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Duplex – A new generation of stainless steels for desalination plants

Jan Olsson*, Malin Snis*

Outokumpu Stainless, Avesta Research Centre, Box 74, SE-77422 Avesta, Sweden
Tel: +46 226 81000; Fax: +46 226 81077
email: jan.olsson@outokumpu.com malin.snis@outokumpu.com

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Abstract

The paper describes austenitic-ferritic or duplex stainless steels in technical terms and gives reasons why they are such good alternatives to traditional austenitic grades of the 300-series for the construction of desalination plants. Duplex grades possess the same, or even better, corrosion resistance as their austenitic counterparts and they have higher strength, at least twice that of the austenitic grades, enabling gauge, weight and cost reductions. The paper also describes a number of applications within desalination, both membrane and distillation processes, where the advantages of duplex stainless steels have been utilized. Four major engineering companies involved in thermal desalination have realised that duplex stainless steel is a cost effective alternative to traditional materials for such plants. It also describes some applications from other industrial sectors showing that desalination is not a type of guinea-pig industry; it has rather been very slow to adopt the concept with duplex stainless steels.

Keywords: Stainless steel; Distillation; Evaporators; Condenser tubes; Reverse osmosis; High-pressure piping

1. Introduction

Austenitic stainless steels in the ASTM 300-series have by tradition been the predominant material for a number of components in desalination plants. And when the corrosion resistance has been inadequate, the remedy has been higher alloyed grades beyond the 300-series, most commonly austenitic 6Mo grades such as 254 SMO®, also implying higher costs due to more costly alloying elements.

*Corresponding author.

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However, a new generation of stainless steel, austenitic-ferritic or duplex grades, is entering this industrial sector by to a number of reasons. The duplex stainless steels have good resistance to corrosion, especially to stress corrosion cracking (SCC), they have twice the strength of austenitic grades, they are less costly due to lower contents of mainly nickel and molybdenum, and they are excellent engineering materials. The reason for not being so common in the past is that the modern versions, with good engineering properties, did not even exist when stainless steel was introduced to the desalination industry, i.e. during the 1970s.

This paper will describe different duplex grades suitable for a variety of applications, ranging from handling of the most corrosive compounds such as acids, seawater and brine, to less aggressive species such as alkaline solutions, brackish water, product water and distillate.

It will also describe existing and decided installations, including large scale use for modern SWRO plants such as Ashkelon, Singapore and Perth and MSF and MED plants such as Melittah, Taweelah B, Jebel Ali, Ras Abu Fontas, Sharja and Hidd. The discussion will include the use of duplex condenser tubes for the Aruba MSF plant in the West Indies.

Experience from some other industrial sectors will be described as well in order to develop ideas about new applications, e.g. for product water storage tanks and also building elements for civil engineering, although a more comprehensive description can be found elsewhere [1].

2. Metallurgy

Duplex stainless steels were originally developed more than 70 years ago, i.e. during late 1920s, the oldest test results recorded at Avesta Research Centre are dated December 23 in 1930, Fig. 1. However, these old grades were not designed as engineering materials, the metallurgical processes available were not suitable to produce grades with the right austenite-ferrite balance and alloying with nitrogen was not feasible, so fabrication was limited to cast products and possibly forgings [2].

The introduction of the AOD-process (argon-oxygen-decarburisation) in the late 1960s and early 1970s opened up for possibilities to produce modern duplex grades, i.e. duplex grades with a low carbon content in combination with a high chromium content, a high content of nitrogen, and a favourable balance between austenite and ferrite. The first commercial such grade, today mainly known as 2205, was developed and introduced by the German steel producer Krupp in the mid-1970s, and the success of this grade encouraged other steel producers to continue with lower alloyed duplex grades, often referred to as lean duplex grades, and higher alloyed, superduplex, grades.

The chemical compositions and other technical data of such grades available for desalination plant designers are described in Table 1.

The different grades are also described in the section "Steel grades" below.

3. Applications and experience from desalination plants

3.1. Reverse osmosis

Poor experience of conventional austenitic 300 series grades such as 1.4404 (ASTM 316L) and 1.4438 (317L) for high pressure parts in seawater plants has made highly alloyed grades of type 6Mo, e.g. 254 SMO, more or less mandatory for large SWRO plants. And the experience reported from such plants, e.g. in Cyprus, Malta, Saudi Arabia and Spain, is generally satisfying [3].

However, recent price increases for important alloying elements, above all nickel and molybdenum, have implied an in many cases unacceptable cost increase for these grades and more cost effective options have been

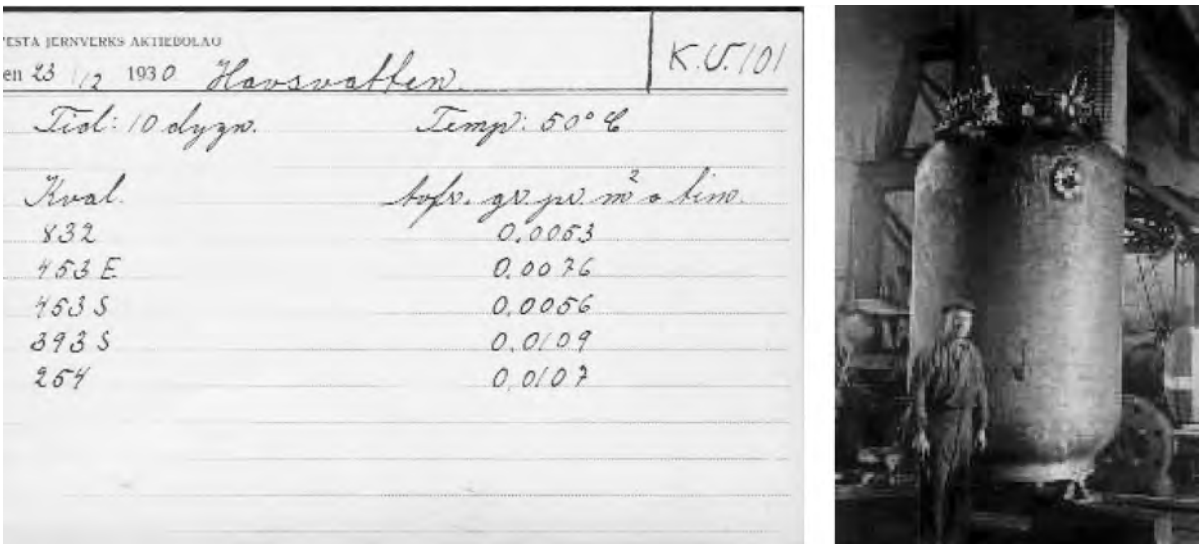

Fig. 1. Protocol from 1930 describing a test with stainless steels, including the 25%Cr–1.5%Mo duplex grade 453 S, a forerunner to ASTM 329 (left), and a reactor vessel for production of gun powder, made of the same grade, supplied to a Belgian chemical industry in August 1933 (right).

looked for. One solution is by several reasons a superduplex grade, e.g. SAF 2507. It has almost the same resistance to pitting and crevice corrosion as 254 SMO, it has twice the strength, and the cost is lower. The first plant with SAF 2507 for critical components is Ashkelon in Israel where the energy recovery system (DWEER) is made of SAF 2507 and the same solution was selected for the new plant in Singapore, Fig. 2.

Table 1
Typical chemical compositions, mechanical properties, PRE-numbers and CPT-values of duplex stainless steels and some austenitic grades for reference

Outokumpu	EN	ASTM	C	Cr	Ni	Mo	N	$R_{p0.2}$[1] (MPa)	R_m[1] (MPa)	PRE[2]	CPT[3] (°C)
LDX 2101®	1.4162	S32101	0.03	21.5	1.5	0.3	0.22	450	680	26	18
2304	1.4362	S32304	0.02	23	4.8	0.3	0.10	400	630	26	20
4404	1.4404	316L	0.02	17.2	10.1	2.1	0.04	220	520	25	20
2205	1.4462	S32205	0.02	22	5.7	3.1	0.17	460	640	35	50
904L	1.4539	N08904	0.01	20	25	4.3	0.04	220	520	36	52
SAF 2507®	1.4410	S32750	0.02	25	7	4	0.27	530	730	43	82
254 SMO®	1.4547	S31254	0.01	20	18	6.1	0.20	300	650	43	83

1. Min values for plate according to EN. ASTM values differ in few cases.
2. PRE (Pitting Resistance Equivalent) = %Cr + 3.3x%Mo + 16x%N
3. Critical pitting temperatures acc. to ASTM G 150.
®Registered trade names, Outokumpu and Sandvik.

Fig. 2. Energy recovery systems (DWEER) made of SAF 2507 for Ashkelon (left) and Singapore SWRO plants (Courtesy of VID and DWEER respectively).

Also the high pressure piping in Singapore is made of SAF 2507 and the same grade was selected for most of the piping at the Perth plant in Australia.

For second pass piping where the desalted feed has a TDS of may be 300–500 ppm less costly grades could be used, but they should still be selected from the duplex family. The critical parameters are temperature and chloride content and available engineering diagrams strongly promote the use of LDX 2101 or 2304, at least for TDS levels of close to 500 ppm [4]. At higher TDS levels 2205 will be the best alternative.

The feed for BWRO plants is often higher in salinity than the second pass of SWRO plants and the grade has to be selected accordingly, but the duplex 2205 should be a natural option.

3.2. Multi stage flash—evaporator shells

The duplex grade 2205 was proposed for MSF evaporator shells already at the IDA conference in Yokohama in 1993, but the first plant designed accordingly did not come on stream until 2004 when the 15,840 m^3/day Melittah in Libya, built by the Italian engineering company Reggiane, started to produce water [5,6]. The second plant built with solid duplex stainless steel evaporator shells was Skikda in Algeria, erected in 2005 by the American engineering company Aquatech, Fig. 3.

This design concept has later been accepted and specified also for large plants engineered by FISIA, Taweelah B extension in Abu Dhabi, Jebel Ali L in Dubai and Ras Abu Fontas in Qatar. These projects include even a "dual duplex" concept, i.e. the use of 2205 for more hostile environments and LDX 2101 for less corrosive environments.

3.3. Multi stage flash—condensers

The tube side of the condensers is exposed to either deaerated conditions in the heat

Fig. 3. MSF evaporators made of solid duplex stainless steel, 2205, for Melittah (left) and Skikda (Courtesy of Reggiane and Aquatech respectively).

recovery stages or air saturated and chlorinated conditions in the heat reject stages. Deaerated conditions should be harmless to stainless steels and condenser tubes made of duplex 2205 will be installed in the heat recovery stages of Aruba, a 6000 m^3/day plant being built by Aquatech. The same material will also be used for the brine heater tubes.

One important issue for surface condensers and other heat exchangers is their heat transfer capability. Copper base alloys, both brass and copper nickel, have high coefficients of thermal conductivity while some other materials, e.g. titanium and stainless steel, are inferior in this respect. However, Maurer presented a comprehensive review of data on heat transfer in 1980, showing that other factors than the coefficient of thermal conductivity were more important, water side films and water side fouling being two examples [7]. These findings have also been confirmed by measurements in Swedish nuclear power plants [8]. The total heat transfer was increased by 17% when using titanium tubes and soft ball cleaning instead of Al-brass tubes despite the more than 80% lower coefficient of heat transfer (17 and 100 W/m°C respectively).

The experience from installations of close to 600,000 m of 254 SMO tubes as replacement for copper base alloys (brass and copper nickel) in Finnish power plants is the same, i.e. no drop in total heat transfer [9]. Also Siemens KWU has reported an almost 100% "change-over" from copper base alloys to stainless steel and titanium for power plant condenser tubes with an increase from 2.6 millions of meters of stainless steel tubes in 1980 to more than 14 millions in 1995 without any experience of loss in heat transfer [10].

Duplex 2205 could also be an option for tube sheets, baffle plates and water boxes and even more so LDX 2101 considering the excellent machining properties of this grade.

3.4. Multi effect distillation—evaporator shells

The "dual duplex" concept, i.e. a highly corrosion resistant duplex grade such as 2205 for parts exposed to more hostile conditions combined with a lower alloyed duplex grade for less harsh environments, has also been accepted for large MED plants.

The first such plant, with a capacity of 72,500 m^3/day, is in early 2006 being erected by Sidem in Sharjah in UAE. The same

concept has also been specified for Hidd phase 3, with a capacity of 275,000 m^3/day. The grades used for both these plants will be 2205 in combination with 2304. The selection of 2304 was based on two years successful in-plant testing in the West Indies [11]

3.5. Others

The duplex grade 2205 has also been used for other, less critical components in distillation plants, e.g. for product water processing, Fig. 4.

4. Applications and experience outside desalination plants

Duplex stainless steels are extensively being used within a number of industry sectors outside desalination, e.g. for chemical tankers, for pressure vessels, storage tanks and machinery within the pulp and paper industry, and also for civil engineering. The grade selected depends on the environmental conditions. Out of these applications the storage tanks have really bearing also to the desalination industry. By using duplex stainless steel it is possible to reduce the weight and cost and it should be a very cost effective option for the storage of not only product water, but also liquid additives used for the processes. Some examples of storage tanks made of duplex stainless steel are shown in Fig. 5.

The tanks made of LDX 2101 were for the storage of marble slurry at a paper mill in Norway and the initial specification called for 1.4301 (ASTM 304). By using the high strength LDX 2101 it was possible to reduce the total plate weight by 43% (from 65 to 37 tons) and the plate cost by 34%. On top of that, less bevelling, less welding and easier erection, which further reduced the cost.

LDX 2101 and 2304 can handle product water with a TDS of close to 500 ppm at a temperature of 40°C and close to 1000 ppm at the same temperature if the higher alloyed 2205 is being used for critical crevice sites, e.g. sealing surfaces in connection with flanges at manholes, nozzles etc.

5. Steel grades

5.1. LDX 2101

This is a new duplex grade, which has a resistance to pitting and crevice corrosion

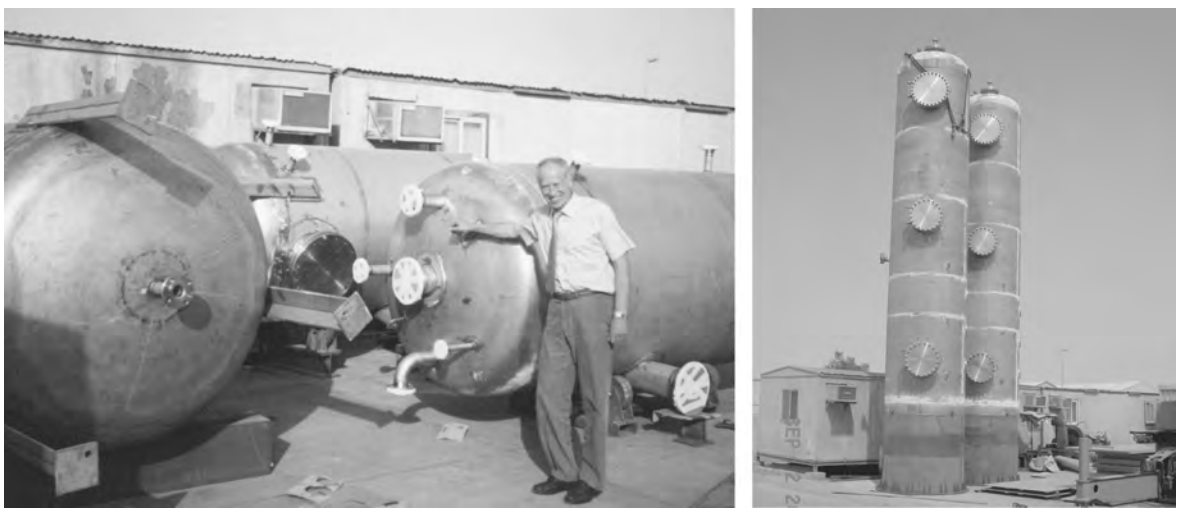

Fig. 4. Filters and CO_2 absorbers made of 2205 (Courtesy of Ferrofab).

Fig. 5. Storage tanks of duplex stainless steels, SAF 2507 upper left, 2205 upper right, 2304 bottom left and LDX 2101 bottom right.

that is far superior to the resistance of 1.4307 (304 L) and very close to 1.4404 (316 L). The high strength should imply possibilities to reduce the gauge with up to 50% in comparison with austenitic 300 series grades for components where design is based on the proof strength. However, restrictions in design codes limit the real savings to around 35–40% [12].

On top of this it has also excellent machining properties. It should be an ideal material for parts of the evaporator shells and internals, not least tube sheets and baffle plates; better corrosion resistance than 1.4307 (304 L) and very cost effective when compared with 1.4404 (316L). It has been specified and supplied for several large MSF projects in the Arabian Gulf countries during 2005–2006.

5.2. 2304

This is an established duplex grade, which has a resistance to pitting and crevice corrosion that is slightly superior to the resistance of 1.4404 (316 L). The high strength should imply possibilities to reduce the gauge with up to 40% in comparison with austenitic 300

series grades for components where design is based on the proof strength. However, restrictions in design codes limit the real savings to around 30% [12].

SAF 2304 has been commonly used for liquor tanks within the pulp and paper industry, for blast walls on offshore platforms and within the food and beverage industry. It has been specified and supplied for large MED projects in the Arabian Gulf countries during 2005–2006.

5.3. 2205

This is an established duplex grade, the real workhorse of the duplex family, which has a resistance to pitting and crevice corrosion that is on the same level as the resistance of the highly alloyed austenitic grade 904 L. The high strength should imply possibilities to reduce the gauge with up to 50% in comparison with austenitic 300 series grades for components where design is based on the proof strength. However, restrictions in design codes limit the real savings to around 35–40% [12].

The first installations within desalination were for high-pressure piping in SWRO plants, in Gibraltar, in connection with the Eurotunnel between UK and France and in Australia to mention a few [13–15]. The experience clearly demonstrated that 2205 should not be used for SWRO plants, but it will still be an ideal material for BWRO plants with a TDS of around 2000–3000 ppm depending on the temperature of the feed.

It is also an excellent material for a number of components within distillation plants. The main application is for evaporator shells, Fig. 3, but it can also be used for other applications, e.g. parts of the vent systems, deaerators, make-up items for water to be supplied to distribution net, Fig. 4, to mention a few examples.

5.4. SAF 2507

A superduplex grade, which has a higher PRE-number than any other superduplex grade. The resistance to pitting and crevice corrosion is on the same level as for the 6Mo austenitic grades. It has also higher strength than other duplex grades. The high strength should imply possibilities to reduce the gauge with more than 50% in comparison with austenitic 300 series grades for components where design is based on the proof strength. However, restrictions in design codes limit the real savings to around 35–40% [12].

6. Discussion

It was shown already at the IDA conference in Yokohama in 1993 that the use of duplex stainless steels could reduce the cost for evaporators in MSF plants and it was also discussed at the EDS conference in Las Palmas 6 years later [16]. However, this design concept was not accepted by the desalination industry until 2003 when first Melittah was erected and then FISIA promoted it at the IDA conference in Bahamas [17].

There is no doubt, however, that the ball has started rolling. The concept with solid duplex stainless steel, or even dual duplex, will be used for Taweelah B extension, Jebel Ali L and Ras Abu Fontas, three major MSF projects, and also for new MED plants in Sharjah and Bahrain. And a small MSF plant in North Africa, Skikda.

This implies that four large engineering companies, Aquatech, FISIA, Reggiane and Sidem, and also their clients and consultants involved, have realised that duplex or even dual duplex, will result in more cost-effective design in combination with, not a lowered but improved technical quality, i.e. reduced investment cost, reduced maintenance cost and, above all, a reduced water cost.

And duplex stainless steel will most probably also be used even more for condenser tubing in heat recovery stages and brine heater tubing. The deaerated conditions of the brine-seawater mix should be harmless to stainless steel and most likely even lower alloyed grades than 2205 will be used in the future, e.g. 2304 or LDX 2101.

MSF once through is a third concept for distillation plants and solid stainless steel has successfully been used for such plants in Libya and Chile [18]. The feed into the first stage is air saturated with higher demands on the corrosion resistance of the stainless steel to be used than for MSF recycling plants. Highly alloyed austenitic grades, 254 SMO in Chile, have shown adequate corrosion resistance, but a superduplex grade such as SAF 2507 would be an even more cost-effective option.

More highly alloyed grades could also be an alternative for deaerators in MSF and MED plants.

254 SMO and similar austenitic grades are the only having shown adequate corrosion resistance for the first pass of SWRO plants in the past, but the superduplex grade SAF 2507 has been used for recently built plants, e.g. in Singapore and Perth, and there is no doubt that such grades will be more used due to cost reasons.

Lower alloyed duplex grades such as LDX 2101 and 2304 could be used for the second pass of SWRO plants while the chloride level of the feed for BWRO plants could imply a need for 2205.

7. Summary and conclusions

- There are different grades of duplex stainless steels able to cope with different process environments in desalination plants.
- Superduplex grades are for the moment used in first pass high-pressure piping and energy recovery devices in SWRO plants, but could be viable options for first stages flash chambers in MSF once-through plants and deaerators for MSF and MED plants. And also for piping and tubing in vent systems.
- The duplex grade 2205 is presently used for evaporator shells in MSF recycling plants and MED plants, occasionally in combination with lower alloyed and less costly duplex grades such as LDX 2101 and 2304. It is also used for condenser tubing in MSF plants, for high-pressure piping in BWRO plants and for different items in connection with product water processing.
- Lower alloyed duplex grades such as 2304 and LDX 2101 are used in combination with 2205 for MSF and MED evaporator shells, but should also be ideal materials for distillation plant internals, for second pass high-pressure piping in SWRO plants and product water storage tanks.

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