MULTI Alloys

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STAINLESS STEELS AND NICKEL ALLOYS FOR USE IN SULPHURIC ACID.

In this e-Book you will learn more about the grades of stainless steel and nickel alloys that have adequate corrosion resistance to warrant consideration of their use in sulphuric acid service. The content is intended to serve as a guide to metals that may be suitable for duty in the acid but consultation and testing are recommended to support a decision on the material of construction.

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SULPHURIC ACID - OVERVIEW

Sulphuric acid (H_2SO_4) may be produced directly from sulphur but it is also by-product of mining - the processing of sulphur containing ores. Volcanic activity and fossil fuel combustion result in the release of sulphur dioxide into the atmosphere which in turn gives rise to “acid rain”. Although the latter (fossil fuels) are now subjected to Flue Gas Desulphurisation the resultant chemical is not the acid but gypsum, a stable calcium sulphate compound.

USES OF SULPHURIC ACID

H_2SO_4 is a very strong acid and is an important basic chemical that may be a feedstock to manufacture further chemicals such as fertilisers and explosives, pigments and detergents, pharmaceuticals and inorganic salts. It is used in oil refining and in the processes to recover metals after mining has taken place. It may be used to treat the surface of metals prior to coating and it is the electrolyte in lead acid batteries. A reason for the widespread usage of H_2SO_4 is its effectiveness in chemical processes as well as it’s availability.

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SULPHURIC ACID – CORROSIVITY

The corrosion characteristics of H_2SO_4 are not straight forward and need to be understood in order to make material selection choices.

The corrosion of metals is an electrochemical process during which the metal is dissolved at the anode whilst the balancing reaction at the cathode may be one of a number depending on the nature of the chemical. In a **reducing acid** the cathodic reaction is usually the reduction of hydrogen ions resulting in the formation of hydrogen gas. Hydrochloric acid, HCl is an example of a reducing acid. On the other hand in **oxidising acids** the cathodic reactions may vary. As an example, in nitric acid, HNO_3, it may be $HNO_3 + 3H^+ + 3e^- = NO + 2H_2O$

This simple characterisation of acids based on the metal – acid reaction is also influenced by the following:

- the nature of the metal – **see overleaf**.
- contaminants that may create “oxidising conditions” in a reducing acid by providing an alternative cathodic reaction.
- flow conditions and dissolved oxygen may have a similar effect

Turning specifically to H_2SO_4 , the cathodic reactions in commercial grade acid is influenced by its concentration. Below 60-70% concentration, for many metals hydrogen is evolved and the acid is considered reducing whilst at the higher concentrations the acid is oxidising. Material selection needs to take in to account the reducing or oxidising nature of the solution.

“Boiling 55% H_2SO_4 is a reducing acid to steel or 18-8 (stainless steel), liberating hydrogen, while it is oxidising to the cast silicon-nickel alloy, the sulfate ion being reduced to sulfur dioxide and hydrogen sulfide”

C P DILLON

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STAINLESS STEELS

There exists an extensive library of iso-corrosion curves for various alloys in commercial purity H_2SO_4 and these provide a useful guide to their suitability as a function of temperature and concentration. Table 1 has been drawn up from these curves with the focus on acid concentrations up 80%. Since several alloys may have a similar resistance to H_2SO_4 at a given concentration, pitting corrosion resistance may be a distinguishing property and thus included in the Table is a value for the pitting resistance equivalent (PRE) based on the empirical formula established for stainless steels.

PRE = %Cr+3.3%Mo+16%N

316L (17Cr-10Ni-2Mo) may be used at ambient temperatures up to 20% concentration as well in the oxidising range from 90%. As indicated, there are several factors that can change the character of the acid and thereby enhance the passivity of stainless steels and thus in commercial service the useful range of 316L may be increased. Equally if chlorides are present, it may be decreased. The addition of copper to stainless steels is advantageous in diminishing corrosion in sulphuric acid. Grades such as Alloy 255 (25.5Cr-6Ni-3.3Mo-1.7Cu-N), S32760 (25Cr-6.9Ni-3.8Mo-Cu-N) and 904L (25Ni-20Cr-4.3Mo-Cu) may be used across the full concentration range but with each having temperature limitations as indicated in the Table. Alloy 20 (33.5Ni-20Cr-2.3Mo-3.5Cu-Nb) having almost equal amounts of Fe and Ni also contains a significant addition of copper.

STAINLESS STEELS

As a generalisation, higher chromium contents are advantageous in oxidising conditions and this is illustrated by the low corrosion rate of 310 (25Cr-20Ni), ideally a very low carbon variant, in hot concentrated acid. Super-duplex stainless steels have similar chromium contents to 310 and are also useful in concentrated acid.

The addition of silicon to stainless steels is known to enhance their resistance in strongly oxidising conditions and so there are several proprietary austenitic stainless steels which have a high silicon content and thus have good corrosion resistance in hot concentrated H_2SO_4. They are of value in plants producing the acid.

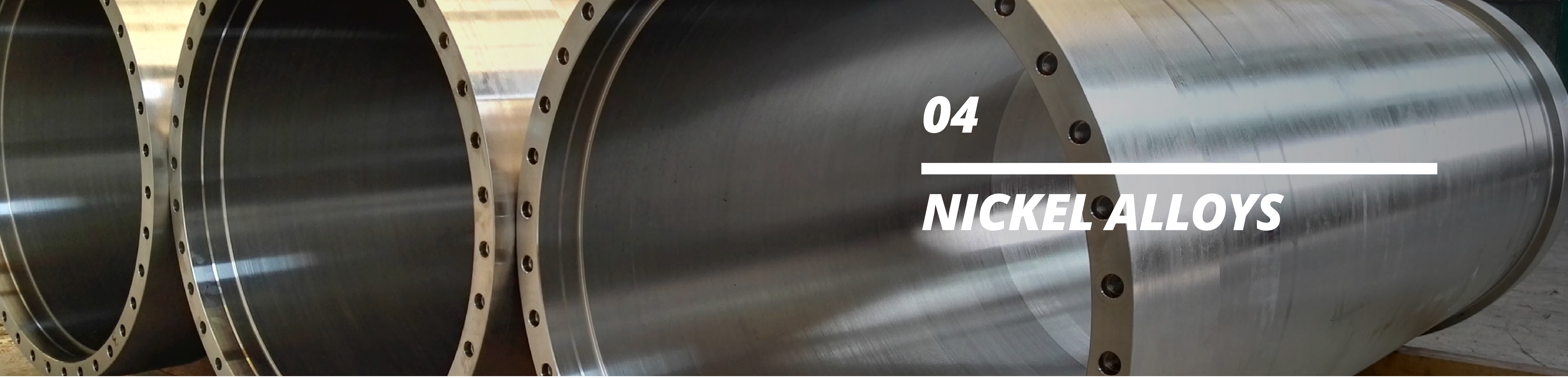
Table 1: H_2SO_4 CORROSION DATA

Temperature (°C) at which 0.1mm/yr corrosion rate is reached in commercial acid

(Corrosion rates are higher above this temperature; read from iso-corrosion curves)

ALLOY	PRE	TEMPERATURE (°C)							
		Acid Concentration (%)							
		10	20	30	40	50	60	70	80
316L	24	55	35	20					
904L	34	80	70	65	55	45	40	35	35
Alloy 2507	43	90	78	48	30				
S32760	42	100	78	60	48	42	40	42	52
Alloy 255	40	92	82	80	75	65	58	55	62
Alloy 20	28	82	70	65	62	60	57	57	58
Sanicro 35	52	90	75	65	55	48	40	NR	
Alloy 825	31*	92	73	61	55	48	48	48	51
Alloy 625	52*	92	89	86	83	76	73	67	48
Alloy C276	68*	85	80	80	70	70	70	70	70
Hastelloy C2000	75*	95	90	90	90	80	80	80	70

**- Calculated using the same formula as for stainless steel although a preferred alternative for nickel alloys is PRE = %Cr+1.5(%Mo+%W+%Nb)*



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NICKEL ALLOYS

Ni-Cu and Ni-Mo alloys are well suited for use in reducing acids and this is true for H_2SO_4 up to about 70% concentration as well. However in practice the acid is rarely reducing as may be expected for reagent grade acid since there are other process chemicals or contaminants present and the effect of these is to render the solution oxidising in which case these alloys may in fact suffer very rapid corrosion.

> ***"RECOMMENDATION: Never use Ni-Mo or other oxidation vulnerable alloys unless conditions are proven to be reducing, preferable by a corrosion test."***
>
> ***G N KIRBY***

Alloy 825 (42Ni-28Fe-21Cr-3Mo-2Cu) is a well-established alloy for sulphuric acid service across a broad range of concentrations and temperatures. Alloy 625 (61Ni-21Cr-9Mo-2.5Fe-3.6Nb) and Alloy C276 (57Ni-16Cr-16Mo-5.5Fe-4W) are 2 nickel alloys intended for use in demanding corrosion conditions and this includes H_2SO_4. Hastelloy® C2000 (60Ni-23Cr-16Mo-1.6Cu) a further development in the "Alloy C-Family" offers, a distinct benefit in H_2SO_4 over C276.

A characteristic of the "Alloy C-Family", and there are more in the range than the 2 mentioned above, is their resistance to corrosion in both oxidizing and reducing conditions even though there may be other alloys better suited to one or other behaviour. The molybdenum and chromium in the various alloys, albeit in different amounts for each of them, imparts this versatility and alloy developers conduct screening tests to demonstrate this. They have focussed development work on alloys which potentially have very good corrosion resistance across the broadest set of conditions. Hastelloy® Hybrid-BC1® (61Ni-22Mo-15Cr) is one such alloy that may be useful in H_2SO_4 under demanding conditions. It was developed for reducing media but it can tolerate oxidising species.

Sanicro® 35 (35Ni-31Fe-27Cr-6.5Mo-Cu), a relatively new alloy, has a general corrosion rate similar to that of some of the super-duplex stainless steels. However, the composition of the alloy is such that it has superior pitting and crevice corrosion resistance.

CONCLUSION

This e-book is an overview of possible materials of construction for applications that involve sulphuric acid. In the interest of brevity, the electro-chemistry associated with the dual nature of the acid has been covered briefly and the iso- corrosion curves for the individual alloys and those associated with the effects of the known contaminants such as ferric and chloride ions have been omitted. Mild steel and titanium which, may be used in H_2SO_4 in some very specific conditions are not included in this review.

Should you require more information relating to alloys for use in sulphuric acid please contact us.

> ***"While the actual choice of an alloy for an application is made on the basis of field experience, it is hoped that this (paper) will enable an initial selection of a set of alloys to be made for further field testing in a given environment."***
>
> ***N SRIDHAR***

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