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Duplex and Super Duplex Stainless Steels, and Their Applications in Steam Assisted Gravity Drainage (SAGD)

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Abstract

As oil reserves decrease, the level of difficulty to extract oil increases. With this increased difficulty, the service conditions involved in Steam Assisted Gravity Drainage (SAGD) are increasingly more aggressive. In an effort to maintain low raw material prices without sacrificing performance, duplex and superduplex stainless steels have been used for many applications to resist corrosion from chlorides, withstand extremely high pressure and still stay cost competitive. This summary of case histories shows where duplex stainless steels have been successfully utilized in the Alberta Oil Sands as well as across the globe. Duplex stainless steels have replaced leaner austenitic stainless steels and low alloy steels because of their increased corrosion resistance. In other cases, duplex and superduplex stainless steels have replaced higher nickel-chromium-molybdenum grades because of their lower cost and similar performance. For example, super duplex stainless steel has already been used as an alternate to six percent molybdenum grades in brine concentrators throughout Alberta, Canada.

What is Steam Assisted Gravity Drainage (SAGD)?

Steam Assisted Gravity Drainage (SAGD) is the process that makes the recovery of heavy crude oil found deep in tar sands possible. The process consists of two parallel wellbores drilled into the oil reservoir about 15 feet apart. The top wellbore is used as the injection wellbore; carrying high pressure steam to the reservoir. The steam is used to decrease the viscosity of the oil containing tar sands in the well, allowing the mixture to drain to the lower wellbore. The lower wellbore is used in the oil retrieval process as it pumps the lower viscosity bitumen to the surface where it can be processed to separate the oil from the mixture.

Increased demand for SAGD

It is no secret that the need for oil has become more prevalent in recent years. As easily recoverable sources of oil become depleted and reserves become harder and harder to recover, newer technologies (like SAGD) will need to be utilized more to ensure that the high demand for oil is met. While horizontal wells have been used in the past, many of the reservoirs using horizontal drilling for heavy oil production have not been able to extract all of the oil in the well as most of the reserves have stayed in the ground. The tar sands located in Alberta Canada have great potential to fill the need for increased oil consumption. Over 100 mechanical zero liquid discharge systems are now in operation worldwide using RCC* Brine Concentrator and Crystallizer technologies, including two SAGD heavy oil recovery projects currently underway in Alberta¹. The delay in using these resources is due to the difficulty of extracting oil trapped in the tar sands. As the cost of crude oil increases, the higher cost of extracting the tar sands in western Canada becomes feasible. Oil reservoirs using SAGD techniques are now able to extract 60% of the heavy crude oil in a well².

Corrosion in SAGD

In the SAGD process, there are many areas where corrosion can take place. Each different stage of the process ranging from steam generation to downhole drilling to water treatment can each have different methods of corrosion that could cause problems for the process as a whole. While many different types of corrosion could be present in the various stages of a SAGD facility, a few types of corrosion are more prevalent than others.

Chloride Stress Corrosion Cracking.

One of the biggest potential failures in SAGD applications is due to chloride stress corrosion cracking (CSCC). The water used to loosen the oil and sand mixture is typically very high temperature (above 120°F) and often contains high levels of chlorides. This combination is prime for CSCC and extremely detrimental for 300 series stainless steels. Solutions at elevated temperatures with various levels of chlorides in them, promote CSCC. For CSCC to occur three conditions must be met. The first condition is very simple; there has to be a source of chlorides in the fluid. The second condition is that elevated temperatures (above 120°F) must be present. This criterion is easily met in this case as steam is being pumped into the well. The third condition for CSCC to occur requires that there is a source of stress on the material. This can be either mechanical or thermal and is usually both³. Pressurized steam presents a relatively aggressive environment for CSCC as the steam provides both mechanical stresses from the pressure and thermal stresses from the heating process. In SAGD the elements for CSCC are all present which makes this type of corrosion a true concern. The key to resist CSCC is either to use a high nickel alloy with over 20% nickel or a low nickel alloy that is at least partially ferritic. Figure 1 shows the relationship between nickel content and potential for chloride stress corrosion cracking.

Pitting and crevice corrosion.

In any wet chloride application, there is a limit for each alloy where pitting or crevice corrosion will occur. The higher concentration of the corrosive media combined with elevated temperatures can cause pitting or crevice corrosion to occur. The chemistry of each alloy determines the limits of pitting or crevice corrosion. In other words, even if the temperature is low enough to avoid failure due to chloride stress corrosion cracking, the alloy may still form pits and eventual failure. Chlorides, such as NaCl, are found in the service water in SAGD applications. On some occasions the solution is concentrated to a brine to encourage holding the heat from the steam generators¹. For this reason, a fully ferritic alloy like 410 stainless may not suffer CSCC, but the high chlorides will cause rapid pitting and failure due to material loss. The key to resisting pitting and crevice corrosion is to utilize an alloy with high levels of chromium, molybdenum, nitrogen, tungsten and other elements that assist in forming a strong, tightly adhering passive layer⁴.

Microbially-Influenced Corrosion (MIC).

Microbially-influenced corrosion is most common in water systems that have the potential to operate intermittently leaving stagnant water in the system for periods of time. The stagnant water optimizes conditions for microorganism growth. Some sulfate-reducing bacteria will produce hydrogen sulfide. The hydrogen sulfide can cause sulfide stress cracking in carbon steels and other alloys depending on the hardness. Other bacteria actually form sulfuric acid which rapidly pits 300 series stainless steels. If sulfuric acid levels are high enough, even 22 percent chromium duplex stainless steels, such as UNS S32205 can pit. Figure 2 shows the isocorrosion curves for 316L, duplex and 6% molybdenum alloys in sulfuric acid. Chlorine can be added into the water to help control the effects of MIC, by reducing bacteria levels. Even though the

chlorine limits the amount of MIC attack, the chlorine at high temperatures may cause corrosion similar to that of sodium chloride found in ocean fed service water piping systems³.

Alloys Used in SAGD

Various materials are used in the SAGD process ranging from mild steels through highly corrosion resistant stainless and duplex stainless steels.

In some areas where chloride concentrations and temperatures are low, commodity stainless steels, like 304L and 316L are used successfully. In most areas above and below the ground, higher alloys such as 6% molybdenum grades have been used. For example many brine concentrators have used the 6.3% molybdenum alloy N083675. With 24% nickel the N08367 also has good resistance to CSCC. In more recent years, raw elemental prices have changed rapidly. The extreme rise and fall of nickel ore has encouraged the use of a leaner alloy.

Due to the high temperatures and possible corrosive activity in the numerous systems in a SAGD facility, duplex stainless steels are being used more often to be able to handle the corrosive nature of the environments. These alloys are also being used to keep strength levels high and costs low. The duplex grades have several benefits including high strength, low cost and excellent resistance to CSCC. For example, 2205 duplex stainless has only 5% nickel which keeps the cost very competitive with 300 series stainless steels. Higher grades like superduplex S32760 have corrosion resistance similar to that of a 6% molybdenum alloy while maintaining a much lower price due to only 7% nickel. In addition to price and corrosion resistance, the duplex grades are nearly twice the strength of a 300 series austenitic stainless⁴.

Standard duplex (UNS S32205) and superduplex stainless steels (UNS S32750, S32760) are already being supplied into Canadian SAGD plants to handle the corrosive environments associated with brackish water. These same alloys are also used in many other areas throughout production. Tanks, tubes and above ground piping systems are now made from duplex grades.

Overview of Duplex Stainless Steels

“Duplex” describes the family of stainless steels that are neither fully austenitic; like 304; nor fully ferritic, like 430 stainless. Rather, the structure of a duplex stainless steel is comprised of a roughly 50/50 phase balance of both austenite and ferrite. These alloys consist of austenite formations submerged in a continuous ferrite matrix. Due to this phase balance, the alloy combines many of the positive features of both austenitic and ferritic phases. The austenite in the alloy promotes good formability and ductility along with good general corrosion resistance. The ferritic matrix promotes resistance to chloride stress corrosion cracking and higher strengths than common stainless grades.

Duplex stainless steels are currently used in many industries including marine environments, chemical process industry, oil and gas, and desalination. They are produced in all product forms that are currently made in 300 series grades. Duplex stainless steels have also been formed, welded and otherwise fabricated for numerous applications. Due to the 50/50 mixture of ferrite and austenite it is important to limit the service temperature to below 600°F.

Advantages of Duplex Stainless Steels

As previously stated, the duplex family of stainless steels has many advantages over standard austenitic or ferritic stainless steels. The corrosion resistance of duplex grades is significantly greater than that of common 304 or 316 stainless steels. This is in part, due to the ferrite in the phase structure that has very good corrosion resistance. In addition to the continuous ferrite phase in the alloys, the chemistry also plays a large role in corrosion resistance. Alloys with higher chromium and molybdenum contents have higher resistances to pitting corrosion. Table 1 shows comparative data for the pitting resistance of an alloy based on the pitting resistance equivalency equation listed below.

$$PRE(N) = \%Cr + (3.3)*\%Mo + (16)*\%N \quad Eq.1$$

Duplex stainless steels also resist chloride stress corrosion cracking. CSCC penetrates the alloy through the grains causing branching cracks. This cracking can cause sudden failure and leakage. Due to the microscopic nature of some of the cracks, the material is very difficult to weld repair as all of the cracks causing leaks may not be visible to the naked eye. Both 304L and 316L stainless steels failed U-bend tests in boiling 26% NaCl in less than 1,000 hours. Alloys S32205 and S32760 are both very resistant to the corrosive nature of CSCC due to the duplex grain structures as well as the lean nickel contents in the chemistry for both alloys.

In addition to the many corrosion resistant advantages of duplex stainless steels, the strength of these alloys cannot be overlooked. Duplex stainless steels have yield strengths that are at least twice the value of that of common grades of stainless like 304 and 316. The strength increases found in duplexes can be utilized by thinning down section thicknesses. Decreased

section thicknesses ultimately result in lower costs⁷. Table 2 shows the minimum allowable yield and tensile strength for several alloys according to ASTM A240.

Applications and Case Histories

Most of the water used in SAGD is recycled and put back into service. Since the water is recycled it must go through separators to remove any solids and then concentrated to decrease the moisture and therefore increase the salt concentration. Rolled Alloys has supplied various alloys including 2205 duplex and S32760 super duplex stainless steel for various applications in SAGD service. The most common use for these alloys is in the brine concentrators. Brine concentrators, such as those designed by GE Power & Water have high levels of chlorides combined with elevated temperatures. GE sites that over 100 of these concentrators have been produced for the oil sands in western Alberta Canada¹. Various manufacturers have also utilized 2205 duplex stainless steel for separators. Duplex stainless steels are beneficial in this service because they not only have increase corrosion resistance compared to 300 series stainless steels, but they also have higher strength and hardness to reduce wear from the abrasive solids.

Conclusion

As oil reserves decrease, the level of difficulty to extract oil increases. With this increased difficulty, the service conditions of alloys involved in Steam Assisted Gravity Drainage (SAGD) are increasingly more aggressive. In an effort to maintain low raw material prices without sacrificing performance, duplex and superduplex stainless steels have been used to resist corrosion from chlorides, withstand extremely high pressure and still stay cost competitive. It is likely that this trend will continue to grow as service conditions become more aggressive and the demand for oil and gas increases.

Table 14: Corrosion resistance of several stainless steels

Alloy	% Mo	CCCT, F	CPT, F	PRE _N
316L (S31603)	2.1	<28	68	24
2205 (S32205)	3.1	68	120	35
Z100 (S32760)	3.5	108	180	41
6% Mo (N08367)	6.3	110	172	44

CCCT - 10% FeCl₃ • 6H₂O, per ASTM G 48 Practice B, CPT - 1 M NaCl, per ASTM G 150, PRE_N = Cr + 3.3 Mo + 16N

Table 24: Yield and tensile strength of several stainless steels

Alloy	Yield Strength, MPa	Tensile Strength, MPa
316L (S31603)	205	515
2205 (S32205)	450	655
Z100 (S32760)	550	750
6% Mo (N08367)	310	655

Figure 16: Copson curve showing likelihood of stress cracking versus nickel content

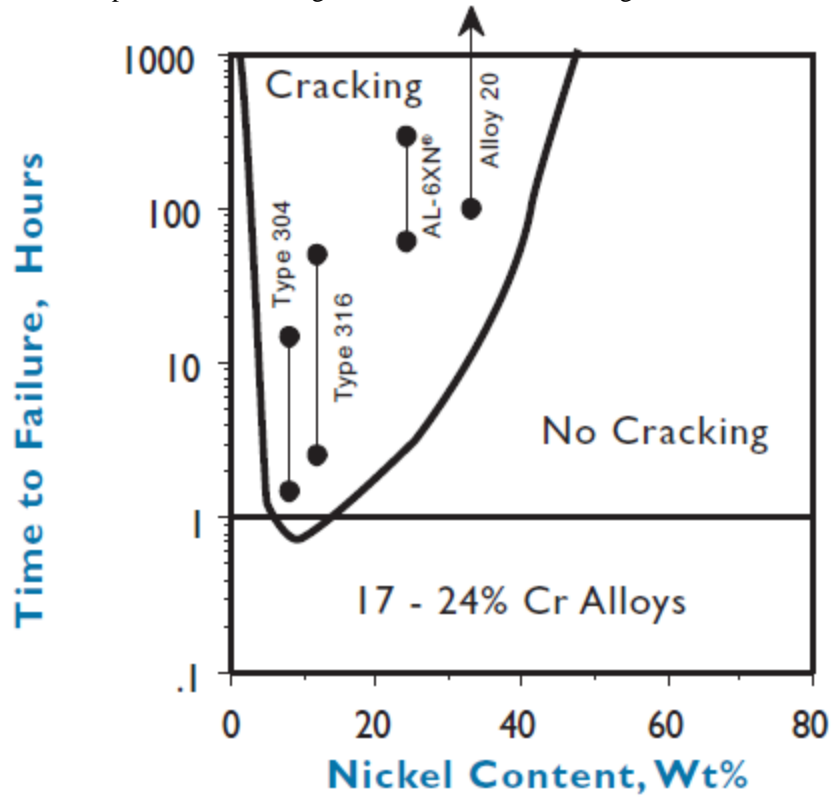


Figure 24: Sulfuric Acid – Iso-corrosion Curves, 4 mpy for Several Stainless Steels

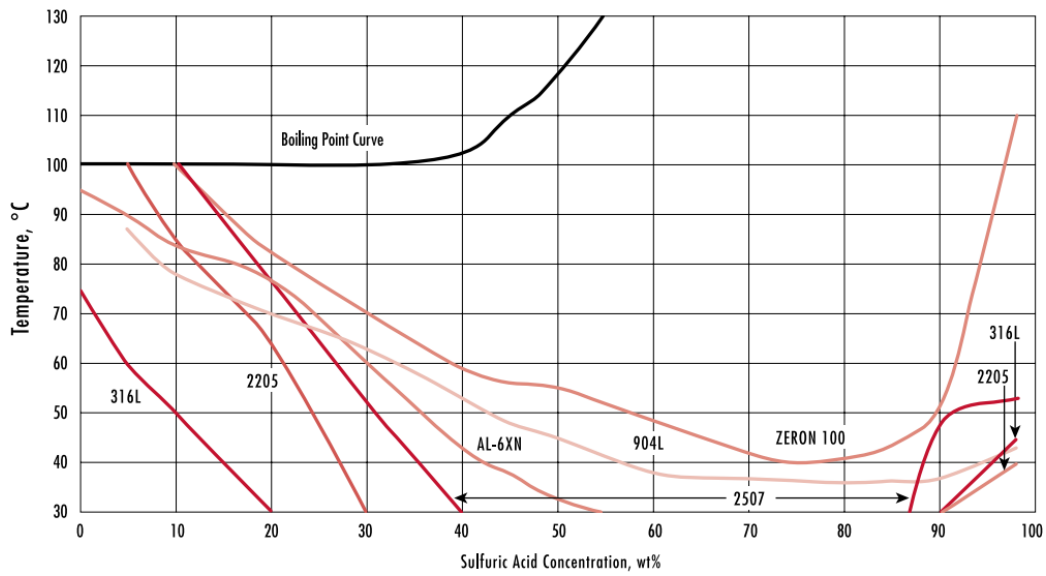
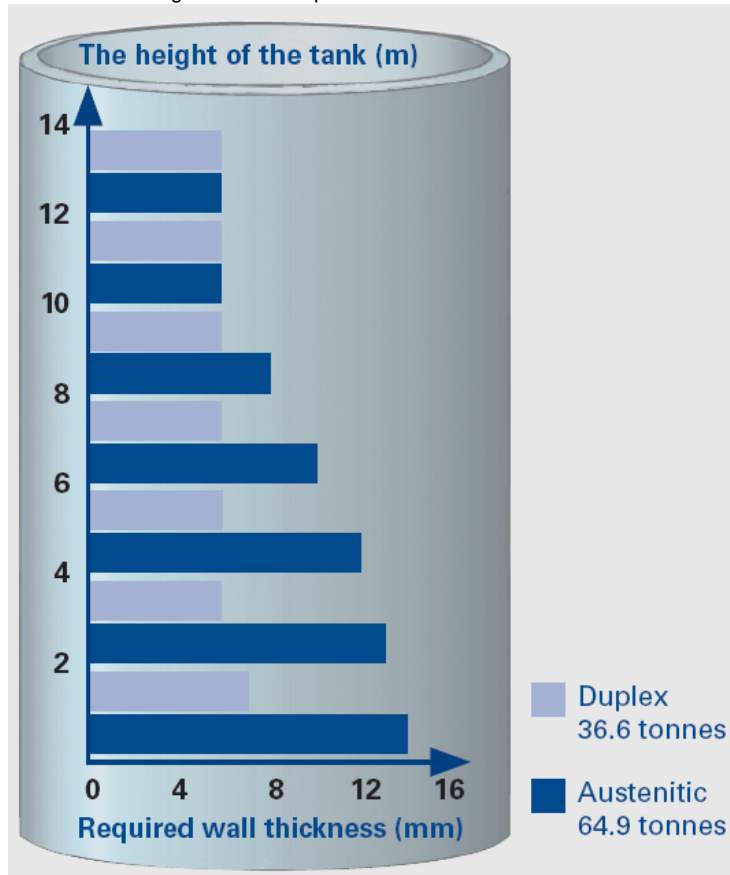


Figure 37: Required Wall Thickness for API Storage Tanks in Duplex and Austenitic Stainless Steels



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