Stainless steels for chemical process equipment


NiDI
NICKEL DEVELOPMENT INSTITUTE
NiDI Reprint Series No. 14 038

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Effective Use of Stainless Steels for Chemical Process Equipment

Chemical process equipment, piping systems and instrumentation all make extensive use of austenitic stainless steel materials of construction. Most commonly used are wrought AISI types 304L and 316L and the cast version of 316 known as CF-8M. A vast body of knowledge is available on the properties and applicability of these alloys, much of it in bulletins published by the Nickel Development Institute (NiDI).

This article provides practical guidance on ten issues most often raised by designers, plant engineers and maintenance people on stainless steels in process equipment applications. These issues are often the key to successful operation of plant equipment and represent the kind of information that is disseminated at NiDI seminars.

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Specific topics covered are as follows:
1. Dual marking and corrosion evaluation of wrought stainless steels
2. Key property differences between stainless steel and carbon steel
3. Effect of reduced molybdenum content on corrosion resistance of 316L stainless steel
4. Using ASTM specifications for stainless steel castings
5. Repair welding of corrosion resistant castings
6. Post-fabrication cleaning of stainless steel
7. Corrosion of stainless steel equipment from temporary process upsets
8. Material mix-ups
9. Corrosion of stainless steel under wet insulation
10. Microbiologically influenced corrosion (MIC) of stainless steels in waters
1 DUAL MARKING AND CORROSION EVALUATION OF WROUGHT STAINLESS STEELS

Background
Prior to the 1980s, the most commonly used 300 series stainless steels in the chemical process industry were available in two grades, those with regular carbon content ('straight grade') and those with extra low carbon content ('L-grade'). They were identified as 304 and 316, or 304L and 316L, respectively. When welding the straight grades, it was possible to 'sensitise' the base metal adjacent to the weld. Sensitisation occurs when alloys containing more than .08 per cent carbon are held in the 1200 to 1900°F (650 to 1040°C) temperature range. Excess carbon combines with some of the chromium carbides leaving the surrounding region depleted in chromium, which is the alloying element chiefly responsible for corrosion resistance. Consequently, the alloy develops local regions of significantly impaired corrosion resistance to specific environments. Sensitisation during welding is avoided in L-grades by restricting carbon to .03 per cent.

Dual Marking
Improved stainless steel melting practices have reduced the cost of lowering carbon content, so that the L-grade is now cost competitive with the straight grade. Since the reduction of carbon is achieved at the expense of strength, producers then began to add nitrogen to offset the loss. Thus the dual marked grades (304/304L and 316/316L) appeared, with the carbon content of an L-grade and the strength of a straight grade.
Initially, there was no national code acceptance for dual marked grades. Designers were obliged to use L-grade stress values. To get around this, people were known to grind off the unacceptable part of the dual marking designation and deliver whatever grade was initially specified. The ASME has now formally stated that dual marked grades may be used at straight grade stresses for all product forms and piping to 1000°F (540°C).

Corrosion Evaluation
Back when it was necessary to determine whether an alloy was L-grade and thus immune to sensitising during welding — a corrosion evaluation test per ASTM A262 was performed. A corrosion evaluation test is a quality control check involving exposure of test samples of material that has been held in the sensitising temperature range, to a highly corrosive environment under standardised conditions. Sensitised material that fails corrosion evaluation testing may perform perfectly well in service. This is because the highly oxidising environments used for corrosion evaluation testing may not typify the service environment. Therefore, corrosion evaluation testing should only be performed when it is known that a sensitised alloy would fail prematurely in the service environment.
Now that dual marked alloys predominate in the market, the requirement for corrosion evaluation is even more questionable.

Summary
For dual marked stainless steels, consider:
- Permitting dual marked stainless steels where the design specifies a straight grade.
- Not using a material marked only as L-grade where a straight grade is
called for in the design.
• Using dual marked grades in designs that originally called for L-grade to take advantage of higher allowable stresses and possible speed up in delivery.
• Specifying corrosion evaluation for services where it is known to be absolutely necessary.

2 KEY PROPERTY DIFFERENCES BETWEEN STAINLESS AND CARBON STEELS

Background
Stainless steels are principally selected over carbon steel for superior corrosion or scaling resistance. However, consideration must also be given to many other properties that affect design, fabricability and service performance. Because many designers, fabricators, and end-users are familiar with carbon steel it is useful to compare and contrast the characteristics of stainless steels with those of carbon steel.

Property Comparisons
Welding. Arc welding is affected by the thermal and electrical properties of an alloy as well as its composition and microstructure. The melting point of 304 stainless steel is 200-300°F (93-149°C) lower than that of carbon steel. Consequently, fusion of 304 requires less heat, and thus faster welding for the same heat input or less heat for the same speed. The electrical resistance of 304 is much greater than that of carbon steel. Therefore, arc welding of 304 gives more heat for the same current or the same heat for less current than when welding carbon steel. The low thermal conductivity of 304 promotes greater temperature gradients and distortion than in carbon steel. Lower rates of heat flux also mean a tendency to remain in the temperature range for sensitisation for a longer time.

Thermal Expansion. The greater rate of thermal expansion and contraction of 304 compared with carbon steel means that extra allowances must be made for movement, warping, and development of stresses in the stainless steel. For example, if stainless steel tubes are substituted for carbon steel, a design analysis is required to see if the shell requires an expansion joint.

Forming. Stainless steel frequently uses the same forming equipment as does carbon steel. In forming operations such as bending, stainless steels often require more power because of higher work hardening rate. This can result in greater springback. For grades that are hot formed, stainless steels require more power than does carbon steel due to their higher high temperature strengths. Cold upsetting of many stainless steels is limited by their tendency to work harden.

Machining. On a relative scale of cutting properties, the machinability of free-machining stainless steels ranges between 75-90 per cent that of carbon steel. The relative machinability of most other grades is only 40-85 per cent that of carbon steel. Stainless steels are considered gummy and tend to tear, have greater power requirements, tend to work harden, and require more cooling due to lower rates of heat conductivity.

Low Temperature Properties. While carbon steels retain much of their tensile properties to about 0°F, their impact resistance and ductility are markedly reduced. In contrast, wrought stainless steels lose little of their room temperature toughness and ductility to temperatures of 300°F or lower.

Summary
Successful fabrication and application of stainless steels requires understanding of their properties and performance. Those familiar with properties and behaviour of carbon steel can build on this knowledge to understand the similarities and differences with stainless steels.
• Welding—Recognise higher heat retention, lower thermal conductivity and greater thermal expansion give more opportunity for distortion.
• Thermal Expansion—Recognise greater capability for movement.
• Forming—Recognise greater tendency to work harden.
• Machining—Recognise tendency to gall and work harden.
• Low Temperature—Take advantage of superior toughness and ductility.

3 EFFECT OF REDUCED MOLYBDENUM CONTENT ON CORROSION OF 316L STAINLESS STEEL

Background
In the 1970s, technology called argon oxygen decarburisation (AOD) for refining stainless steel allowed manufacturers much greater control over the percentage of alloying elements present. In commercial terms, AOD technology permits expensive alloying elements to be reduced to the minimum specified. Prior to AOD, the manufacturers generally used the midpoints as aim in order that normal variations would not run the melts below specification minimum. With the new technology, this was not a constraint.

Molybdenum in Stainless Steel
Molybdenum (Mo) is one of the most important elements added to some stainless steels to improve resistance to chlorides and reducing acids. The greater the amount of Mo, the better the resistance. For example, 316L is the workhorse in hot acetic acid. With AOD-refined alloys, Mo content is now close to the 2.00% minimum, versus older content in the 2.4-2.6% range, both of which are within the ASTM specification tolerance of 2.0-3.0%. In some cases, the lower Mo content has resulted in corrosion rates as much as six to eight times higher, with no changes in the chemical process environment.

Corrosion Testing
If you find that you are experiencing shorter life in new stainless steel equipment and the change cannot be attributed to obvious process variations, what can be done? The first thing to do is some corrosion testing. This should include coupons with both the low minimum Mo content and the older mid-range level. If there is no difference in the corrosion rate, then Mo content is not the answer, and some change, even subtle, in the process is likely. If low Mo is the problem, it may be possible to specify a minimum of 2.4% in the material, but it is likely to cause delivery problems. The more realistic approach is to change the specification to 317L. This alloy has a Mo range of 3.0-4.0%. As with the 316L, it will have a Mo level at the low end of the range, but that will be higher than the mid-range level of the old 316L stainless steel.

Summary
• Expose stainless steel corrosion coupons with various Mo levels to help predict equipment life in borderline situations.
• Specify higher Mo stainless steel, e.g. 317L, if you determine that lower Mo is the cause of reduced corrosion resistance.

4 USING ASTM SPECIFICATIONS FOR STAINLESS STEEL CASTINGS

Background

Although most people have heard of 316 stainless steel, few recognise CF-8M as the correct name for the cast equivalent of 316. For ease of communication most of us use the more familiar terminology for the wrought alloys. When referring to the cast grades, keep in mind that if you request a 304 or 316 pump or valve, you are technically requesting it to be of wrought construction.

Availability of cast vs. wrought

In the annealed condition the mechanical properties of cast and wrought alloys are similar, but the wrought alloys have the capability to be cold worked which can greatly enhance their tensile properties. For example, cast CF-8M will have typical yield strength of 40,000 psi while 316 plate or bar can be cold worked to strengths at least twice that of its cast equivalent. In service these mechanical differences are not an issue because each piece of equipment is designed to the specific mechanical properties of the alloy. It is a common practice to specify cast pump and valve alloys to match the wrought piping but this may not be possible. For example, wrought 304 is available as 316 but cast CF-8M is much more available for pumps and valves than CF-8 which is the cast equivalent of 304. The reason is that CF-8M has much broader application than CF-8 and manufacturers have tended to standardise on CF-8M for manufacturing and inventory reasons. A purchaser should look at their casting selection separately from the piping not only for availability, but also for price. Usually CF-8M is priced more attractively compared to CF-8 than 316 is to 304.

Composition

The compositional differences between cast and wrought alloys are minor but intentional in order to enhance either castability or fabricability as the case may be. These minor compositional differences for the most part do not significantly affect the corrosion resistance of either group. Therefore, the corrosion resistance of properly produced cast alloys should be similar to that of the wrought alloys. The key point here is ‘properly produced’, and this is where the ASTM specifications come into play.

ASTM Specifications

The preferred ASTM specification for cast stainless steels is A744 because of its mandatory post-weld heat treat (PWHT) requirement. The PWHT is necessary to minimise the intergranular corrosion that a study has determined represents over 50 per cent of the industry’s corrosion problems. However, some valve manufacturers promote the use of ASTM A351 because it is the only cast stainless steel specification recognised by ASME (the Boiler and Pressure Vessel Code) on account of the emphasis placed on mechanical properties in A351. Tensile properties for the austenitic stainless steels (300 series) are not particularly relevant if they are made to the required chemistry since their mechanical properties are not influenced by heat treatment. But their corrosion resistance certainly is and hence A744 is preferred. ASTM specifications only determine the basic minimum requirements for the alloys and there is considerable latitude within the specifications as to how a manufacturer produces them. For example, the compositional limits are fairly broad and they do not address the control of secondary elements that are either intentionally added, e.g., for deoxidation purposes, or are present as a residual contaminant. Also, some of the specifications like A351 do not define heat treat requirements and even ones that do, such as A744, only define minimum temperatures. The implications of these shortcomings are that the corrosion resistance and quality of alloys can be adversely affected. An incorrect deoxidation choice can sometimes result in corrosion rates two to three times higher for certain alloys. Also, the optimum heat treat temperature for an alloy can vary depending on where in the broad compositional range it is produced.

The user of cast pumps and valves can minimise problems and achieve optimum performance by working with suppliers who are familiar with the ASTM specifications and their limitations. The availability of cast alloys will greatly differ from wrought alloys, and therefore their selection and purchase should be considered separately from wrought equipment.

Summary

For optimum service life from stainless steel castings:

• Work with suppliers who are familiar with ASTM specifications and their limitations.
• Understand differences between availability of different grades of cast alloys compared with their wrought equivalents.
• Consider specification and purchase of cast corrosion resistant stainless steels separately from wrought equivalents.

5 REPAIR WELDING OF CORROSION RESISTANT CASTINGS

Background

Occasionally a need arises for weld repair of corrosion-resistant stainless steel castings damaged by corrosion, erosion, wear or other means. Weld repair is also used to fix minor defects in the initial manufacture of corrosion resistant castings. The primary factor to consider before attempting weld repair is how to maintain corrosion resistance of the weld and heat-affected zone.

Sensitisation

Stainless steel castings are used in the solution annealed condition for maximum corrosion resistance when carbides are fully dissolved in the alloy. Welding may cause localised sensitisation, which reduces corrosion resistance, i.e., by precipitation of carbides in a normal carbon content casting (e.g., CF-8 or CF-8M). The quench welding technique has been used to avoid sensitisation if solution annealing is not possible.

Summary

• Select a low carbon weld filler metal such as E308L or E316L.
• Keep heat input low and weld for no Stainless Steel World
more than 20 seconds per weld bead.

- After welding, immediately quench the weld bead with a water spray or water-soaked rag.
- Continue quench welding until the repair is complete.

**6 POST-FABRICATION CLEANING OF STAINLESS STEEL**

**Background**
It is often necessary to clean stainless steel equipment before placing it into service after fabrication. Cleaning is done to ensure either optimum performance of the material in service or maximum corrosion resistance, or both.

Many stainless steel fabricating operations involve the need to clean before or after individual stages, such as degreasing or descaling before welding. Cleaning may include removal of oxides from hot fabrication steps and heat treatment, removal of iron contamination, and removal of machining fluids and other dirt, grease, grime, debris, and stains that occur during fabrication, handling, and storage.

**Cleaning Philosophy**
Cleaning and fabrication steps should be planned to prevent contamination and to prevent undoing the results of earlier cleaning. Contamination can result from exposure to fumes, sprays and mists, dust, iron particles, marking devices, adhesives, fingerprints, and even packaging. Cleaned material should be kept away from dirt and from dirty areas and equipment. Preventing contamination usually costs less than its removal.

**Cleaning Methods**
Descaling and cleaning methods include pickling, abrasive blasting, mild cleaning, hot alkaline cleaning, and passivation.

Pickling removes adherent oxides formed during hot processing, commonly using strong acids such as hydrofluoric, nitric, sulphuric, or mixtures. Methods used depend on the type and extent of scale and the stainless steel involved. These chemicals are hazardous and corrosive and require great care in handling, use, and disposal.

Abrasive blasting removes heavy scale and is often followed by pickling. New, clean stainless steel grit or shot must be used to reduce the risk of contamination from sand.

Mild cleaning with detergents and non-scratching abrasives is followed by rinsing with clean water and drying. Removal of finger and ink marks can usually be done with fairly non-aggressive solutions.

Hot alkaline cleaning removes drawing compounds and lubricants and is followed by water rinsing and drying, and/or solvent degreasing. Electrolytic cleaning may be employed to enhance alkaline methods. Degreasing may use liquids or vapours, or a solid-fluid mixture used in vapour blasting.

Passivation removes superficial iron or rust contamination and restores the protective oxide film with nitric acid solution or a passivating paste.


**Summary**

- Recognise the level of cleaning required for fabrication or maintenance and select a method that accomplish the task with minimum impact on equipment integrity and disposal of solvents.
- Special precautions must be taken to control exposure to chlorides and chlorinated compounds during cleaning of stainless steels to prevent pitting and cracking risks.

**7 CORROSION OF STAINLESS STEEL PROCESS EQUIPMENT FROM TEMPORARY PROCESS UPSETS**

**Background**
One of the dilemmas sometimes facing operators of batch process or pilot plants is, “What is the risk of temporarily running my stainless steel equipment outside of its stated range of corrosion resistance?” Such situations may occur when it is required to raise temperature, increase chloride concentration, or add a reducing acid such as acetic or formic.

**Factors Affecting Corrosion Resistance**
Before permitting stainless steel process equipment to be operated beyond its normal corrosive boundaries, one must understand how temporary conditions affect stainless steel’s protective, corrosion-resistant film. If the protective film can be maintained or reformed after upsets that cause it to breakdown, temporary operation is allowable. Stainless steel cookware is a classic example of equipment that operates outside of its boundaries for short periods of time because it is regularly cleaned and thereby repassivated.

Forms of corrosion that break down the protective film include crevice corrosion, general corrosion and stress corrosion cracking.

Crevice Corrosion is localised metal loss under surface deposits, enhanced by chlorides in the process environment when they concentrate in the deposits. The most susceptible location is the vapour space of reactors above the liquid level where deposits can bake on walls or inside nozzles.

General Corrosion is uniform metal loss in corrosive environments that reduce or remove the protective film. Reducing acids such as formic or very dilute sulphuric may cause general corrosion, particularly at elevated temperatures. Time of exposure is a key consideration because metal loss is a function of corrosion rate and time exposed.

Stress Corrosion Cracking (SCC) is a network of cracking into the wall thickness, most often occurring under deposits where the chlorides concentrate, such as splash zones or flash zones. Time of exposure and operating temperature are key to whether SCC will occur.

**Summary**
When considering operation of stainless steel equipment temporarily outside of normally accepted corrosion boundaries, consult a materials engineer who will use the following type of decision-making process:

- Analyse temporary conditions for presence of a reducing environment, chlorides, temperature, etc., above and beyond normal operating conditions, and their effect on the integrity of stainless steel’s protective film.
- Determine whether rapid electrochemical or crevice coupon corrosion tests are required to predict increased susceptibility to pitting or crevice corrosion under the temporary conditions.

- Develop agreement on how and
when the equipment will be cleaned to restore the surface after temporary operation or between batches. Effective clean out is the way of ensuring equipment integrity.

- Determine post-visual inspection and non-destructive testing required to ensure that the temporary operation has not compromised equipment mechanical integrity.

8 MATERIALS MIX-UPS

Background
Mix-up of materials is a real problem facing industry. Many materials look identical, but can react differently under certain process conditions. Failures have occurred when incorrect materials were accidentally fabricated or built into chemical process systems. For example, 304L and 316L stainless steels differ principally in that 316L contains 2-3% of molybdenum, improving corrosion resistance in many applications. However, in hot concentrated nitric acid, 304L actually performs better and should be used over 316L.

Identification Methods
Many materials cannot be identified simply by visual inspection; for example, 304L and 316L look the same. Identification through markings or by analysis is the only means for accurately determining material type. All properly produced plates, pipes and fittings should be marked with identifying stamps by the manufacturer. Use of a magnet is not a positive identification tool and can only be used for primary sorting of non-magnetic austenitic from magnetic ferritic and martensitic (400 series) stainless steels. Unfortunately, materials can sometimes be mismarked or accidentally or intentionally switched. It is important that everyone, from purchasing and receiving, to fabrication, installation and maintenance, check and verify all materials used to insure that they are correct. When material quality control is critical, field checks for chemical or alloy content may be necessary. These tests include:
- Chemical Spot Tests
- X-ray Fluorescence Portable Analyzers
- Portable Spectrographs

9 CORROSION OF STAINLESS STEEL UNDER WET INSULATION

Background
Piping and equipment are insulated to maintain temperature, conserve energy and protect personnel. However, insulation also can serve to trap moisture against the metal and hide any corrosion that takes place. Corrosion may proceed undetected until failure occurs. Stainless steel is subject to stress corrosion cracking (SCC) due to chlorides. Such corrosion attack can lead to failure and leaks.

SCC Conditions
SCC of austenitic stainless steels results from a combination of moisture, chlorides, tensile stress, and temperatures between approximately 140°F (60°C) and 300°F (150°C). A minimum (parts per million) level of oxygen is also necessary. Change of one or more of these factors is necessary to prevent SCC. The chosen stainless steel may be the most cost-effective material for the process condition and not easily changed. It is usually difficult to eliminate and prevent stress in fabricated equipment. Therefore, the temperature may be necessary for the process, and oxygen is almost certain to be present. So preventing external corrosion of insulated stainless steel depends upon preventing contact of moisture and chlorides with the metal.

Prevention Philosophy
Prevention of corrosion under insulation requires an integrated approach from materials selection, design and fabrication through to application/installation and finally to ongoing inspection and maintenance. The first line of defense is to keep moisture and chlorides out, the second is to apply coatings to prevent wetting of the metal, and the third is a program of inspection and maintenance to ensure dry insulation and/or detection of any wetting that occurs.

Summary
The following are methods of preventing SCC of stainless steel under insulation:
- Design:
  - Ensure that insulation is necessary.
  - Design and fabricate to exclude water, making provisions for valves, nozzles, flanges and other protrusions.
  - Select and apply protective coatings suitable for liquid immersion service.
- Installation:
  - Keep insulation and metal dry before insulating and cladding.
  - Avoid damage to protective coating during insulation.
  - Provide adequate materials and application procedures for coating, insulating, jacketing and caulking.
  - Support piping outside rather than through insulation.
  - Provide sealed inspection portholes if metal thickness checks are required.
  - Provide protection against abuse and impact.
- Operation:
  - Prevent abuse and impact, such as climbing, standing, and walking on insulated lines.
  - Avoid hosing down of insulated piping and equipment.

10 MICROBIOLOGICALLY INFLUENCED CORROSION (MIC) OF STAINLESS STEELS IN WATERS

Background
There have been numerous cases of stainless steel corrosion by microbiological organisms (MIC) in waters used for hydrostatic testing, cooling, settling, ballast, run-in, fire protection, etc. Piping, storage tanks, heat exchangers, etc. have been affected and required extensive repair or replacement. Iron containing bacteria appear to be the dominating microbial species involved. Although others have been implicated.

Failure Experience
MIC failures are exceptions to the nor-
Data on selected Austenitic stainless steels

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MIC Mechanism
Stagnant and low flow conditions promote attachment of bacteria to metal surfaces. Attachment is followed by colonization and formation of discrete deposits, starting as a film (biofilm) and frequently developing as a bulky deposit (biofilm). Composition of the deposit is significantly different from and more corrosive than the bulk water environment. Thus, under-deposit corrosion occurs, and localized attack with penetration rates as high as one-eighth inch in one month for 304L and in four months for 316L.

Summary
Considerations for prevention of MIC include the following:
- Use 'clean' waters over raw water, such as steam condensate, demineralized water or filtered and chlorinated potable water. Drain and dry immediately following a hydrostatic test, and monitor to assure compliance.

Avoid crevices where possible. They are preferred sites for attachment and growth of microbial colonies.
- Specify full penetration welds and removal of heat tint scale from weld heat-affected zones by grinding, abrasive blasting, pickling or electro-polishing. Use clean blasting media and uncontaminated grinding media.
- Chemically treat waters with biocides, dispersants, corrosion inhibitors and/or pH elevators. Consult water treatment specialist for applicable treatments.
- Regardless of the quality of the water, drain and dry and inspect to assure dryness immediately following.
Nominal mechanical properties

<table>
<thead>
<tr>
<th>Tensile strength</th>
<th>Yield strength (0.2% offset)</th>
<th>Elongation in 2&quot; (Rockwell)</th>
<th>Hardness</th>
<th>Product form</th>
</tr>
</thead>
<tbody>
<tr>
<td>ksi</td>
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<td>ksi</td>
<td>%</td>
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<tr>
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</tbody>
</table>

Suggested filler metals for welding selected stainless steel

<table>
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<tr>
<th>Base metal</th>
<th>Covered welding electrode AWS Name</th>
<th>Bare welding electrode/rod AWS Name</th>
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</thead>
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<tr>
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<td>ER 308[1]</td>
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<tr>
<td>347</td>
<td>E 347</td>
<td>ER 347</td>
</tr>
</tbody>
</table>

Note: (1) The L or low carbon grade or a stabilised grade is always used for welded fabrication except in a few instances where the slightly higher strength of the grades is more important than best corrosion resistance.

the test, i.e., within 3 to 5 days; this virtually guarantees avoidance of MIC.

Conclusions
Effective usage of austenitic stainless steels in the chemical industry is achieved by taking advantage of their many beneficial characteristics during design, fabrication, operation and maintenance. Although austenitic stainless steels are the most widely used corrosion resistant materials of construction, it is important to recognise pitfalls, which might prevent their successful application.

Acknowledgement
This paper was originally presented at the 97 Chem Show, held at the Javits Convention Center, New York, from 18–20 November 1997.
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