

Impact of Availability and Economics on Alloy Selection

Paul Whitcraft
Regional Metallurgist – Eastern US
Rolled Alloys
Barnegat, NJ 08005

Zach Schulz
Project Manager
Rolled Alloys
125 West Sterns Rd.
Temperance, MI 48182

Devin Wachowiak
Director of Metallurgical Services
Rolled Alloys
125 West Sterns Rd.
Temperance, MI 48182

ABSTRACT

Cost, availability, and performance are all driving factors in material selection.¹ Duplex stainless steels have long been of interest to the pulp and paper industry and biomass conversion due to lean alloying and good corrosion resistance. Product form availability and lead times can influence alloy selection. This paper reviews factors that should be considered when selecting a duplex stainless steel in today's market. As nickel prices rise and fall the relative cost savings may be large and/or insignificant depending on surcharges at the time material is ordered. Other factors, such as availability can also be a hindrance. Lean duplex stainless steels have been successful in replacing 300 series austenitic stainless in storage tanks where the only product forms used are plate and weld wire. In systems where multiple product forms are required, a combination of duplex alloys may be necessary to optimize the configuration.

INTRODUCTION

The use of duplex stainless steel has grown substantially, as shown in Figure 1. The pulp and paper, oil and gas, desalination and CPI industries have all increased their demand for duplex stainless steels. This significant growth is due to a combination of market growth combined with change in material selection. In 2008, the total worldwide production of duplex stainless reached about 260,000 metric tons.² Although this is a fast growth rate, it still represents only about 1% of the total stainless usage. There is room for duplex stainless steels to grow.

Duplex stainless steels are often characterized as being in one of three groups: lean duplex, standard duplex, and super duplex. There is a stark contrast in the usage between the duplex stainless steel families. The standard duplex consists of 2205 (UNS S31803/S32205). This standard duplex accounted for 22,000 metric tons per month in 2008, which was roughly 48% of the total duplex market.² In contrast, a lean duplex grade like S32304 had 17% market share in 2008, and the super

duplex grades S32750 and S32760 shared a combined market share of around 7%² A fourth group of duplex alloys, the hyper duplex materials, is emerging. Although, the entire duplex market has grown, the 2205 standard duplex still maintains the largest portion of the market. This paper is intended to provide insight into the growth of each of these duplex families.

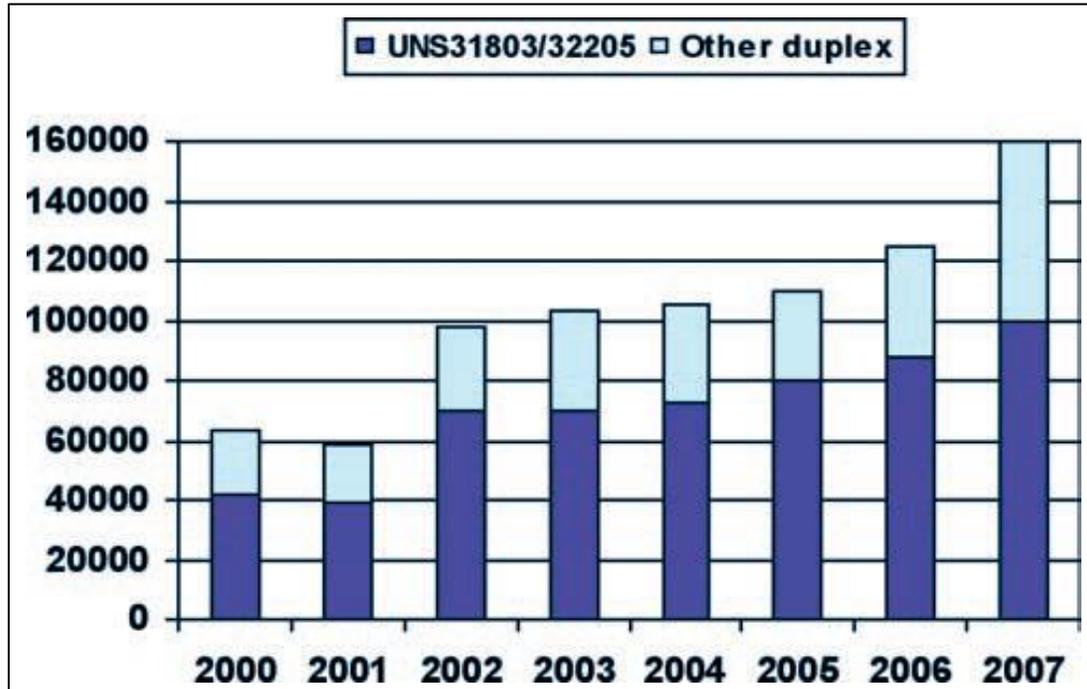


Figure 1: Crude Productions of Duplex Stainless Steel According to Global Markets²
Annual Sales (metric tons)

Despite the contrast in use between the duplex families, all grades of duplex stainless steel have increasing global demand. In fact, duplex stainless steel usage has increased over 250% from 2001 through 2007.³ This trend matches the overall stainless market.⁴

The challenge in optimizing material selection is in balancing accounting (cost), procurement (availability), and engineering (performance). All three of these criteria must be satisfied for a project to be successful. With well established materials in a stagnant economy, these choices are straight forward. In a growing market, with new technologies, new alloys, and escalating raw material costs, balancing these three factors has become more challenging.

MATERIAL SELECTION PROCESS

There is a process for selecting the most cost effective material, and it is an iterative process that considers multiple factors.⁵ The first consideration is general corrosion resistance. There are databases which offer general corrosion data for a wide range of materials and environments. Additional information may also be available from alloy producers. Once alloys with the general resistance needed are identified, consideration must be given to localized corrosion issues, such as pitting, crevice corrosion or stress corrosion resistance. While general corrosion is uniform and predictable, localized corrosion is very difficult to quantify. In addition, once it begins it can propagate rapidly, so it is desirable to select a material or design that is not susceptible to this form of attack.

After alloys that offer suitable corrosion resistance to the environment are identified, other factors need to be considered. Product form availability is often the next parameter to consider. Some materials are only available in certain forms or dimensions. This could be because of metallurgical or commercial reasons. Making a component or system of components may require the use of multiple alloys, but be careful not to create combinations that could result in significant galvanic effects. Demand also has a significant effect on availability.

Fabrication issues should be considered next. Some alloys do require more time for machining or welding than others. While these considerations won't normally be reason to rule out a material, ease of fabrication can be an overall cost factor. Strength is another parameter to consider that typically won't rule a particular material in or out. However, higher strength materials might afford the opportunity to reduce component weight, raw material costs (less material), or reduce heating or cooling costs.

Last, but certainly not least, overall cost often governs the final material selection. If cost was not a concern we could simply select the most corrosion resistant material for everything, however, this wouldn't be cost effective. But, choosing the least expensive raw material is not the most cost effective path either. Our goal should be to optimize the Total Design Life Cycle Cost. Any benefit from using a higher cost material must be offset by a combination of increased service life, reduced maintenance costs, superior product quality, less down time and less risk to the environment.

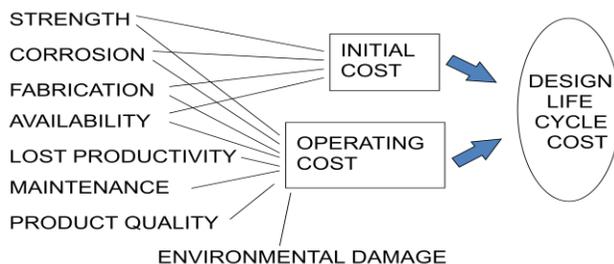


Figure 2: Design Life Cycle Costs

Often, these hidden costs are overlooked in favor of a lower initial capital cost. But in the longer run, proper material selection can have a much greater impact on operating costs.

PERFORMANCE

All duplex stainless steels offer advantages over the basic 300 series stainless grades offering roughly double the strength and excellent resistance to chloride stress corrosion cracking. Disadvantages include limited upper and lower operating temperatures as well as more planning, preparation and time for fabrication.

Lean Duplex

Most of the lean duplex stainless steels were created as alternates to a 200 or 300 series stainless steel. Much of the corrosion data generated is focused around comparison to 304L and 316L stainless. The PRE_N values in Table 1 shows how each of these grades compare in pitting resistance. Since these two grades are the largest volume in stainless steels used around the world, developing alloys to take even a small share of this market is a worthwhile endeavor. Since the duplex stainless steels have both a ferritic and austenitic phase combined with high chromium, the general corrosion resistance of the lean duplex grades is typically on par with 304L, and in few cases can offer resistance comparable to 316L. In any case, the greatest advantage of duplex microstructures over austenitic alloys is the resistance to stress corrosion cracking.

**Table 1
Nominal Chemistries for Common Duplex and Austenitic Grades⁶**

Type	Alloy	UNS	Cr	Ni	Mo	N	Cu	Mn	*PRE _N
Austenitic SS	304L	S30403	18	9	-	-	-	1	18
Austenitic SS	316L	S31603	17	10-14	2.5	-	-	1	24
Austenitic SS	317L	S31703	18	11.6	3.1	0.05	-	1.5	29
Lean DSS	2001	S32001	20	1.7	0.3	0.15	0.3	5	23
Lean DSS	2304	S32304	23	4	-	0.10	-	1	24
Lean DSS	2101	S32101	21.5	1.5	0.3	0.2	0.3	5	26
Lean DSS	2202	S32202	22.7	2	0.3	0.21	0.2	1.3	27
Lean DSS	2003	S32003	20	3.5	1.7	0.15	-	2	28
Standard DSS	2205	S32205	22.1	5.6	3.1	0.16	-	-	35
Super DSS	F255	S32550	25.5	5.7	3.1	0.17	1.8	0.8	38
Super DSS	2507	S32750	25	7.0	4.0	0.3	-	0.1	41
Super DSS	Z100	S32760	25	7.0	3.5	0.22	0.7	0.5	41
Nickel Alloy	625	N06625	22	64	9.0	-	-	0.2	52

$$*PRE_N = Cr + 3.3Mo + 16N$$

2205 Duplex

All duplex stainless steels resist the Achilles heel of the 300 series - chloride stress corrosion cracking. The original duplex alloy Type 329 offered useful corrosion resistance and high strength while having less than 30% austenite. Modern day duplex alloys, like 2205, are balanced to typically have 50% austenite and further optimize performance and ease of fabrication. Duplex alloys overall offer good general corrosion resistance and higher strength with the benefit of a cost saving. We know today that 2205 has approximately double the strength of 300 series stainless and is similar to 317L with respect to general corrosion. Due to the cost competitive supply of 2205, it has replaced 304L, 316L, 317L and even carbon steel for many applications. The higher strength allows for weight savings by permitting lighter section thickness. The improved corrosion resistance lengthens the overall life expectancy. The strength and corrosion benefits have made 2205 a competitor to many different austenitic stainless steels.

Super Duplex

Super duplex alloys extend the range of the same benefits offered by the lower duplex grades. Super duplex is an alternate to some more highly alloyed stainless steels and even high nickel grades due to lower cost and comparable corrosion resistance. Historically, materials such as alloy 400, 90-10 Cu-Ni, and the 6% Mo grades have dominated applications in seawater. Recently, super duplex has replaced these alloys for marine applications, seawater reverse osmosis, offshore oil rigs and even subsea applications. In fact, super duplex has allowed the oil and gas industry to produce pipe that handles

pressures of up to 15,000 psi (1,034 MPa) using heavy wall pipe that is stronger than nickel alloy 625. With a fraction of the cost, combined with high strength and resistance to seawater, the upstream oil and gas market widely utilizes super duplex stainless. ZERON 100 was the first super duplex produced as a cast pump housing for use in the North Sea during the 1980's. By employing critical production methods and careful fabrication, duplex grades are expected to be even more widely used as oil wells become deeper with higher pressures.⁷

AVAILABILITY

Although availability was briefly mentioned in the section on material selection, retired metallurgist Jim Kelly always said, "Availability is a material's most important property." He was correct since, even if a material has excellent corrosion resistance and extremely low cost, it is irrelevant if you can't find the alloy in the product forms you need, when you need them. High volume usage effects not only cost, but availability, too. High turnover items are more likely to be replaced and to be available off-the-shelf. Some alloys are proprietary with no stocking suppliers or are produced in only one product form. Restricted availability is not a problem for large capital projects that require large amounts of material and have generous lead times. However, an extra piece of pipe or a few fittings might be impossible to find. This availability dilemma is contrasted even within the duplex family.

2205 Duplex

2205 duplex is the most available duplex stainless steel around the globe. 2205 is particularly cost competitive, in part due to the many global mills and stockists. It is produced in nearly every product form, most of which are available from inventory. This availability has made 2205 a viable option for large and small projects as well as repair and replacement. Most new products in any industry need to create a demand in order to ramp up production and increase availability. New alloys can struggle to gain traction because mills are not willing to produce large volumes of material without firm orders. Similarly, stocking suppliers are hesitant to invest in a stocking program without an identifiable customer base. On the flip side, users are not willing to specify an alloy that is not readily available. 2205 has overcome this hurdle in recent years and has become a commodity alloy similar to 304L and 316L. This acceptance has taken some time and was aided by the fact that 2205 was never a patented alloy.

Lean Duplex

The availability of lean duplex stainless steels is somewhat a different story. Instead of one generic lean duplex grade, there are many varieties of lean duplex. Many, but not all, of these lean duplex grades are under patent and trademark. One manufacturing mill may develop a proprietary lean duplex that fits a specific application, need, or price range. They continue to market that alloy solely through their manufacturing and distribution chain. This is not an uncommon philosophy with many brands, such as Inconel[®], Hastelloy[®], or even AL-6XN[®] Alloy. In order to bring a solid financial return for the investment of creating a new alloy, each supplier may choose to brand and patent that material. Although this directs all the profits back to a single supplier, it has a downside. The downside to these branded products is the product form availability is limited to the expertise of the supplier, and the material inventory is limited to current customers of that mill. This scenario is compounded by an ever expanding list of lean duplex stainless steels in the market. With patented products like, LDX 2101[®], LDX 2404[®], ATI 2102[®], ATI 2003[®], etc., the opportunity for any particular lean duplex alloy is diluted. Less demand for a single alloy slows the progress of increasing availability in that grade. Where 2205 is now treated as a commodity, these lean duplex grades are limited to projects and often require a mix-and-match alloy list to complete a complex fabrication or system. This philosophy dampens the support of end users and further slows progress. For example, lean duplex plate is often sold for tanks

[®] Inconel, Hastelloy, AL-6XN, LDX 2101, LDX 2404, ATI 2102, ATI 2003 are all registered trademarks

and vessels. Since pipe, fittings, flanges, and weld wire are not readily available; these items are often sourced in 2205 duplex. Although this may be suitable for performance, it reduces the cost benefit of choosing a leaner alloy and complicates the project specification process.

Super Duplex

Super duplex stainless steels offer a better availability scenario than lean duplex. There are a handful of super duplex grades; all are proprietary, but none are still under a patent. The super duplex grades have been produced, at least in Europe, since the 1980's.⁷ Although super duplex is not as widely used as 2205 duplex, it has grown over the years. Extensive use in Europe has increased the supply chain with many qualified mills in Western Europe. In the past 5-10 years, other areas of the world, such as North and South America have begun stocking and using super duplex.¹ For this reason, super duplex is readily available from inventory in a wide range of sizes and product forms. Similar to lean duplex, the super duplex market is divided among several primary super duplex grades including S32760, S32750, and S32550. The fact that these alloys are in the public domain permits multiple producers to use their expertise in supplying the needed range of product forms. Sourcing less common items, like fasteners, or unusual forgings is possible, but still need to be made to order. Although the story for super duplex alloys is getting better, they still lag the availability of 2205 duplex.

COST

Cost is always important, but material costs are only part of the picture. Design life cycle costs for fabricated equipment must be evaluated to properly compare alternatives and to optimize cost effectiveness.

Before a material can be a viable option, it must fall within budget constraints. It doesn't matter how well something performs or how easily it can be obtained, if the benefits of using a more costly alloy can't be justified, it will not go forward. Life cycle cost analysis is critical to evaluating the use of higher cost alloys. Additional benefits such as reduced down time, better product quality and less risk to the environment should also be considered. Because 304L and 316L are the workhorses in chemical process environments, alloy costs of alternate materials will typically be compared to these alloys as a benchmark. For example, lean duplex stainless steels will look more favorable to 304L and 316L due to a comparable price per pound, in contrast to duplex and super duplex.

Many material suppliers monitor nickel prices on the London Metal Exchange (LME) on a daily basis. The reason for tracking nickel is because it is a leading factor in the surcharge calculation for stainless steels. Unfortunately, nickel ore and other raw elements, such as chromium and molybdenum are subject to market variations. Over the past 10 years, spot nickel prices have varied from roughly \$3/lb up through \$24 per pound and, increasing slowly at this time, are currently near \$8.50 per pound.^{8,9} Since 2005 surcharges have also included an energy factor. This roller coaster of surcharges causes great uncertainty in predicting the cost of long term projects. Duplex stainless steels are generally low in nickel content, ranging from about 1.5 to 7 wt% nickel as shown in Table 1. This contrasts with austenitic stainless and nickel alloys, which vary from 8 to 76 wt% nickel. The significant reduction in nickel content means that duplex stainless steel surcharges do not fluctuate as much when nickel costs change. Figure 3a illustrates this point by plotting the ratios of the surcharges of several alloys to the surcharge for 316L. For the selected months shown, nickel has ranged from a low of \$4.85/# to a high of \$14.57/#. The surcharges for the 6Mo alloy and 625 are significantly higher than the other stainless grades. When nickel was at the low point of \$4.85 in this plot, the surcharge for 625 was 10.6 times greater than the surcharge for 316L. However, when nickel prices peaked, the surcharge for 625 was only 4.6 times greater, significantly reducing the differential between these two alloys.

Relative Surcharge

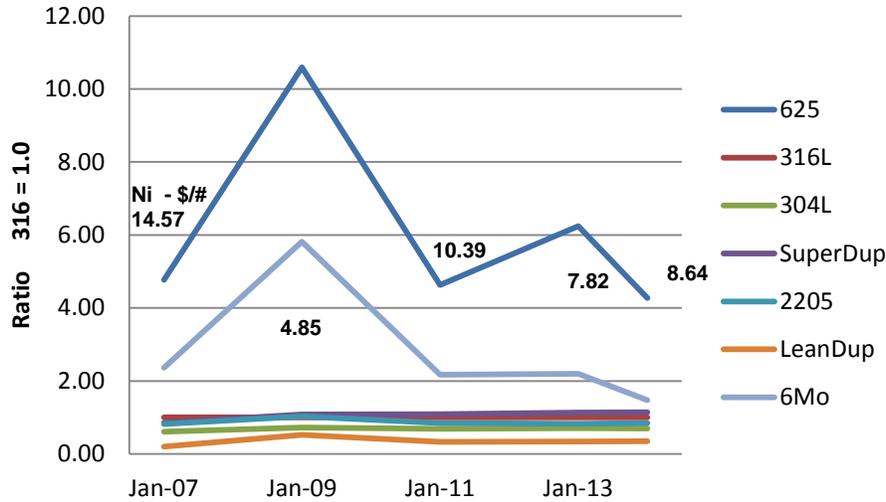


Figure 3a^{8,9}: Relative Surcharge. Ratio to 316L surcharge (y-axis) Plotted against Date (x-axis) and showing Nickel Surcharge Basis Price

Relative Surcharge

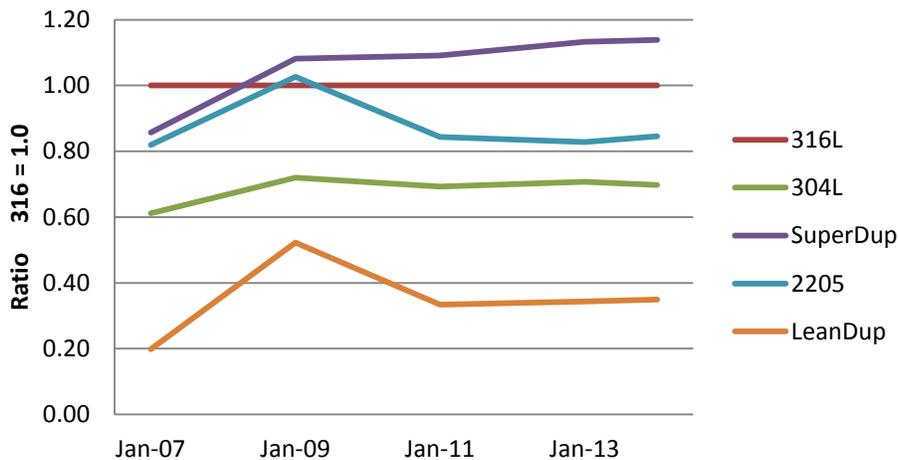


Figure 3b^{8,9}: Relative Surcharge. Same as 3a except excluding the high nickel alloys.

Figure 3b is a closer look at the lower portion of the plot in 3a. This illustrates that, at what appear to be more common levels for raw materials costs, the surcharge for Alloy 2205 is less than the surcharge for 316L. As the raw material and energy costs rise, the surcharge for duplex alloy 2205 is even more attractive and can even result in surcharges for the superduplex alloys that are less than those for 316L. The graph also shows that the surcharge for lean duplex stainless steels is substantially below the surcharge for 304L. This means that a project designed in a duplex alloy will be less subject to price fluctuation due to escalating raw material costs than one designed with an austenitic stainless steel.

Please keep in mind that this discussion pertains to the surcharge only and does not include the base metal price to which the surcharge is added. Base prices for alloys are dependent on a number of factors, not just alloy content. In addition to alloy content, base prices must also take into account the costs to convert the ingot to a particular shape, normal yield losses during processing, and economies of scale (demand).

CASE HISTORIES

Lean Duplex 2101 for Chemical Storage Tank

Lean duplex 2101 (UNS S32101) stainless steel was chosen for a storage tank at a chemical company located in the southeastern U.S. The tank stores a chemical intermediate used to make plastics at an approximate capacity of 1.25 million US gal (4.7 million L). This 50 ft. (15.2 m) diameter, 48 ft. (14.6 m) high tank was fabricated using approximately 75 tons of S32101 plate. S32101 was chosen as the material of construction for this storage tank over 316L stainless steel due to increased strength and resistance to chloride SCC. Because of the high strength of lean duplex, the wall thickness was reduced for three of the six elevations versus 316L, reducing material weight by over 11,000 lbs (5,000 kg). This resulted in a 10% material reduction for the tank walls.

Entire Family of Duplex Stainless Used at Pulp & Paper Plant

All varieties of duplex including lean duplex S32101, duplex 2205, and super duplex S32760 and S32750 have been used at a pulp and paper plant in the southeastern US. Lean duplex S32101 was used for various capacities including a black liquor tank and a caustic tank. Lean duplex was also used for evaporators over 300 series stainless steel due to its high strength and good resistance to chloride SCC. Standard duplex 2205 was used for various process vessels. Super duplex S32760 and S32750 were used in various acid tanks including one handling sulfuric acid and another handling sodium chlorite.

2205 and 2304 Duplex Used in Batch Digesters

Batch digesters are typically 8 to 13 feet in diameter and up to 60 feet in length. The mixture of chips and pulping liquor cook for approximately 2 hours at up to 338°F. At the end of the cooking cycle the contents of the digester are blown out the bottom of the digester into what is referred to as a blow tank. Here the impact of the pulp falling into the blow tank breaks apart the fibers.

As paper mills increase throughput at the digesters, temperatures are raised and the composition of the pulping liquors adjusted. Both have lead to increased corrosion rates.

Historically, most batch digesters were constructed out of heavy carbon steel plate. The recent trend has been to construct digesters out of solid duplex stainless plate; most commonly using 2205 or 2304 duplex. Duplex grades 2205 and 2304 are stronger than 304 or 316L stainless. Because of this, solid duplex digesters can be fabricated with a lighter wall than steel digesters designed to hold the same pressure.

2205 and 2304 Duplex Used in Continuous Digesters

The majority of continuous digesters are of the Kamyr design. Continuous digesters are vertically oriented and feature one or two cylindrical digester shells. A continuous digester can be between 25 to 30 feet in diameter and over 200 feet tall.

In the one shell design the wood chips continuously move from the top of the vessel toward the bottom. As they descend they are impregnated with cooking liquor, cooked, washed, and then discharged to the blow tank.

In the two shell design pulping liquors are introduced to the wood chips in the first vessel or impregnation vessel. The cooking of the chips and washing is then performed in the second vessel.

The majority of continuous digesters are constructed of A516 Grade 70 material. In some cases this material is roll clad or lined with 304L stainless sheet. Recently some have been built of 2205 stainless. Continuous systems offer fewer opportunities than batch digester systems for duplex use. These systems have fallen out of favor as they offer less production flexibility than batch systems.

Digesters constructed of steel are subject to caustic stress corrosion cracking in non-stress relieved areas near welds. Prior to 1980, the ASME Code did not require stress relief of vessels below 1-1/4" thickness. In 1980, a catastrophic failure occurred in a steel vessel. As a result stress relief is now standard on all steel digesters. This adds additional costs and as a result make thin walled 2205 or 2304 digesters more economically competitive. Steel digesters are also subject to general corrosion in higher temperature pulping processes and pitting corrosion if not properly inhibited during acid cleaning.

CONCLUSIONS

Cost, availability, and performance must all be considered in the material selection process. Duplex stainless steels have long been of interest to the pulp and paper industry and biomass conversion due to lean alloying and good corrosion resistance. Total design life cycle costs can vary significantly as the relative alloy costs change with fluctuating prices in raw materials. As nickel prices rise and fall the relative cost savings may be large, or insignificant, depending on surcharges at the time material is ordered. Poor availability can also be a roadblock to specifying non-commodity type alloys. Lean duplex stainless steels have been successful in replacing 300 series austenitic stainless in storage tanks where the only product forms used are plate and weld wire. In plate there are many lean duplex steels to choose from that are readily available from both distribution and mill delivery. In contrast, it may not be as easy or economical to switch a piping system or heat exchanger from a 300 series austenitic to a lean duplex. In situations where certain product forms are not available, a combination of lean duplex and 2205 duplex may be the most cost effective solution. Although the range of super duplex alloys is more narrow, the availability of product forms and sizes is actually better than that of the lean duplex family.

REFERENCES

1. Z. Schulz, D. Wachowiak, P. Whitcraft, Availability and Economics of Using Duplex Stainless Steels, NACE Corrosion 2014, March 2014.
2. J. Chater, "The European Market for Duplex Stainless Steels: Rapid Growth Expected," Duplex Steel World, March 2010.
3. J. C. Gagnepain, "Duplex Stainless Steels: Success Story and Growth Perspectives," Stainless Steel World America, December 2008.
4. J. Rowe, "Stainless Steel in Figures 2013," International Stainless Steel Forum (ISSF), Brussels, Belgium, May 2013.
5. P. K. Whitcraft, "Try Aerospace Specialty Alloys in the CPI Plant", Chemical Engineering Progress, May 1995.
6. Annual Book of ASTM Standard - Iron and Steel Products, Volume 1.03, ASTM A240-13, ASTM International, West Conshohocken, PA, 2013.
7. R Francis, G Byrne, "Experiences with Superduplex Stainless Steel in Seawater," NACE Corrosion 2003, Paper No. 03255 (Houston, TX; NACE International, March 2003).
8. ATI Surcharges, <http://www.atimetals.com/businesses/ATIFlatRolledProducts/Tools/Pages/surcharges.aspx>, June 2014.
9. Outokumpu Surcharges, <http://www.outokumpu.com/en/pricing-aaf/surcharges-north-america/Pages/default.aspx>