oxidizing media.

Chromium and molybdenum levels were determined from the request to improve general performance above that of Type 316L stainless steel.

Copper level was established to improve resistance at lower concentrations of sulfuric acid and the addition of iron was added to minimize cost of alloy, where the upper iron level was established to avoid sigma phase embrittlement.

Mechanical Properties

Considerable time was spent on evaluating the thermal stability and on annealing studies. Table 2 reports tensile properties of Alloy D205 (Ref. 1).

Corrosion Properties

In view of both the severe conditions existing in a sulfuric acid plant, the special requirements/conditions of a semi-welded plate heat exchanger and already existing Fe-Si steels, it was deemed appropriate to both perform extensive laboratory work and also, for comparison, a Fe-based steel with an identical Si content was tested in many of these media.

Sulfuric Acid

In Figure 6, comparative corrosion rates in concentrated commercial grade sulfuric acid at 265°F (130°C) are shown (Ref. 1). The same comparative rates are shown in Figure 7 at 200°F (93°C) but for lower concentration of reagent grade sulfuric acid (Ref. 1).

In Figure 8, an isocorrosion curve for 5mpy (0.13mm/year) shows that it is clearly in the oxidizing environment; the D205 alloy shows superiority over the traditional C276/C22 alloys.

Operational Experience

The first operational unit went in to an acid plant at Outokumpu Oy at Kokkola, Finland. The unit, an M10-BW, started up in April 1992 as a test unit in parallel with an anodically protected PHE. A test piece of Hastelloy C276 and Hastelloy D205 was also put in the acid stream for comparison. The test pieces were taken out of operation after 10 months with the temperature about 195 ° - 200°F from April - October with peaks of 215°F. Between November and March, the temperature was about 215°F with peaks of 230°F. The measured Alloy 276 corrosion rate was slightly less than 5mpy (0.13mm/year), while the corrosion rate was practically nil for Alloy D205. Approximately the same result has been found in our other European operational units at Metal Europe, Sachtleben, and Sudchemie, all in Germany. Our only D205 units operating in any length of time in North America are at TexasGulf, Aurora, NC. One gasketed unit replaced a Hastelloy C276 PHE in July 1993 and a second semi-welded PHE replaced another PHE in Hastelloy C276 unit at the end of January 1994. TexasGulf found that the corrosion rate of Hastelloy C276 was higher than expected with their 95% acid at 182°F. They also wanted to go to semi-welded units due to the wish to reduce the amount of gaskets, but the urgency of delivery forced us to delivery the first unit gasketed. The small unit, delivered to Simplot in Lathrop, CA, is a test for a full-scale unit and the 3 units for Simon-Carves, Fenco, Canada, are just in the delivery stage going to Disputada, Chile. No bad experience has been experienced to date with any delivered unit.

Chloride Containing Environment

The general performance of D205 Alloy in chloride containing environment was tested and the tests verified that the Chromium and Molybdenum levels improve the D205 performance in comparison to stainless steel 316L, which was the intention (Ref. 1). This is an important major difference between D205 Alloy and Fe-Si-alloys and makes D205 Alloy usable for not only cooling water of BFW quality.

Corrosion Resistance in Laser Welds

Laser welding is the selected welding method of a semi-welded PHE cassette of two reasons:

- To limit the heat effective zone to a minimum
- To eliminate any additional electrode material in the welding.

However, to confirm properties of the welded cassette, a welded and non-welded sample was tested in 96% acid at 215°F (100°C) and 250°F (120°C). No difference in corrosion rate was detectable.

SUMMARY

In summary, the semi-welded PHE in Hastelloy D205 represents a significant advance in technology for sulfuric acid coolers. Not only does it possess higher resistance to sulfuric acid than high-silicon stainless steels with identical Si content, but also is considerably more resistant to chloride-containing environment. The PHE technology, furthermore, offers a much higher flexibility and possibilities for much higher economical energy conservation.

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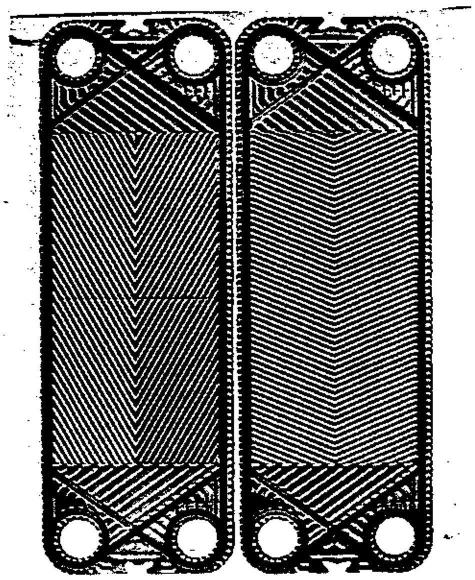


FIGURE 1: Corrugation of Plates

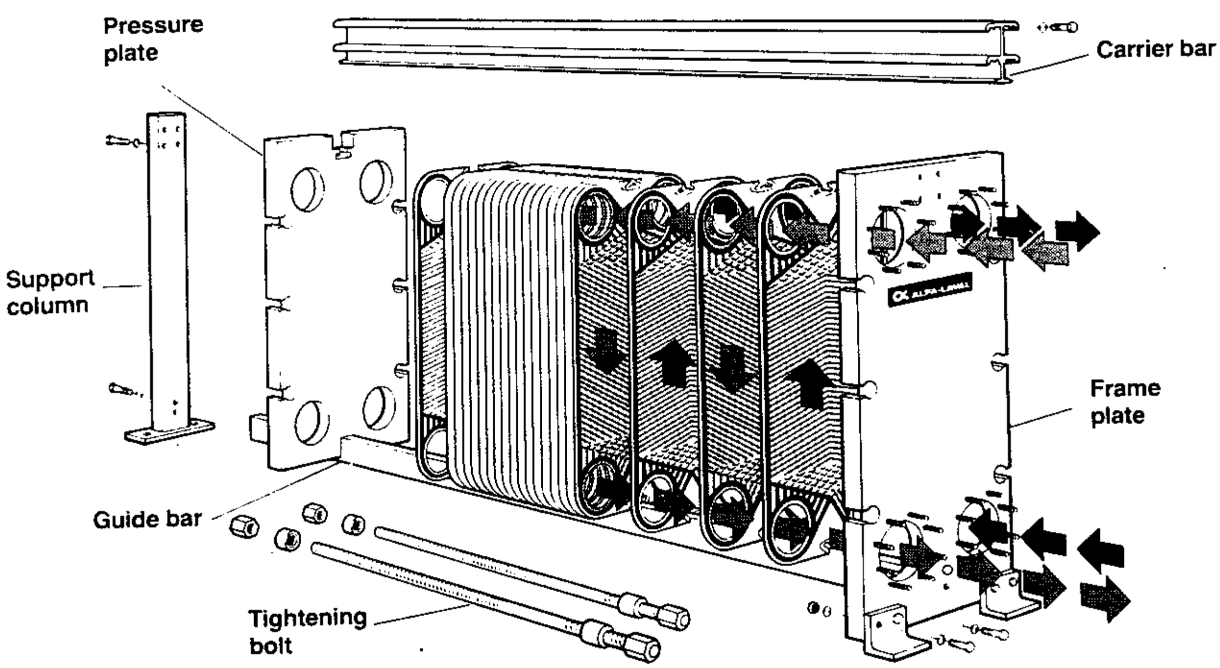


FIGURE 2: Flow Pattern in Plate Heat Exchanger

The welded plate heat exchanger for aggressive fluids

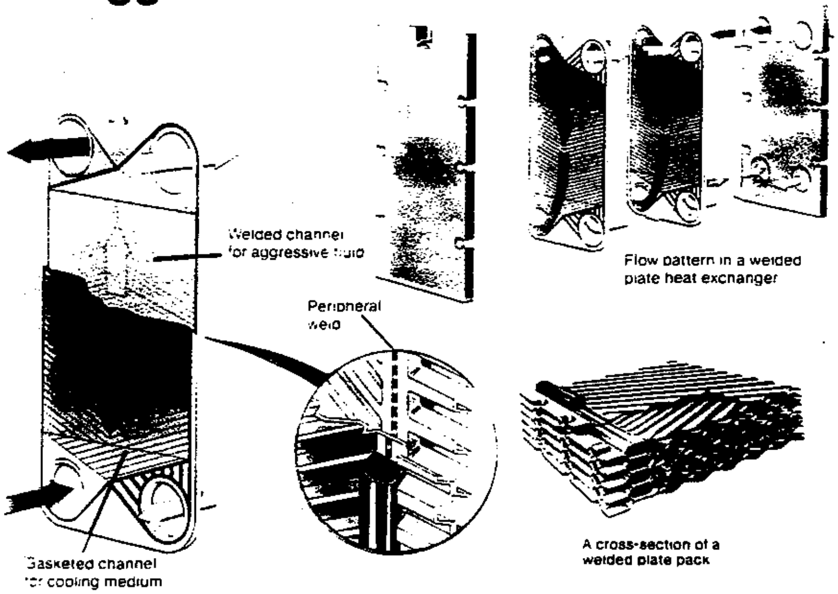


FIGURE 3

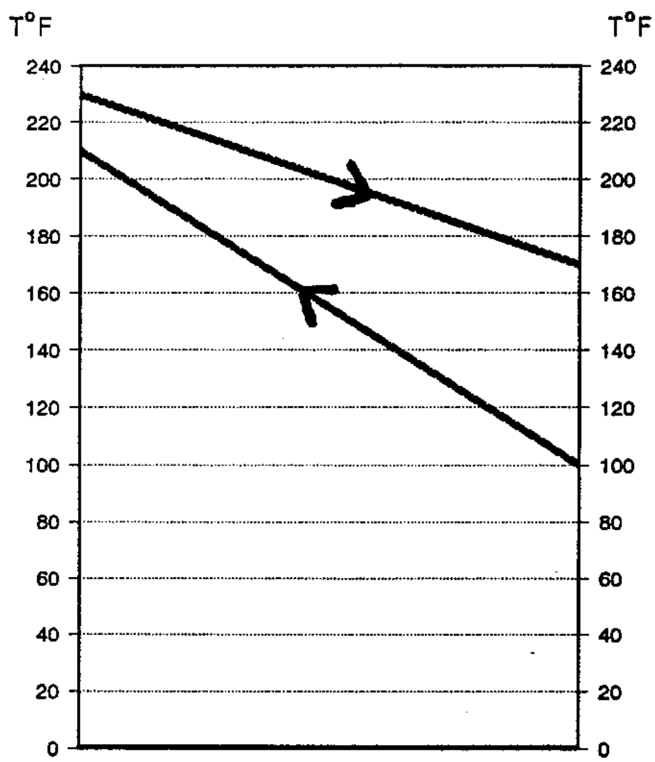


FIGURE 4: Crossing Temperatures
Are No Problem in PHE's.

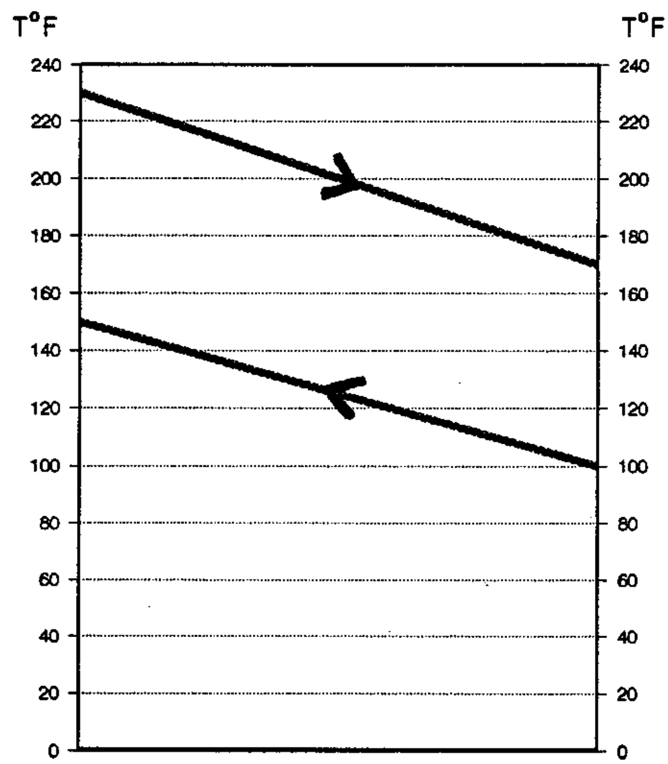


FIGURE 5: Typical N.A. Acid Duty.
No Temperature Crossing.

FIGURE 6: Comparative Corrosion Rates In Commercial Grade Sulphuric Acid at 130°C

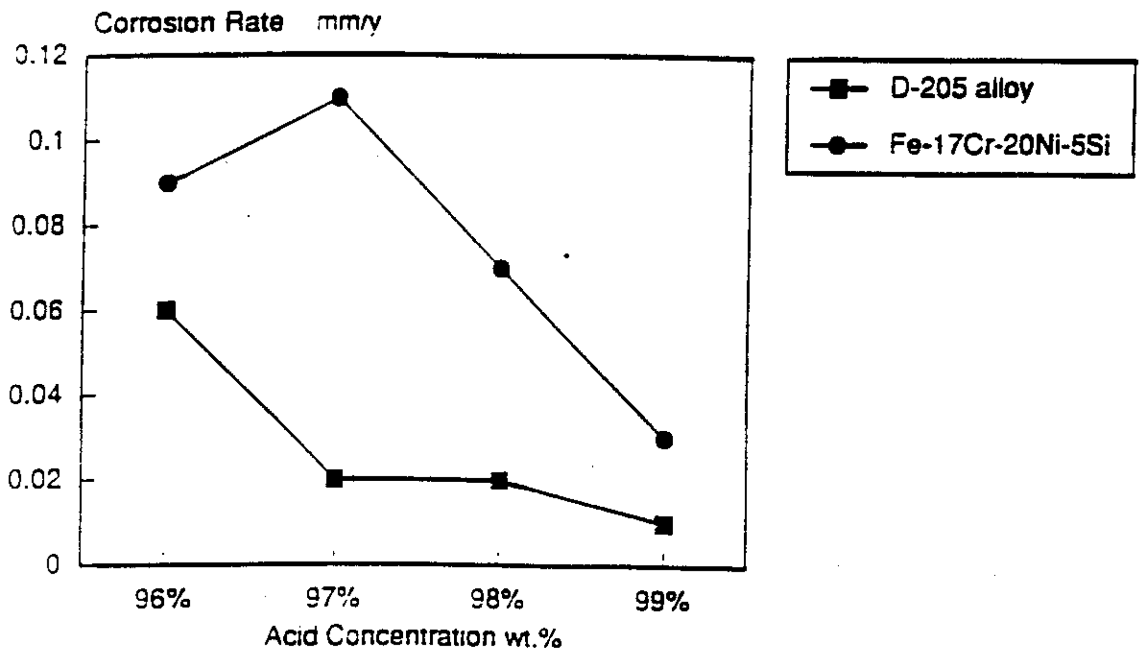
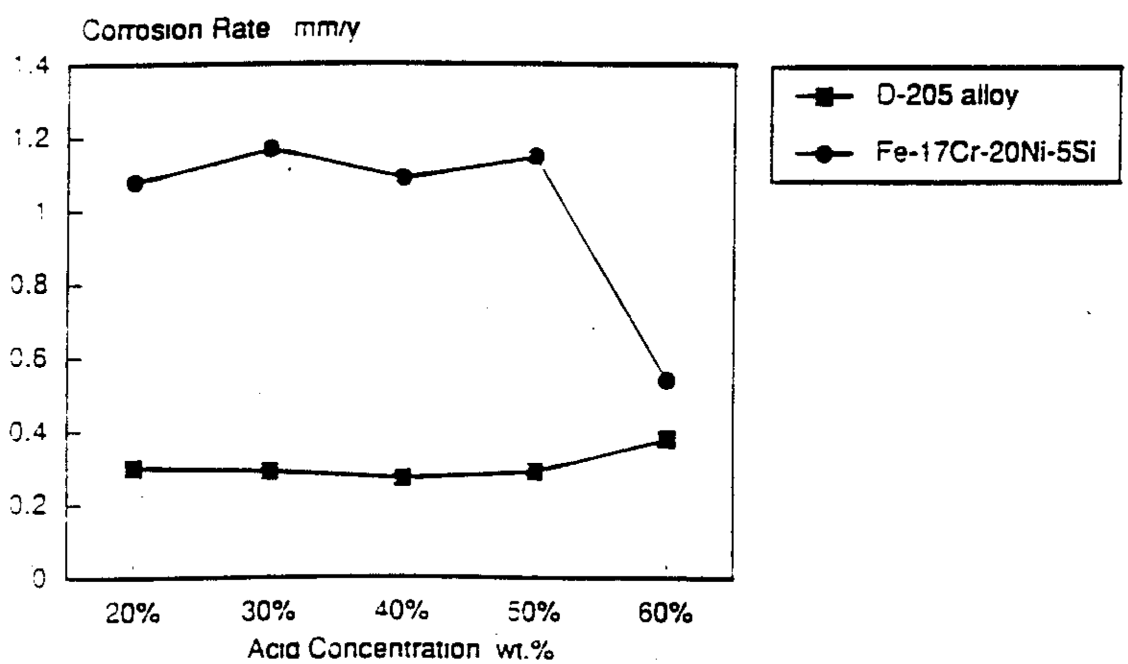


FIGURE 7: Comparative Corrosion Rates In Reagent Grade Sulphuric Acid at 93° C



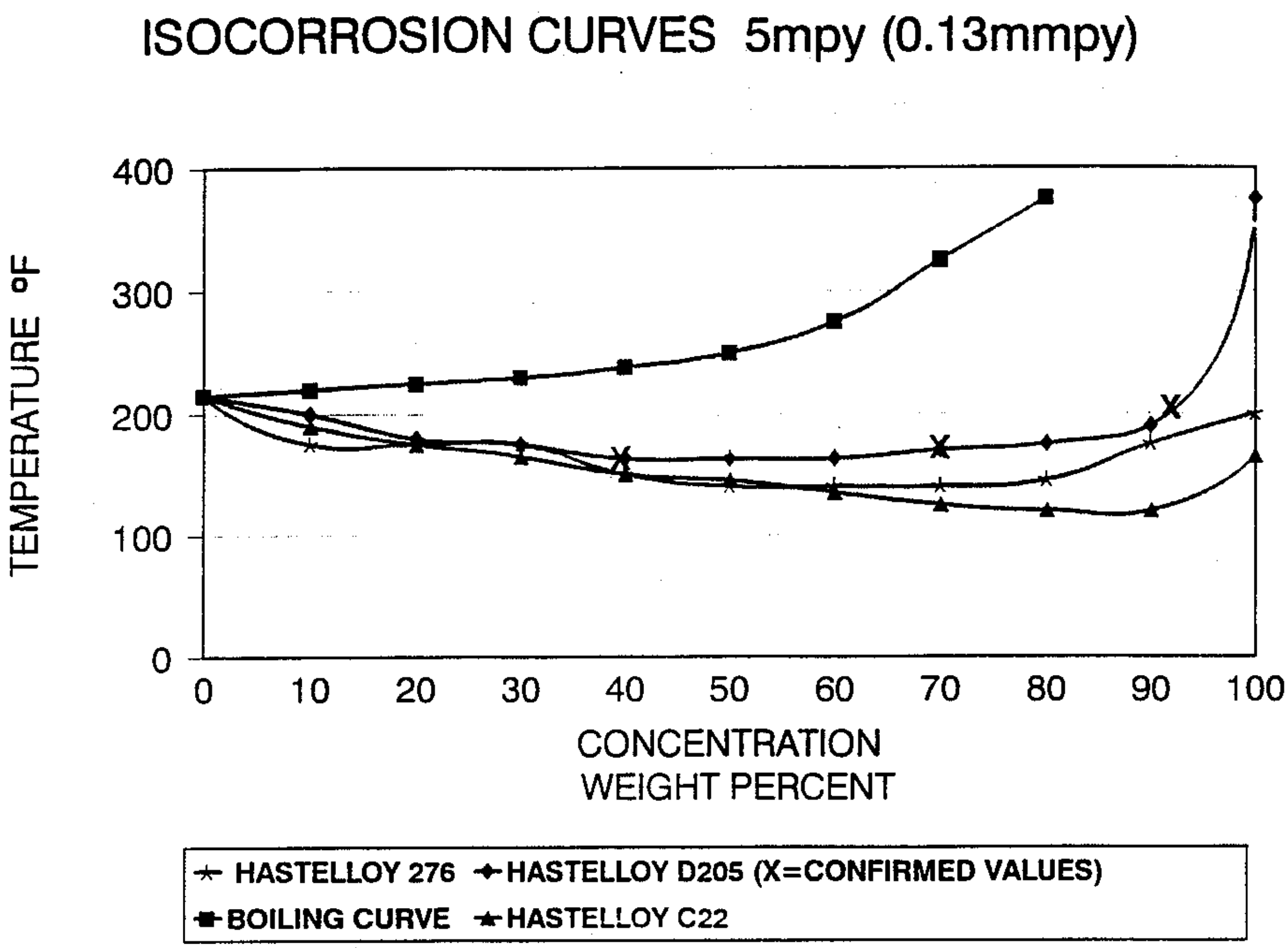

ISOCORROSION CURVES 5mpy (0.13mmpy)
TEMPERATURE °F
400
300
200
100
0
0
10
20
30
40
50
60
70
80
90
100
CONCENTRATION
WEIGHT PERCENT
HASTELLOY 276
HASTELLOY D205 (X=CONFIRMED VALUES)
BOILING CURVE
HASTELLOY C22

FIGURE 8.

TABLE 1. TYPICAL COMPOSITION OF METALS FOR USE IN HEAT EXCHANGERS

	CR	NI	MO	CU	OTHERS
AISI 316	17	12	2.		
904 L (W.1.4539)	20	25	4.5	1.5	
AVESTA 254 SMO	20	18	6.1	0-7	N 0.20
INCOLOY 825 (NICROFER 4221)	22	42	3	2.5	
INCOLOY 625 (" 6020HMO)	22	60	9		
INCOLOY 686 (" 6020HMO)	21	57	16		FE 2, W 4
HASTELLOY C276	15.5	58	16		W
HASTELLOY G-30	29.5	40	5		W 2.5 FE 18-21
HASTELLOY C-22	21	44	13.5		W 3 FE 2-6
HASTELLOY B-2	1.0	68	28		
NICKEL 200		99.2			
TITANIUM					
PD-STAB TITANIUM					
TANTALUM					
HASTELLOY D205	20	BAL	2.5	2	SI 5, FE 6

TABLE 2. HASTELLOY D-205 INSTALLATIONS

SITE	ACID CONC. %	MAX. TEMP. °C (°F)	START-UP	PHE TYPE/FT.²
Outokumpu, Finland	98.8	105 (221)	April, 1992	1 M10-BW
Sudchemie, Germany	98.5	120 (248)	Nov., 1992	1 M10-BW
Metal, Europe, Germany	98.5	100 (212)	April, 1993	2 + 1 AM20-W
Sachtleben, Germany	98.5	105 (221)	April, 1993	2 + 2 AX30-BW/7700
South Pacific Viscose, Indonesia	98.0	90 (195)		1 A15-BW
Outokumpu, Finland	98.5	90 (195)		2 A15-BW/2000
Texasgulf, NC	95.0	82 (180)	July, 1993	1 A15-B/1480 1 A15-BW/1480
Indo Bharat Rayon, Indonesia	98.5	85 (185)		4 A15-BW/2450
Thai Rayon, Thailand	98.5	90 (195)		4 A15-BW/2450
Courtlaulds, UK	98.5			2 AM20-W/1800
J. R. Simplot, CA	98.5			1 M6-M
Rhone-Poulenc, TX	99.0	126 (260)	March, 1994	2 M10-B/670
Disputada, Chile	96.0	103 (218)	May, 1994	3 AM20-W/1400
Outokumpu, Finland	98.5	116 (240)	June 1995	3 MS30-W/21000