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ALLOY 31 - A HIGH ALLOYED NI-CR-MO-STEEL - PROPERTIES AND APPLICATIONS FOR THE PROCESS INDUSTRY

ALLOY 31 - VISOKO LEGIRANO Ni-Cr-Mo JEKLO - LASTNOSTI IN APLIKACIJE ZA PROCESNO INDUSTRIJO

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Alloy 31 (Nicrofer 3127 hMo) is an austenitic nickel-chromium-molybdenum steel comprising about 0.2 wt.-% nitrogen to stabilize the austenitic structure. The alloy was developed to fill the gap between the commercial stainless steels and the nickel-base alloys. It is a material for many high-severity applications where conventional stainless steels have proven inadequate. On the other hand, alloy 31 shows a high resistance to pitting and crevice corrosion in neutral and acid aqueous solutions, coming close to that of higher nickel alloyed materials. Laboratory tests in different aqueous solutions have proven that alloy 31 is characterized by an excellent resistance to both reducing and oxidizing media. The corrosion resistance to oxidizing media is caused by the high chromium content and is not impaired by the molybdenum content of about 6.5 wt.-%. Additionally, the high resistance to pitting and crevice corrosion corresponds to the additions of molybdenum and nitrogen. The paper describes some typical industrial and practical applications of alloy 31. For example the material is successfully used for filter systems and mixer components in phosphoric acid plants, in pickling plants, for waste sulfuric acid recovery and for FGD (flue gas desulfurisation) systems. For such applications not only corrosion and erosion-corrosion resistance but also high strength, high ductility and ease of fabrication such as welding are important parameters.

Key words: alloy 31, Nicrofer 3127 hMo, pitting corrosion, crevice corrosion, corrosion resistance, erosion-corrosion resistance, wet corrosive applications, phosphoric acid plants, pickling plants, waste sulfuric acid recovery, FGD-systems

Alloy 31 (Nicofer 3127 hMo) je avstenitno nikelj-krom-molibdenovo jeklo s približno 0.2 mas.% dušika, ki stabilizira avstenitno strukturo. Alloy 31 je bila razvita zato, da bi zapolnila vrzel med komercialnimi nerjavnimi jekli in zlitinami na osnovi niklja. Namenjena je za uporabo v pogojih, kjer so se nerjavna jekla izkazala za neuporabna. Po drugi strani pa kaže Alloy 31 visoko odpornost proti jamičasti koroziji, proti neutralnim in kislim vodnim raztopinam, podobno kot zlitine legirane z visokim deležem niklja. Laboratorijski testi v različnih vodnih raztopinah so pokazali, da je Alloy 31 odporna tako na oksidativne kot reduktivne medije. Korozijsko odpornost na oksidativni medij zagotavlja visoka vsebnost kroma in ne vsebnost 6,5 mas.% molibdena. Dodatno pa molibden in dušik zagotovita odpornost proti jamičasti in špranjski koroziji. V članku so opisane nekatere tipične industrijske in praktične aplikacije Alloy 31. Na primer material se uspešno uporablja za sistem filtrov in komponent mešalnikov pri proizvodnji fosforne kisline, v lužilnicah, pri predelavi odpadne žveplene kisline in za FGD sisteme, za razžveplanje dimnih plinov. Za tovrstne aplikacije so pomembni parametri ne samo korozijska in erozijsko-korozijska odpornost ampak tudi visoka trdnost, duktilnost ter lahka izdelava kot npr. varjenje.

Ključne besede: alloy 31, nicofer 3127 hMo, jamičasta korozija, špranjasta korozija, odpornost proti koroziji, erozijsko-korozijska odpornost, mokri korozijski postopki, obrat za proizvodnjo fosforne kisline, lužilnice, obrat za predelavo odpadne žvepelne kisline, FDG sistem

1 INTRODUCTION

For many applications in the process industry the service conditions are too severe for the use of conventional stainless steels. In such cases the superaustenitic stainless steel alloy 31 (Nicrofer 3127 hMo) is a cost effective alternative if over-engineering has to be avoided. The material is particulary well suited to applications in the chemical and petrochemical industries, environmental engineering, and oil and gas production. The paper describes some practical applications of alloy 31 for industrial processes.

2 CHARACTERISTICS OF ALLOY 31

The nominal chemical composition of alloy 31 (Nicrofer 3127 hMo) is given in **Table 1**. The chromium content of about 27 wt.-% and the molybdenum content of about 6.5 wt.-% are of decisive importance for a high degree of resistance to pitting and the related crevice corrosion[1]. The pitting resistance equivalent (PRE) of 47 for alloy 31, which is higher than that of the conventional stainless steels and very close to that of the nickel base alloys, can be estimated by using the well-known relation

$$PRE = \%Cr + 3.3\%\ Mo \quad (1)$$

A corrected PRE of 53 takes into account that the nitrogen content also improves pitting resistance of the above material according to the modified equation

$$PRE = \%Cr + 3.3\%\ Mo + 30\%\ N \quad (2)$$

Futhermore, the addition of 0.2 wt.-% nitrogen improves the strength, decreases the tendency to weld segregation, reduces the tendency to precipitation of intermetallic phases and stabilizes the austenite. The latter effect, the positive influence on the austenite stability, allows to add 6.5% molybdenum to this alloy which would otherwise be unstable. The material comprises approx. 1.2 wt.-% copper in order to ensure a good resistance to reducing diluted acids. Moreover, alloy 31 represents a very low carbon alloy. Its carbon content of 0.010 wt.-% is far below the limit value of max. 0.03 wt.-% specified for low-carbon steel grades and thus helps to prevent the formation of chromium carbides as well as a sensitization during heat treatment and welding. The sulfur content of max. 0.005 wt.-% is sufficiently low to exclude pitting attack which can be induced by the existance of MnS precipitates[2,3].

Table 1: Nominal chemical composition (wt.%) of alloy 31 (Nicrofer 3127 hMo)

Ni	Cr	Mo	Cu	N	Mn	C
31	27	6.5	1.2	0.2	1.7	0.010

The mechanical properties at room temperature, which compare well to those of other stainless steels and nickel-base alloys are given in **Table 2**. According to previous investigations[4] welding does not impair the excellent ductility. Alloy 31 can be welded by all conventional processes (GTAW, hot wire GTAW, plasma arc, manual metal arc and GMAW/MAG). For most applications, the material is welded with overalloyed filler metals such as alloy 59 (Nicrofer 5923 hMo) to compensate their tendency for molybdenum and chromium segregation, in particular in the welded zone[5]. If appropriate welding parameters are used, no difference in the corrosion resistance to intergranular attack of both welded sample and parent metal was found[6].

Table 2: Mechanical properties of alloy 31 at 20°C (flat products, solution-treated condition)

0.2% Yield strength ($R_{P0.2}$)	Tensile strength (R_m)	Elongation A_5	Brinell hardness (HB)	ISO-V-notch
min. 280 N/mm^2	min. 650 N/mm^2	min. 40%	max. 220	≥185 J/cm^2

3 APPLICATIONS FOR THE PROCESS INDUSTRY

In the following section some typical industrial and practical applications of alloy 31 will be described. For example the material is successfully used in phosphoric acid plants, in pickling plants, in FGD-systems and in waste sulfuric acid recovery plants. Further typical applications are represented in[4,7].

Phosphoric acid production

In most cases phosphoric acid is produced by the wet digestion process at 80°C according to the following reaction

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 + 6\ H_2O \rightarrow \\ \rightarrow 2\ H_3PO_4 + 3\ CaSO_4 \cdot 2\ H_2O \qquad (3)$$

Depending on the water content of the resulting byproduct, calcium sulfate, usually two process variants, the conventional and wide-spread dihydrate process ($CaSO_4 \cdot 2H_2O$) or the modern hemihydrate process ($CaSO_4 \cdot 0,5\ H_2O$) are prefered. Using low quality phosphate ores, impurities with different concentrations may arise in the production of phosphoric acid, such as chlorides, fluorides, sulfates, sulfides, oxidizing metal ions which increase the aggressivity of wet-process phosphoric acid. As a result, conventional alloys which are corrosion-resistant in chemically pure phosphoric acid may no longer be adequate for mixer components etc. Therefore, the high alloyed nickel-chromium-molybdenum steel alloy 31 was considered as an alternative material for the concentration range > 50% H_3PO_4. In laboratory experiments specimens of alloy 31 were tested for 21 days in two technically relevant phosphoric acid solutions at 80°C. The chemical composition of the simulating media and the calculated corrosion rates are shown in **Table 3**. As can be seen from these results, alloy 31 seems to have a good corrosion resistance under the above conditions. Another important criterium for the use of alloys as plant components in the phosphoric acid production is the erosion-corrosion resistance. Erosion-corrosion measurements of different alloys were performed in wet process phosphoric acid plant conditions[8]. The simulation of erosion-corrosion was achieved by using a rotating electrode. The composition of the alloys tested is given in **Table 4**; the results of these measurements are represented in **Figure 1 and Figure 2**. In a non agitated phosphoric acid solution (28% P_2O_5) the corrosion rates of all alloys are below 0.049 mm/a **(Figure 1)**. On the other hand the corrosion rates increase to values up to 1.4 mm/a if erosion-corrosion was simulated by the rotation (100 rot./min) of the electrode **(Figure 1)**. In **Figure 2** the erosion-corrosion resistance of the same alloys was tested in different phosphoric acid media. Again, especially in comparision to the high alloyed materials (on the right hand side of alloy 31 in **Figure 1 and Figure 2**), alloy 31 shows the best results under the above conditions. As a result, alloy 31 is used for filter systems and mixer components in high-severity phosphoric acid plants.

Table 3: Corrosion rates (mm/a) of Nicrofer 3127 hMo in technically-relevant phosphoric-acid solutions

Test medium	Temperature	Corrosion rate
$52\%P_2O_5+4.5\%H_2SO_4+0.9\%H_2SiF_6+1.5\%Fe_2O_3+400ppmCl^-$	80°C	0.02 mm/a
$30\%P_2O_5+2.4\%H_2SO_4+2.3\%H_2SiF_6+1\%Fe_2O_3+1000ppmCl^-$	80°C	0.015 mm/a

Table 4: Chemical composition (wt.%) of the alloys shown in **Figure 1 and Figure 2**

Uranus B6	44.5Fe-21Cr-25.5Ni-4.5Mo-2.0Mn-1.5Cu-1.0Si-0.02C
Sanicro 28	37.5Fe-27Cr-31Ni-3.5Mo-2.5Mn-1Cu-0.02C
Avesta 654 SMO	45.7Fe-24Cr-22Ni-7.3Mo-0.5Cu-0.5N-0.02C
Lewmet 25 Cast	15Fe-29Cr-38Ni-4.5Mo-3Mn-3Cu-0.5Si-6Co-0.05C
Hastelloy G30 Cast	15Fe-29.7Cr-41.3Ni-5Mo-1.5Mn-1.7Cu-5Co-0.8Si-0.03C

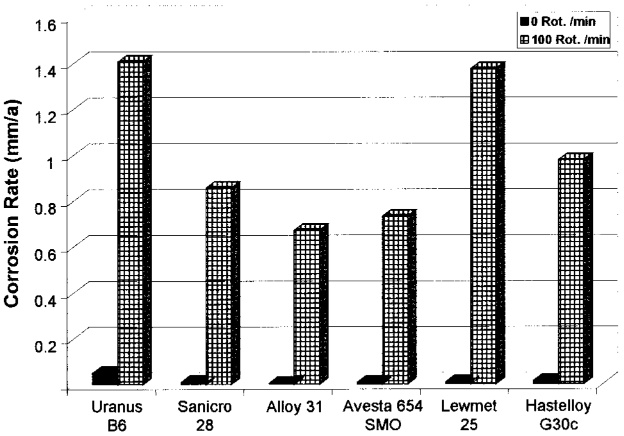

Figure 1: Erosion-corrosion rates of different alloys in phosphoric acid (28% P_2O_5)[8]
Slika 1: Stopnje erozije-korozije za različne zlitine v fosforni kislini (28% P_2O_5)[8]

Figure 3: Vertical spray pickling plant at Krupp VDM with solid metal segments in alloy 31 in highly stressed areas
Slika 3: Vertikalna razprševalna lužilnica v podjetju Krupp VDM s trdnimi kovinskimi deli iz zlitine alloy 31 v visoko tlačnih predelih

Pickling plants

Another typical application field for alloy 31 is shown in **Figure 3**. In the production process of sheets at Krupp VDM, sheets pass through a vertical continuous spray-pickling plant which has been rebuilt with solid metal segments in alloy 31 in the highly stressed areas. Before using alloy 31 as a material for this pickling plant welded samples of the alloy were inserted in the pickling plant for 7000 h. The pickling spray contains a mixture of 20% HNO_3 and 4% HF, the spray pressure is 0.4 MPa and the temperature is about 50°C. The results of these tests are given in **Table 5**. The material was manual welded by the GTAW (gas tungsten arc welding) process, the welding filler metals were Nicrofer S 3127 and Nicrofer S 5923 hMo. As can be seen the corrosion rates of both weldments are low under these conditions, anyhow, alloy 31 as a matching filler metal is recommended today.

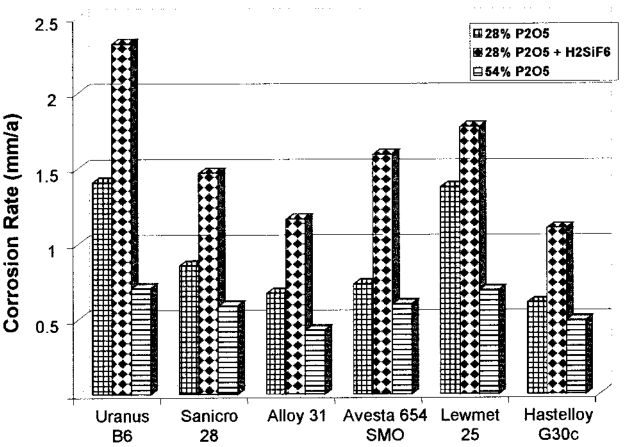

Figure 2: Erosion-corrosion rates of different alloys in three phosphoric acid solutions (100 rot./min)[8]
Slika 2: Stopnje erozije-korozije za azlične zlitine v treh različnih fosfornih kislinah (28% P_2O_5)[8]

Table 5: Corrosion rates of welded samples of alloy 31 after inserting for 7000 h in the pickling plant at Krupp VDM GmbH

Filler metal	Corrosion rate (mm/a)
Nicrofer S 3127 hMo	0.05
Nicrofer S 5923 hMo	0.05

FGD-systems

Air pollution control requires the installation of FGD (flue gas desulfurisation) systems in fossil-fuel-fired power stations. In such systems oxidation products of the sulphur and of the accompanying HCl/HF gases from the combustion processes of organic materials (coal, lignite, oil) are removed by chemical gas scrubbing. For the construction of these FGD-systems the use of high alloyed materials is necessary because in some areas, for instance in the raw gas inlet of spray absorbers, extremely corrosive conditions may appear. Under these conditions the resistance against pitting and crevice corrosion has to be proven. One screening test for the alloy's resistance against pitting and crevice corrosion is ASTM G-48, in which the critical pitting corrosion temperature (CPT) and critical crevice corrosion temperature (CCT) is determined in a 10% solution of hydrated ferric chloride. In order to establish the CPT and CCT, specimens are immersed into the solution, starting at room temperature. After 24 hours each, the temperature was increased by 2.5°C. The CPT is the temperature at which initial pitting becomes visible on the surface. This applies analogously to the determination of the CCT. To this end, artificial crevices are produced with slotted teflon discs according to MTI[9]. The results are compiled in **Figure 4**. A comparision with other materials shows that alloy 31 possesses the best resistance to chloride media of all high-alloyed stainless steels and exhibits a resistance close to that of the high-molybdenum containing nickel material alloy 625. The CPT and CCT measured in this aggressive test indicate an excellent resistance to local corrosion of alloy 31 in practical chloride containing media of low pH-values.

Additionally, in approximation to FGD practice, a simulating FGD test solution with the chemical composition pH = 1 (H_2SO_4), 7% Cl^- (NaCl), 0.01% F^- (NaF), 20% FGD-gypsum ($CaSO_4$, $CaCO_3$, $MgCO_3$) was developed. The medium was aerated and gently stirred throughout the experimental period. An additional time lapse effect is achieved by using Teflon crevice blocks, whereby a crevice block is attached to each specimen side with a defined torque. In this way it is also possible to distinguish the attack on exposed surfaces and the reaction under crevice conditions such as may occur in a FGD-plant. The temperature of 65°C was maintained by means of a silicon oil bath. The total test duration was 90 days. The results of the visual inspections and the determinations of the weight losses are collected in **Table 6**. Whereas the reference materials suffered localised attack, alloy 31 has a good corrosion resistance under these conditions as shown by the low corrosion rates for both the welded and the base metal.

Table 6: Resistance of alloy 31 and reference materials under flue gas desulfurization conditions: Simulating test solution: 7% Cl^-, 0.01% F^-, 20 wt.-% gypsum, pH = 1 (H_2SO_4), O_2 saturated, T = 65°C, t = 90 days. TIG welding conditions, surface relation weld/base metal of corrosion test samples 1:5

Alloy	Base metal	Welded sample
Nicrofer 3127 hMo	< 0.01 mm/a	0.01 mm/a
Nicrofer 3127 LC	0.04/0.06 mm/a pitting corrosion crevice corrosion	0.18 mm/a pitting corrosion crevice corrosion
Cronifer 1925 hMo	0.08/0.14 mm/a pitting corrosion crevice corrosion	0.03 mm/a pitting corrosion crevice corrosion

Waste sulfuric acid recovery

The corrosion resistance of alloy 31 in reducing sulfuric acid with no impurities and in concentrations of 20% to 80% is remarkably good, as shown in the isocorrosion diagram in **Figure 5**. In this diagram the limiting lines of the resistance in pure, slightly agitated and aerated sulfuric acid in the concentration range 0 to 100 wt.% H_2SO_4 were determined by immersion tests according to DIN 50905. The isocorrosion lines for 0.1 mm/a and 0.5 mm/a are plotted as a function of temperature and concentration. The area below 0.1 mm/a gives the concentration temperature points up to which the alloy can be used without restriction. The conclusion is that alloy 31 shows exceptionally good resistance in pure H_2SO_4 up to 60% and 100°C and in 80% H_2SO_4 up to 80°C.

Figure 6 represents the behaviour in reconcentrating waste acid from a titanium dioxid plant. As a result of these experiments alloy 31 was selected for some components of such a waste-acid reconcentration system. Similar low corrosion rates have been demonstrated in viscose rayon plants and other acid sulfate media.

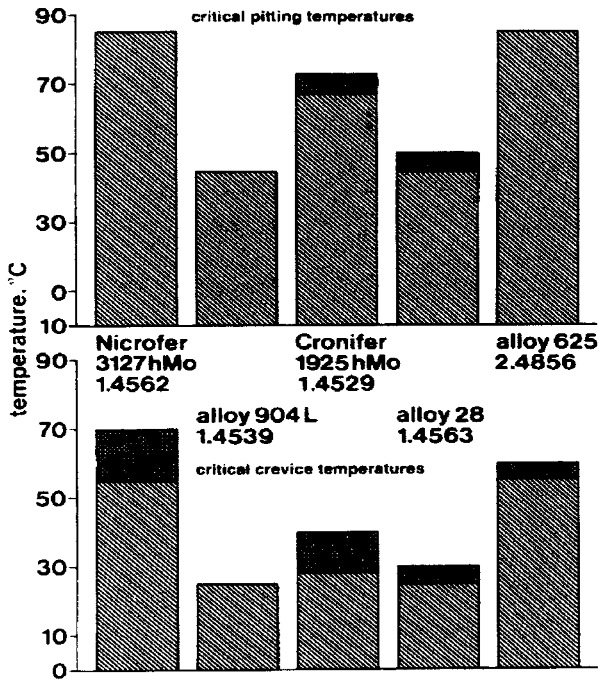

Figure 4: Pitting corrosion resistance and crevice corrosion resistance of alloy 31 in the 10% $FeCl_3.6H_2O$ test. Comparision to other high alloyed materials

Slika 4: Odpornost na jamičasto in špranjasto korozijo Alloy 31 v 10% $FeCl_3.6H_2O$ in primerjava z drugimi visoko legiranimi materiali

For industrial applications of alloy 31 in waste sulfuric acid plants the exact knowledge of the operating parameters is important. Amongst others the effect of minor traces of oxidizing contaminants has to be considered[10]. Alloy 31 has a high corrosion resistance in 60% sulfuric acid if sufficient aeration is guaranteed. The maintenance of passivation of the material was confirmed by electrochemical measurements, as shown in

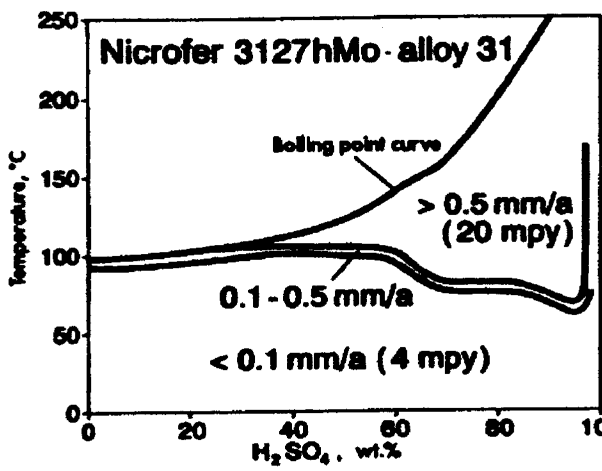

Figure 5: Isocorrosion diagram of alloy 31 in sulfuric acid. The corrosion rate was calculated from immersion tests over at least 120 h

Slika 5: Izokorozijski diagram zlitine Alloy 31 v žvepleni kislini. Stopnja korozije je bila izračunana iz testa potapljanja, ki je trajal najmanj 100 ur

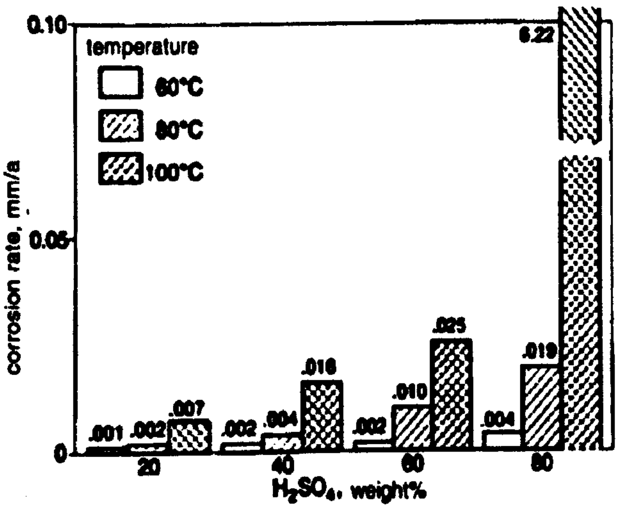

Figure 6: 120 h exposure tests of alloy 31 in reconcentration of waste sulfuric acid from titanium dioxide production
Slika 6: Izpostava Alloy 31 za 120 ur in ponovna koncentracija odpadne žveplene kisline pri proizvodnji titanovega dioksida

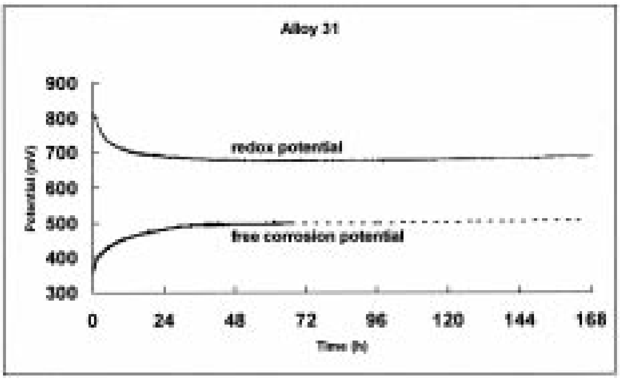

Figure 7: Free corrosion potential and redox potential of alloy 31 in 60% sulfuric acid saturated with oxygen gas at 80°C measured continously for 7 days
Slika 7: Prosti korozijski potencial in redoksi potencial zlitine alloy 31 v 60% žvepleni kislini nasičeni s kisikom pri 80°C, merjena kontinuirno 7 dni

Figure 7. The constant and stable free corrosion potential of about 500 mV and the stable redox system of about 700 mV indicate the oxygen induced passivation of alloy 31, which allows the application of the material under such conditions.

The pronounced effect of impurities on the corrosion behaviour of alloy 31 under conditions of 80%/80°C is summarized in **Table 7**. It was shown in **Figure 6** that alloy 31 has a corrosion rate of only 0.019 mm/a at 80°C in H_2SO_4 of technical grade purity. At the same conditions, however, the corrosion rate in analytical grade acid, which is free from oxidizing impurities, rises to over 4 mm/a. The addition of only 100 ppm Fe^{3+} to this analytical grade acid reduces the corrosion rate to a level comparable to that obtained in the industrial grade acid used for other lab tests.

Table 7: Effect of minor variations in sulfuric acid composition on the corrosion rate of alloy 31 (80°C/80% H_2SO_4)

Test conditions	Corrosion rate, mm/a
'Analysis grade', no agitation, no aeration (<2 ppm Fe)	4.34
'Analysis grade', nitrogen bubbled	2.67
'Analysis grade'+100 mg/l Fe^{3+}, nitrogen bubbled	0.03
'Chemical grade', nitrogen bubbled	2.33

4 CONCLUSIONS

The superaustenitic steel alloy 31 (Nicrofer 3127 hMo) has an exceptional corrosion resistance under widely-varying conditions. It exhibits an excellent resistance to pitting and crevice corrosion in neutral and acid solutions, to oxidizing and reducing media. Therefore typical application areas for alloy 31 are the following:

- equipment for phosphoric acid production
- pickling plants
- FGD of fossil-fired power generation
- waste sulfuric acid recovery
- sea-water-related industries
- components for pulp and paper industries.

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