

NiDI

Nickel
Development
Institute

Selection and use of stainless steels and nickel-bearing alloys in nitric acid

by C.M. Schillmoller

NiDI Technical Series N° 10 075

The material presented in this publication has been prepared for the general information of the reader and should not be used or relied on for specific applications without first securing competent advice.

The Nickel Development Institute, its members, staff and consultants do not represent or warrant its suitability for any general or specific use and assume no liability or responsibility of any kind in connection with the information herein.

C.M. Schillmoller
is a consultant
in the United States to the
Nickel Development Institute

Selection and use of stainless steels and nickel-bearing alloys in nitric acid

C. M. SCHILLMOLLER

Nitric acid is the second most important industrial acid after sulphuric. It is a strong oxidizer and a very corrosive acid. Even though most stainless steels do not resist 100% HNO₃, they are resistant to corrosion by the 60% to 70% concentrations that result from ammonia/air oxidation processes, and the low-carbon or stabilized stainless steels play a major role in the production and handling of nitric acid over a wide range of temperatures and concentrations.

This article examines the selection criteria for several stainless steels and nickel-bearing alloys in the production and handling of nitric acid and in its use, both in the production of ammonium nitrate fertilizers and as an acid mixture with HF for descaling.

The Bibliography at the end of the article contains references that will provide more detailed information on many of the specific subjects included in this article.

Table I lists the alloys referred to in the article.

Table I **Representative stainless steels and high-nickel alloys for nitric acid service.**

Designation		Nominal Composition, % by mass									
Traditional	UNS*	C	Cr	Ni	Mo	Cu	Nb	Ti	Fe	Al	Other
Type 304	S30400	<0.08	18.0-20.0	8.0-10.5					Bal		
Type 304L	S30403	<0.03	18.0-20.0	8.0-12.0					Bal		
Type 321	S32100	<0.08	17.0-19.0	9.0-12.0				≥5x%C	Bal		
Type 347	S34700	<0.08	17.0-19.0	9.0-13.0			≥10x%C		Bal		
Type 316	S31600	<0.08	16.0-18.0	10.0-14.0	2.0-3.0				Bal		
Type 317	S31700	<0.08	18.0-20.0	11.0-15.0	3.0-4.0				Bal		
Type 316L	S31603	<0.03	16.0-18.0	10.0-14.0	2.0-3.0				Bal		
Type 317L	S31703	<0.03	18.0-20.0	11.0-15.0	3.0-4.0				Bal		
Type 310Nb	S31040	<0.08	24.0-26.0	19.0-22.0			Nb+Ta 1.10 ≥10x%C		Bal		
Type 329Mod	S32950	<0.03	26.0-29.0	3.5-5.2	1.0-2.5				Bal		N 0.15-0.35
1815LCSi	S30600	<0.018	17.0-18.5	14.0-15.5					Bal		Si 3.70-4.30
Alloy 20 Nb3	N08020	<0.07	19.0-21.0	32.0-38.0	2.0-3.0	3.0-4.0	≥8x%C		Bal		
Alloy C276	N10276	<0.02	14.5-16.5	Bal	15.0-17.0				4.0-7.0		Co <2.5 W 3.0-4.5
Alloy G30	N06030	<0.03	28.0-31.0	Bal	4.0-6.0	1.0-2.4	0.30-1.50		13.0-17.0		W 1.5-4.0 C0 <5.0
Alloy 690	N06690	<0.05	27.0-31.0	≥58.0					7.0-11.0		
Alloy 800	N08800	<0.10	19.0-23.0	30.0-35.0				0.15-0.60	Bal	0.15-0.60	
Alloy 825	N08825	<0.05	19.0-23.5	38.0-46.0	2.5-3.5	1.5-3.0		0.60-1.20	Bal		
Type 430	S43000	<0.12	16.0-18.0						Bal		
Type 446Mod	S44627	<0.01	25.0-27.0		0.75-1.5		0.05-0.20		Bal		
Silicon Iron	F47003	0.70-1.10							Bal		Si 14.2-14.75
1100 Aluminium	A91100					0.05-0.20				≥99.0	
3003 Aluminium	A93003					0.05-0.20				≥97.5	Mn 1.0-1.5

*Unified Number System

Nitric Acid Production

Nitric acid is almost always made by mixing gaseous ammonia with air, converting it to nitric oxide (NO) in a reactor over a platinum-rhodium catalyst at 800°C to 950°C, and further oxidizing the NO to NO₂. The nitric oxide is passed through an absorber column for conversion to 60%-65% HNO₃, which is bleached with air and sent to storage. Off-gas from the bleaching operation is recycled to the absorber. Some details of the plant layout may vary, but the basic design is imposed by the nature of the process. *Figure 1* is a schematic diagram of a typical plant.

The azeotrope of HNO₃ and water at atmospheric pressure is 67% HNO₃. Higher concentrations of acid—90% to 100%—are produced by distilling the dilute acid with a dehydrating agent, e.g., concentrated sulphuric acid, and condensing the fuming nitric acid vapors from the dehydration tower overhead.

Materials Selection

Common Stainless Steels

Nitric acid is a very strong oxidizing medium, and therefore, chromium content plays an extremely important role in corrosion resistance of stainless steels and nickel alloys. The most widely used grades of stainless steel for nitric acid are the low-carbon or stabilized austenitic grades: Type 304L (S30403), Type 321 (S32100), and Type 347 (S34700). They are resistant to corrosion over a wide range of temperatures and concentrations up to 60% HNO₃ at the atmospheric boiling point. Stainless steels with higher levels of carbon,

such as Type 304 (S30400), that are not stabilized are subject to intergranular attack in nitric acid at the heat-affected zone near welds as a result of sensitization due to the precipitation of chromium carbides at the grain boundaries.

Molybdenum additions, found in Types 316 (S31600), 317 (S31700), 316L (S31603), and 317L (S31703), are generally considered to improve the resistance of stainless steels to acid corrosion. However, in nitric acid, Type 304L generally performs better than the molybdenum grades because the molybdenum tends to promote the formation of sigma phase, which is less resistant to nitric acid attack. Except in mixed acids or contaminated nitric acid containing halides, Type 304L is preferred to Type 316L for nitric acid service on the basis of both cost and corrosion resistance.

Table II shows some of the locations where Type 304L stainless steel and the stabilized stainless steels are being used as materials of construction in a nitric acid plant. *Figure 2* shows an isocorrosion diagram for Type 304L stainless steel in nitric acid.

Special Stainless Steels

Selective corrosion along grain boundaries can occur when stainless steels are exposed to strong nitric acid at elevated temperatures. Type 304L can be optimized with extremely low carbon and low silicon, phosphorus, and sulphur residuals to be extremely resistant to intergranular corrosion after sensitization. Sometimes called Type 304L Special, it is electroslag refined to obtain the low levels of non-metallic residuals and optimum microstructure.

Type 310 stainless steel (S31000) with low carbon or

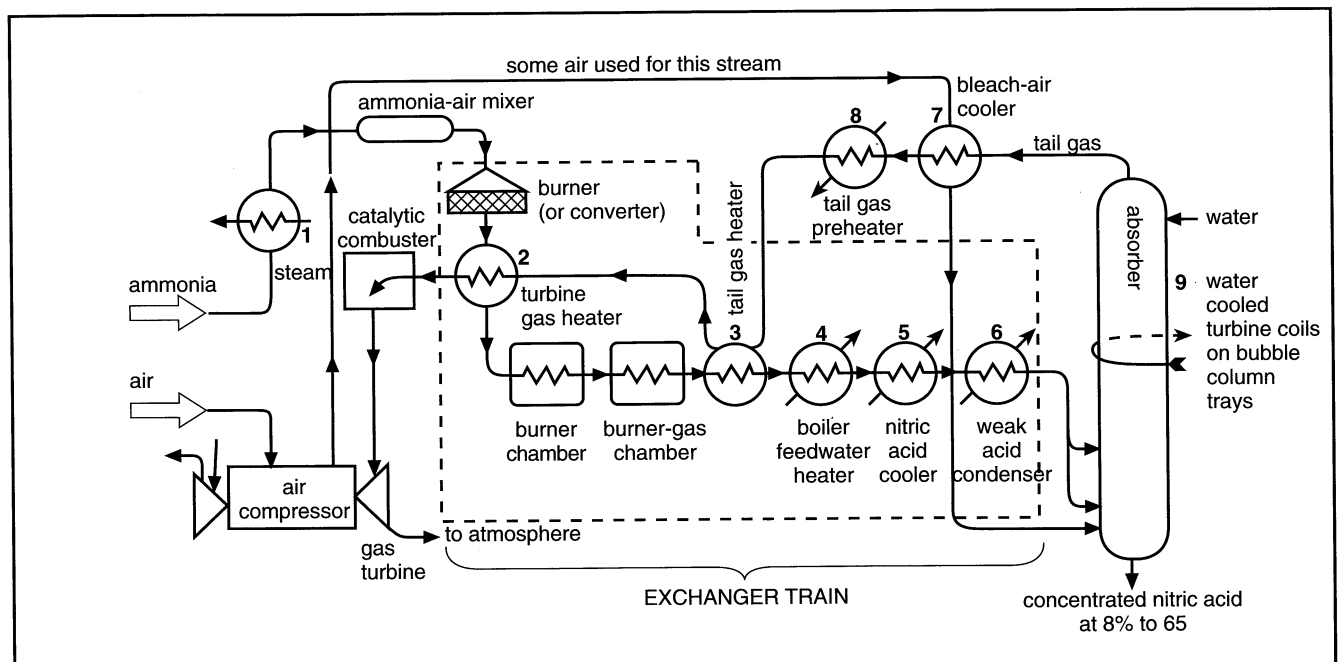


Figure 1 Flow diagram of nitric acid plant.

stabilized with niobium, is more resistant than Type 304L Special to corrosion by nitric acid up to 67% because of its higher chromium content. Again, the composition and microstructure are optimized. These optimized grades of Types 304L and 310L are often referred to as "nitric acid grades of stainless steel."

Type 329 duplex stainless steel (S32950) has provided excellent service in nitric acid tube-side and shell-side cooler condensers operating at low to intermediate temperatures. The alloy also offers useful resistance to chloride stress-corrosion cracking (SCC). Its use is restricted to temperatures below 260°C.

Elements other than chromium can influence the rate of scale formation in nitric acid under constant temperature conditions. A proprietary grade known as 1815LCSi (S30600) contains 4% silicon and is remarkably effective in resisting nitric acid above 95% HNO₃. This alloy is used for piping systems and equipment for reactions involving highly concentrated nitric acid at temperatures up to the boiling point. Several other proprietary stainless steels containing 5% or 6% silicon are available and used for even more severe conditions in concentrated acid.

Figure 3 shows isocorrosion rate curves of 0.1 mm/yr for the special stainless steels: 304LSp, 310LSp, and 1815LCSi in nitric acid.

Iron-Nickel-Chromium Alloys

Higher alloy materials such as Alloy 20 Nb-3 (N08020), Alloy C276 (N10276), Alloy G-30 (N06030), Alloy 690 (N06690), Alloy 800 (N08800), and Alloy 825 (N08825)

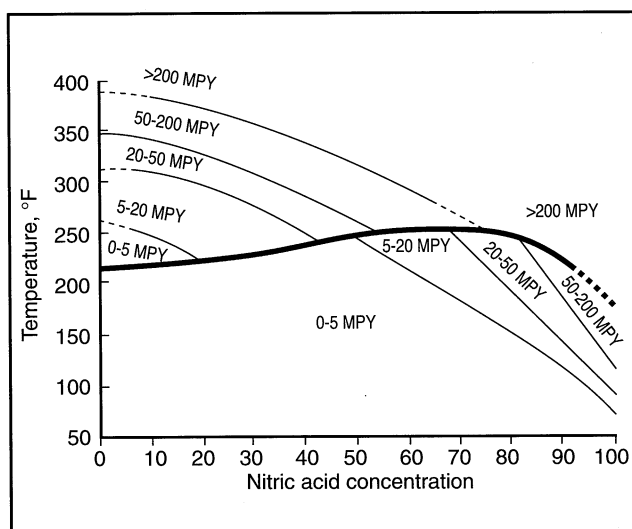
Table II **Stainless steels in nitric acid manufacture.**

Service	Preferred Material	
Absorption tower	all 304L	
Ammonia to mixer	304L	
Ammonia converter	347	
65% acid storage	304L	
Acid mixing tank	304L	
Acid concentrator	304L	
Storage, 95 Wt%	304L	
Piping	304L	
Shipping	304L	
	Shell	Tubes
Ammonia evaporator	steel	304L
Ammonia superheater	steel	304L
Tail gas heater	304L	304L
Tail gas preheater	steel	304L
Boiler feedwater heater	steel	304L
Weak acid condenser	304L	304L
Turbine gas heater	321/347	321/347
Nitric gas cooler	steel	304L
Bleach air cooler	steel	304L

Sources: Crooks (1986) and Newman and Miller (1967).

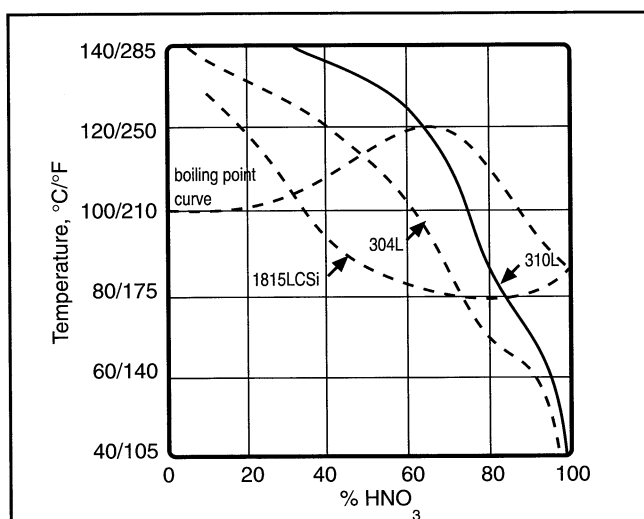
sometimes are used for specific applications in nitric acid environments, but the less expensive austenitic stainless steels are usually more economical and just as good. Some conditions in which higher alloys are useful include high velocity, mixed acids, or contaminated nitric acid.

Tubular equipment, such as acid coolers and cooler condensers are sometimes problem areas in nitric acid plants. The cooling media on the water side may contain chlorides and cause SCC in the austenitic stainless steels. Cooler condensers may present additional problems if the design allows condenser acid to migrate to warmer portions of the condenser where it can re-evaporate. Alloy 690 or G-30 may be useful.



Source: Fontana and Greene, 1967.

Figure 2 Isocorrosion diagram for AISI Type 304L stainless steel in nitric acid.



Source: Sandvik Steel Company, 1985.

Figure 3 Diagram showing isocorrosion in nitric acid for AISI 304L, 310L and 1815LCSi at a corrosion rate of 0.1 mm/yr (4 mpy).

Alloys Containing No Nickel

The presentation would not be complete without a comment on some metals and alloys that do not contain nickel but which can sometimes be used with nitric acid.

There are applications for the ferritic stainless steels such as Type 430 (S43000) and a low-interstitial modification of Type 446 (S44625). Both alloys are more difficult to fabricate than the austenitic stainless steels, and both have experienced failures due to crevice corrosion. Their main application is in piping and heat exchanger tubing.

Alloy F47003, a 14% silicon iron, is very resistant to nitric acid with greater than 50% HNO_3 . Its main application is in castings.

Aluminum alloys are good for "fuming" nitric acid at concentrations from 86% to 100% HNO_3 at ambient temperatures. Any dilution of the acid will cause accelerated attack. Aluminum alloys A91100 and A93003 are frequently used for storage tanks of concentrated nitric acid above 95% HNO_3 . Type 304L stainless steel is used for lower concentrations. The effect of nitric acid concentration on the corrosion rate of aluminum and stainless steel is shown graphically in *Figure 4*.

Titanium can be used with most concentrations of nitric acid at room temperature, but as temperature increases, the corrosion rate increases, particularly in the range between 20% and 60% HNO_3 . Titanium is never used with red fuming nitric acid because a pyrophoric reaction can occur. In acid solutions above 90% HNO_3 , titanium can be subject to stress-corrosion cracking.

Zirconium is resistant to nitric acid at all concentrations up to the boiling point, and it is frequently

used to solve the cooler-condenser corrosion problems mentioned above if design adjustments cannot be made. Zirconium is also used to overcome vapor-phase corrosion, which can be severe in acid reboiler tubing. Zirconium can be subject to stress-corrosion cracking in nitric acid in concentrations above 20% HNO_3 .

Industrial Applications for Nitric Acid

There are a number of major markets for nitric acid, all requiring facilities for storage and handling. It is good engineering practice to use Type 304L stainless steel for storage tanks, tank trucks, rail cars, piping, valves, and pumps.

Nitric acid is used in the production of acrylonitrile textile fibers (nylons), dyestuffs, and high explosives. Type 304L is widely used for production equipment in each of these. In nuclear fuel processing, Alloy 825 and Alloy 690 are used to handle solvents for dissolving fuel elements of uranium and uranium oxide together with their cladding elements. These solvents include nitric acid up to 45% HNO_3 at the boiling point, sulphuric acid, and caustic soda.

Mixtures of acids are frequently encountered in chemical and metallurgical processes. A mixture of nitric and hydrofluoric acids is used in the pickling of stainless steel to remove oxide films due to heat treating and to remove embedded iron left as a residue from fabrication. Type 304L stainless steel is usually inadequate for this service and exhibits a corrosion rate typically about 25 mm per year (1000 mils per year). Alloy 690 exhibits a corrosion rate of about 0.25 mm per year (10 mils per year) and can be used for heating coils in this corrosive acid mixture.

Stainless steels may exhibit marginal corrosion performance in sulphuric acid solutions up to 60% H_2SO_4 . The addition of 0.5% to 1.5% of nitric acid often restores passivity to Type 316L stainless steel or Alloy 20 in sulphuric acid and acts effectively as a corrosion inhibitor. Stainless steels are not recommended for mixtures of nitric and hydrochloric acid in which the chloride ion induces high corrosion rates and pitting of stainless steels. Below 10% hydrochloric acid concentration in nitric acid, Alloy C22 and Alloy G30 exhibit low corrosion rates.

The largest industrial application for nitric acid is in the fertilizer industry, where it is used for the production of ammonium nitrate and potassium nitrate. Type 304L stainless steel is the preferred material for mixers, evaporators, crystallizers, pumps, piping, and tanks. The nitrate is frequently stored in concentrated solutions of 83% or 92% at 85°C. Alloy 800 or Type 329 stainless steel are sometimes used in heat exchangers where one might be concerned about SCC.

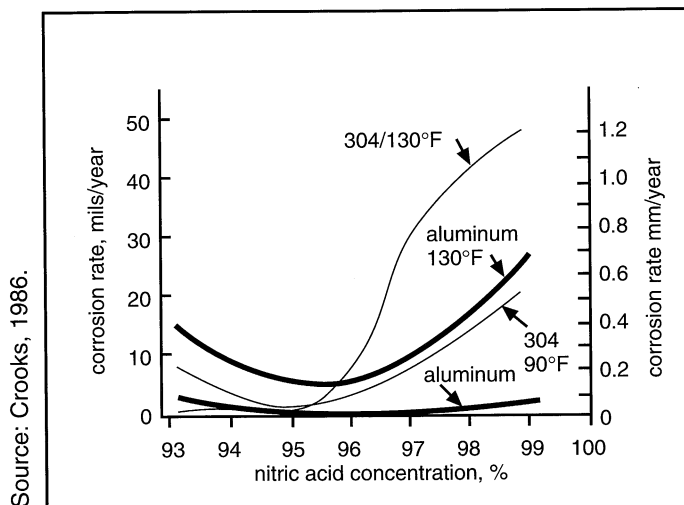


Figure 4 Corrosion rate of aluminum A93003 and stainless steel S30400 in concentrated nitric acid.

SUMMARY

Because of the strong oxidizing conditions, the stainless steels are able to handle most of the conditions encountered in the production of nitric acid and in its industrial applications. Type 304L stainless steel is the most widely used and is capable of handling nitric acid over a wide range of temperatures and concentrations up to about 60% at the atmospheric boiling point. For more severe conditions, special nitric acid grades of Types 304L and 310L containing low carbon and non-metallic residual elements have been developed for even greater resistance to intergranular corrosion at heat-affected zones near welds.

Several nickel iron-nickel-chromium alloys are used in nitric acid under extreme conditions, in mixed acids, or in contaminated nitric acid where stainless steels are inadequate.

Figure 5 is a summary chart to serve as a guide for alloy selection.

Readers seeking more information on any of the subjects covered by this article should refer to the Bibliography.

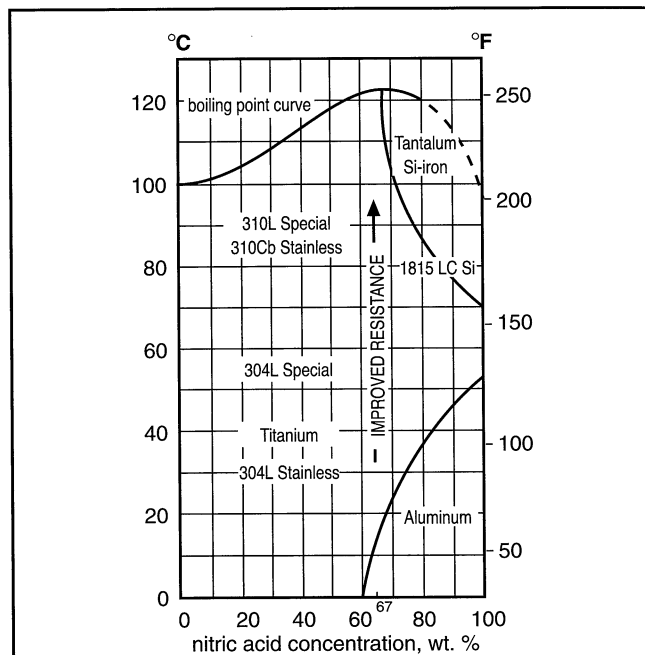


Figure 5 Nitric acid selection guide.

Source: Schillmoller and Althoff, 1982.

BIBLIOGRAPHY

"Corrosion by Nitric Acid", NACE Publication 5A256, *Corrosion*, June 1956

"Handling Nitric Acid", *Chemical Engineering*, Nov 11, 1974, pp 129-132

Product Information on Stainless Steel for the Nitric Acid Industry, Vereinigte Edelmetalle Werke, TOK31/08.82

Sandvik Stainless Steel Products Manual for the Process Industries, Sandvik Steel Company, Tubular Products Division, May 1985

R. D. Crooks, "Materials of Construction for Nitric Acid", *Process Industries Corrosion*, Houston TX, 1986

G. L. Delaney and T. F. Lemke, "Corrosion resistance of Nickel Alloys in Aqueous Environments", *Corrosion Australasia*, Vol 6, pp 4-6, 1981

C. P. Dillon, "Corrosion of Type 347 Stainless Steel and 1100 Aluminum in Strong Nitric and Mixed Nitric-Sulfuric Acids", *Corrosion*, Vol 12, No 5, 1957

C. P. Dillon, "Corrosion of Stainless Steels by Nitric Acid", *Materials Protection*, July 1992

M. G. Fontana and N. D. Greene, *Corrosion Engineering*, McGraw Hill, 1967

T. Gladman, "A Nitric Acid Grade (NAG) Type 304L Austenitic Stainless Steel", *Materials Protection*, Feb 1989

G. Hochoertler and E. M. Horn, "Improvements of Si-bearing Austenitic Stainless Steels for Applications Involving Highly Concentrated Nitric Acid", A Bayer Report, 1982

J. Husbands and P. K. Whitcraft, "High-Chromium Duplex Stainless Steel for Nitric Acid Production", *Materials Protection*, July 1992

M. J. Johnson, J. R. Kearns, and H. E. Deverell, "The Corrosion of the New Ferritic Stainless Steels in Nitric Acid", *Corrosion/84*, Paper 144, NACE, 1984

R. Kirchheiner, U. Heubner, and F. Hoffmann, "Increasing the Lifetime of Nitric Acid Equipment Using Improved Stainless Steels and Nickel Alloys", *Corrosion/88*, Paper 318, NACE, 1988

M. Kobayashi et al, "Development of Nitric Acid Resistant Stainless Steels", *Corrosion/84*, Paper 145, NACE, 1984

A. Kratzer et al, "A low Carbon Stainless Steel for Use in Nitric Acid at Higher Concentrations and Temperatures", *International Conference on Metallic Corrosion*, Vol 1, June 1984

D. W. McDowell, "Handling Mixed Nitric and Sulfuric Acids", *Chemical Engineering*, Nov 11, 1974, pp 133-135

D. J. Newman and R. Miller, "Making Nitric Acid in All-Stainless Plants", *Chemical Engineering*, July 31, 1967

C. M. Schillmoller and J. Althoff, "High Technology Stainless Steels for the Fertilizer Industry", *Fertilizer Industry Annual Review*, 1982

N. Sridhar, J. B. C. Wu, and S. M. Corey, "The Effect of Acid Mixtures on Corrosion of Nickel-Base Alloys", *Corrosion/86*, Paper No. 182, NACE, 1986

M. W. Wilding and B. E. Paige, "Survey on Corrosion of Metals and Alloys in Solutions Containing Nitric Acid", ERDA ICP-1107, December 1976

**The Nickel
Development
Institute is
an international
nonprofit
organization
serving the needs of
people interested
in the application of
nickel and
nickel-containing
materials.**

Members of NiDI

Companhia Níquel Tocantins
Empresa de Desenvolvimento
de Recursos Minerais "CODEMIN" S.A.
Falconbridge Limited
Inco Limited
Morro do Níquel S.A.
Nippon Yakin Kogyo Co., Ltd.
Outokumpu Oy
P.T. International Nickel Indonesia
Pacific Metals Co., Ltd.
QNI Limited
Sherritt Inc.
Shimura Kako Company, Ltd.
Sumitomo Metal Mining Co., Ltd.
Tokyo Nickel Company Ltd.
Western Mining Corporation Limited

North America

Nickel Development Institute
214 King Street West - Suite 510
Toronto, Ontario
Canada M5H 3S6
Telephone 1 416 591-7999
Fax 1 416 591-7987

Europe

Nickel Development Institute
42 Weymouth Street
London, England W1N 3LQ
Telephone 44 171 493 7999
Fax 44 171 493 1555

Nickel Development Institute
European Technical Information Centre
The Holloway, Alvechurch
Birmingham, England B48 7QB
Telephone 44 152 758 4777
Fax 44 152 758 5562

Japan

Nickel Development Institute
11-3, 5-chome, Shimbashi
Minato-ku, Tokyo, Japan
Telephone 81 3 3436 7953
Fax 81 3 3436 7734

Central & South America

Nickel Development Institute
c/o Instituto de Metais Não Ferrosos
Av. 9 de Julho, 4015, 01407-100
São Paulo-SP, Brasil
Telephone 55 11 887 2033
Fax 55 11 885 8124

India

Indian Nickel Development Institute
c/o India Lead Zinc Information Centre
Jawahar Dhatu Bhawan
39 Tughlaqabad Institutional Area
Mehrauli-Badarpur Road
New Delhi 110 062, India
Telephone 91 11 698 0360
Fax 91 11 698 9522

Australasia

Nickel Development Institute
P.O. Box 28, Blackburn South
Victoria 3130, Australia
Telephone 613 9878 7558
Mobile 61 18 346 808
Fax 613 9894 3403

South Korea

Nickel Development Institute
Olympia Building, Room 811
196-7 Jamsilbon-Dong, Songpa-Ku
Seoul 138 229, South Korea
Telephone 82 2 419 6465
Fax 82 2 419 2088