

Availability and Economics of Using Duplex Stainless Steels

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ABSTRACT

Cost, availability, and performance are all driving factors in material selection. Duplex stainless steels have long been a point of interest to the pulp and paper industry and biomass conversion due to lean alloying elements and good corrosion resistance. The caution with using duplex stainless steels is in understanding relative price compared to similar austenitic alloys and realistic availability. This paper reviews decisions to be made when considering a duplex stainless steel in today's market. Lean duplex has been successful in replacing 300 series austenitic stainless in storage tanks where the only product forms used are plate and weld wire. In contrast, it may not be as easy or economical to switch a piping system or heat exchanger from 316L to a lean duplex. In situations where certain product forms are not available, a combination of lean duplex and 2205 duplex can be used. This story of supply and demand is not a new phenomenon. Even 2205 duplex was once a "new" grade, but is now readily available from many suppliers in nearly every product form at an economical price. Some positive experiences are when an end user finds a need (demand) and works with a supplier to develop the product and increase availability (supply). These are growing pains that need to be understood or users will either waste money or never develop new products.

Key words: Duplex, Super Duplex, Lean Duplex, Availability, Performance, Cost, Surcharge

INTRODUCTION

Duplex stainless steel usage has increased drastically as shown in Figure 1. All industries, including pulp and paper, have 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 duplex usage globally reached about 260,000 metric tons.¹ Although this is a fast growth rate, it is still only about 5% of the total stainless usage. There is room for duplex stainless steels to grow.

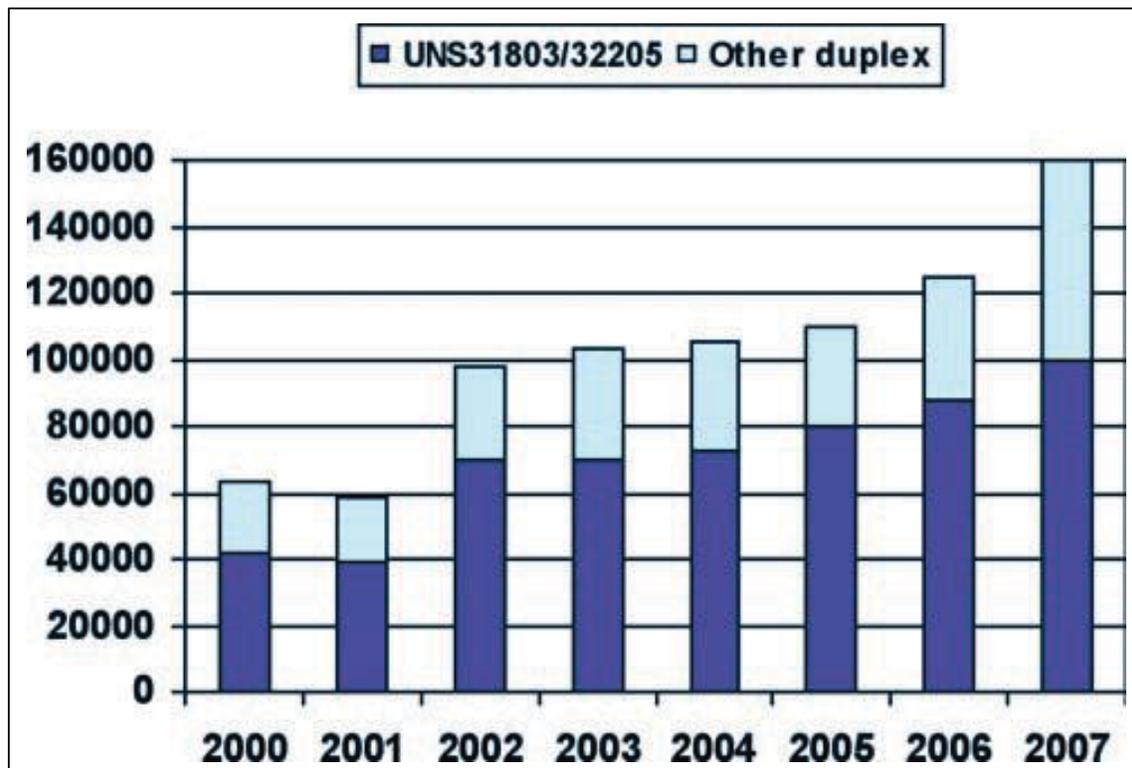


Figure 1: Crude Productions of Duplex Stainless Steel According to Global Markets²
Annual Sales (metric tons)

The selection process of raw material for any application should always consist of considerations of the cost, availability, and performance of the material. The challenge is optimizing the balance between 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 easy. In a growing market, with new technologies, and more steel mills and alloys coming online, these three factors have become variables. This paper reviews the history and current conditions for the use of duplex stainless steels in the pulp and paper industry. Although the pulp and paper industry was one of the first industries to adopt duplex stainless steels, it is still important to analyze duplex stainless growth and development.

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.¹ 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%.¹ 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.

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 2007.² This trend matches the overall stainless market.³

AVAILABILITY

Retired metallurgist Jim Kelly always said, “Availability is a material’s most important property.” He was correct because 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. There are many alloys that look great on paper, but are not realistically available. These are jokingly referred to as Unobtainium.⁴ Duplex stainless steels have a wide range of availability. Some alloys are proprietary with no stocking suppliers or are produced in only one product form. This works great for large capital projects that only require large amounts of plate. 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 of equipment. 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 a customer base. On the other side of the story, users are not willing to specify an alloy that is not readily available. 2205 has overcome this hurdle in recent years and is verging on joining the commodity classification along with 304L and 316L, which have been the leaders in the stainless realm for many years. This process has taken a long time and was pushed forward by the fact that 2205 is not under patent and is often viewed as a commodity. This motivates any stainless supplier to produce and stock the grade with a high confidence level that it can, and will, be widely consumed.

Lean Duplex

Lean duplex stainless steels carry a different story than 2205. 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 develops 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 AL-6XN[®]. In order to bring a solid financial return for the investment of creating a new alloy, each supplier must 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 becomes watered down. Less focus on a single alloy slows the progress of increased 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 piece of equipment. This philosophy dampens the support of end users and further slows progress. For example, lean duplex plate is often sold for tanks 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 lessens the cost incentive and confuses the specification.

Super Duplex

Super duplex stainless steels carry a slightly different 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

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have been produced, at least in Europe, since the 1980's.⁵ 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 relatively available from inventory. Unfortunately, there are still only a handful of suppliers and a handful of stockists. Similar to lean duplex, the super duplex market is divided among several primary super duplex grades including ZERON[®] 100 (S32760), SAF 2507[®] (S32750), and Ferralium[®] 255 (S32550). Dividing the market share means that some grades are available in seamless pipe, while others have better availability in bar or plate. Sourcing odds and ends, like fasteners, or unusual forgings is possible, but still need to be made to order. Although this story is getting better, it is still far behind that of 2205 duplex.

PERFORMANCE

Now that availability has been discussed, performance is the next factor to consider. Just because an alloy is easier to find, doesn't mean it will be a suitable alternative. Duplex stainless steels in general have similar properties, such as high strength and good resistance to chlorides and other corrosion. Disadvantages include limited upper and lower operating temperatures as well as special care during fabrication.

Lean Duplex

Most of the lean duplex stainless steels are manufactured to compete with 300 series stainless steels. Much of the corrosion data generated is focused around 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 corrosion resistance of the lean duplex grades is typically at least on par with 304L and in some cases can offer an improvement over 316L.

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

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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 using less nickel. Modern day duplex alloys, like 2205, further optimized 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 in regards 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 to counteract any cost increase. 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 has replaced many stainless steels and even high nickel grades due to lower cost and comparable corrosion resistance. Historically, alloys such as alloy 400, 90-10 Cu-Ni, and 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 625 nickel alloy. 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. In fact, 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.⁵

COST

Cost is always important. Overall, material and equipment costs must be affordable to maintain production profits. Material costs would ideally be consistent and or predictable to manage long term projects. Material costs must also be evaluated to comparable alternatives to avoid over spending.

At the end of the day, economics drives all construction projects. 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 justifying the use of higher cost alloys. Additional benefits such as reduced down time, reduced maintenance and less risk to the environment should also be considered. Because 304L and 316L are the workhorses in chemical process environments, alloy costs of new materials will always 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, raw nickel prices have varied from roughly \$3/lb up through \$24 per pound and back down to current prices at \$6 to \$7 per pound.⁷ This roller coaster of surcharges causes great pain 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 materials, which vary from 8 to 76 wt% nickel. The significant reduction in nickel content means that duplex stainless steel surcharges do not fluctuate as greatly when nickel costs change. Figure 2 shows the last 3 years of surcharges for some common duplex grades and austenitic grades. In these three years, the price of nickel has varied from \$7.50/lb to \$12.82 as noted by each month at the bottom of the plot. The alloy 625 surcharge is significantly higher than the other grades. With about 64% nickel, changes in nickel surcharge more drastically affect the final cost of the alloy 625. Although 316L stainless has a much lower surcharge, it is still higher than all the duplex grades. This means that a project designed in 316L stainless will have greater fluctuation in total estimated cost over time compared to a duplex like 2205. Please keep in mind that this is a surcharge only and does not include the base metal price. For example, the surcharge for super duplex is currently lower than 316L stainless but the total sell price with base price + surcharge is higher than 316L.

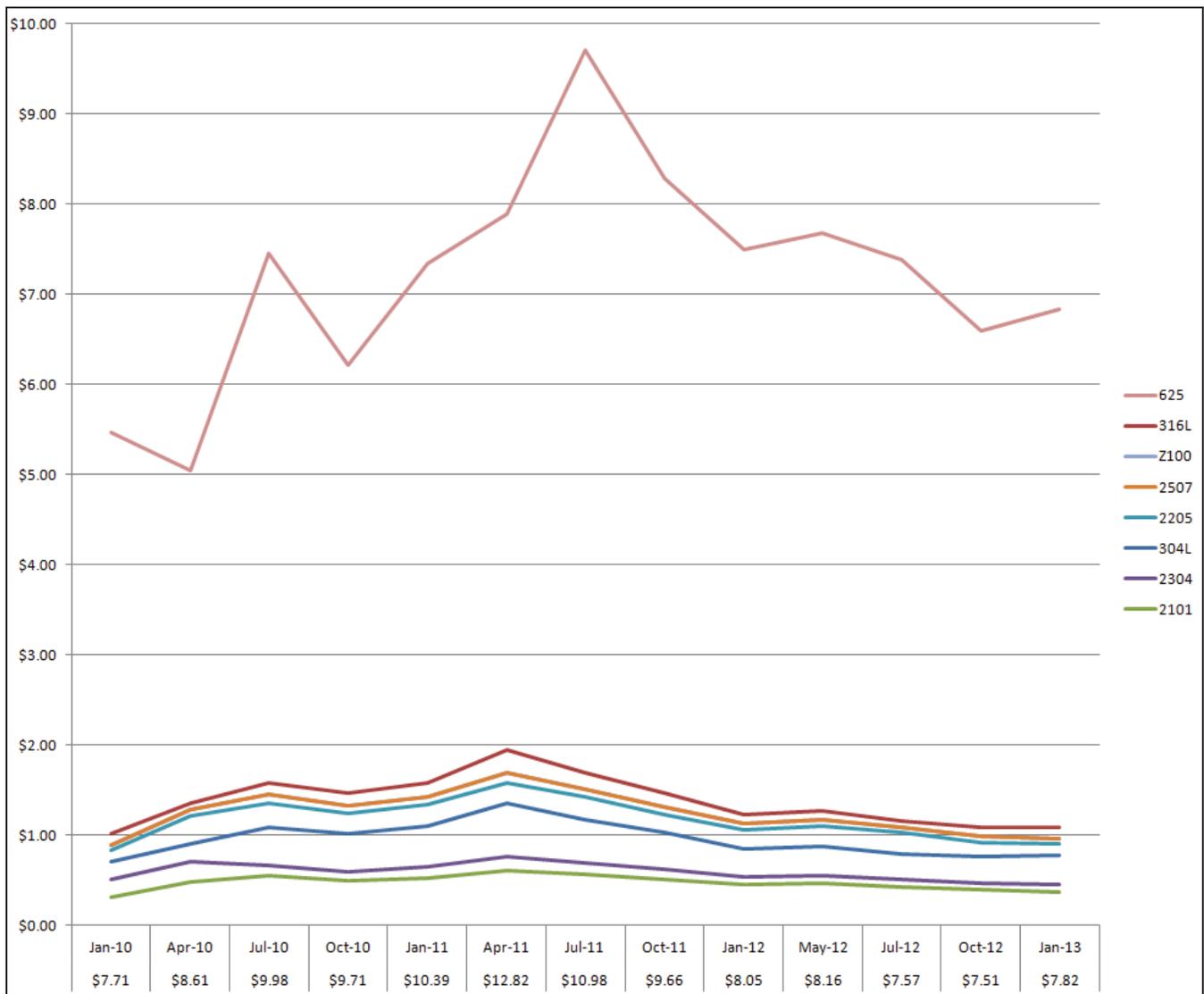


Figure 2⁷: Historical Surcharge. Surcharge (y-axis) Plotted against Date (x-axis) with Nickel ore Surcharge at Each Individual Month

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 are all driving factors in material selection. Duplex stainless steels have long been a point of interest to the pulp and paper industry and biomass conversion due to lean alloying elements and good corrosion resistance. The caution with using duplex stainless steels is understanding the relative price compared to similar austenitic alloys and the realistic availability. As nickel prices rise and fall the relative cost savings may be large 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 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 are used. This story of supply and demand is not a new phenomenon. Even 2205 duplex was once a "new" grade, but is now readily available from many suppliers in nearly every product form at an economical price. Lean duplex stainless steels are still catching up. Some positive experiences are when an end user finds a need (demand) and works with a supplier to develop the product and increase availability (supply). These are growing pains that need to be understood or users will either waste money or never develop new products.

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