Presented at **INTERPHEX - USA 1994**

CONSIDERATIONS IN SELECTING A STAINLESS STEEL for BIOPROCESS EQUIPMENT

by

Paul K. Whitcraft
Director, Application Engineering/QA
Rolled Alloys
Temperance, MI 48182

ABSTRACT

An approach to selecting stainless materials for bioprocess equipment under defined conditions is presented. Using defined process conditions, the wide variety of stainless materials available can be reduced to a relatively few likely to be cost effective. Product form availability, ease of fabrication and technical support become important factors in developing a final material selection. Some suggestions regarding material specifications are offered.

Using the engineering approach presented, a specialty high nickel stainless alloy, UNS N08367, is shown to be worthy of consideration in the construction of bioprocess equipment. The material, designated as AL-6XN® Alloy, contains 25% nickel, 21% chromium and 6% molybdenum along with a small alloying addition of nitrogen. The alloy is characterized by excellent general corrosion resistance, exceptional pitting and crevice corrosion resistance, and virtual immunity to chloride stress corrosion cracking.

Wide acceptance of this material in the Power Generation, Chemical Process and Pulp & Paper industries has made the alloy readily available in all major product forms. Fabrication of components is accomplished using the same general methods appropriate for the common Type 304L and 316L stainless alloys. Standard fittings, valves and pump components are also available.

INTRODUCTION

Due to improved technology and an increasing demand for more highly corrosion resistant materials, extensive research led to an explosion of new materials over the past fifteen years. Stainless alloy selection was never an easy task, but more aggressive environments, more demanding equipment performance and a long list of candidate materials has complicated the task even further.

Much of the alloy development effort was intended to at least match the general corrosion resistance of a Type 304 stainless, while significantly improving the localized corrosion resistance in halogenated environments. Halogens, particularly chlorides, are detrimental to the performance of basic stainless alloys, resulting in some form of pitting, crevice or stress assisted corrosion. Highly alloyed nickel base alloys have been in existence for a number of years and have provided an alternative to stainless materials. For many applications, however, these materials are too costly to provide an overall economic advantage, despite their high level of effectiveness.

Recent alloy development efforts have focused on two basic alloy systems. The first area involves duplex stainless steels, which contain both austenite and ferrite in roughly 50-50% concentrations. These alloys exhibit good resistance to both pitting and stress cracking mechanisms. The second area is the use superaustenitic stainless alloys containing high levels of molybdenum. These materials offer even greater resistance to chloride pitting and crevice attack, as well as excellent resistance to stress corrosion cracking (SCC).

A SELECTION METHOD

Carpenter Technology Corporation simplified the selection of stainless alloys in the early 1960's when they introduced the Selectaloy® method. This approach was based primarily on matching a particular application with a stainless alloy's general corrosion resistance and strength. This method is still useful in many situations, particularly when machinability is also a major consideration. However, this method does not consider localized corrosion resistance which is a factor in many of today's more severe environments.

Corrosion resistance, both general and localized, is the predominant reason for considering stainless alloys. The selection process, however, can not be restricted to only considering this factor. Other criteria must also be evaluated including fabricability (machining, forming, joining) and product form availability. Mechanical properties and material availability (delivery time) become factors once the field of potential candidates has been narrowed. A closer look at these individual areas is warranted.

General Corrosion. Since corrosion is the primary reason for considering a specialty alloy, this is the most logical place to start the selection process. An approach such as the Selectaloy method can be employed to identify the general class of material and amount of alloying required. Most laboratory corrosion testing is performed to develop general corrosion resistance data. Much of this data is published in either standard reference books or the manufacturer's technical literature.

Localized Corrosion. Localized corrosion in stainless alloys is most often caused by halogen ions (i.e. chlorides) and appears as either pitting, crevice corrosion or SCC. Data on this type of corrosion is not as readily available as for general corrosion, and is subject to interpretation. Localized corrosion test data are prone to variation in results. Additionally, a wide variety of tests have been employed to evaluate pitting and crevice corrosion resistance. These tests are useful in comparing materials, but normally do not directly relate to actual performance in real service. The results can be affected dramatically by minor changes in temperature, pH, crevice geometry and the type and concentration of corrodent. Comparison of alloys must be made using data generated under identical test conditions, preferably tested side by side.

The difficulty in interpreting and correlating laboratory data to actual service underscores the value of in-situ testing. Test racks containing various candidate materials can often be placed in a unit under actual service conditions. This can be extremely useful for highly complex service environments. In-situ testing of coupons, followed by a small scale version of a process can be worthwhile steps in selecting a material if allowed by time constraints and justified by the potential risk and size of the final process system.

Fabricability. For process equipment, the most significant factor in terms of fabrication is weldability. Forming characteristics and machinability must also be factored into overall design and cost considerations, but are not normally limiting constraints. It is desirable for the material to be weldable using standard stainless welding techniques. This also means that a suitable welding consumable has been identified. Properties of the weld joint, both mechanical and corrosion resistant, must closely approximate those of the base metal. For most process equipment these properties are required in the as-welded condition since post weld heat treatment is usually not practical.

Product Form Availability. Process equipment components -- vessels, piping, heat exchangers, valves, pumps, screens, etc., require nearly all wrought product forms. An alloy should be capable of being produced in all of the forms, from heavy plate to large bar to fine wire, if it is to be considered a truly useful engineering material. The metallurgy of some alloy systems limits the ability to produce all the required forms and sizes. Selecting a material without considering this issue can mean, at a minimum, qualifying an additional alloy.

Mechanical Properties. In reality, mechanical properties are not a significant consideration for most process equipment operating below 600° F. The largest impact is usually related to decreasing the weight of the material required by taking advantage of reduced section thicknesses from stronger materials. While this can lower raw material costs, the impact on finished components is small. In some alloy systems, toughness must be taken into consideration. Some materials can exhibit ductile to brittle transition temperature effects at room temperature. Other alloy systems can undergo phase transformations which can cause a loss of toughness at temperatures as low as 500° F.

Material Availability. Material availability refers to the lead time required for delivery of a particular product form and the minimum quantity that must be bought. These are important considerations at the design stage even though at this early stage, long lead times can usually be accommodated. It is a more important consideration for long term operation of equipment where smaller components might need replacement on short notice. Specification coverage is also an important aspect of material availability. Various standards organizations exist which provide specifications detailing material requirements judged to cover the needs of the majority of end users. These specifications should be used as base ordering documents and modified only when additional requirements can be economically justified. Most materials which are available as stock items are inventoried to these specifications. Increasing requirements on a basic material specification will not only increase cost, but also decrease availability.

Cost. All of the previous factors must be taken into consideration before the cost of a system can be developed. Once the other selection criteria are satisfied, this factor controls the final selection. The selection process really involves successive iterations of the above steps with each of the potential candidate materials. Cost is not the overriding factor. Selecting the lowest cost material at the sacrifice of missing a market opportunity by three months due to availability, design changes during fabrication or fabrication problems is not a cost effective choice. Total design life cycle cost should also be carefully considered. Clearly, the actual alloy chosen will impact the service life of the unit. The other factors discussed above also have an impact on initial costs, operating costs, or both, as shown in the figure below. Maintenance costs, lost productivity and product quality often become much more significant costs over long term operation than the initial equipment costs alone.

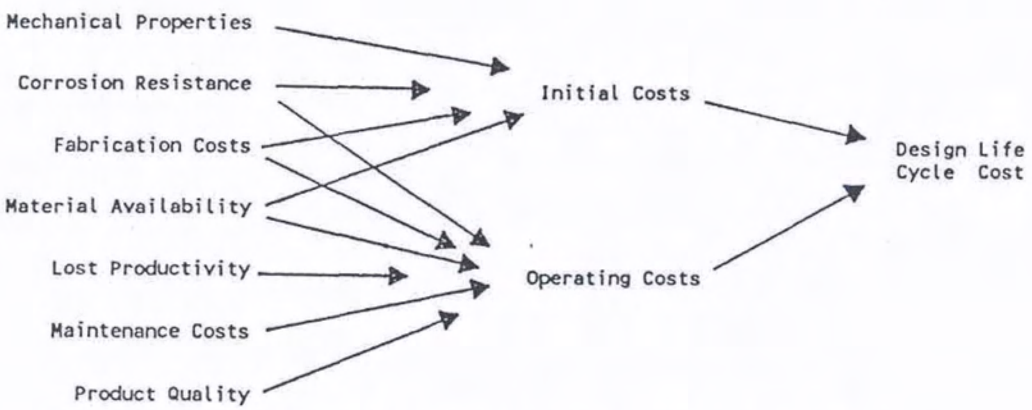

FIGURE 1 - DESIGN LIFE CYCLE COST FACTORS

APPLICATION OF METHOD

The evaluation of one candidate alloy for the construction of a bioprocess equipment system will be made using the following process design considerations. The material must be biocompatible. This generally rules out materials containing high levels of copper as alloy additions since free copper can act as a poison. The pH during processing will be neutral. Chloride concentrations in the media are expected to be as high as 10,000 ppm. During cleaning operations, both inorganic acid and caustic exposure are anticipated. Temperatures during the process cycle are not planned to exceed 120° F. During cleaning, temperatures may exceed 250° F with pressures only slightly over atmospheric.

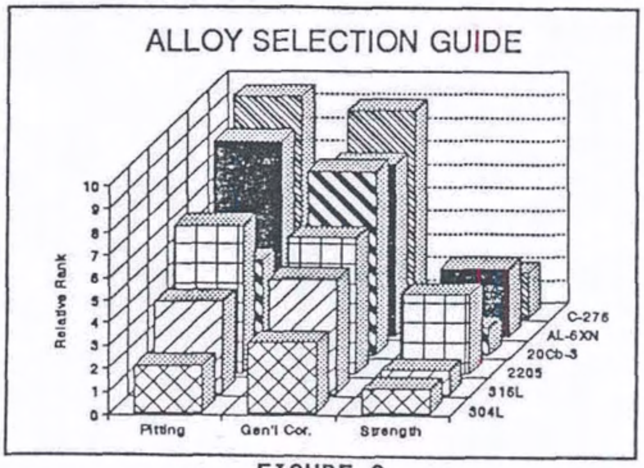

FIGURE 2

These general conditions, and current experience indicate that type 316L stainless steel be considered a base alloy from the standpoint of general corrosion resistance. The presence of chloride ions in concert with elevated temperature exposure indicate the need to consider materials with added resistance to chloride pitting, crevice corrosion and SCC. Examination of Figure 2 can help focus attention on the types of alloys to be considered.

AL-6XN Alloy (UNS N08367) is a superaustenitic stainless alloy with general corrosion resistance and resistance to halogens exceeding that of type 316L. Some general corrosion data for this alloy is shown in Table 1. The material shows excellent resistance to both strong acid and base solutions. The 2205 Alloy is a duplex stainless steel.

Environment	316L	2205	AL-6XN
10% H_2SO_4 Boiling	635	206	84
85% H_3PO_4 70° C	2.5	0.4 [a]	0.1

a - 66° C

TABLE 1 - GENERAL CORROSION RESISTANCE (MPY)

Resistance to various types of localized corrosion is illustrated in Table 2. Both the pitting and crevice corrosion data for AL-6XN Alloy reveal outstanding levels of resistance to these forms of attack compared to non-standard austenitic stainless alloys. The Critical Pitting Temperature (CPT) is the lowest temperature at which pitting begins to occur in the test media. The Critical Crevice Corrosion Temperature (CCCT) is the lowest temperature at which crevice corrosion will occur in the test media. Crevice conditions accelerate corrosion attack. While the duplex alloy can provide a high degree of resistance, the margin of safety offered by the AL-6XN Alloy is significant.

Environment	316L	2205	AL-6XN
CPT [a]	25° C	40° C	80.5° C
CCCT [b]	-3° C	17.5° C	43° C
25% NaCl Boiling U-Bends	Cracked 24-72 Hrs.	No Cracks 1000 Hrs.	No Cracks 1000 Hrs.

a - 6% $FeCl_3$ per ASTM G48A. 24 Hour periods. 2.5° C Intervals.
b - 6% $FeCl_3$ per ASTM G48B Modified. 24 Hour periods. 2.5° C Intervals.

TABLE 2 - LOCALIZED CORROSION RESISTANCE

The formability of AL-6XN Alloy is comparable to common austenitic stainless steels, such as 316L, exhibiting good ductility. Since the material is alloyed with nitrogen, the yield strength is greater than 316L and forming operations will require more power. The machining of austenitic stainless steels requires slower speeds than those used for low alloy steels. Because of the relatively high nickel content of AL-6XN Alloy, machining parameters approximate those of nickel base alloys. Surface finishes similar to those for 316L are obtained. Electropolishing of AL-6XN Alloy components has also been accomplished using the same electrolytes used for 316L, although modified parameters and current densities may be necessary. Most fabrication is accomplished by welding. AL-6XN Alloy has been welded using the standard stainless steel techniques, including GTAW, GMAW, SMAW and SAW. The filler metal used must be over alloyed relative to the base metal. Alloy 625 fillers (E/ER NiCrMo-3) are normally employed. Autogenous welds must be annealed prior to placement in service.

AL-6XN Alloy is available in all product forms. The addition of nitrogen to the alloy content makes the production of thick sections possible. Forgings with thicknesses up to 6″ have been successfully produced. Fine wire and sheet products, as well as heavy plate are practical product forms.

The nitrogen strengthening of the AL-6XN Alloy does offer a slight advantage in terms ASME of allowable design stresses. While strength is not a particular concern in this application, some minor weight savings could be obtained by utilizing slightly lighter section thicknesses. Design allowable stress values established by the ASME for the construction of pressure vessels in accordance with the rules of Section VIII, Division 1 are presented in Table 3. The impact toughness of the AL-6XN Alloy is good even at sub-zero temperatures where duplex alloys lose toughness. Also, unlike the duplex type alloys, the usefulness of the material can extend above the 600° F range.

Temperature	316L	2205	AL-6XN
100 F	16.7	22.5	25.0
200 F	14.1	22.5	25.0
300 F	12.7	21.7	23.7
400 F	11.7	20.9	22.2
500 F	10.9	20.4	20.4
600 F	10.4	20.2	19.5
700 F	10.0	NP	18.6
800 F	9.6	NP	18.0

NP - Not permitted due to 885° F embrittlement.

TABLE 3 - ASME DESIGN ALLOWABLE STRESS VALUES (KSI)

Because of the wide acceptance of AL-6XN Alloy in other industries, availability of the alloy in a wide range of product forms is excellent. Plate and sheet products are inventoried in standard thicknesses ranging from 22 gauge to 2.5″. Heat exchanger tubing inventories are maintained as well as a full complement of pipe and welding fittings. Solid bar, hollow bar and billet items ranging from 1/8″ through 8″ are also on-hand. A leading manufacturer of sanitary tubing fittings and systems has also incorporated AL-6XN Alloy components as part of their product line. All of these products are produced in accordance with standard ASTM/ASME specification coverage. The USDA and FDA have both approved AL-6XN Alloy for use in food contact articles.

The cost of corrosion resistant alloys generally coincides with their increasing corrosion resistance. Alloy content is the major and most obvious reason for this correlation. Specialized manufacturing practices can also increase costs. The relative costs for several materials is represented in Table 4. These ratios are engineering approximations only, since they can vary considerably depending on market conditions and do vary with product form.

Material	Approximate Ratio
316L	1.0
2205	2.6
AL-6XN	3.0
C-276	5.3

TABLE 4 - RELATIVE BASE MATERIAL COSTS

SUMMARY

The alloy selection process should begin by defining the expected operating conditions along with other practical engineering and commercial considerations. Designers should seek the assistance of the basic material supplier in making alloy selections. For applications involving halogen ions, careful evaluation of localized corrosion test data is required. The final material selection decision must take into consideration not only the general and localized corrosion resistance of the material, but also the fabricability, availability and total design life cycle costs.

REFERENCES

1. R. Davison and J. Redmond, "Practical Guide to Using Duplex Stainless Steels", Materials Performance, January 1990, NACE, Houston, TX, 1990.

2. M. Henthorne, "Corrosion Causes and Control", Chemical Engineering, May 1971-April 1972, McGraw-Hill, 1971-1972.

3. J. Husbands and P. Whitcraft, "High Chromium Duplex Alloy in Nitric Acid Production", Corrosion 91, Paper No. 171, NACE, Houston, TX, 1991.

4. J. McConnell and I. Franson, "Applications of 6% Mo Superaustenitic Alloy In Severe FGD System Environments", AirPol/92, NACE, Houston, TX, 1992.

5. J. Nordstrom and B. Rung, "Digesters and Pulp Storage Towers of Duplex Stainless Steels - Saving Weight and Costs", 1993 TAPPI Engineering Conference, TAPPI Press, Atlanta, GA, 1993.

6. P. Whitcraft, "High-Tech Steels to the Rescue", Chemical Engineering, January 1992, McGraw-Hill, 1992.