NATIONAL METAL DISTRIBUTORS, INC.

Suppliers of acid, corrosion, heat and wear resistant alloys

Super Duplex Stainless Steel
UR52N+ (255)

Duplex Stainless Steel
UR45N+ (2205)

Contents

UR52N^{+} - ALLOY 255

TECHNICAL SPECIFICATIONS

URANUS® 52 N$^+$

A 25 Cr Super Duplex stainless steel with PREN ≥ 40

URANUS 52N$^+$ (UR 52N$^+$) is a super duplex stainless steel with 25% Cr and a PREN value higher than 40. The minimum guaranteed yield strength is 550 MPa which allows the designer to reduce weight. The molybdenum and nitrogen additions have been optimized in order to obtain the best corrosion resistance properties even for heavy plates. High nitrogen content improves the structure stability particularly in HAZ. Its corrosion resistance is much better than UR B6/N08904 and roughly equivalent to 6 Mo super austenitic alloys.

Copper additions increase the corrosion resistance properties, particularly in sulphuric acid media.

URANUS 52N$^+$ is a cost efficient grade designed for offshore, marine, phosphoric acid, sulphuric acid applications... as well as pollution control equipments.

STANDARDS

EURONORM .... 1. 4507 - X2 Cr Ni Mo Cu N 25.6.3
AFNOR.. Z3 CNDU 25.07 AZ
ASTM. .... UNS S32550/S32520

CHEMICAL ANALYSIS

Typical values (Weight %)

C	Cr	Ni	Mo	N	Others
< 0.030	25	6.5	3.5	0.25	Cu ≥ 1.5
PREN = [Cr %] + 3.3 [Mo %] + 16 [N %] ≥ 40					

MECHANICAL PROPERTIES

Tensile properties - minimum values

°C	Rp 0.2 MPa	Rp 1.0 MPa	Rm MPa	°F	YS 0.2% KSI	YS 1.0% KSI	UTS KSI	El %
20	550	570	770	*68*	78	83	111	25
100	485	500	700	*212*	70	72	102	25
250	400	420	640	*500*	57	61	92	25

Typical temperature range of use : -50°C/+ 270° C (*-58°F /+518°F*)
For lower temperature applications, please contact us.

Impact strength (KV typical values)

	-50°C (-58°F)	-20°C (-4°F)	0°C (32°F)	20°C (68°F)
KV plates (guaranteed)	> 70 J	> 85 J	> 90 J	> 95 J
KV weld metal (typical)	> 30 J	> 40 J	> 50 J	> 55 J

Impact values of welds are closely related to the microstructure (α / γ balance) and the control of chemical analysis (oxygen, nitrogen, nickel) which depend on welding processes and parameters. The best results are obtained for high austenite contents (75-60 %) and low oxygen levels. High nitrogen contents associated with high ferrite levels must be avoided. For more information, please contact us.

Hardness values - Typical values

HV_5 : 250 to 280 HRC < 28

PHYSICAL PROPERTIES

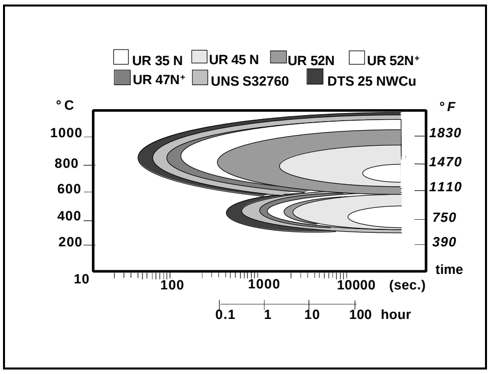
Density : 7,820 kg/m^3 - 0.28 lb/in^3

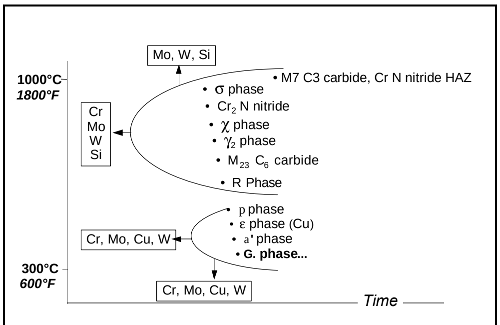
Interval Temper °C	Thermal expansion αx10^{-6}K^{-1}	°C	°F	Resistivity (μΩ cm)	Thermal conductivity (W.m^{-1}.K^{-1})	Specific heat (J.kg-1.K^{-1})	Young modulus E (GPa)	Shear modulus G (GPa)
20-200	13.5	**20**	**68**	85	17	450	200	75
20-300	14	**100**	**392**	95	18	500	190	73
20-500	14.5	**200**	**392**	100	19	530	180	70

STRUCTURE STABILITY

25 Cr super duplex grades are subject to intermetallic phase precipitations (σ, χ...) particularly when improperly heat treated. Higher molybdenum and tungsten additions increase the sensitivity to sigma phase transformation. CLI equipments and heat treatments are optimised in order to control the composition, structure and properties of the products. We use a batch furnace to control time and temperature for each individual plate. This makes CLI duplex quality. The microstructure free of intermetallic phases contributes to an increase of both toughness properties and corrosion resistance properties.

Nitrogen additions have been increased compared to the former UR 52N grade (0.18→0.25%) in order to increase both corrosion resistance properties and structure stability, particularly in HAZ.





Possible precipitations in super duplex stainless steels

Heat treatment :

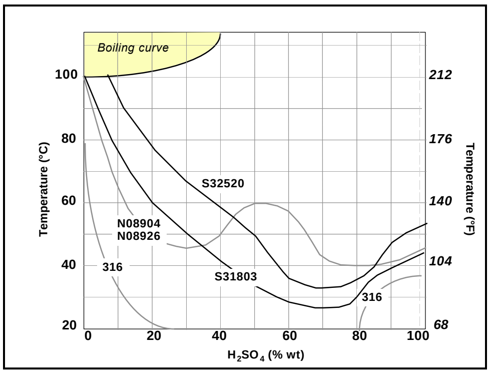
UR 52N+ is delivered in the solution annealed and water quenched conditions (1080/1120°C - *1976/2018°F*). The chemical analysis and heat treatment are optimised in order to reach a 50% α / 50% γ microstructure.

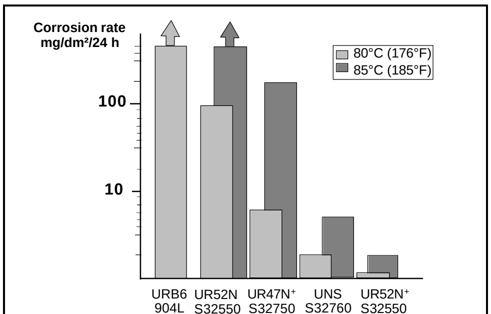
CORROSION RESISTANCE

General corrosion

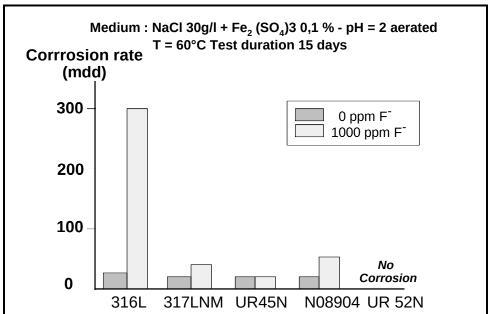
UR 52N+ performs particularly well in sulphuric and phosphoric acid solutions, even in presence of chlorides. The duplex microstructure which provides high mechanical properties explains why the alloy behaves particularly well in abrasion-corrosion conditions (agitators, screws, rakes...).

Mixed acids are often associated with chlorides and in pollution control equipments. Due to high chromium, molybdenum and copper additions, UR 52N+ behaves well in scrubber systems. In Pulp and Paper industries, UR 52N+ is used in the most severe conditions encountered for example in digester (resistant to hot wall problems), chips presteaming vessels or in some bleaching equipments.

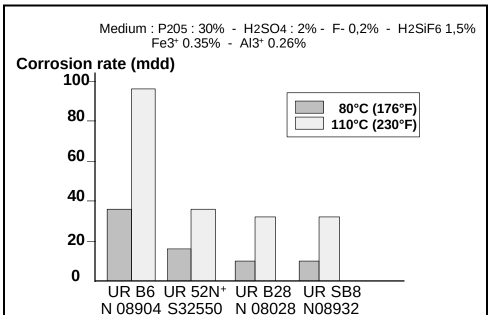




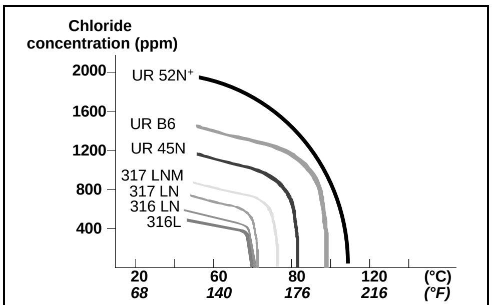
Corrosion rate in 10% H_2SO_4 + 500 ppm Cl^- aerated, at 80°C and 85°C (176°F and 185°F)



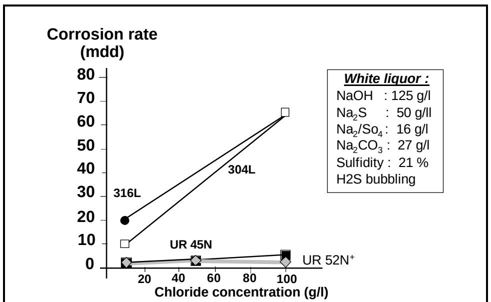
Pollution control equipments
Effects of fluoride contents on the uniform corrosion rate



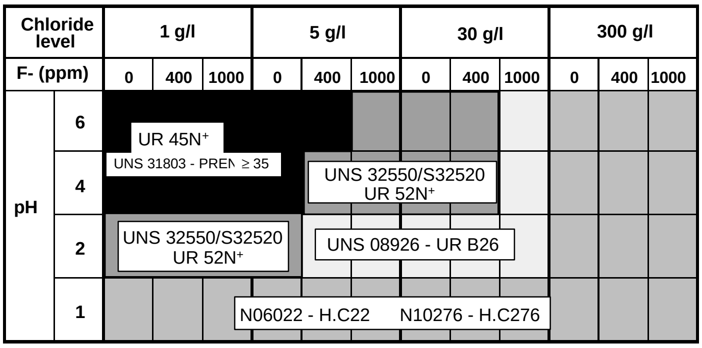
Phosphoric acid production
Effect of the attack temperature on the corrosion rate



Safe use limits of stainless steels versus chloride content and temperature in 54 % P205



Heat transfer (solution 140°C - Sample 80°C)
Pulp and Paper industry
Corrosion rate versus chloride content in Kraft media

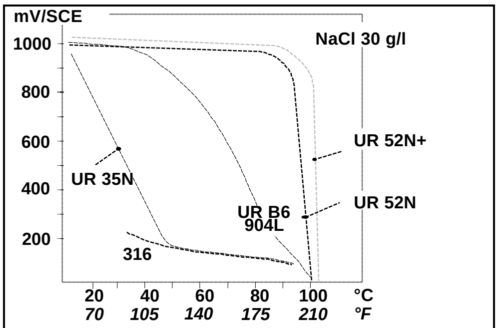


MATERIAL GUIDE FOR USING IN FGD EQUIPMENTS - 60°C (140°F)

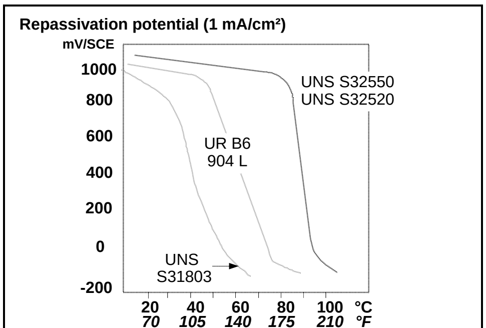
Based on extensive tests results

Pitting and crevice corrosion

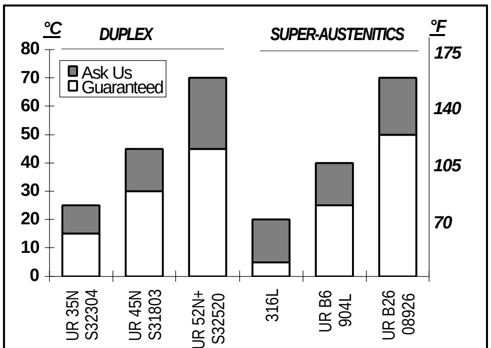
The minimum PREN value of 40 also explains why the alloy is highly resistant to pitting corrosion and crevice corrosion. The alloy behaves much better than 904L and is, for pitting corrosion resistance, nearly equivalent to 6 Mo super γ grade. In some cases, the crevice corrosion resistance is slightly higher than 6 Mo alloys due to the 25% Cr additions.



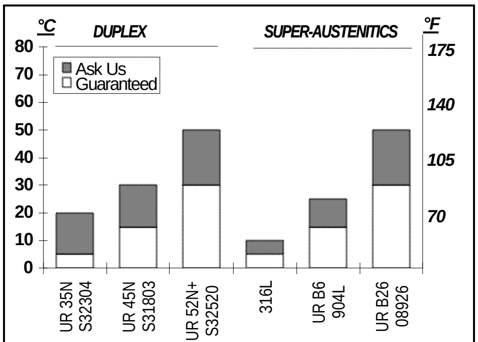
Pitting potential taken from polarization curves for different stainless steels



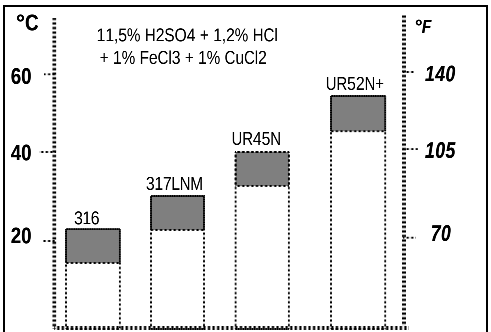
Repassivation potential in 15% NaCl solution CO_2 saturated



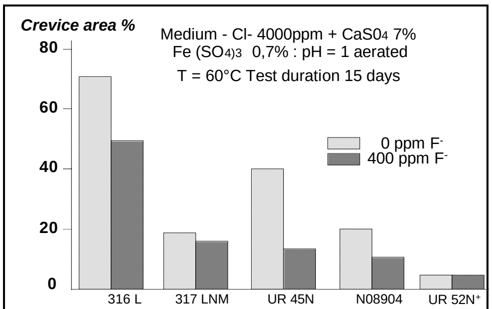
Test ASTM G48A PITTING in a 6% $FeCl_3$ solution



Test ASTM G78 CREVICE in a 6% $FeCl_3$ solution



GREEN DEATH - CRITICAL PITTING TEMPERATURE

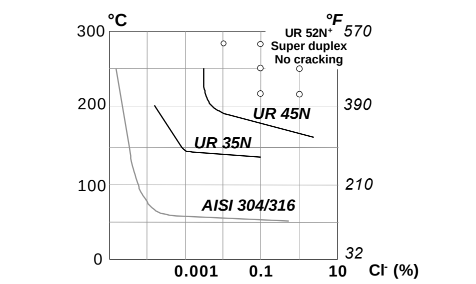


Pollution control equipments
Crevice corrosion test on samples fitted with multi-crevice washers - effect of fluoride content

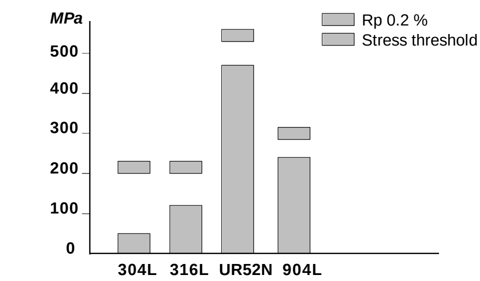
Stress corrosion cracking resistance

The stress corrosion resistance properties of URANUS 52N+ is excellent in high temperature chloride containing solutions as well as in sour gas applications.

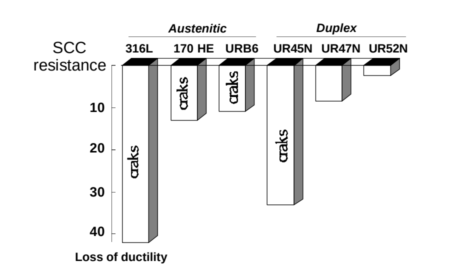
FABRICATION



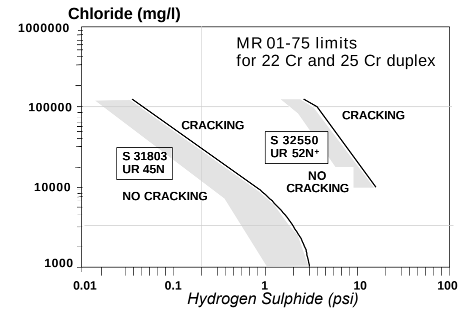
Constant-strain tests in autoclave
Above the curve, SCC occurs.
Open circles means no SCC for UNS 32550/UR 52N+



Stress corrosion cracking in chloride media :
300 g/l NaCl - T = 110°C - pH = 1
Threshold stress without crack after 1 month



Slow strain rate tests (10^{-6}/sec) in NaCl, 40% pH=2 (HCl), 110°C - Elongation in air - Elongation in corrosive medium



Suggested limits for Duplex
and Super duplex stainless steels

Cold forming

Due to its higher mechanical properties, the cold forming of UR 52N+ requires more strength than austenitic grades. For cold deformations higher than 20 %, an intermediate heat treatment is required (solution annealing 1080/1120°C (*1976/2018°F*) + water cooling).

Detailed guidelines for cold forming of unwelded and welded plates are available upon request.

Hot forming

Between 1150°C and 1000°C (*2102 and 1832°F*). After hot forming, a new solution annealing heat treatment in the range 1080/1120°C (*1976/2018°F*) + water cooling is necessary.

Pickling

Same conditions as for 316L grade, but the pickling time is at least twice that of 316L grade. An increase of the temperature of the pickling bath reduces the pickling time.

WELDING

URANUS 52N+ can be welded using the following processes : SMAW, GTAW (with filler), GMAW, PAW (with filler).

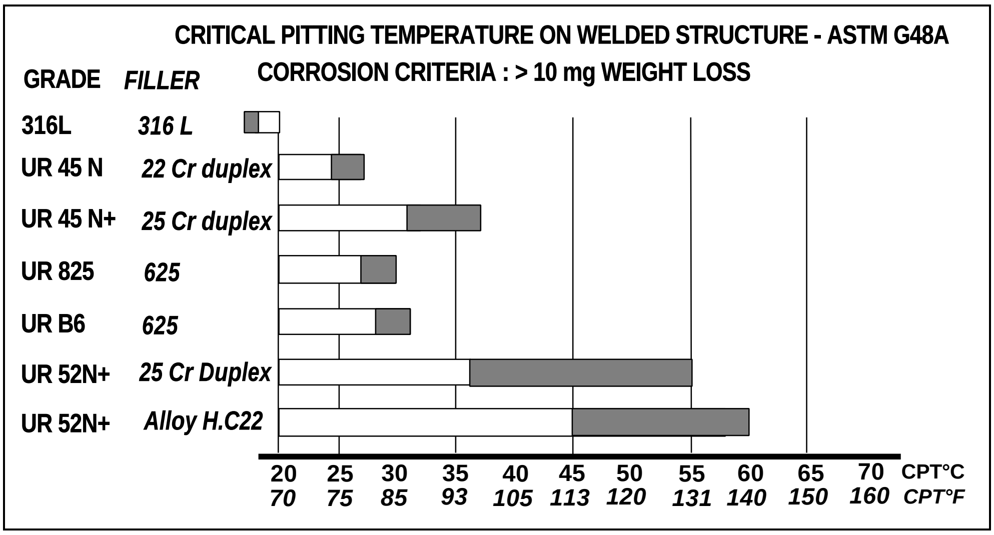
The welding procedures are similar to those of other duplex stainless steels :

- no pre-heating,
- heat input between 0.5 KJ/mm and 2 JK/mm is recommended (depending on the process and on the thickness of the plate). Precise welding parameters for each type of process and thicknesses are available on request.
- interpass temperature less than 150°C (*302°F*) and preferably less than 120°C (*248°F*)
- no PWHT, except solution annnealing at 1080/1120°C (*1976/2048°F*) + water cooling.

As in welded conditions, the ferrite ratio in the heat affected zone should be lower than 70% between 20 to 60% for the weld metal ; for SMAW, FCAW and SAW weld metal aim for the lower part of the range (20 to 40%).

In order to control the structure and properties, over alloyed filler materials are recommended (nickel and/or nitrogen additions). Excessive dilutions must be avoided.

Filler materials and shielding gases guaranteeing PREN > 40 have been developed (wire, metallic cored wire, electrodes) - a list of tested filler materials is available on request.



Corrosion resistance properties of welded structures are very dependant on welding parameters and surface condition. Avoid oxyde scales or contaminations. Brushed or pickled welds perform better. The best results are obtained for solution annealed welds. The use of nickel based weld consumables allow to increase the corrosion resistance of welded structures (avoid 625 alloys but use Nb free grades like H.C22 or SG Ni Cr 23 Mo 16 or PHYWELD NCM (Nb free 625).

DESIGN

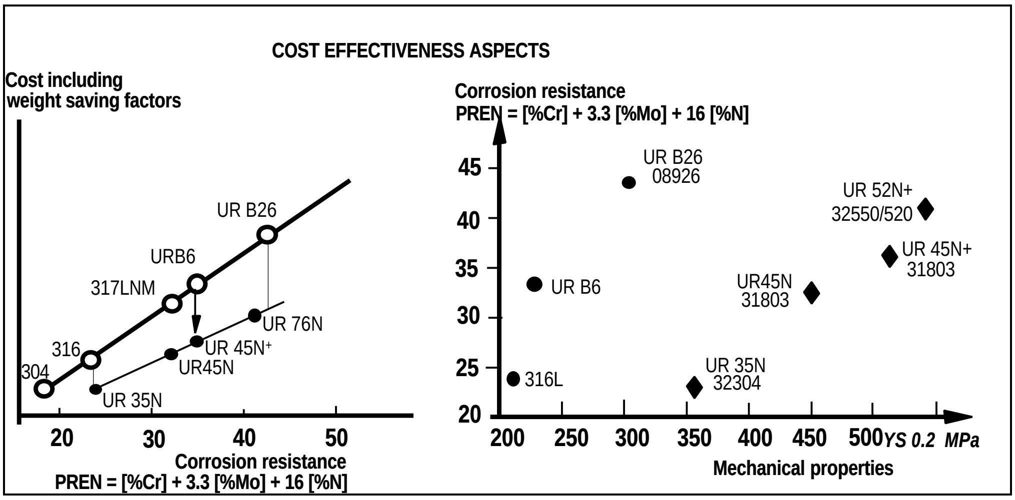
Cost factor considerations

Maximum allowable stresses given by several pressure vessel codes are shown here. The high mechanical properties of URANUS $52N^+$ allow thickness and, consequently, cost reductions..

We are happy to offer assistance in evaluating potential cost savings related to pressure vessel or structural design and the excellent corrosion resistance properties of UR 52N+.

Design stress values (Typical values)

Country	Code	Room temperature (MPa)				Saving factors
		316	UR 45N 31803	UR B6 904L	UR $52N^+$ 32550/520	UR$52N^+$/ URB6
USA	ASME VIII, DIV1	108	155	123	190	35 %
F	CODAP 90, f.1	166	275	176	287	38 %
UK	BS 5500	128	289	173	294	42 %
D	ADW 2	128	300	167	327	49 %



APPLICATIONS

- Seawater systems and applications (diving spheres...),
- Oil and gas Industry including sour gas applications,
- Petrochemical industry including PVC strippers,
- Pulp and paper industry (digesters, bleaching towers...),
- Chemical industry including organic acid applications,
- Sulphuric acid plants,
- Phosphoric acid plants,
- Truck-lorries multipurpose containers,
- Pollution control equipments (scrubbers),

...

SIZE RANGE

	Hot rolled plates	Cold rolled plates	Clad plates
Thickness	5 to 150 mm 3/16" to 6"	2 to 14 mm 5/64" to 5/8"	6 to 150 mm 1/4" to 6"
Width	Up to 3300 mm Up to 130"	Up to 2300 mm Up to 90.5"	Up to 3300 mm Up to 130"
Length	Up to 12000 mm Up to 472"	Up to 8250 mm Up to 325"	Up to 14000 mm Up to 551"

Other sizes are available on request, including 4100mm (161,5")width plates

NOTE

This technical data and information represents our best knowledge at the time of printing. However, it may be subject to some slight variations due to our ongoing research programme on corrosion resistant grades. We therefore suggest that information be verified at time of enquiry or order.

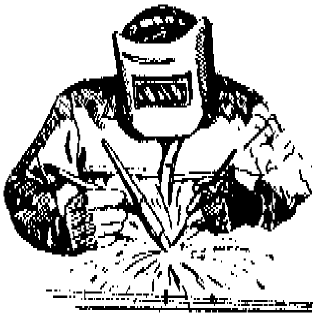
Furthermore, in service, real conditions are specific for each application. The data presented here is only for the purpose of description, and may only be considered as guarantees when our company has given written formal approval.Further information may be obtained from the following address.

For all information : NATIONAL METAL DISTRIBUTORS, INC.

P.O. Box 1499
Vancouver, WA 98668
Sales Tel (800) 878-3675
Fax (800) 878-9709

UR52N$^+$ - ALLOY 255

FORMING AND WELDING



URANUS 52N$^+$

FORMING and WELDING PROCEDURES

THE PRODUCT

UR 52N$^+$ is a super duplex stainless steel with 25 % Cr and a PREN value higher than 40. The minimum guaranteed yield strength is 550 MPa which allows the designer to reduce thickness of equipments.

The molybdenum and nitrogen contents have been optimized in order to obtain the best corrosion resistance properties even for the heaviest plates. Its high nitrogen addition improve the structure stability particularly in HAZ (Heat Affected Zone).

Copper addition increases the corrosion resistance, particularly in sulfuric acid media.

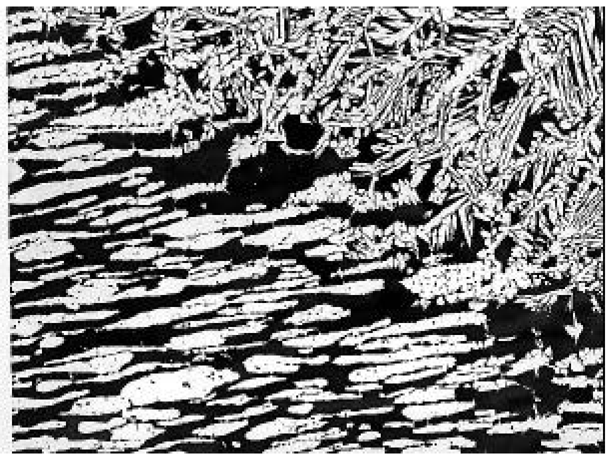
UR 52N$^+$ is a cost efficient grade designed for offshore, marine, phosphoric acid and pollution control equipments.

URANUS 52N$^+$ answers to the following standards :

EURONORM................ 1.4507 - X2 Cr Ni Mo Cu N 25.6.3
AFNOR........................ Z3 CNDU 25.07 AZ
DIN.............................. W. Nr 1.4507
ASTM.......................... UNS S32520

Chemical analysis of URANUS 52N

C	Cr	Ni	Mo	N	Others
.030	25	6.5	3.5	0.25	Cu ≥ 1.5
PREN = [Cr %] + 3.3 [Mo %] + 16 [N %] ≥ 40					

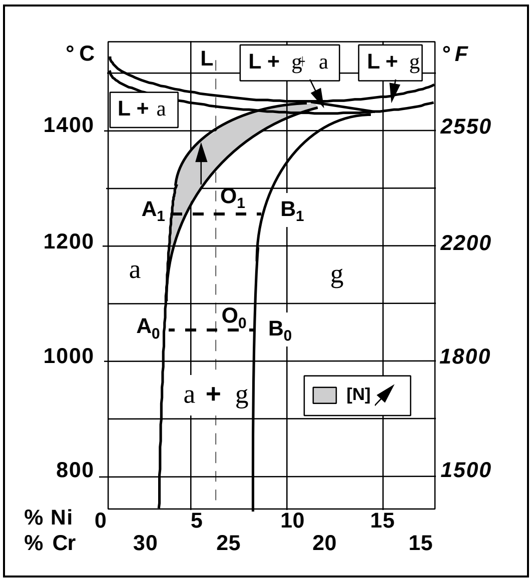


Microstructure of UR 52N$^+$ HAZ welded joint

METALLURGY

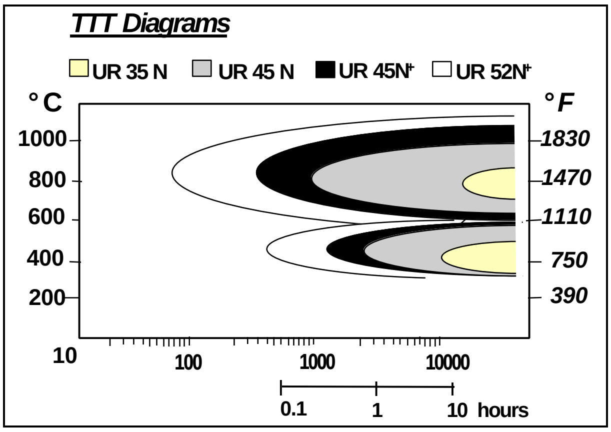
URANUS 52N+ has roughly equivalent volume fractions of ferrite and austenite (slightly more austenitic). This is obtained by work-hardening, followed by solution annealing + water quenching, and involves the simultaneous control of the chemical composition and annealing temperature. The figure shows a schematic isoplethal section of the Fe-Cr-Ni diagram, for an iron content of 68%. The proportions of each of the phases and their respective compositions are indicated for a given alloy analysis and annealing heat treatment.

The figure shows that the duplex microstructure solidifies in the ferritic phase and that the austenite forms only when the steel is cooling down. Over-heating (1150-1450°C - *2102-2642°F*) of a solution annealed, water quenched, plates (HAZ for example) of duplex steels may result in the formation of more ferrite which may retransform in austenitic when again cooling down. Too fast cooling rate may reduce this α-γ retransformation process and explain why welding consumables are over alloyed in nickel.

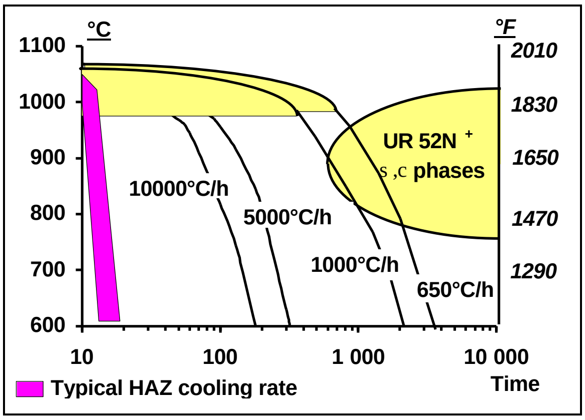


As regards the high temperature stability of the duplex structure, it is important to note the gamma stabilising action of nitrogen.

The TTT diagrams for the grades UR 35N, UR 45N, UR 45N+ and UR 52N+ here presented are conservative, and do not imply that the mechanical properties or corrosion resistance are modified as soon as the boundaries indicated are reached. This is particularly true for the low temperature ferrite hardening field. The TTT curves are mainly affected by molybdenum, chromium and tungsten additions.



Continuous cooling diagram shows that intermetallic phase transformation in duplex 52N+, and even more easily in UR 45N+ grade can be avoided by a control of the cooling rate which is obtained by a control of the heat input.



HOT FORMING

Hot forming is carried out between 1150 and 1000°C (*2102 - 1832°F*).
It should be kept in mind that ferritic-austenitic stainless steels have low strength at high temperatures. So, precautions must be taken to avoid possible deformations (wedging and support of pieces).

At temperatures below 1000°C (*1832°F*), embrittlement can appears due to intermetallic phase precipitations especially when material is strained.

After hot forming, a solution annealing heat treatment in the range 1080 - 1120°C (*1976 and 2018°F*) with water cooling is necessary.

COLD FORMING

Due to its higher yield strength, forces required for the cold forming of UR 52N$^+$ are more important than for austenitic steels.
Edges will be grinded and surfaces (absence of scratches...) will be checked before cold forming.

For cold deformations higher than 20 %, an intermediate treatment is required (solution annealing between 1080 and 1120°C (*1976 and 2018°F*) with water cooling). This heat treatment performed after cold forming is always required when the deformation exceeds 10%.

® ***Detailed recommendations for cold forming or bending of welded and unwelded duplex and super duplex plates are available upon request.***

MACHINING

Generally, the same technologies and tools can be used as for conventional stainless steels.

For drilling, high speed steel tools must preferently be used with a speed cutting of 10 to 15 m/min. The drilling speed depends on the hole diameter.

For machining with carbide tools, the cutting speed is the same as the cutting speed used for 316 L type austenitic steels.

Operation	Tool	Lubrication	CONDITIONS					
			Depth of cut		Feed		Speed	
			mm	*inch*	mm	*inch*	m/min	*feet/min*
Turning	High speed steel	Cutting oil	6	*0.23*	*0.5*	*0.019*	15-20	*49.2-65.6*
			3	*0.11*	0.4	*0.016*	23-28	*75.5-91.9*
			1	*0.04*	0.2	*0.008*	30-35	*98.4-114.8*
	Carbide	Dry or cutting oil	6	*0.23*	0.5	*0.019*	75-85	*246.1/278.9*
			3	*0.11*	0.4	*0.016*	90-100	*295.3-328.1*
			1	*0.04*	0.2	*0.008*	110-120	*360.9-393.7*
Parting off	High speed steel	Cutting oil	Blade width		Feed			
			1.5	*0.06*	0.03	*0.0012*	23-28	*75.5-91.9*
			3	*0.11*	0.04	*0.0016*	24-29	*78.7-95.1*
			6	*0.23*	0.05	*0.0020*	25-30	*82.-98.4*
Drilling	High speed steel	Cutting oil	Drill Ø		Feed			
			1.5	*0.06*	0.25	*0.0010*	10-14	*32.8-45.9*
			3	*0.11*	0.06	*0.0024*	11-15	*36.1-49.2*
			6	*0.23*	0.08	*0.0031*	11-15	*36.1-49.2*
			12	*0.48*	0.10	*0.0039*	11-15	*36.1-49.2*
Milling /profiling	High speed steel	Cutting oil			Feed			
					0.05/0.10	*.002/.0039*	12-22	*39.4-72.2*

HEAT TREATMENT

UR 52 N$^+$ is delivered in the solution annealed and water quenched conditions (1080/1120°C - *1976/2018°F*).

The chemical composition of UR 52N$^+$ is optimised in order to obtain after heat treatment nearly a 50 α / 50 γ microstructure.

These solution annealing conditions must be respected for final or intermediate heat treatment in case of forming and when a solution annealed or a stress relieved treatment is required after welding.

All other heat treatments, particularly the one with holding time or with slow cooling in 300 to 1000°C (*572-1832°F*) range must be avoided. Heat treatments at 400°C (*742°F*) used for dimensional stability of austenitic stainless steels are not acceptable for UR 52N$^+$.

WELDING

Welded joints preparation

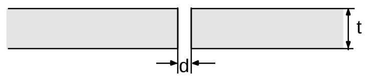
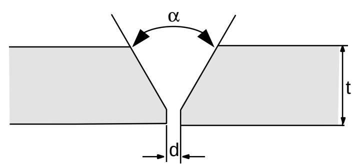
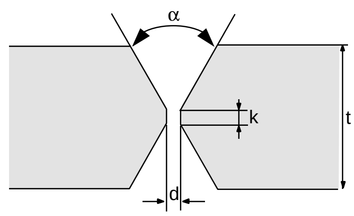
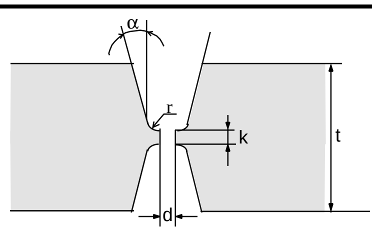
The joint must be designed in such a manner that the penetration weld could be realised without an excessive dilution of base meta or a Burn through. Groove type must be designed in order to have a good gaseous shielding protection (GTAW, GMAW, PAW, FCAW) ; a good accessibility for welding guns in the bottom of the joint must be obtained.

Some examples of welded joints preparation, are presented on the following tables which can be used for the butt welding of UR 52N$^+$ (different plate thicknesses).

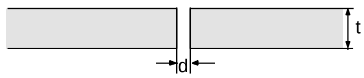
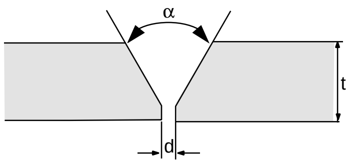
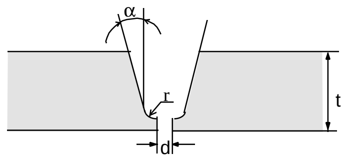
Grooving will be realised by machining or thermal cutting (oxy-acethylenic gas with iron powder or plasma) followed by grinding to eliminate oxyded and heat-affected zones.

As for all others stainless steels, the welding zone will be carefully cleaned with unchlorided solvent in order to eliminate grease or paint marks.

Joint design for Butt welding from both sides

GROOVE	**Process**	**Thickn. th(mm)**	**GAP d (mm)**	**ROOT k (mm)**	**BEVEL a (°)**
	GTAW	3 - 5	1 - 3	-	-
	GMAW	3 - 6	1 - 3	-	-
	SMAW	3 - 4	1 - 3	-	-
	SMAW	4 - 15	1 - 3	1 - 2	55 - 65
	GTAW	3 - 8	1 - 3	1 - 2	60 - 70
	GMAW	5 - 12	1 - 3	1 - 2	60 - 70
	SAW	9 - 12	0	5	80
	SMAW	> 10	1.5 - 3	1 - 3	55 - 65
	GMAW	> 10	1.5 - 3	1 - 3	60 - 70
	SAW	> 10	0	3 - 5	90
 R=6--8mm	SMAW	> 25	1 - 3	1 - 3	10 - 15
	GMAW	> 25	1 - 3	1 - 3	10 - 15
	SAW	> 25	0	3 - 5	10 - 15

Joint design for one-sided butt welding

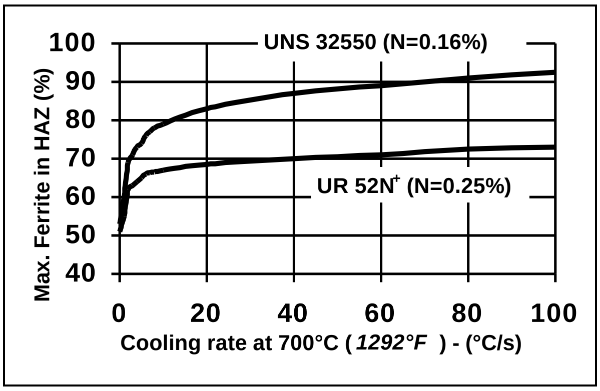
GROOVE	Process	Thickn. th(mm)	GAP d (mm)	ROOT k (mm)	BEVEL a (°)
	GTAW	< 3	0 - 2	-	-
	GMAW	< 3	0 - 2	-	-
	SMAW	< 3	0 - 2	-	-
	SMAW	3 - 15	2 - 3	1 - 2	60 - 70
	GTAW	2.5 - 8	2 - 3	1 - 2	60 - 70
	GMAW	3 - 12	2 - 3	1 - 2	60 - 70
	SAW	4 - 12	2 - 3	1 - 2	70 - 80
 r = 6-8 mm	SMAW	12 - 60	1 - 2	2 - 3	10 - 15
	GTAW	> 8	1 - 2	1 - 2	10 - 15
	GMAW	> 12	1 - 2	2 - 3	10 - 15
	SAW	> 10	1 - 2	1 - 3	10 - 15

General welding conditions

▪ **Welding metallurgy**

As for other ferritic-austenitic stainless steels, the weld metal of 52N+ has a whole ferritic microstructure when solidifying.

Due to high increase of temperature range (1150-1450°C - *2102-2642°F*) the HAZ may also increase its ferrite content by $\gamma \rightarrow \alpha$ transformation.



SMAW Process
Effect of the cooling rate on maximal ferrite content in HAZ

It's only during cooling that a part of the high tempe-rature ferrite retransforms into austenite, giving to the weld a ferritic-austenitic microstructure.

Consequently, the ferrite content in HAZ and in weld metal is directly linked to the cooling rate as indicated on the above graph.

If the cooling rate is too high, microstructure is too ferritic.
For 52N+, moreover, too low cooling rates could cause a beginning of ferrite transformation into intermetallic phases. This has also to be avoided since intermetallic phase precipitations reduce the corrosion resistance properties and the mechanical properties.

To obtain the best as-welded microstructure of weld, the optimal cooling rate must be ensured by a strict control of the heat input and interpass temperatures. A minimum and maximum value of the heat input is then recommended for each welding procedure. Typical data are provided here after. More specific informations are provided when requested.

- **Pre-heating**

Preheating of UR 52N+ is not necessary, and not recommended.
Preheating acts mainly on cooling rate at low temperature. Therefore, preheating is not very efficient for the transformation the ferrite into austenite which happens at high temperature while slow cooling rate may result in deleterious phase precipitation processes.

- **Interpass temperature**

Too high interpass temperatures decrease the cooling rate so that intermetallic phases, nitride or carbide precipitations are likely to occur.

The maximum allowed interpass temperature for UR 52N+ weldings is 150°C (*302°F*).

- **Heat input**

For a given thickness of plate, welding process and a welding configuration, the cooling rate is inversly proportionnal to the heat input which is calculated accordingly to the following relation :

$$HI_{(kJ/mm)} = \frac{I_{(A)} x U_{(v)}}{W_{S(mm/min)}} x \frac{60}{1000}$$

I and U are read on welding machine, W_s is the welding speed of the gun or the welding electrode.

The table hereafter, shows the heat input ranges for some welding processes which can be used to weld UR 52N+.

Welding process	Heat inputs used for UR 52N+ (kJ/mm)
SMAW	0.4 to 1.4
Pulsed GMAW	0.4 to 1.4
GMAW	0.5 to 1.7
SAW	0.3 to 1.4
GTAW - PAW	0.6 to 2.2

However, the best results are obtained for more occurate heat input ranges determined by the welding parameters, including plate thickness, welding process, welding type (butt or filet weld).

→ ***Optimum heat input ranges calculated from welding parameters of the user are communicated on request by Marketing Department of CLI.***

As a general guide, the lowest heat input are recommended for the welding of the thinner plates.

- **Post-heating**

Post-heating is not recommended and even dangerous when temperature exceeds 290°C (*554°F*).

- **Hot straightening**

Hot straightening is not used for UR 52N+ insofar as any maintain at a temperature > 290°C (*554°F*) could deteriorate the microstructure and corrosion resistance of this duplex.

Welding processes

As indicated in the table hereafter, most of welding processes can be used to weld URANUS 52N+.

Welding processes for Duplex and Superduplex	With filler metal	Without filler metal*
Industrial processes	- SMAW - SAW - FCAW - GMAW - Pulsed GMAW - GTAW - PAW	- GTAW - PAW
Processes not very used or being studied	- ESW	- LW - EBW - RW - FW

* A solution annealing heat treatment after welding or nitrogen addition in welding gas is recommended

The only restrictions concern welding processes without filler material for which it is difficult or impossible to counteract the loss of nitrogen content in molten metal by a nitrogen addition in the welding gas.

In this case, a solution annealing post-welding heat treatment of UR 52N+ allows to obtain a correct microstructure and satisfactory corrosion resistance of the weld metal.

- **Shielding metal arc welding**

This process can be used from a thickness of 3 mm. Rutile, basic-rutile or basic type of covered electrode are available to weld UR 52N+.

The highest levels of toughness and the highest capacities of deformation are obtained with basic covered electrodes. These basic electrodes will preferably be used if the weld should support strong deformation (heads forming) or if the weld should have a good level of toughness at low temperature.

The choice of electrode diameter will take into account the recommended heat input range. The weld will be made with stringer beads (the width of weave s-hould not exceed twice the electrode diameter).

When a covered electrode is used to make the root pass, a backing shielding gas, as used for GTAW, is recommended. In the opposite case, the penetration will be finily grinded.

In all cases, the welder will hold a short arc to avoid an atmospheric nitrogen pick up which leads to an unacceptable level of porosities, for an already nitrogen al-loyed duplex weld metal.

- **Submerged-arc welding**

This welding process is used for flat position with thickness of plate from 10mm.

Basic flux leads to the best toughness and ductility in weld metal whereas rutile flux gives an easier removal of slag and often a lower sensibility to porosity. Small filler diameter (often Ø 2,4 mm) will be chosen to respect recommended heat inputs (Nevertheless, that SAW thermal efficiency is very high, ≈ 1).

For a given heat input, the choice of welding parameters I, U, Ws is important. The use of both moderate amperage and low welding speed (Ws < 45 cm/min) reduces strongly the risk of shrinkage voids or porosities which could be unacceptable according to the most often used specifications of compactness (X-Ray exams ASME VIII for instance).

Too fitted passes (backing pass after gouging and too narrow grinding) must be avoided. Width of bead should always be higher than its depth.

- **Flux cored arc welding**

There are two types of flux cored wires to weld UR 52N$^+$:

- Metallic cored wires (without mineral powders) can be used with solid flux or with shielding gas (particularly GTAW),
- Mineral flux cored wires can be used with GMAW and Ar+CO_2 18% shielding gas.

The high shielding gas activity and the rutile type of the cored wires lead to rather low resilience levels but acceptable for applications at room or higher temperature.

Those mineral flux cored wires give a good compactness of weld metals. Their pitting corrosion resistance measured by ASTM G48A test is the same as the corrosion resistance obtained with others welding processes.

- **Gas metal arc welding and pulsed GMAW**

These semi-automatic or automatic welding processes are used for thicknesses of 3 mm or more.

- The short-circuiting transfer is used for low heat inputs and therefore for the lower plate thicknesses.
- The spray-arc transfer or axial transfer which is obtained with high amperage and voltage leads to a stable arc and high deposition rates.
- The pulsed arc transfer is obtained with special power sources. The current has its peak in the spray-arc transfer range and its low level in the short-arc transfer. This process allows to benefit of spray-arc advantages with reduced heat inputs and makes it possible to perform weldings in all positions

The UR 52N$^+$ welding with GMAW process has been tested with the three transfer modes but the most used process is the pulsed GMAW.

The shielding gas composition is very important for duplex weldings when using GMAW or pulsed GMAW processes.

The shielding gas must avoid both nitrogen losses of weld metal and weld metal oxydation.

Some ternary gases (Ar+CO_2+N_2) or quaternal gases (Ar+CO_2+He+N_2) can be used for GMAW and pulsed GMAW welding of UR 52N$^+$ (Sales references delivered on request).

The quality of the shielding g as must be stable. Flight of water cooled gun system or pick-up of atmospheric nitrogen are to be avoided since lack of compactness, *i.e.* porosities in the weld metal may then be created.

The use of welding speed inferior to 40 cm/min is adviced when a good compactness is required after X-Ray examination.

When GMAW is used to realise the root pass, the same backing shielding gas as for GTAW weldings is adviced.

▪ **Gas tungsten arc welding**

GTAW, manual or automatic is very used to weld UR 52N+ when the thicknesses of plates are lower than 15 mm. This is also the case to perform penetration passes before filling with SMAW or SAW processes.

The GTAW welding process leads to the purest weld metals (the lowest oxygen contents) and is the less sensitive to lack of compactness phenomenon.

GTAW process without filler material is used to weld very low thicknesses of plates (< 3 mm). The welding gas used must contain nitrogen addition.

The recommended shielding gas is a Ar 98%+N_2 2% mixture. More nitrogen additions can be used but can also lead to a deterioration of tungsten electrode. The nitrogen addition in the shielding gas is important to keep a satisfactory microstructure and corrosion resistance even when selected filler material is a nickel overalloyed grade.

The flow rate must be carefully set according to nozzle diameter and the use or not of a gas diffuser. Turbulence (too high flow rate) which can introduce atmospher in molten bath must be avoided

Moreover, the tungsten electrode extension can never exceed twice or three times its diameter, except when the torch has gas lens. In this case, an electrode length of about 20 mm can be used to resolve difficult accesses. If not, uncontrolled nitrogen addition in duplex or superduplex weld metal may occur. As a result, too low ferrite content and lack of compacity may be obtained.

A backing shielding gas is necessary and will be ensured by pure argon (Ar > 99,95%).

Welding will be realised with stringer beads and moderate thickness beads. Too thick passes are more sensitive to porosity (more difficult degasing).

Choice of filler materials and weld metal composition

Two types of weld metal compositions can be used to weld UR 52N+.

a) Mostly a 25% Cr, Ni, ferritic-austenitic product.
The pure chemical composition should be similar from this indicated below :

Elements

	C	S	P	Si	Mn	Ni	Cr	Mo	Cu	N_2
Mini %	0.015	-	-	0.300	0.500	9.6	25.0	3.60	-	0.220
Maxi %	0.035	0.015	0.025	0.750	1.500	10.2	27.0	4.00	1.50	0.250

b) A nickel alloy filler materiel with high chromium and molybdenum additions.

Two chemical compositions can be used :

- Alloy C22 type, E Ni Cr Mo 10 according to AWS or ASME,
- Alloy 59 type, SG Mo Cr 23 Mo 16 according to DIN.

The use of the second solution depends on the final application, and gives to the weld metal an increased corrosion resistance. Nevertheless, this weld metal has lower tensile properties than a super duplex weld metal.

® ***For these differents welding solutions, lists of filler materials* used to weld URANUS 52N$^+$ can be obtained on request from CLI Marketing Department.***

****The supply of filler materials lists by CREUSOT-LOIRE INDUSTRIE doesn't take away responsability from supplier of filler material and fabricator who are totally in charge of their welding products quality.***

Wire/flux or wire/gas couples proposed by the filler material suppliers can't be separated without great problem regarding weld metal properties.

Covered electrodes and flux will be carefully dried in accordance with suppliers instructions.

Welding gas with hydrogen addition are not allowed for UR 52N$^+$ welding.

Welding of URANUS 52N$^+$ with other steels

URANUS 52N$^+$ can be welded with carbon steels, others stainless steels or nickel based alloys.

Processes described for matching welding of UR 52N$^+$ can be used insofar as a filler material can be used .

Superduplex, duplex or 309 L Mo type filler materials can be used to weld UR 52N$^+$ with carbon steel or low alloy steels or with austenitic stainless steels.

To weld URANUS 52N$^+$ with super austenitic steels or nickel alloys, nickel alloys filler materials with high chromium and molybdenum contents, but without niobium (E Ni Cr Mo 10 or SG Ni Cr 23 Mo 16) will be used.

These heterogeneous welds will be done with the same precautions than matching welds (respect of heat input range, drying of filler materials...).

Cleaning and Pickling and Passivation of welds

The cleaning of welded zones is made by mechanical or chemical methods.

Welds can be finily grinded and polished, sand-blasted or micro-beaded (products without iron particles).

Complementary or, instead of these mechanical methods, pickling can be made with the same fluonitric baths or pastes as for others stainless steels but with a longer time (twice longer than 316 L grade).

Tidy washing must be realised after pickling.

These operations must be realised with high security (ventilation, protective clothing and rubber gloves).

Ferrite determination

The control of ferrite content in URANUS $52N^+$ welds is very important insofar as a too high ferrite content in HAZ or weld metal leads to a too low tenacity, a low ductility and a lower corrosion resistance of the weld.

- **Calculation methods**

The ferrite content in weld metal can be predicted from its chemical composition with using formulas and ESPY diagram (results in ferrite per cent) or these of diagram WRC 93 (results in Ferrite Number or FN).

The others methods (SCHAEFFLER or DELONG) which don't take care of nitrogen or copper additions can't be used for UR $52N^+$ welds.

- **Measurement methods**

The more usual measurement methods to determine ferrite content in weld metal are magnetic methods as ferritscope (results in % or FN) or magnegage (results in FN).

These methods can't be used for very localized measurement of ferrite content. For instance, in HAZ, metallographic grid method (ASTM E 562) with sufficient magnification ($\geq$ 400 x) is the only one which gives a significant result.

- **Expression of results**

The ferrite content results expressed with % or FN are not equivalent.

In fact, there is a correlation between ferritscope or grid method results (F%), and those obtained by magnegage expressed in FN.

For ferritic-austenitic steels and in accordance with IIW II 1196-92, the relation between F% and FN values of ferrite is as follow :

$$F\,\% = 0{,}54\ FN + 9{,}7$$

- **Ferrite contents recommended in UR $52N^+$ weld**

In lack of all required values by the user, the following values of ferrite content in UR $52N^+$ as welded weld metal should be obtained :

Welding processes	Localisation	Method	Ferrite %
SMAW - FCAW SAW	Weld metal	Espy	15 to 35
		Ferritscope	20 to 40
GMAW - GTAW PAW	Weld metal	Espy Ferritscope	15 to 50 20 to 60
All processes	HAZ	Point grid at ≥ 400 x	< 70

Inspection :
non-destructive testing and qualification tests of welds

If it's easy to weld UR 52N$^+$, advices given in this document make it to improve the properties of the welded structures.

The weldings must be carried out by personnel who is qualified for welding of steels or alloys used for severe corrosive medias.

About non-destructive testings, dye-penetrant testing and X-Ray inspection can be used without any problem.

On the other hand, ultrasonic control is more difficult to do and requires operators familiar with US control of stainless steels.

In addition to controls required by main international codes, ASME, CODAP EN 288, some more specific tests are often required to qualify duplex or super duplex welds.

Metallographic ferrite content measurement and ASTM G 48A pitting corrosion test in Fe Cl_3 solution are very often required. These tests are only carried out, by laboratories which are competent in ferritic-austenitic stainless steels.

Le Creusot Research Center is totally able to realise all specific testings of duplex and super-duplex welds.

For all information ***: NATIONAL METAL DISTRIBUTORS, INC.***
P.O. Box 1499
Vancouver, WA 98668
Sales Tel (800) 878-3675
Fax (800) 878-9709

UR52N^{+} - ALLOY 255
PHOSPHORIC ACID APPLICATION

SELECTION OF STAINLESS STEEL FOR USE IN PHOSPHORIC ACID PLANTS, NEW TRENDS AND EXPERIENCE

Jean-Pierre Audouard & Michel Verneau, CREUSOT-MARREL INC./CLI, Wayne, PA
Michel Barloy, BARTEC, New York, NY & Mulberry, FL
William Shelton, METRO TECHNICAL SERVICES, Gautier, MS

Summary - Laboratory tests as well as field tests have shown that the super-duplex grade UNS 32520/UR52N$^+$ is more resistant to corrosion and erosion-corrosion in industrial phosphoric acids than the conventional N 08904 alloy. This is explained by the combination of high chromium content and Mo-Cu and N additions together with high mechanical properties .

These properties, which in some circumstances permit thickness reductions, when combined with the low Ni content and the good ability of this material to be cut, formed and welded led to a relative low cost which explain why UNS 32520/UR52N$^+$ has been considered as a candidate material for manufacturing several major equipment in two phosphoric acid plants in US.

In addition to lower initial capital costs, the savings due to lack of down time and expense due to rubber and refractory repairs is immense. Such items as adding a pump suction to an attack tank can be accomplished without a major capital outlay. We feel this practical material has perhaps many other applications yet to be realized for this industry.

CORROSION PERFORMANCE EVALUATION

Industrial phosphoric acid solutions are chemically complex and their analysis change from one plant to another, depending on the quality of phosphate rocks and on the process utilised. So, in order to elaborate an accurate basis for material selection, a reference synthetic solution representative of the average aggressivity of industrial acids was designed [1].

Then, the effects of the main corrosion determining parameters like free fluoride, hydrofluorsilisic acid, sulfuric acid in excess and chlorides were investigated by adding these elements to the reference solution. The effect of process temperature was also studied. Finally, erosion-corrosion tests were carried out using a laboratory equipment especially designed to simulate the effect of actual industrial parameters which are considered as to be rate determining for this form of corrosion [2].

The corrosion tests were carried out in the Research Centre for Materials of CREUSOT-LOIRE INDUSTRIE (CLI) in Le Creusot, France ; various stainless steels were tested (Table 1).

Table 1 - Average composition of the candidate stainless steels and alloys

AISI UNS	CLI Trademark	C	Cr	Ni	Mo	Cu	N2
		Average composition (% weight)					
Austenitics							
316 L	ICL 164 BC	0.02	17	12	2.2		
316 LN	ICL 166 HE	0.02	18	11	2.7		0.15
317 L	ICL 168 BC	0.02	19	15	3.2		
317 LN	ICL 168 HE	0.02	19	15	3.5		0.15
317 LNM	ICL 170 HE	0.02	18	15	4.5		0.15
N 08 904	UR B6	0.02	20	25	4.3	1.5	
Super Austenitics							
N 08 028	UR B28	0.01	27	31	3.5	1	
N 08 926	UR B26	0.01	20	25	6.2	1	0.20
Duplexes							
31 803	UR 45N	0.02	22	5.3	2.8		0.16
32 520	UR 52N$^+$	0.02	25	6.5	3.5	1.5	0.25

1- EFFECT OF IMPURITIES (Attack Stage)

The very detrimental effect of free **hydrofluoric acid** is shown in Fig.1. In particular, the corrosion rate of the UNS 08904 grade increases from 0.08 mm/y to 0.15 mm/y when the HF content increases from 0 to only 0.2 %. The duplex grade UNS 32520 (UR 52N+) and the super austenitic grade UNS 08926 (UR B26) are less affected when the HF content increases, but this acid remains very detrimental. It appears quite clearly that high chromium countaining grades exhibit the best corrosion resistance.

Hydrofluorsilisic acid is less agressive than hydrofluoric acid, as shown by electrochemical tests which consisted in measuring the passive domain taken from polarisation curves (Fig.2). Thus, adding 1.5 % H_2SiF_6 to the synthetic solution has very little effect when compared to HF.

The effect of **sulfuric acid** concentration is shown in Fig.3. An increase of 2 % (from 2 to 4 %) has about the same influence as the one observed with HF additions in the range 0 to 0.2 %. High chromium containing austenitic grades either austenitics or duplexes are the best resistant materials.

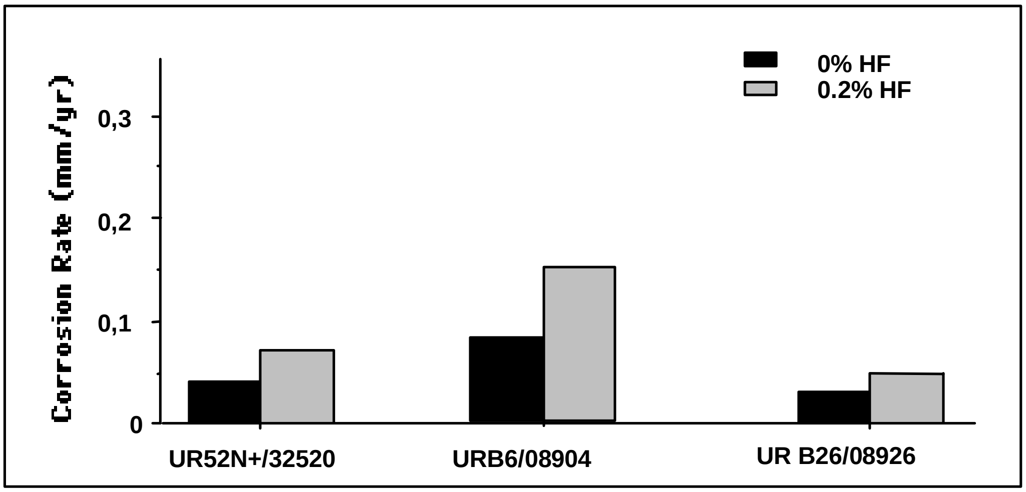


Fig. 1 - Effect of Hydrofluoric Acid on the corrosion rate of stainless steels. Temperature 80°C/176°F.

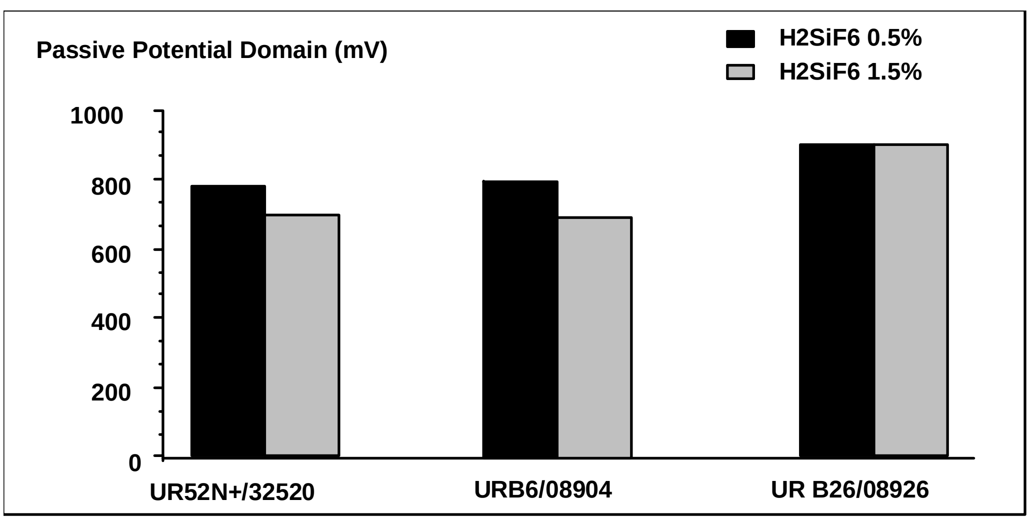


Fig. 2 - Effect of hydrofluosilicic acid on the corrosion rate of stainless steels.
Temperature 80°C/176°F.

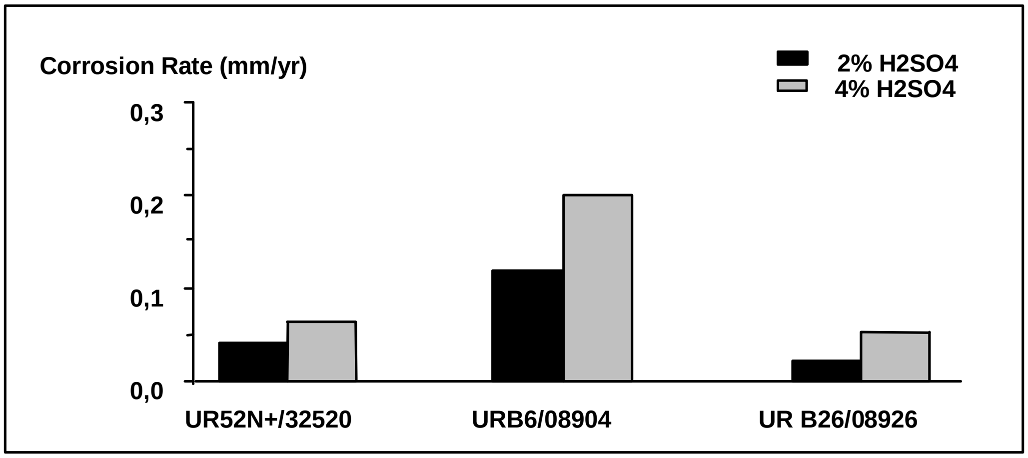


Fig.3 - Effect of excess of Sulfuric Acid on the corrosion rate of stainless Steels.
Temperature 80°C/176°F.

The effect of **chloride** concentration on uniform corrosion was also investigated. Fig.4 summarizes the results of tests with several chloride concentrations from 600 to 4600 ppm at 80°C. It clearly appears that chromium, molybdenum and nitrogen additions increase the resistance to corrosion; thus, the threshold chloride concentration is directly dependant on the concentration of these alloying elements. In this respect, the PREN value = Cr% + 3.3 Mo% + 16 N% which is generally utilized to rank the resistance of stainless steels to localised corrosion in chloride containing media seems to be rate determining for corrosion in the tested conditions.

In regular industrial conditions, i.e. when the chloride concentration does not exceed 1000 ppm, the UNS 08 904 grade can be utilized in erosion free conditions; in solutions containing higher chloride levels, one must select either the super-duplex grade UR 52N^{+} or the super-austenitic grade UR B26 up to about 2000 ppm and the super austenitic-grade UNS 08 028 up to about 3000 ppm.

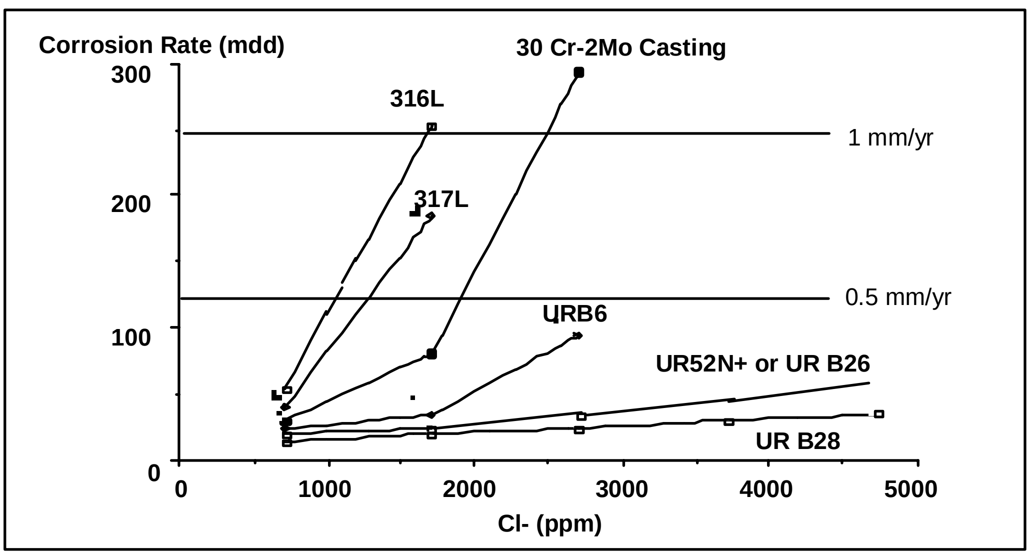


Fig. 4 - Effect of Chloride concentration on the corrosion rate of stainless steels.
Temperature 80°C/176°F.

2- EFFECT OF ATTACK TEMPERATURE

Corrosion tests were carried out at 110°C (230°F) in order to simulate the conditions of hemi-hydrate processes. Figure 5 shows the corrosion rate of all the tested grades to be multiplied by three when the temperature increases from to 80°C/176°F to 110°C/230°F.

At the highest temperature, the UNS 08904 grade is no longer recommended while the grades with high chromium content (25 %) exhibit a corrosion rate of about 0.15 mm/y.This means that either UNS 32520 ($UR52N^+$) or UNS 08926 (URB26) grades can be considered as candidate materials to build phosphoric reacting vessels but the higher mechanical properties of the super-duplex grade provide a decisive advantage compared to the super austenitic grade.

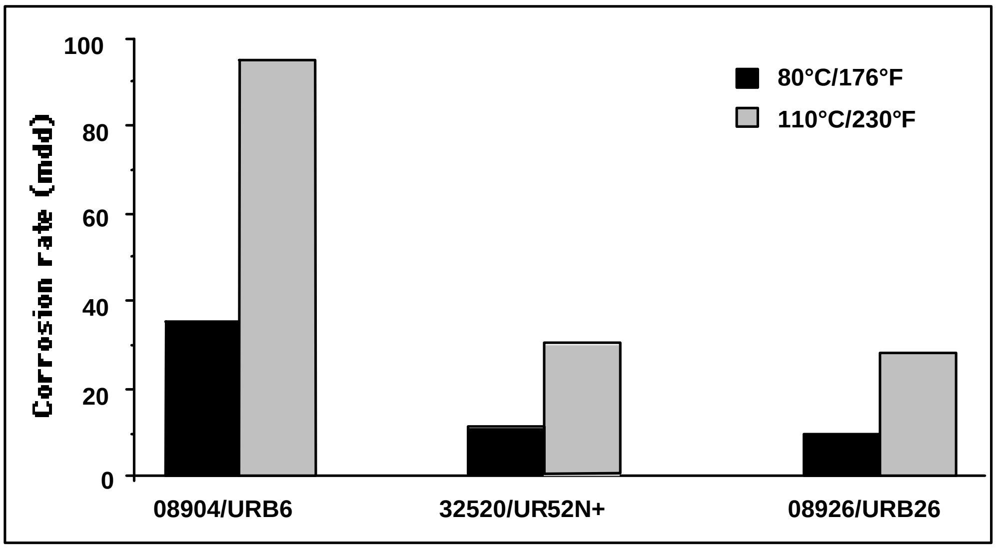


Fig. 5 - Effect of Temperature of Attack on the corrosion rate of stainless steels.

3- EROSION-CORROSION

The main central agitator and more particularly surface agitators used in some processes for mixing reacting products must resist to a severe abrasion phenomenon (due to gypsum and non reactive silica) and to general corrosion due to temperature and sulfuric acid addition. They are currently made from UNS 08904 grade with some rubber lined parts (sometimes from 29Cr-4Mo casting, especially for small surface agitators) but the operating conditions are generally so agressive that agitators must be replaced annually or every two years, depending on the process.

Pumps utilized to transfer the phosphoric mixture from the reacting vessel to the filter are also submitted to very severe abrasion so that they have to be replaced every year.

Laboratory tests carried out by means of a specific device using 100 microns silicon carbide as abrasive particles [1] in the synthetic solution at 80°C/176°F shown that abrasion increases drastically the corrosion rate of stainless steels (Fig.6). For example, the UNS 08904 grade exhibits a corrosion rate of about 1.2 mm/yr. In the same conditions, the corrosion rate of the 25% Cr grades is only about 0.6 mm/yr i.e. 50% lower. One must stress that the super-duplex grade UNS 32520 (UR 52N+) is as resistant as the super-austenitic UNS 08926 grade (UR B26).

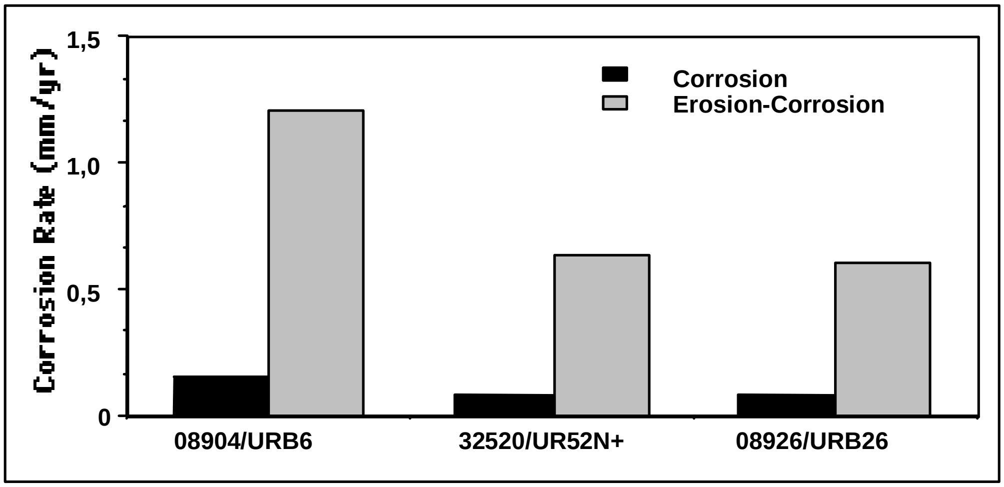


Fig.6 - Effect of Erosion by Solid Particles in suspension in Phosphoric Acid. Temperature 80°C/176°F.

4- STORAGE OF 54% PHOSPHORIC ACID: EFFECT OF CHLORIDES

The 54 % P_2O_5 acid solution is not as aggressive as the 30 % mixture. Normal contents in fluoride and chloride containing compounds are in fact notably lower than in the mixture. However, the most economical material must be selected taking into account the actual storage conditions i.e. the temperature and the Cl^- concentration in the acid

Results of laboratory tests conducted in an actual concentrated industrial phosphoric acid at several temperatures and several Cl- contents (Fig.7) indicate the threshold chloride vs temperature values for which localized corrosion does not appear on industrial hot rolled stainless steel samples.

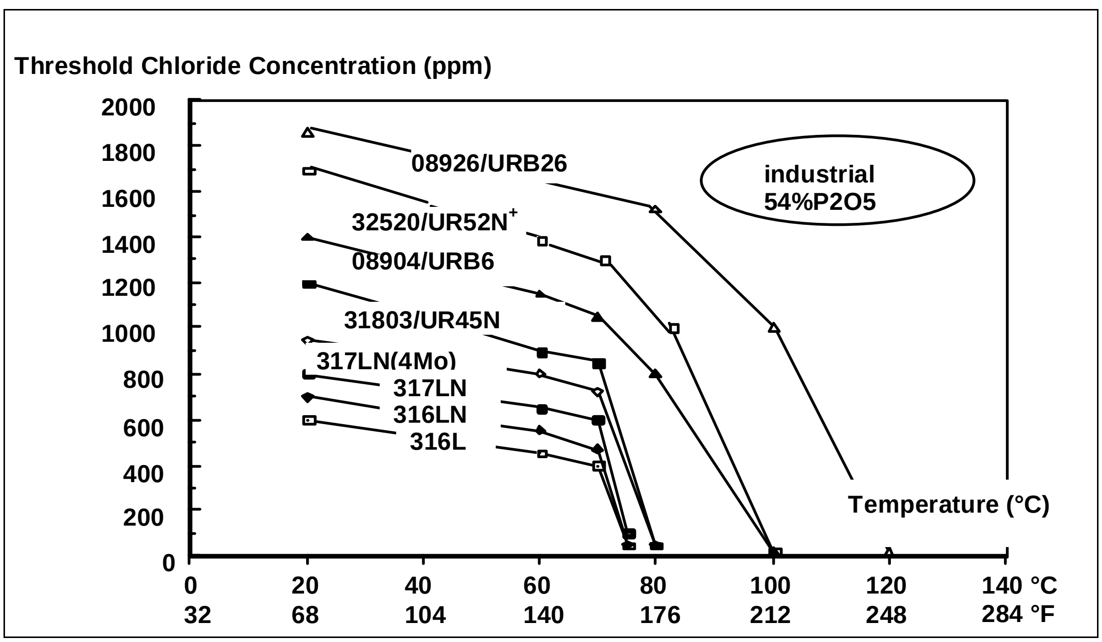


Fig. 7 - Selection of stainless steels for transportation of 54 % P205 as a function of Chloride content.

If one consider 900-1000 ppm chlorides which is probably representative of the upper content in actual 54% P2O5 industrial acids, the duplex grade UNS 31803 withstand localized corrosion up to 60°C/140°F while the super-duplex grade UNS 32 520/UR $52N^+$ has to be selected at 80°C/176°F. Types 316L, 316LN and even 317LNM are much less resistant.

Such results, together with the good resistance to erosion-corrosion as previously shown, suggest that UNS 32 520/UR 52N+ is a very good candidate for construction of phosphoric acid storage tanks.

5- FIELD TESTING

Field tests were carried out in two plants using di-hydrate Rhône-Poulenc processes in Belgium and in Greece. Samples taken from industrial hot-rolled plates (N 08 904, N 08 028, N 08 932, 32 550 and Nickel Base N 06 625 grades) were attached on surface agitator blades during several months.

The results in Fig. 8 and 9 show that super-austenitics and super-duplexes are about twice as resistant to erosion-corrosion than 08 904 grade in these very agressive conditions. The super-duplex grade UR 52N+ exhibits the best performance among all the materials tested including N06 625 Nickel Base alloy.

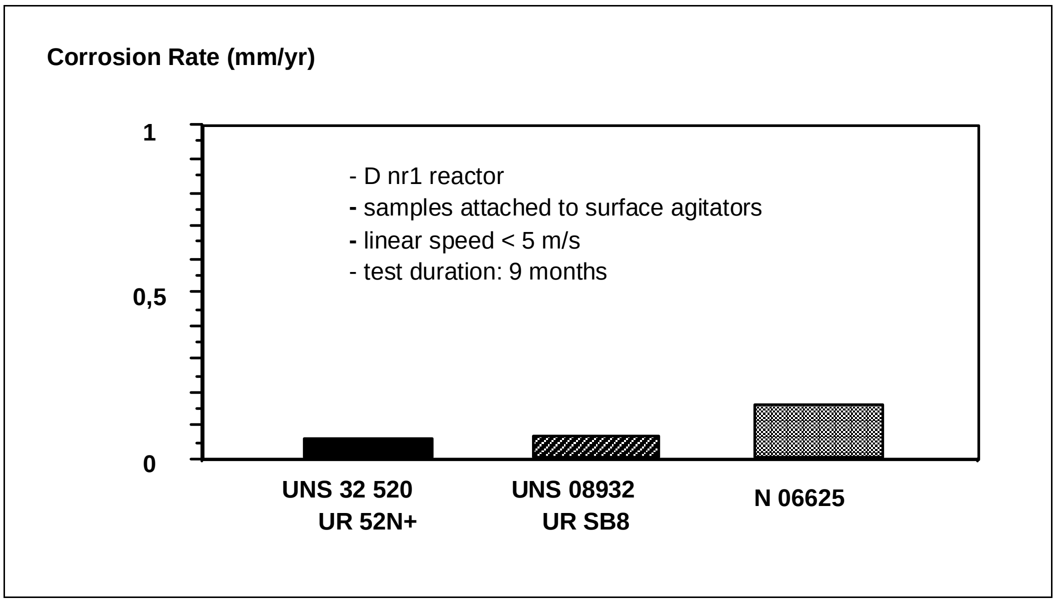


Fig. 8 - Field Tests in a Rhône-Poulenc Plant, Greece.

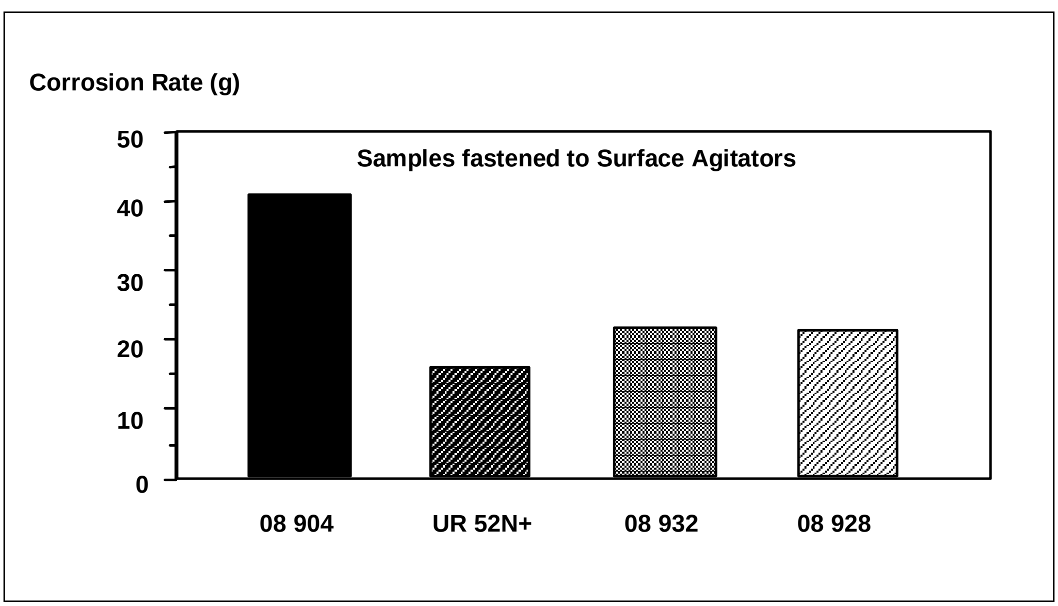


Fig. 9 - Field Tests in a Rhône-Poulenc Plant, Belgium.

MECHANICAL PROPERTIES

The minimum guarantied values for mechanical properties of various stainless steels are mentionned in Table 2. One can observe that whatever the microstructure, higher alloyed grades exhibit higher yield and ultimate tensile values. Particularly, nitrogen is the most beneficial element.
Nevertheless, the combination of austenite and ferrite in the duplex microstructure provides very high mechanical properties which are at least twice those observed on austenitic grades like the N 08904 commonly used in phosphoric acid industry.
The high corrosion resistance of the duplex grade UR 52N+/UNS 32520 combined with its high mechanical characteristics generally permit to reduce the thickness of the plates and consequently to save money.

Table 2 - Mechanical characteristics of stainless steels.

AISI or UNS	TRADENAME	Y.S. 0.002		U.T.S.		E
AUSTENITICS		Mpa	KSI	Mpa	KSI	%
316L		225	33	520	75	45
316LN		250	36	590	86	40
317LNM		290	42	580	85	40
N08904	UR B6	245	36	550	80	40
N08926	UR B26	320	46	650	94	40
N08028	UR B28	220	32	500	73	40
DUPLEX						
S31803	UR 45N	480	69	680	98	25
S32520	UR 52N+	550	80	760	115	25

FABRICATION WITH UR 52N+ IN THE US PHOSPHATE INDUSTRY

Uranus 52N+(S 32 520) has proven to be a durable, cost effective, and relatively easy metal with which to fabricate corrosion resistant vessels and devices for the phosphate industry.

To date this material has been used to fabricate preneutralizers, attack tanks, piping, fittings, and other proprietary devices. Vessels have ranged in size from small five feet diameter vessels to thirty feet diameter attack tanks. After designing, fabricating, and using this material in the phosphate industry, the following observations and suggestions are made concerning it’s use:

1- FORMABILITY –This material has been rolled, formed, and broken to the various required shapes. While these processes can be accomplished, in some cases, for example, the fabricator chose to cut out the top leg of a rolled angle as this proved easier. In any case, the material can be formed within advised limits.

2- WELDING – We recommend researching the material, developing a welding procedure, and then working closely with Creusot-Marrel Inc./CLI to check the procedure. CLI's policy is to develop a very close cooperation between its corporate metallurgists and welding experts and their client conterparts (fabricators and end users) in order to insure the best performance of the equipment in service.

Vessels to data have been constructed using FCAW in the flat position and stick electrodes for all other positions. A tabulation of approved filler materials for these and other methods was supplied by Creusot-Marrel Inc./CLI. The fabricators reported no particular problems with welding.

3- ISOLATION FROM CARBON STEEL EXTERNAL SUPPORTS – Digesters designed from Uranus 52N+ typically will be low overhead, externally supported API 650 type vessels. In construction to date, care was taken with welded external connections to carbon steel supports to avoid dilution contamination of wetted plates. External welded connections on vessels in service to date were designed with isolation pads to prevent such contamination. Bolted connections are another options for external supports such as that necessary for digester construction. Nevertheless, duplex stainless steels can be welded directly onto carbon steel using duplex filler material without any microstructural problem. This is an advantage when compared to 316L for which a first pass with 20Cr-25Ni type filler material has to be used in order to avoid cracking due to martensite.

REFERENCE OF URANUS 52 N +
IN THE US FERTILIZER INDUSTRY

1- MISSISSIPPI PHOSPHATES - Pascagoula **-** MS

The main equipment built in Uranus 52 N^+ are :

- An additional **attack tank** in the phosphoric acid unit of about 100,000 gallons working volume. The metal thickness is ¼" at the bottom, 3/8" on the shell and ¼" for the cover, and includes 0.125" corrosion allowance. The total weight of stainless steel is 44,244 pounds.

  Except for protection of the bottom against abrasion with an acid resistant material, there is no other lining on the stainless steel. This solution was less expensive than any other material requiring a rubber and brick lining.

- A new **preneutralizer** in the DAP granulation unit of about 30,000 gallons working volume. As with the attack tank, there is no lining except the bottom protection with an acid resistant material. Total weight about 19,500 pounds.

- A new **central valve**. A first valve in 904 L of similar design was commissioned in January 1989 as part of the additional 24 C filter. As soon as the company was granted a permit for a long term operation, the decision was made to modify the filtration section of the other 24 C filter with the design of the first one. The main difference is the material of construction of the last valve which is Uranus 52 N +.

All this equipment was designed by Metro Technical Services and commissioned in March 1998. They have since behaved well.

2- AGRIFOS - Pasadena **-** TX

The plant is located in the port of Houston and was purchased by Agrifos from Mobil in September 1998. Agrifos decided to uprate the capacity of the phosphoric acid unit by 50 %, using Bartec technology for the process design and Metro Technical Services for the detailed engineering and project management. The first phase of the uprate is planned to be commissioned in July 1999, and the second phase in 2000. Many large and small equipment are or will be made in Uranus 52 N + for a total weight of 800,000 pounds. The main equipment in this material are:

- The **vapor head** of the new evaporators, 18' 4" diameter, 28' high, about 1" thick, are special Bartec design with dished heads on top and bottom. First they were considered in rubberlined carbon steel with the rubber protected against temperature and water blasting by a carbon tiles lining on the bottom and on the shell. Then it was found not much more expensive to make the whole vessels in stainless steel.

- The **condensers** of the new evaporators are also in Uranus 52 N +. Although condensers in rubberlined carbon steel would not have included carbon tiles, the smaller diameter of these vessels allowing a thinner wall made the material attractive as regards all advantages.

- The **circulation loop** including the pipes and the strainer are made in Uranus 52 N +. The pipes are quite large in diameter due to the large flow needed to get an acid velocity of 10.6 ft/sec in the tubes of the heat exchanger.

- The **acid desupersaturation unit** is totally made in Uranus 52 N^+, including the circulation tank, the vacuum cooler and the condenser. The purpose of this section is to release part of the supersaturation of the acid from the filter by forced circulation in a small vacuum cooler. That decreases the further precipitation of impurities in the downstream equipment and particularly in the heat exchangers of the evaporators while increasing the acid strength by 0.5 % and removing more impurities from the 29 % settling tank.

- Studies will be made to decide whether or not **large storage tanks of phosphoric acid** could be economically made in stainless steel clad plates. The answer will probably depend on the acid quality and corrosiveness and on the size of the tanks.

- The new **filter pans** of Bartec design are not made in Uranus 52 N^+ because there is no requirement for a grade highly resistant to corrosion. For corrosive slurries, for example when the rock has a high chlorine content and with hemihydrate route, Uranus 52 N^+ is preferentially selected since it is more corrosion resistant, has better mechanical properties and is less expensive than 904 L.

3- WHY BARTEC IS MAKING A LARGE USE OF STAINLESS STEEL

Bartec is owned by the fertilizer producer Agrifos, and thereby is designing the process equipment in close collaboration with the people in operation to meet their requirement for an easy and maintenance free operation, while still taking care of low capital cost. Bartec is also innovative in the design of its process and proprietary equipment and has the opportunity to test new unconventional and efficient solutions in Agrifos facilities. In this respect, the use of new grades of stainless steel at relatively low cost has the following advantages :

- Rubberlining is troublesome, particularly in evaporators running at high temperature where damage in rubberlining results in clogging the heat exchangers, air leaks, maintenance and down time. Water blasting rubber and carbon brick erodes the surface which is afterward scaling faster and harder. An equipment in stainless steel resistant to corrosion is trouble free for a life time.

- Some Bartec equipment may have to be optimized after commissioning or to be adapted later on to some changes in the design or operating conditions such as rock quality, capacity or others. A rubber or brick lined equipment cannot be easily modified, and doing it is expensive and requires a down time for curing. A stainless steel equipment can easily be modified by adding, removing or modifying nozzles, overflows, internals etc …

The detailed engineering, the selection of the fabrication shops and the supervision of fabrication is made by Metro which has a good expertise of Uranus 52 N + after designing the equipment for Mississippi Phosphates. That made the selection of the equipment in this material easier and speeded the detailed design.

CONCLUSION

Industrial phosphoric acid solutions are very agressive due to impurities coming from natural phosphate rocks. Solid particles of silica and gypsum lead to erosion-corrosion processes which depassivate stainless steel equipment, particularly agitators and pumps during the attack stage.

Laboratory tests showed the 25Cr super-duplex grade UNS 32520/UR $52N^+$ to be much more resistant to corrosion and erosion-corrosion than the conventional austenitic alloy N 08 904 grade which has been widely utilized for more than 30 years now . Among 25% chromium containing grades, the super-duplex grade appeared to be at least as resistant as the super-austenitics which are more expensive. These results are confirmed by long term exposure field tests.

By the use of the super-duplex grade UNS 32 520/UR 52N+ and other innovative design methods, a low cost, durable vessel such as a preneutralizer and an attack tank were constructed completely free from expensive rubber and acid brick. Additionnal equipment are planned to be built using this material. In addition to lower initial capital costs, the savings due to lack of down time and expense due to rubber and refractory repairs is immense. Such items as adding a pump suction to an attack tank can be accomplished without a major capital outlay. We feel this practical material has perhaps many other applications yet to be realized for this industry.

BIBLIOGRAPHICAL REFERENCES

[1] J-P Audouard, D. Catelin, P. Soulignac, "Application of Stainless Steels in Wet Process Phosphoric Acid", NACE Symposium "Corrosion Prevention in the Process Industries", Amsterdam, The Netherlands, 8-11 Nov. 1988.

[2] J-P Audouard, "Etude de l'influence d'éléments d'alliage sur la passivité d'un acier inoxydable à base de chrome et de nickel soumis à l'abrasion de particules solides en suspension dans un milieu corrosif", Thèse d'Université, Institut National Polytechnique de Grenoble, France, 12 Décembre 1980.

UR45N+ - ALLOY 2205

TECHNICAL SPECIFICATIONS

URANUSò 45 N^{+}

a 22 % Cr austenitic-ferritic duplex stainless steel

URANUS 45N^{+} (UR 45N$^{+)}$ is a nitrogen alloyed austenitic-ferritic Duplex stainless steel (22.05), with a minimum PREN value guaranteed of 36 due to over-alloying in Molybdenum and Chromium. This alloy presents higher mechanical and corrosion resistance properties than duplex 22 Cr stainless steels.

Its yield strength is about twice that of standard austenitic grades and well in excess of that of nitrogen alloyed austenitics.

Operation temperature of UR 45 N^{+} is generally limited from -50°C to 280°C (-58°F to 536°F). Lower temperature used particularly for welded structures may also be considered, but needs technical background.

STANDARDS

EURONORM..............................1.4462 - X2 Cr Ni Mo N 22.5.3
AFNOR ....Z3 CND 22.05.AZ
WERKSTOFF ....Nr 1.4462
ASTM.......................................UNS S 31803/S 32205

CHEMICAL ANALYSIS

Typical values (%)

C	Cr	Ni	Mo	N	Others
.020	22.6	6	3.4	.18	S = .001
PREN = [Cr %] + 3.3 [Mo %] + 16 [N %] ³ 36					

MECHANICAL PROPERTIES

Tensile properties - Minimum guaranteed values

°C	Rp 0.2 MPa	Rp 1.0 MPa	Rm MPa	°F	YS 0.2% KSI	YS 1.0% KSI	UTS KSI	A/Elong %
20	510	540	720	*68*	74	78	104	25
Plates th £ 50 mm (2 inches)								
50	460	500	670	*122*	67	72	97	
100	420	450	640	*212*	61	65	93	25
150	380	420	620	*302*	55	61	90	
200	350	390	600	*392*	51	56	87	20
250	320	350	600	*482*	46	51	87	
300	310	340	600	*572*	45	49	87	20

Plates th ≥ 50 mm (2 inches)

°C	Rp 0.2 MPa	Rp 1.0 MPa	Rm MPa	°F	YS 0.2% KSI	YS 1 .0% KSI	UTS KSI	A/Elong %
50	440	480	650	*122*	64	70	94	
100	400	430	620	*212*	58	62	90	
150	360	400	600	*30*	52	58	87	
200	330	370	580	*392*	48	64	84	
250	300	330	580	*482*	44	48	84	
300	290	320	580	*572*	42	46	84	

UR 45 N^+ should not be used over 280°C (*536°F*) for long periods.

Impact values

KCV + 20°C	*+ 68° F*	120 J/cm² average 90 J/Cm² mini	87 Ft.lbs 65 Ft.lbs
KCV - 50°C	*- 58° F*	90 J/cm² average 75 J/cm² mini	65 Ft.lbs 54 Ft.lbs

PHYSICAL PROPERTIES

Specific mass 7800 kg/m^3

Interval Temper °C	Thermal expansion ? x10^{-6}K^{-1}	°C	°F	Resistivity (μW cm)	Thermal conductivity (W.m^{-1}.K^{-1})	Specific heat (J.kg^{-1}.K^{-1})	Young modulus E (GPa)	Shear modulus G (GPa)
20-100	12	20	*68*	80	17	450	200	75
20-200	12.5	100	*212*		18	450	194	73
20-300	13	200	*392*		19	500	186	70
		300	*572*		20	550	180	67

Structure

The UR45 N^+ alloy is a two-phase microstructure contaning, 50% α, 50% γ

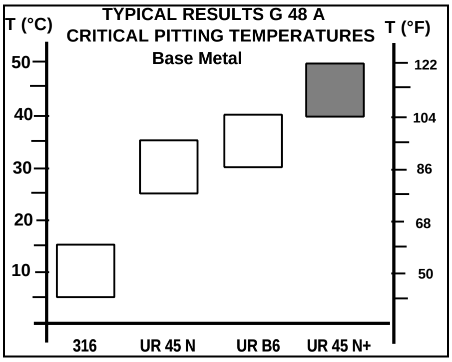
CORROSION RESISTANCE

General corrosion

UR 45N^+ has a general corrosion resistance better than a 316 L steel (Z3 CND 17.12.03) and equivalent or better than a 904 L alloy (UR B6)

Pitting corrosion

	PREN Value
316 L	≥ 23
URANUS 45N	≥ 33
URANUS 45N^+	≥ 36
URANUS B6 (20 Cr/25 Ni/4.5 Mo/Cu)	≥ 32



Crevice corrosion

Better than 316L ; equivalent to UR B6 / 904L

Stress corrosion cracking

Duplex structure gives to UR45 N^+ a definite advantage over austenitic steels (chloride containing media at temperatures up to 280°C (*536°F*).

Intergranular corrosion

UR 45N^+ is resistant to Strauss test (A262E) as delivered and as welded conditions

FABRICATION

Heat treatment

The heat treatment for delivery is 1040-1100°C (*1904/2012°F*)

Air cooling for thicknesses < 8 mm is agreed, but water quenching is advised. For thicknesses of 8 mm and above, water quenching is necessary. Special precautions must be taken during heat treatment to avoid deformation.

Cold forming

Due to its higher mechanical properties, UR 45 N^+ requires more strength than a classical austenitic stainless steel. Deformation higher than 20% requires an intermediate heat treatment.

Hot forming

Recommended between 1150°C and 1000°C (*2102 and 1832°F*)
After forming, a new heat treatment is necessary to obtain optimal mechanical properties and microstructure stability

Pickling

Pickling solution acceptable for 316L may be used, but the pickling time required is at least twice that of 316L.

Machining

Machining is yet another example of a fabrication process in which the employed techniques (eg. tools and lubricants) are very similar to those used for conventional stainless steels).

Machining characteristics of UR 45N$^+$ are better than those of Z3 CND 17.12.02 (316 L grade).

Oper.	**Tool**	**Lubri-** cation	**Depth of cut** mm (*inch*)	**Feed** mm *inch*)	**SPEED (m/min) -*SPEED (feet/min)*** m/min	feet/min	m/min	feet/min
					Ur B6		**Ur 45 N$^+$**	
Turning	High speed steel	Cutting oil	6-*0.23*	*0.5-0.19*	6-11	*19.7-36.1*	15-20	*49.2-65.*6
			3-*0.11*	0.4-*.016*	9-14	*29.5-45.9*	23-28	*75.5-91.9*
			1-*0.04*	0.2-*.008*	15-20	*49.2-65.6*	30-35	*98.4-114.8*
	Carbide	Dry or cutting oil	6-*0.23*	0.5-*.019*	25-35	82-114.8	75-85	*246.1/278.9*
			3-*0.11*	0.4-*.016*	45-55	*147.6-180.4*	90-100	*295.3-328.1*
			1-*0.04*	0.2 -*.008*	65-70	*213.3-229.7*	110-120	*360.9-393.7*
Parting off	High Speed steel	Cutting oil	**Blade width**					
			1.5-*0.06*	0.03 -*0.0012*	10-13	*32.8-42.7*	23-28	*75.5-91.9*
			3-*0.11*	0.04 -*0.0016*	11-14	*36.1-45.9*	24-29	*78.7-95.1*
			6-*0.23*	0.05 -*.0020*	12-15	*39.4-49.2*	25-30	*82.-98.4*
Drilling	High speed steel	Cutting oil	**Drill Ø**					
			1.5-*0.06*	0.25 -*0.0010*	6-10	*19.7-32.8*	10-14	*32.8-45.9*
			3-*0.11*	0.06 -*0.0024*	7-11	*23.-26.1*	11-15	*36.1-49.2*
			6-*0.23* 12-*0.48*	0.08 -*0.0031* 0.10- *0.0039*	7-11 7-11	*23.-26.1* *23.-26.1*	11-15 11-15	*36.1-49.2* *36.1-49.2*
Milling profiling	High speed steel	Cutting oil		.05/0.10 *.002/.0039*	10-20	*32.8-65.6*	12-22	*39.4-72.2*

WELDING

UR 45N$^+$ is an austenitic-ferritic Duplex grade, and the ferrite/austenite ratio is controlled by :

- its chemical analysis, designed to obtain between 45 and 55 % of ferrite and the complement austenite after heat treatment at 1050/1080°C (*1922/1976°F*),
- the thermal cycle undergone by the alloy, a higher heat treatment temperature (>1100°C is *2020°F*) resulting in a higher amount of ferrite.

After thermal cycle (heat at high temperature and rapid cooling), HAZ structure is enriched by ferrite compared to the heat treated structure. Nevertheless, the high nitrogen level of UR 45N$^+$ allows an excellent control of the structure in HAZ. The chemical composition of UR 45N$^+$ has been calculated so that ferrite does not exceed 75 % to guarantee a good corrosion resistance and a good ductility. Austeno-ferritic structure of UR 45N$^+$ steel (primary solidificatIon) excludes all risk of hot cracking.

UR 45 N$^+$ is easily welded by the following processes :

- TIG welding, both manual and automatic	- MIG welding
- Plasma welding	- Manual arc welding with covered electrodes
- Flux Cored Arc Welding (FCAW)	- Submerged Arc Welding (SAW)

Special care must be taken in controlling the ferrite content of the weld deposit, which is usually between 20 and 60 %, and, depending on the application, a low ferrite content will be recommended (20-40 % of ?) *i.e.* for SMAW, SAW and FCAW

Chemical composition has to be adapted to stabilise austenite (generally, nickel or nitrogen overalloying compared to the base metal). Using of a Cr and Mo overalloyed filler metals is recommended.

Welding in several passes helps to limit ferrite content.

As for austenitic grades :

- No preheat is necessary prior to welding,
- The heat input must be controlled (10 to 25 KJ/cm is generally counselled).
- Interpass temperature must be limited to 150°C (*302°F*)
- No post weld heat treatment is necessary, except if, in particular cases, or for a particular welding, a lower ferrite content is necessary. Treatment will be realised at a sufficient temperature to avoid any transformation in phase. A higher temperature can be required when using welding products on alloyed steels 1080/1100°C (*1976/2012°F*).

- Usual precautions including cleaning and degreasing of weld area, protection against weld spatters must be taken to ensure corrosion resistance of finished product.
- Careful final descaling and/or cleaning of the weld is highly recommended.

1. Plasma + TIG welding

- Typically used for thicknesses 5 to 12 mm.
- Normal 22.09 wire, or overalloyed wire (25.10.4 type) will be used for plasma pass.
- If no filler metal is used for the plasma arc, Ar + (2-3)% N_2 will be used as shielding gas.
- Ferrite content will be between 30 and 60 %. Complementary TIG welding will also be realised with normal 22.09 wire or overalloyed wire. The ferrite content will also be between 30 and 60 %.
- Nitrogen addition (2-3%) to the shielding gas can be recommended to improve corrosion behaviour and stabilize the microstructure. Technical assistance is available for special cases. In each case, contamination of shielding gas by hydrogen must be avoided.

2. Manual metal arc welding

A standard 22.09 wire or 25-10-4 grade allowing overalloy of deposit metal will be used. The ferrite content is between 20 and 40 %. For more information, please contact us.

3. Submerged arc welding

This process can be used for single pass or multipass welds for high thicknesses (≥ 10mm) or to complete a plasma pass. The filler metal is a duplex wire and basic fluxes should be preferred. Ferrite content will be controlled between 20 and 40% in order to avoid cold cracking risks ; use only well dryed fluxes to avoid hydrogen pick-up.

APPLICATIONS

Gas transportation on- offshore	Other uses	
- tubes for platforms - tubes for transportation of acid gas to refining stations - wet carbonic gases collecting unit	- Bulk tankers for transportation of chemical products - acid areas (H_2SO_4 diluted, phosphoric acid, production and storage of phosphates)	- urea production - truck, lorries - pollution control industry - pulp and paper industry - plastic industry - food industry - chloride areas

SIZE RANGE

	Hot rolled plates	Cold rolled plates	Clad plates
Thickness	5 to 150 mm 3/16" to 6"	2 to 14 mm 5/64" to 5/8"	6 to 150 mm 1/4" to 6"
Width	Up to 3300 mm Up to 130"	Up to 2300 mm Up to 90.5"	Up to 3300 mm Up to 130"
Length	Up to 12000 mm Up to 472"	Up to 8250 mm Up to 325"	Up to 14000 mm Up to 551"

Other sizes are available on request, including 4100mm (161,4") width plates

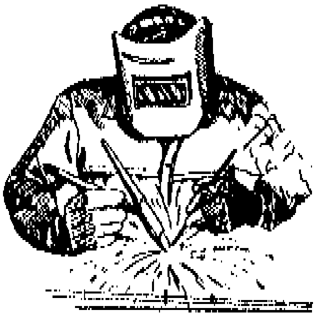
NOTE

This technical data and information represents our best knowledge at the time of printing. However, it may be subject to some slight variations due to our ongoing research programme on corrosion resistant grades. We therefore suggest that information be verified at time of enquiry or order.

Furthermore, in service, real conditions are specific for each application. The data presented here is only for the purpose of description, and may only be considered as guarantees when our company has given written formal approval.Further information may be obtained from the following address.

For all information : NATIONAL METAL DISTRIBUTORS, INC.
P.O. Box 1499
Vancouver, WA 98668
Sales Tel (800) 878-3675
Fax (800) 878-9709

UR45N+ - ALLOY 2205
FORMING AND WELDING



URANUS 45N+

FORMING and WELDING PROCEDURES

THE PRODUCT

UR 45N+ is an overalloyed 2205 duplex stainless steel with PREN value higher or equal to 36. The minimum guaranteed yield strength is 500 MPa which allows the designer to reduce thickness of equipments.

The molybdenum and nitrogen contents have been optimized in order to obtain the best corrosion resistance properties even for the heaviest plates. Its high nitrogen addition improves the structure stability particularly in HAZ (Heat Affected Zone).

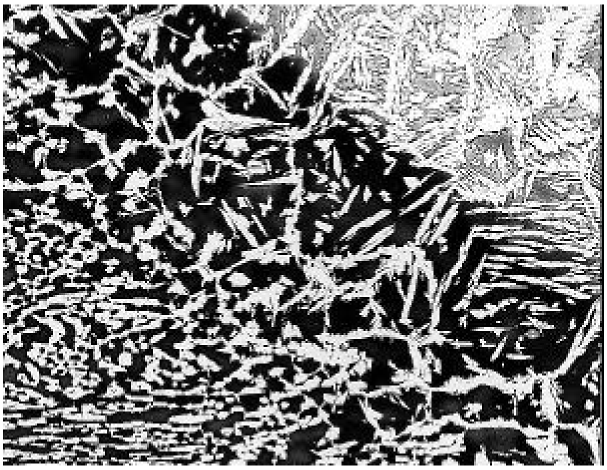
UR 45N+ is a cost efficient grade designed for offshore, marine and pollution control equipments.

UR 45N+ answers to the following standards :

EURONORM................ 1.4462 - X2 Cr Ni Mo N 22.5.3
AFNOR .... Z3 CND 22.05 AZ
DIN................................ W. Nr 1.4462
ASTM........................... UNS S32205

Chemical analysis of URANUS 45N+

C	Cr	Ni	Mo	N	Others
.020	22.6	6	3.3	.18	S = .001
PREN = [Cr %] + 3.3 [Mo %] + 16 [N %] $\geq$ 36					

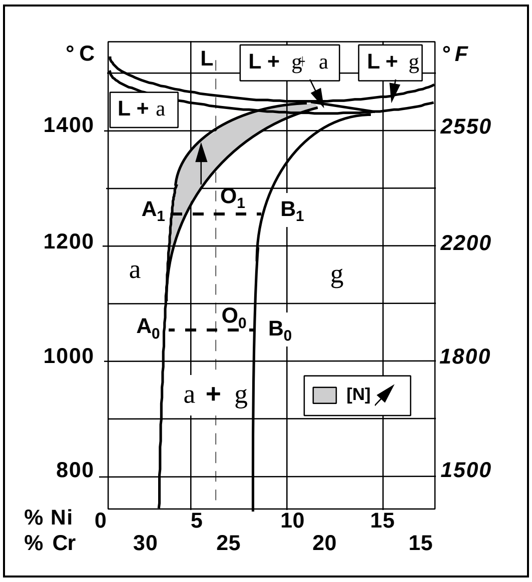


Microstructure of UR 45N+ HAZ welded joint

METALLURGY

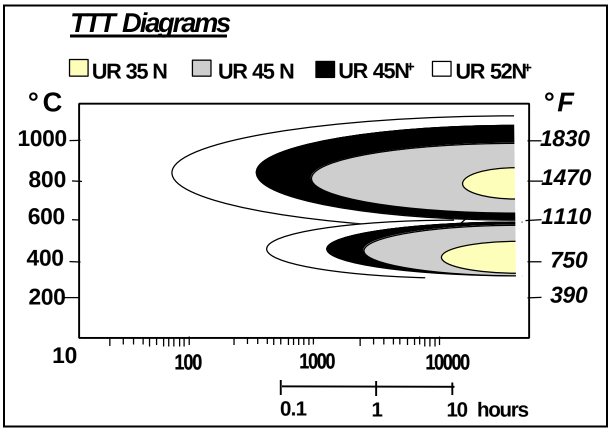
URANUS 45N+ has roughly equivalent volume fractions of ferrite and austenite (slightly more austenitic). This is obtained by work-hardening, followed by solution annealing + water quenching, and involves the simultaneous control of the chemical composition and annealing temperature. The figure shows a schematic isoplethal section of the Fe-Cr-Ni diagram, for an iron content of 68%. The proportions of each of the phases and their respective compositions are indicated for a given alloy analysis and annealing heat treatment.

The figure shows that the duplex microstructure solidifies in the ferritic phase and that the austenite forms only when the steel is cooling down. Over-heating (1150-1450°C - *2102-2642°F*) of a solution annealed, water quenched, plates (HAZ for example) of duplex steels may result in the formation of more ferrite which may retransform in austenitic when again cooling down. Too fast cooling rate may reduce this α-γ retransformation process and explain why welding consumables are over alloyed in nickel.

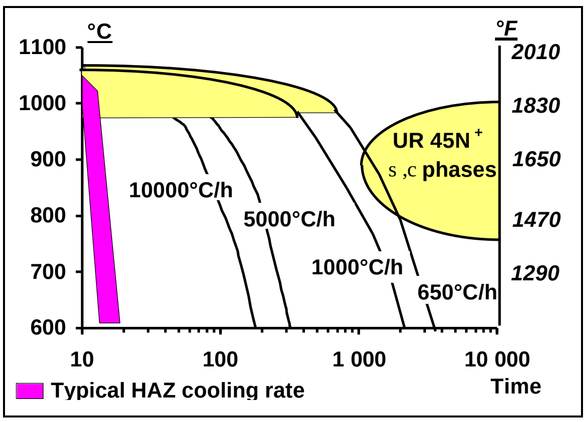


As regards the high temperature stability of the duplex structure, it is important to note the gamma stabilising action of nitrogen.

The TTT diagrams for the grades UR 35N, UR 45N, UR 45N+ and UR 52N+ here presented are conservative, and do not imply that the mechanical properties or corrosion resistance are modified as soon as the boundaries indicated are reached. This is particularly true for the low temperature ferrite hardening field. The TTT curves are mainly affected by molybdenum, chromium and tungsten additions.



Continuous cooling diagram shows that intermetallic phase transformation in duplex 52N+, and even more easily in UR 45N+ grade can be avoided by a control of the cooling rate which is obtained by a control of the heat input.



HOT FORMING

Hot forming is carried out between 1150 and 1000°C (*2102 - 1832°F*).
It should be kept in mind that ferritic-austenitic stainless steels have low strength at high temperatures. So, precautions must be taken to avoid possible deformations (wedging and support of pieces).

At temperatures below 1000°C (*1832°F*), embrittlement can appear due to intermetallic phase precipitations, especially when material is strained.

After hot forming, a solution annealing heat treatment in the range 1040 - 1100°C (*1904 - 2012°F*) with water cooling is necessary.

COLD FORMING

Due to its higher yield strength, forces required for the cold forming of UR 45N$^+$ are more important than for austenitic steels.
Edges will be grinded and surfaces (absence of scratches...) will be checked before cold forming.

For cold deformations higher than 20 %, an intermediate treatment is required (solution annealing between 1040 and 1100°C (*1904 and 2012°F*) with water cooling). This heat treatment performed after cold forming is always required when the deformation exceeds 10%.

® ***Detailed recommendations for cold forming or bending of welded and unwelded duplex and super duplex plates are available upon request.***

MACHINING

Generally, the same technologies and tools can be used as for conventional stainless steels.

For drilling, high speed steel tools must preferently be used with a speed cutting of 10 to 15 m/min. The drilling speed depends on the hole diameter.

For machining with carbide tools, the cutting speed is the same as the cutting speed used for 316 L type austenitic steels.

Operation	Tool	Lubrication	CONDITIONS					
			Depth of cut (mm)(*inch*)		Feed (mm) (*inch*)		Speed (m/min)(*feet/min*)	
Turning	High speed steel	Cutting oil	6	*0.23*	*0.5*	*0.019*	15-20	*49.2-65.6*
			3	*0.11*	0.4	*0.016*	23-28	*75.5-91.9*
			1	*0.04*	0.2	*0.008*	30-35	*98.4-114.8*
	Carbide	Dry or cutting oil	6	*0.23*	0.5	*0.019*	75-85	*246.1/278.9*
			3	*0.11*	0.4	*0.016*	90-100	*295.3-328.1*
			1	*0.04*	0.2	*0.008*	110-120	*360.9-393.7*
Parting off	High speed steel	Cutting oil	Blade width mm - *inch*		Feed mm - *inch*			
			1.5	*0.06*	0.03	*0.0012*	23-28	*75.5-91.9*
			3	*0.11*	0.04	*0.0016*	24-29	*78.7-95.1*
			6	*0.23*	0.05	*0.0020*	25-30	*82.-98.4*
Drilling	High speed steel	Cutting oil	Drill Ø mm-*inch*		Feed mm - *inch*			
			1.5	*0.06*	0.25	*0.0010*	10-14	*32.8-45.9*
			3	*0.11*	0.06	*0.0024*	11-15	*36.1-49.2*
			6	*0.23*	0.08	*0.0031*	11-15	*36.1-49.2*
			12	*0.48*	0.10	*0.0039*	11-15	*36.1-49.2*
Milling / profiling	High speed steel	Cutting oil			Feed mm- *inch*			
					0.05/0.10	*.002/.0039*	12-22	*39.4-72.2*

HEAT TREATMENT

UR 45N$^+$ is delivered in the solution annealed and water quenched conditions (1040/1100°C - *1904/2012°F*).

The chemical composition of UR 45N$^+$ is optimised in order to obtain, after heat treatment, nearly a 50 α / 50 γ microstructure.

These solution annealing conditions must be respected for final or intermediate heat treatment in case of forming and when a solution annealed or a stress relieved treatment is required after welding.

All other heat treatments, particularly the one with holding time or with slow cooling rate in the 300 to 1000°C (*572-1832°F*) range must be avoided. Heat treatments at 400°C (*752°F*) used for dimensionnal stability of austenitic stainless steels are not acceptable for UR 45N$^+$.

WELDING

Welded joints preparation

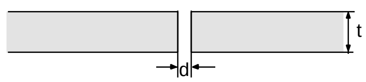
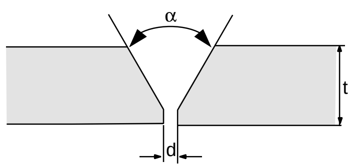
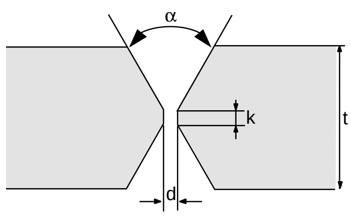
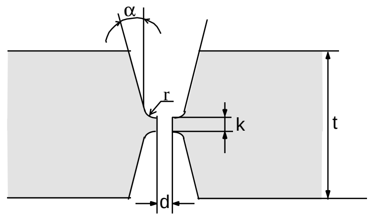
The joint must be designed in such a manner that the penetration weld could be realised without an excessive dilution of base metal or a burn through. Groove type must be designed in order to have a good gaseous shielding protection (GTAW, GMAW, PAW, FCAW) ; a good accessibility for welding guns in the bottom of the joint must be obtained.

Some examples of welded joints preparation are presented on the following tables which can be used for the butt welding of UR 45N^{+} (different plate thicknesses).

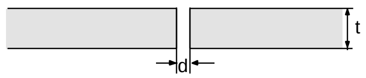
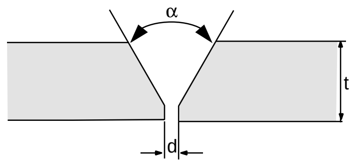
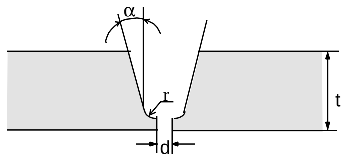
Grooving will be realised by machining or thermal cutting (oxy-acethylenic gas with iron powder or plasma) followed by grinding to eliminate oxyded and heat-affected zones.

As for all others stainless steels, the welding zone will be carefully cleaned with unchlorided solvent in order to eliminate any grease or paint marks.

Joint design for Butt welding from both sides

GROOVE	Process	Thickn. th(mm)	GAP d (mm)	ROOT k (mm)	BEVEL a (°)
	GTAW	3 - 5	1 - 3	-	-
	GMAW	3 - 6	1 - 3	-	-
	SMAW	3 - 4	1 - 3	-	-
	SMAW	4 - 15	1 - 3	1 - 2	55 - 65
	GTAW	3 - 8	1 - 3	1 - 2	60 - 70
	GMAW	5 - 12	1 - 3	1 - 2	60 - 70
	SAW	9 - 12	0	5	80
	SMAW	> 10	1.5 - 3	1 - 3	55 - 65
	GMAW	> 10	1.5 - 3	1 - 3	60 - 70
	SAW	> 10	0	3 - 5	90
 R=6-8mm	SMAW	> 25	1 - 3	1 - 3	10 - 15
	GMAW	> 25	1 - 3	1 - 3	10 - 15
	SAW	> 25	0	3 - 5	10 - 15

Joint design for one-sided butt welding

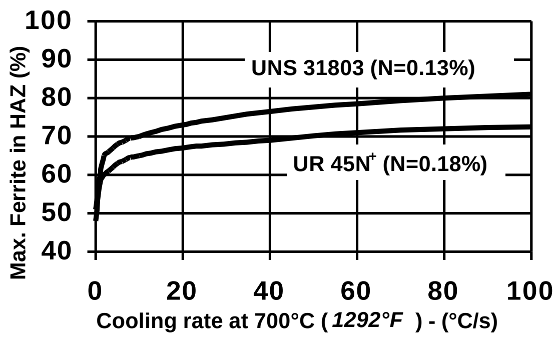
GROOVE	Process	Thickn. th(mm)	GAP d (mm)	ROOT k (mm)	BEVEL a (°)
	GTAW	< 3	0 - 2	-	-
	GMAW	< 3	0 - 2	-	-
	SMAW	< 3	0 - 2	-	-
	SMAW	3 - 15	2 - 3	1 - 2	60 - 70
	GTAW	2.5 - 8	2 - 3	1 - 2	60 - 70
	GMAW	3 - 12	2 - 3	1 - 2	60 - 70
	SAW	4 - 12	2 - 3	1 - 2	70 - 80
	SMAW	12 - 60	1 - 2	2 - 3	10 - 15
	GTAW	> 8	1 - 2	1 - 2	10 - 15
	GMAW	> 12	1 - 2	2 - 3	10 - 15
r = 6-8 mm	SAW	> 10	1 - 2	1 - 3	10 - 15

General welding conditions

- **Welding metallurgy**

As for other ferritic-austenitic stainless steels, the weld metal of 45N+ has a whole ferritic microstructure when solidifying.

Due to high increase of temperature range (1150-1450°C - *2102-2642°F*), the HAZ may also increase its ferrite content by γ → α transformation.



SMAW Process
Effect of the cooling rate on maxim al ferrite content in HAZ

It's only during cooling that a part of the high temperature ferrite retransforms into austenite, giving to the weld a ferritic-austenitic microstructure.

Consequently, the ferrite content in HAZ and in weld metal is directly linked to the cooling rate as indicated on the above graph.

If the cooling rate is too high, microstructure is too ferritic.
For this reason, too high cooling rates should be avoided for the welding of UR 45N+. Moreover, too low cooling rates could cause a beginning of ferrite transformation into intermetallic phases. This has also to be avoided since intermetallic phase precipitations reduce the corrosion resistance properties and the mechanical properties.

To obtain the best as-welded microstructure of weld, the optimal cooling rate must be ensured by a strict control of the heat input and interpass temperatures. A minimum and maximum value of the heat input is then recommended for each welding procedure. Typical data are provided here after. More specific informations are provided when requested.

- **Pre-heating**

Preheating of UR 45N+ is not necessary, and not recommended
Preheating acts mainly on cooling rate at low temperature. Therefore, preheating is not very efficient for the transformation ferrite → austenite which happens at high temperature while slow cooling rate may result in deleterious phase precipitation processes.

- **Interpass temperature**

Too high interpass temperatures decrease the cooling rate so that intermetallic phases, nitride or carbide precipitations are likely to occur.

The maximum allowed interpass temperature for UR 45N+ weldings is 150°C (*302°F*).

- **Heat input**

For a given thickness of plate, welding process and a welding configuration, the cooling rate is inversly proportionnal to the heat input which is calculated accordingly to the following relation :

$$HI_{(kJ/mm)} = \frac{I_{(A)} x U_{(v)}}{W_{S(mm/min)}} x \frac{60}{1000}$$

I and U are read on welding machine, W_s is the welding speed of the gun or the welding electrode.

The table hereafter, shows the heat inputs ranges for some welding processes which can be used to weld URANUS 45N+.

Welding process	Heat inputs used for UR 45N+ (kJ/mm)
SMAW	0,55 to 2,05
Pulsed GMAW	0,55 to 2,05
GMAW	0,70 to 2,45
SAW	0,50 to 1,70
GTAW - PAW	1,00 to 3,45

However, the best results are obtained for more occurate heat input ranges determined by the welding parameters, including plate thickness, welding process, welding type (butt or filet weld).

® ***Optimum heat input ranges calculated from welding parameters of the user are communicated on request by Marketing Department of CLI.***

As a general guide, the lowest heat input are recommended for the welding of the thinner plates.

- **Post-heating**

Post-heating is not recommended and even dangerous when temperature exceeds 290°C (*554°F*).

▪ **Hot straightening**

Hot straightening is not used for URANUS 45N+ insofar as any maintain at a temperature > 290°C (*554°F*) could deteriorate the microstructure and corrosion resistance of this duplex.

Welding processes

As indicated in the table hereafter, most of welding processes can be used to weld URANUS 45N+.

Welding processes for Duplex and Superduplex	With filler metal	Without filler metal*
Industrial processes	- SMAW - SAW - FCAW - GMAW - Pulsed GMAW - GTAW - PAW	- GTAW - PAW
Processes not very used or being studied	- ESW	- LW - EBW - RW - FW

* A solution annealing heat treatment after welding or nitrogen addition in welding gas is recommended

The only restrictions concern welding processes without filler material for which it is difficult or impossible to counteract the loss of nitrogen content in molten metal by a nitrogen addition in the welding gas.

In this case, a solution annealing post-welding heat treatment of UR 45N+ allows to obtain a correct microstructure and satisfactory corrosion resistance of weld metal.

▪ **Shielding metal arc welding**

This process can be used from a thickness of 3 mm. Rutile, basic-rutile or basic type of covered electrode are available to weld UR 45N+.

The highest levels of toughness and the highest capacities of deformation are obtained with basic covered electrodes. These basic electrodes will preferably be used if the weld should support strong deformation (heads forming) or if the weld should have a good level of toughness at low temperature.

The choice of electrode diameter will take into account the recommended heat input range. The weld will be made with stringer beads (the width of weave s-hould not exceed twice the electrode diameter).

When a covered electrode is used to make the root pass, a backing shielding gas, as used for GTAW, is recommended. In the opposite case, the penetration will be finily grinded.

In all cases, the welder will hold a short arc to avoid an atmospheric nitrogen pick up which leads to an unacceptable level of porosities, for an already nitrogen al-loyed duplex weld metal.

▪ **Submerged-arc welding**

This welding process is used for flat position with thickness of plate from 10mm.

Basic flux leads to the best toughness and ductility in weld metal whereas rutile flux gives an easier removal of slag and often a lower sensibility to porosity. Small filler diameter (often Ø 2,4 mm) will be chosen to respect recommended heat inputs (Nevertheless, that SAW thermal efficiency is very high, ≈ 1).

For a given heat input, the choice of welding parameters I, U, Ws is important. The use of both moderate amperage and low welding speed (Ws < 45cm/min) reduces strongly the risk of shrinkage voids or porosities which could be unacceptable according to the most often used specifications of compactness (X-Ray exams ASME VIII for instance).
Too fitted passes (backing pass after gouging and too narrow grinding) must be avoided. Width of bead should always be higher than its depth.

- **Flux cored arc welding**

Mineral flux cored wires can be used with GMAW and Ar+CO_2 18% shielding gas.

The high shielding gas activity and the rutile type of the cored wires lead to rather low resilience levels but acceptable for applications at room or higher temperature.

Those mineral flux cored wires give a good compactness of weld metals. Their pitting corrosion resistance measured by ASTM G48A test is the same as the corrosion resistance obtained with other welding processes.

- **Gas metal arc welding and pulsed GMAW**

These semi-automatic or automatic welding processes are used for thicknesses of 3 mm or more.

- The short-circuiting transfer is used for low heat inputs and therefore for the lower plate thicknesses.
- The spray-arc transfer or axial transfer which is obtained with high amperage and voltage leads to a stable arc and high deposition rates.
- The pulsed arc transfer is obtained with special power sources. The current has its peak in the spray-arc transfer range and its low level in the short-arc transfer. This process allows to benefit of spray-arc advantages with reduced heat inputs and makes it possible to perform weldings in all positions

The UR 45N$^+$ welding with GMAW process has been tested with the three transfer modes but the most used process is the pulsed GMAW.

The shielding gas composition is very important for duplex weldings when using GMAW or pulsed GMAW processes.

The shielding gas must avoid both nitrogen losses of weld metal and weld metal oxydation.

Some ternary gases (Ar+CO_2+N_2) or quaternal gases (Ar+CO_2+He+N_2) can be used for GMAW and pulsed GMAW welding of UR 45N$^+$ (Sales references delivered on request).

The quality of the shielding g as must be stable. Flight of water cooled gun system or pick-up of atmospheric nitrogen are to be avoided since lack of compactness, *i.e.* porosities in the weld metal may then be created.

The use of welding speed inferior to 40 cm/min is adviced when a good compactness is required after X-Ray examination.

When GMAW is used to realise the root pass, the same backing shielding gas as for GTAW weldings is adviced.

▪ **Gas tungsten arc welding**

GTAW, manual or automatic is frequently used to weld UR45N$^+$ when the thicknesses of plates are lower than 15 mm. This is also the case to perform penetration passes before filling with SMAW or SAW processes.

The GTAW welding process leads to the purest weld metals (the lowest oxygen contents) and is the less sensitive to lack of compactness phenomenon.

GTAW process without filler material is used to weld very low thicknesses of plates (< 3 mm). The welding gas used must contain nitrogen addition.

The recommended shielding gas is a Ar 98 % + N_2 2% mixture. More nitrogen additions can be used but can also lead to a deterioration of tungsten electrode. The nitrogen addition in the shielding gas is important to keep a satisfactory microstructure and corrosion resistance even when selected filler material is a nickel overalloyed grade.

The flow rate must be carefully set according to nozzle diameter and the use or not of a gas diffuser. Turbulence (too high flow rate) which can introduce atmospher in molten bath must be avoided.

Moreover, the tungsten electrode extension can never exceed twice or three times its diameter, except when the torch has gas lens. In this case, an electrode length of about 20 mm can be used to resolve difficult accesses. If not, uncontrolled nitrogen addition in duplex or superduplex weld metal may occur. As a result, too low ferrite content and lack of compacity may be obtained.

A backing shielding gas is necessary and will be ensured by pure argon (Ar > 99,95%).

Welding will be realised with stringer beads and moderate thickness beads. Too thick passes are more sensitive to porosity (more difficult degasing).

Choice of filler materials and weld metal composition

Three types of weld metal compositions can be used to weld UR 45N$^+$.

a) An overalloyed 22% Cr and Ni, ferritic-austenitic product.
The pure chemical composition should be similar to that indicated below :

Elements

	C	**S**	**P**	**Si**	**Mn**	**Ni**	**Cr**	**Mo**	**Cu**	**N_2**
Mini %	0.015	-	-	0.300	0.800	8.0	22.5	3.2	-	0.140
Maxi %	0.045	0.015	0.025	0.750	2.000	10.0	23.5	3.60	0.50	0.200

b) A ferritic-austenitic filler material with 25 % Cr like 25.10.4L or 25.10.4L Cu super duplex grade.

This second solution gives to the weld metal an increased corrosion resistance.

c) A nickel based filler material without niobium like E Ni Cr Mo 10 or SG Ni Cr 23 Mo 16 grades. Those products offer the best corrosion resistance properties.

® ***For these differents welding solutions, lists of filler materials* used to weld URANUS 45N+ can be obtained on request from CLI Marketing Department.***

The supply of filler materials lists by CREUSOT-LOIRE INDUSTRIE doesn't take away responsability from supplier of filler material and fabricator who are totally in charge of their welding products quality.

Wire/flux or wire/gas couples proposed by the filler material suppliers can't be separated without great problem regarding the properties of the weld metals.

Covered electrodes and flux will be carefully dried in accordance with suppliers instructions.

Welding gas with hydrogen addition are not allowed for UR 45N+ weldings.

Welding of URANUS 45N+ with other steels

URANUS 45N+ can be welded with carbon steels, other stainless steels or nickel based alloys.

Processes described for matching welding of UR 45N+ can be used insofar as a filler material can be used .

Superduplex, duplex or 309 L Mo type filler materials can be used to weld UR 45N+ with carbon steel or low alloy steels or with austenitic stainless steels.

To weld URANUS 45N+ with super austenitic steels or nickel alloys, nickel alloys filler materials with high chromium and molybdenum contents, but without niobium (E Ni Cr Mo 10 or SG Ni Cr 23 Mo 16) will be used.

These heterogeneous welds will be done with the same precautions than matching welds (respect of heat input range, drying of filler materials...).

Cleaning, Pickling and Passivation of welds

The cleaning of welded zones is made by mechanical or chemical methods.

Welds can be finily grinded and polished, sand-blasted or micro-beaded (products without iron particles).

Complementary or, instead of these mechanical methods, pickling can be made with the same fluonitric baths or pastes as for others stainless steels but with a longer time (twice longer than 316 L grade).

Tidy washing must be realised after pickling.

These operations must be realised with high security (ventilation, protective clothing and rubber gloves).

Ferrite determination

The control of ferrite content in URANUS 45N+ welds is very important insofar as a too high ferrite content in HAZ or weld metal leads to a too low tenacity, a low ductility and a lower corrosion resistance of the weld.

- **Calculation methods**

The ferrite content in weld metal can be predicted from its chemical composition with using formulas and ESPY diagram (results in ferrite per cent) or these of diagram WRC 93 (results in Ferrite Number or FN).

The others methods (SCHAEFFLER or DELONG) which don't take care of nitrogen or copper additions can't be used for UR 45N+ welds.

- **Measurement methods**

The more usual measurement methods to determine ferrite content in weld metal are magnetic methods as ferritscope (results in % or FN) or magnegage (results in FN).

Theses methods cannot be used for very localized measurement of ferrite content. For instance, in HAZ, metallographic grid method (ASTM E 562) with sufficient magnification ($\geq$ 400 x) is the only one which gives a significant result.

- **Expression of results**

The ferrite content results expressed with % or FN are not equivalent.

In fact, there is a correlation between ferritscope or grid method results (F%), and those obtained by magnegage expressed in FN.

For ferritic-austenitic steels and in accordance with IIW II 1196-92, the relation between F% and FN values of ferrite is as follow :

$$F\ \% = 0{,}54\ FN + 9{,}7$$

- **Ferrite contents recommended in UR 45N+ weld**

In lack of all required values by the user, the following values of ferrite content in UR 45N+ as welded weld metal should be obtained :

Welding processes	Localisation	Method	Ferrite %
SMAW - FCAW SAW	Weld metal	Espy	15 to 35
		Ferritscope	20 to 40
GMAW - GTAW PAW	Weld metal	Espy Ferritscope	15 to 50 20 to 60
All processes	HAZ	Point grid at ≥ 400 x	< 70

Inspection :
non-destructive testing and qualification tests of welds

If it's easy to weld UR $45N^+$, advices given in this document make it to improve the properties of the welded structures.

The weldings must be carried out by personnel who is qualified for welding of steels or alloys used for severe corrosive medias.

About non-destructive testings, dye-penetrant testing and X-Ray inspection can be used without any problem.

On the other hand, ultrasonic control is more difficult to do and requires operators familiar with US control of stainless steels.

In addition to controls required by main international codes, ASME, CODAP, EN 288, some more specific tests are often required to qualify duplex or super duplex welds.

Metallographic ferrite content measurement and ASTM G 48A pitting corrosion test in Fe Cl_3 solution are very often required. These tests are only carried out, by laboratories which are competent in ferritic-austenitic stainless steels.

Le Creusot Research Center is totally able to realise all specific testings of duplex and super-duplex welds.

For all information ***: NATIONAL METAL DISTRIBUTORS, INC.***
P.O. Box 1499
Vancouver, WA 98668
Sales Tel (800) 878-3675
Fax (800) 878-9709

SUPER DUPLEX STAINLESS STEELS

CORROSION PERFORMANCE IN FLUE GAS SCRUBBING SYSTEMS

CORROSION PERFORMANCE AND FIELD EXPERIENCE WITH SUPER DUPLEX AND SUPER AUSTENITIC STAINLESS STEELS IN FGD SYSTEMS

Jean-Pierre Audouard & Michel Verneau
CLI-FAFER
BP 56, 71202 Le Creusot Cedex, France

John Grocki
Creusot-Marrel Inc.
Suite 213, 724 Lancaster Avenue, Wayne, PA 19 087, USA

ABSTRACT

A brief description of the process utilized in flue gas scrubbing systems is presented and the corrosion risks are analyzed in relation with the local environments wich are supposed to exist in the main parts of the installation.

Then, Uniform and Localized corrosion performance of welded and non welded super-austenitic and super-duplex stainless steels are investigated and compared to nickel base alloys in laboratory conditions simulating actual flue gas desulphurization environments.

The main corrosion determining parameters investigated are pH, chloride and fluoride concentration as well as temperature.

Results gained from these tests were combined to field experience to design materials selection charts taking into account corrosion risks in various zones of scrubbers. Finally, field experience and references are presented.

INTRODUCTION

Energy production using coal or fuel oil boilers generates exhaust gas polluted by sulphur compounds (SO2, SO3) and halide species (Cl-, F-) which have to be treated to avoid the deleterious effects on human health and environment due to sulphuric (H2SO4) and hydrochloric (HCl) acid production in air. To achieve that, Flue Gas Desulfurisation (FGD) systems have been installed for about 20 years now mainly in United States of America, later in European countries and more recently in Korea, Taïwan and Thaïland.

The most common technology applied in more than 80% of existing installations consists of scrubbing the polluted gas with a slurry of lime Ca(OH)2 or limestone CaO in water (Wet FGD Process). The agressive constitutants of the raw gas are SO2, SO3, HCl and HF but SO2 is the most concentrated. SO2 and SO3 react respectively with Ca++ and H2O leading to sulfate compounds which precipitate as CaSO4. HCl and HF give CaCl2 and NaF which remain in the slurry. The chemical composition of the slurry is continuously monitored in order to insure an efficient neutralizing effect. Then the cleaned gas is blown into the atmosphere.

The process generates agressive conditions in some parts of the FGD Unit which can cause severe corrosion problems ; as a consequence, high corrosion resistant stainless steels have to be selected in order to insure the efficiency of the system .

PROCESS CONDITIONS and CORROSION PROBLEMS

The raw gas produced by burning coal or fuel oil goes through an electrostatic filter in which flying ash is removed. Then, the hot gas (generally 150-200°C/300-390°F) enters the scrubber unit and goes up while it is sprayed by the neutralizing slurry (generally 3 stages).

If the gas is HCl rich, a pre-scrubber unit can be installed to remove this acid before the main scrubbing stage; a mist eliminator is generally placed between the pre-scrubber and the scrubber to reduce gas pollution by wet HCl. When sea water is used to wash the polluted gas, the mist eliminator is compulsory.

The reaction tank where the neutralizing slurry is prepared is placed either at the bottom or near the scrubber ; a pump feeds the spraying system and insures the recirculation . A demister is placed inside the scubber above the upper spray level in order to remove liquid particles from the clean gas which reduces salt deposits. Then the clean gas is blown into the chimney.

As the clean gas is not completely depolluted, some acid condensates can be produced in the chimney causing some corrosion problems. So, in some cases, the clean gas is reheated in order to minimize such a risk. Moreover, during start-up periods, the polluted gas is generally partly by-passed ; this means that by-pass ducts and the chimney are submitted to very agressive conditions due to high temperature and acid-rich condensates.

Significant process parameters and their effect on corrosion

In some areas of the scrubber, the efficiency of the neutralisation reaction between the polluted gas phase and the slurry is not perfect leading to local formation of sulfuric acid. This acid, and the chloride and sometimes fluoride species derived from the coal, produce an agressive environment. Typical analysis for absorber solutions are : 6<pH<3, 10,000 to 50,000 ppm Cl^- (sometimes more in closed-loop systems) and F^- between 0 and 500ppm. In such conditions, and even if the medium is fluoride free, conventionnal stainless steels like 316L are prone to uniform and localized corrosion.

Moreover, the corrosion risk is enhanced in some parts of the scrubbing system where the gas velocity is low. In these parts, condensates may accumulate and concentrate, and scaling develops. The pH can reach values as low as 1 or even 0 and in the same time, the chloride concentration can increase up to 5 or 10%, and if the coal contains fluorides, the fluoride content can increase up to several thousands ppm. Under scaling, the solution becomes more and more agressive due to the lack of oxidizing species. In these conditions, uniform corrosion, pitting corrosion and crevice/underdeposit corrosion can appear.

Thus, from a corrosion point of view, one must consider different situations for which the corrosion mechanisms and consequently the corrosivity are different. Theses situations can be linked with specific locations in the FGD system :

<u>Gas Phase at the entry of the scrubber :</u> when the temperature is higher than the dew-point, condensation is not possible and the corrosion risk is low. Unfortunately, field experience shows that most often, condensation of exhaust gas occurs. The actual chemical composition of the condensates is difficult to evaluate due to complex physical (gas velocity, wall temperature) and chemical effects (mixing of agressive species like SO2, SO3, HCl). The most simple hypothesis consists of considering that SO3,SO2, HCl and HF are fully dissolved in the water contained in the gas ; this permits to calculate a pH value which may be used to evaluate the corrosion risk. This calculation shows that the pH value are very often between 0 and 1 ; moreover, if the slope of the inlet duct is not sufficient or if the flatness of the duct is not perfect, condensates may remain stagnant in certain areas and the local H2SO4 concentration may increase up to several percent. Due to the high temperature, the conditions are very agressive which explain why high Mo containing Ni base alloys have to be selected

<u>Mixing Zone Gas Phase/Liquid Neutralizing Solution :</u> in this part, the hot polluted gas is sprayed with the neutralizing slurry but the mixing of the 2 phases is not perfect everywhere. So, specific areas near the bottom of the absorber can be submitted to condensates or to saturated acid gas with high cloride contents due to the closure of the water circuit.

<u>Slurry Reaction Tank</u> : the slurry is not in itself very corrosive since the pH is generally monitored around 4.5-5.5 but due to closure of water circuits and the composition of some coal grades, the chloride content can be very high and sometimes F- ions are present. Moreover, erosion by solid sulfate salts produced by chemical reaction between S02/H2SO3 and lime or limestone can depassivate some parts of the tank,mainly the agitators.

CORROSION PERFORMANCE

Materials

Hot-rolled plates of various stainless steels including austenitic, super-austenitic, duplex and super-duplex grades have been tested. Some nickel base alloys were also investigated. Table 1 shows the typical chemical composition of these materials as well as their Pitting Resistant Equivalent (PREN) values which are often utilized as an indication for the localized corrosion resistance.

The mathematical expression generally used is Cr + 3.3Mo + 16N, but a modified version taking into account the effect tungsten is proposed in this table, as a result of previous work carried out in CLI-FAFER Research Centre .

Welded samples where also investigated : filler materials and welding processes utilized are indicated in table 3 .

Table 1 - Typical chemical composition of candidate materials

AISI or	CLI-FAFER	Average composition (% weight)								PRENW
UNS	Trademark	C	Cr	Ni	Mo	Cu	N2	W	Mn	[1]
AUSTENITICS										
316 L	ICL 164 BC	0.02	17	12	2.2					24
31725/26	ICL 170 HE	0.02	18	15	4.5		0.15			35
SUPER-AUSTENITICS										
N08 904	UR B6 N	0.02	20	25	4.3	1.5	0.13			36
N08 925/926	UR B26	0.01	21	25	6.4	0.8	0.20			45
31 266	UR B66	0.01	25	22	5.8	1.5	0.45	2	3	55
32 050	SR 50A	0.02	22	21	6.2		0.25			46
31 254	URB25	0.02	20	18	6	0.8	0.20			43
34 565	UR B46	0.02	24	17	4.5	1	0.40		4.5	45
N08 028	UR B28	0.02	27	31	3.5	1				39
DUPLEXES										
31 803	UR 45 N	0.02	22	5.7	2.8		0.16			34
32 205	UR 45 N+	0.02	22.5	6	3.2		0.17			36
32 750	UR 47 N+	0.02	25	7	3.5		0.25			41
32 520	UR 52 N+	0.02	25	7	3.5	1.5	0.25			41
NICKEL BASE ALLOYS										
N 06 625		0.02	21	bal.	9					51
N 10 276		0.01	15.5	bal.	16			4		68
N 06 022		0.015	21.5	bal.	13.5			3		66
[1] PREN = Cr+3,3Mo+16N . PRENW=Cr+3,3(Mo+0,5W) + 16N for URB66										

Testing Conditions

<u>Uniform Corrosion Tests</u> : these tests were carried out in H2SO4 solutions at various concentrations. The effect of pollution due to chloride ions (up to 30,000 ppm) was investigated at pH 0.5 and 0 at 60°C/140°F and 80°C/176°F.

<u>Localized Corrosion Tests</u> : Critical Pitting and Critical Crevice Temperature measurements were achieved in 6% FeCl3 solution according to ASTM G48 and G78 tests.

<u>Electrochemical Investigations</u> : polarization curves were carried out in order to investigate uniform and localized corrosion. The effect of a combined pollution by fluorides and chlorides was studied at pH 3 at 60°C/140°F.

The resistance to crevice corrosion was also investigated in a highly concentrated chloride containing media acidified at pH which simulates the local conditions in a crevice or under deposits. The testing temperature was 80°C/176°F. The uniform dissolution at low potential allows to evaluate the crevice propagation risk due to uniform dissolution in the crevice ; the pitting potentiel permits to evaluate the crevice propagation risk due to the development of new pits inside an existing crevice.

<u>Simulated Absorber Slurry Environment</u> : a multi-partner testing programme has been designed and carried out by CC Technologies Laboratories, Inc. using a special set-up [1]. Non welded and welded samples were submitted for one month to a gazeous environment containing 100 ppm SO2 and 5% O2 and wetted by brines containing 10,000, 20,000, 50,000 and 100,000 ppm chlorides acidified at pH 5. The temperature was monitored to 55°C/131°F and 80°C/176°F.

Main Results

<u>Uniform Corrosion</u> : various stainless steels and Ni base materials were tested in pure H2SO4 acid. The iso-corrosion chart showing the maximum temperature at a given H2SO4 concentration for which the maximum corrosion rate is 0.2mm/yr is shown in Fig.1. The concentration range between 0 and 40% is probably the most usefull for use in FGD systems including the inlet ducts and the chimney.

High Mo containing Ni base materials are obviously much more resistant than conventionnal stainless steels ; as an exemple, alloy N06022 is resistant up to about 110°C/230°F in dilute H2SO4 and at 80°C/176°F in 40% acid. In 10% acid, 316L is resistant up to 35°C/95°F while super-austenitic grades are resistant up to 65°C/149°F for N 08926 and 95°C/203°F for S31266. The super-duplex grade 32520 is resistant up to 85°C/185°F.

Such results demonstrate that high Chromium content together with Molybdenum and Copper additions are quite efficient for improving corrosion resistance in H2SO4 <40% concentration.

Another series of tests was conducted in chloride containing solutions (up to 30,000 ppm) at pH 0.5 and 0 at 60°C/140°F and 80°C/176°F ; such conditions can be encountered in mixing zones of the scrubbing system when the neutralization is not completed. The results are shown in Table 2.

These tests permitted to establish the limiting conditions for each of the grades tested, according to the measured corrosion rate. At pH=0, 25Cr stainless steels (super-austenitic or super-duplex) can be selected at 10,000 ppm Cl- and it is important to stress that 08926 super austenitic is less resistant than 32 520 super-duplex. At 30,000 ppm chlorides, hogh Mo containing Ni base alloys must be selected .

At pH=0.5, all 6Mo super-austenitic grades with Ni > 22% as well as super-duplex 32520 were found to be resistant at 60°C/140°F while at 80°C/176°F, only Ni base alloys are resistant.

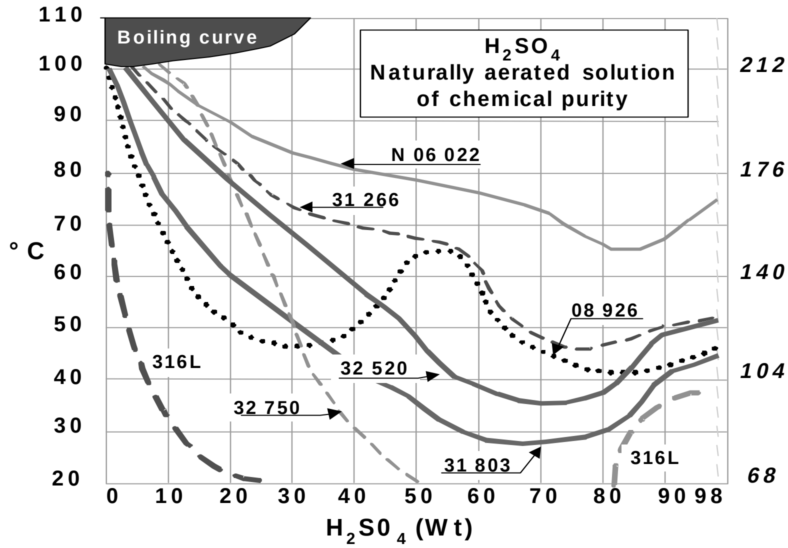


Fig. 1 – Iso-Corrosion diagram (0.2 mm/yr) in H2SO4 solutions.

Table 2 - Uniform Corrosion Tests in H2SO4 solutions (Corrosion Rate in mm/yr)

	317LNM	8926	31266	32520	N06022	N10276
pH 0, Cl- free, 60C/140F	0.05	0.02	0.02	0.02	0.02	0.02
pH 0, 10 000 ppm Cl- free, 60C/140F	2.4	0.5	0.02	0.02	0.02	0.02
pH 0, 30 000 ppm Cl-, 60°C/140F	6	2.1	0.55	2	0.02	0.02
pH 0.5, Cl- free, 60°C/140F	0.02					
pH 0.5, 10 000 ppm Cl- free, 60C/140F	0.02					
pH 0.5, 30 000 ppm Cl- free, 60C/140F	2.2	0.02	0.02	0.02	0.02	0.02
pH 0.5, 30 000 ppm Cl- free, 80C/176F		2.5	2.5	1.5	0.02	0.02

Localized Corrosion Tests : Critical Pitting (CPT) and Critical Crevice Temperature (CCT) values measured on hot rolled materials are mentionned in Fig. 2. For each grade, several heats were tested and the data are the minimum values guarantied. So, individual values are often found to be higher than those indicated in Fig.2.

The ranking for CPT is closely related to the PRENW value, whatever the microstructure of the steel ; this means that super-duplex grades are quite interesting taking into account the fact that they are less expensive than super-austenitics. The super-austenitic grade 31266 is the most resistant of the tested grades including alloy 625 type . Its CPT value is guarantied to be much higher than the CPT of the 6 Mo grade 08926 ; this result is mainly due to the combination of Mo+W+N.

The ranking for CCT is much less related to the PRENW value, but the 31266 grade remain by far the most resistant ; super-duplex grades 32520 and 32750 were found to be as resistant as the 6 Mo grade 08926.

CCT measurements were also carried out on samples welded in conditions generally utilized for manufacturing industrial vessels. Welding process, filler materials and individual CCT values are mentionned in Table 3.

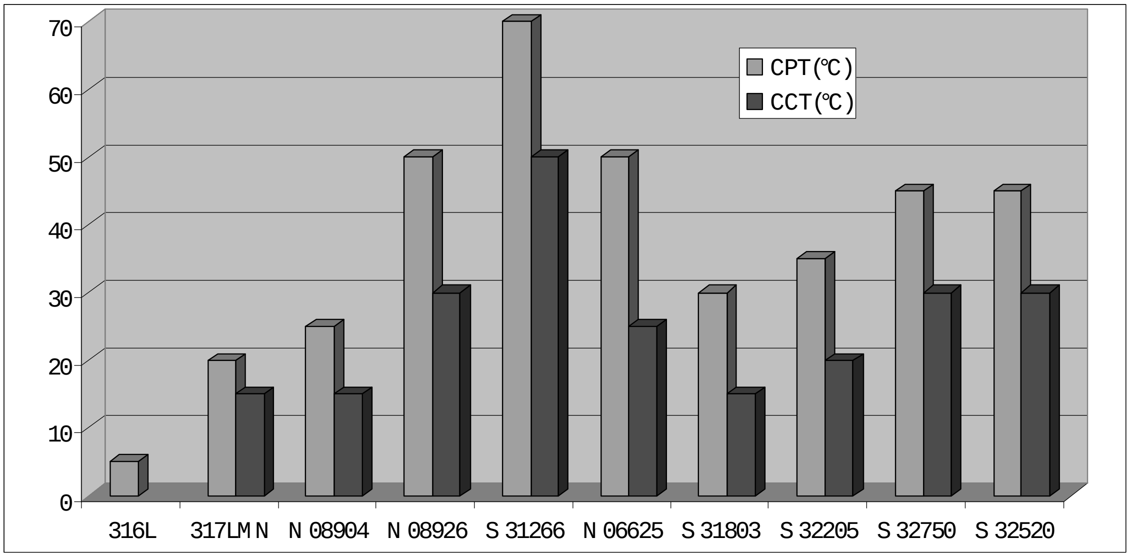


Fig. 2 – Guarantied values for Critical pitting and Crevice Temperatures in ASTM G48 Tests (6%FeCl3)

From these results, one can conclude that it is necessary to select an over-alloyed filler material in order to obtain a CCT value comparable to that of the base material. This is clearly demonstrated for super-duplex grade 31520 and super-austenitic grade 31266 which exhibit CCT values on samples welded using alloy 22 type (N06022) filler material to be comparable to that obtained on base materials.

On the other hand, the use of 625 type filler material is not recommended for welding Nitrogen containing stainless steels since Nb of the filler may react with nitrogen of the base metal, leading to some detrimental microstructure evolution in the fusion line.

Table 3 – Crevice Corrosion Tests on Welded Samples (ASTM G78)

Grades	Base Material	Welded 1			Welded 2		
		CCT	Filler Mat.	Process	CCT	Filler Mat.	Process
317LMN	22	22	Alloy 625	SMAW			
08926	41	37	Alloy 625	SMAW			
31266	60	60	Alloy 22	SMAW	60	Alloy 22	GMAW
06625	35	35	Alloy 625	SMAW			
06022	85	80	Alloy 22	SMAW			
31803	25	25	25Cr DSS	SMAW			
32520	38	30	25Cr DSS	SMAW	38	Alloy 22	SMAW

Electrochemical Investigations : polarization curves plotted in a 15,000ppm Cl- + 15,000 ppm F- solution at pH=3, 60°C/140°F show that stainless steels may suffer from pitting corrosion (Fig.3). In these conditions the 31254 grade is found to be less resistant than the conventionnal 6 Mo grade ; this result is mainly attributed to the lower nickel content of 31254.

Another important result is the very good behaviour of the super-duplex grade 32520 which exhibits the same corrosion resistance as the super-austenitic 31266 grade.

Polarization curves were plotted in NaCl 300 g/l, pH=1, 80°C/176°F which simulates the agressiveness of the medium in regions where crevice corrosion may occur (Fig.4). These conditions are very agressive so that N08904 suffers from crevice propagation due to uniform corrosion (high activity peak) and to pitting inside the crevice (low pitting potential). N08926 is less prone to crevice propagation due to uniform dissolution but some pitting may occur in the crevice.

The super-austenitic grade 31266 is much more resistant than the previous materials and even better than alloy 625 type ; it is almost as resistant as the Ni base N10276 regarding to pitting while its resistance to crevice corrosion in only slightly lower. This demonstrate that 31266 is much more very resistant than 6 Mo grades to uniform and localized corrosion (crevice and pitting) even in acidic and concentrated chloride containing media.

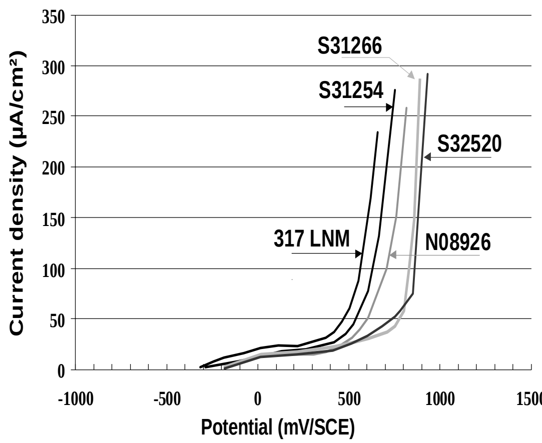


Fig. 3 - Polarization curves in 15,000ppm Cl- + 15,000 ppm F-, pH=3, 60°C/140°F

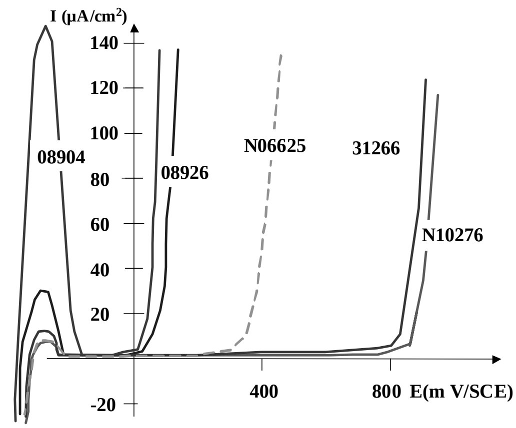


Fig4 - Polarization curves in NaCl 300 g/l, pH=1, 80°C/176°F

- Simulated Scrubbing Environment : the results of these tests [1] combined to CLI-FAFER research presented in this paper and in previous works [2,3] have been used to establish a material selection guide for slurry absorber environment (Fig. 5) and an other guide for other parts of FGD systems (Fig.6) excluding inlet ducts.

For slurry environment including spray pipes, absorber in the spray zone and slurry tank, the main parameters to be taken into account are pH, chloride concentration and temperature. At 55°C/130°F, 316L must be avoided since this material is very sensitive to pitting and crevice.

More alloyed stainless steels (PRENW > 30) may be selected according to Fig. 5 ; in such conditions, pH and chloride content are determining parameters.

pH	CHLORIDE CONTENT (ppm)									
	10 000	20 000	30 000	40 000	50 000	60 000	70 000	80 000	90 000	100 000
7	S 31 726									
6.5			S 32 205	S 32 520		N08 926			S 31 266	
6										
5.5										
5			S 31 266						N 10 276	
4.5										
4										

Fig. 5 - Material selection guide for Absorber Slurry Environments,Temperature 55°C/130°F, Fluoride content < 50 ppm

At 80°C, all materials were found to be more or less sensitive to localized attack whatever the chloride content but among them, super-austenitics 08926 and 31266 and Ni base alloys with high Mo additions may be selected.

For other parts of FGD systems, the chloride content is generally lower but the medium may be more acidic due to H2SO3/H2SO4 rich condensates. When the raw gas is highly polluted by SO2/SO3, the pH of condensates may be very low (<1) so that highly alloyed materials have to be selected. In this case, high Mo containing Ni base alloys must be used.

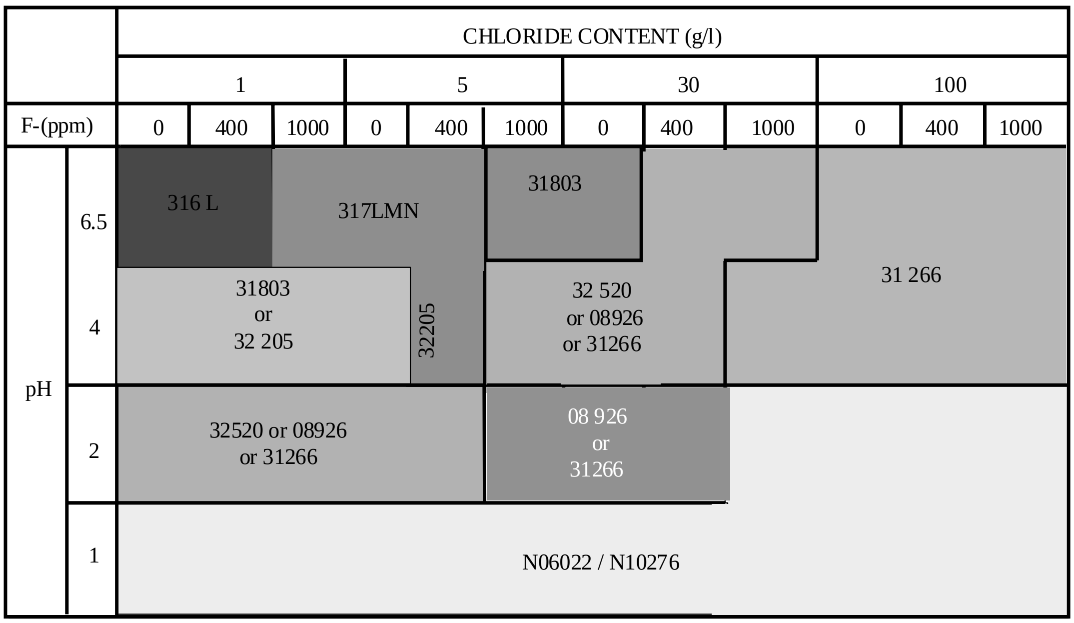


Fig.6 - General material selection guide for FGD systems at 60°C/140°F vs Chlorides, pH & Fluorides

FIELD EXPERIENCE & CLI-FAFER REFERENCES

Field tests were carried out under care of NIDI and LaQue Centre for Corrosion for a multi-client programme. Samples fitted with multi-crevice washers were exposed to several field conditions in various FGD plants in USA and Germany. The results of this programme will be published elsewhere.

An example of the results gained after testing at Orlando Utilities, FL, USA is presented in Fig.7.

316L grade is obviously very sensitive to crevice corrosion. 317LNM and 31803 duplex are more resistant but they experienced some crevice. 6Mo super-austenitic (08926 type) is correctly resistant to crevice. Ni base alloy (N10276) is also very resistant to localized corrosion, but the total weigth loss is slightly higher . This is probably the consequence of some transpassive dissolution due to the oxydizing power of the process conditions. Whatever, N10276 and N08926 were found quite satisfactory.

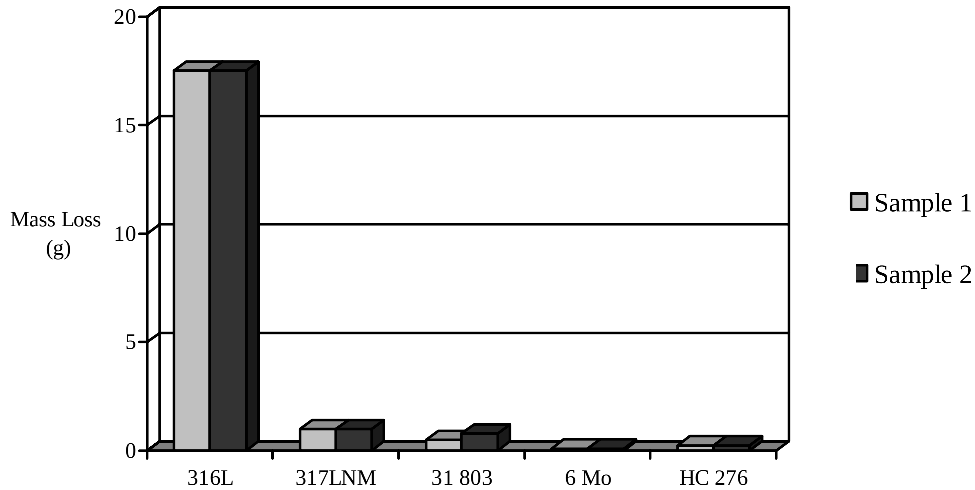


Fig. 7 - NIDI TEST PROGRAM, Orlando Utilities, Fl, USA
60,000 - 80,000 ppm Cl-, pH=5.5, 130F/55°C, 270 days

The main references for use of CLI-FAFER stainless steels and alloys in the world are mentionned below :

- S31726 : more than 2,000 metric tons (first order for Montana Power, Colstrip Units 3&4 in 1980)
- S31803 : more than 1,000 metric tons
- Super-Duplex S32520 : more than 4,000 metric tons were used for FGD systems since 1992 mainly in USA and Korea (first order in USA for TWA Cumberland)
- Super-austenitics : more than 3,500 metric tons (N08926, S 31 266 or S32050) mainly in Germany and Korea
- Ni base alloys : about 2,000 metric tons of clad plates since 1991

CONCLUSIONS

The corrosion properties of several stainless steels including super-austenitic and super-duplex materials have been investigated and compared to lower alloyed grades and to nickel base alloys in unwelded and welded conditions. Field tests were also carried out on some of these alloys.

From these tests, materials selection charts, taking into account the main process parameters like temperature, pH and chloride content were designed.

The super-duplex grade S32520 was found to be much more resistant than S31276 (austenitic) and S31803 (duplex) and close to 6 Mo grades up to 60°C/140°F. Combined to high mechanical properties and moderate cost, this super-duplex grade exhibits a very interesting performance to cost ratio.

Super-austenitic materials with Cr > 20% and Ni >23% with 5 to 6% Mo additions were found to be resistant up to about 80°C in slurry environments with high chloride concentration. More precisely, S32050 (SR50A) and S31266 (URB66) grades exhibit a better corrosion resistance than N06625 and 6Mo grade, close to Ni base alloys type N10276 and N06022. These good properties together with high mechanical characteristics make these alloys very promising for application in FGD systems.

REFERENCES

[1] CC Technologies, Final Report R 212-01 « Investigation of Corrosion Resistance of Duplex and 4-6% Mo-containing Stainless Steels in FGD-Scrubber Absorber Slurry Environments, December 20, 1995

[2] F. Dupoiron, J-P. Audouard, M. Verneau, J. Charles, « Metallic Solutions for Pollution Control Systems : Behaviour of Welded/Unwelded High Alloyed Materials », Corrosion NACE 1995, Orlando, FL.

[3] J.Charles, J-P.Audouard, M.Verneau, « Metallic Answers for FGD Systems », Corrosion NACE'98, New Orleans, LO.

National Metal Distributors, Inc.
P.O. Box 1499
Vancouver, WA 98668

Ph. (800) 878-3675
Fx. (800) 878-9709