

## STAINLESS STEELS FOR DESALINATION PLANTS

Jan Olsson, Outokumpu Stainless, Avesta Research Centre

### Abstract

Stainless steel grades commonly used are, together with more modern grades, evaluated and commented with reference to different types of desalination processes including seawater reverse osmosis and distillation. The possibility to use solid stainless steel as an alternative to clad steel for evaporator vessels in distillation plants is discussed and also the possibility to use austenitic-ferritic or duplex steels instead of grades from the ASTM 300-series. The use of 316L (EN 1.4404) and 317L (EN 1.4438) is conservative in the sense of based on old-fashioned thinking without considering the far more reliable and cost effective concept with modern high strength and highly corrosion resistant duplex grades. Poor experiences from the use of conventional grades as well as installations of modern grades in different processes and process steps are described.

### 1. INTRODUCTION

The first large scale desalination process was no doubt multi stage flash, MSF, where boiling water is evaporated and then condensed in a series of flash chambers, allowing evaporation due to vacuum also at temperatures far below the normal boiling temperature. The history of shell materials ranges from mild steel to mild steel with linings of stainless steel or copper-nickel, clad steel, solid stainless steel of type 316L, and ending with the most recent developments using solid duplex stainless steel.

Later process development, mainly to avoid the risk of scaling, has resulted in another distillation process, low temperature multi effect distillation, LT-MED, where the principle with distillation under vacuum is still applied although the starting temperature is lower, between 60 and 70°C. However, the design concept deviates from the MSF-plants. There has also been a historical development concerning materials for this process starting with coated mild steel shells and aluminium tubes while modern plants normally have stainless steel shells and either copper-nickel or titanium tubes.

The third large-scale process is reverse osmosis or seawater reverse osmosis, SWRO, where the product water is achieved by a type of filtering based on the principle of osmotic pressure. However, instead of utilizing the osmotic pressure, the process is reversed by applying a higher pressure on the high salt concentration side, forcing fresh water through the membranes while preventing salt to do the same. The material development for the high-pressure piping comprehends parts of the ASTM 300-series, i.e. 316L and 317L, the higher alloyed 904L (ASTM N08904, 1.4539), and 254 SMO<sup>®</sup> (S31254, 1.4547), but also the duplex grade 2205 (S32205, 1.4462) and superduplex SAF 2507<sup>®</sup> (S32750, 1.4410).

This paper describes the grades listed in metallurgical terms and the experience reported from the desalination industry.

## 2. METALLURGY

### 2.1 Chemical compositions and mechanical properties

The chemical compositions and mechanical properties of candidate steel grades for desalination plants are given in Tables 1 and 2 respectively.

Table 1. Chemical compositions and PRE-number of some stainless steels.

Outokumpu	EN	ASTM	Cr	Ni	Mo	N	PRE <sup>1)</sup>
4404	1.4404	316L	17	11	2.1	0.06	25
LDX 2101 <sup>®</sup>	1.4162	S32101	21	1.5	0.3	0.22	25
4438	1.4438	317L	18	13	3.2	0.06	30
904L	1.4539	N08904	20	25	4.5	0.06	36
2205	1.4462	S32205	22	5.5	3.1	0.17	35
254 SMO <sup>®</sup>	1.4547	S31254	20	18	6.1	0.20	43
SAF 2507 <sup>®</sup>	1.4410	S32750	25	7	4	0.27	43

1)  $PRE = \% Cr + 3.3 \times \% Mo + 16 \times \% N$ .

2) Registered trade names by Outokumpu Stainless and Sandvik (SAF 2507).

From the chemical compositions (PRE-numbers) it is obvious that the duplex grade LDX 2101 should have approximately the same resistance to pitting and crevice corrosion as 1.4404, the duplex grade 2205 will be similar to 904L and SAF 2507 will not deviate much from 254 SMO.

Table 2. Mechanical properties of some stainless steels.

EN	R <sub>p0.2</sub> MPa	R <sub>m</sub> MPa	A <sub>5</sub> %	Design stress (MPa) at	
				100°C	200°C
1.4404	220	520	45	143	130
1.4162 <sup>1)</sup>	450	650	30	-	-
1.4438	220	520	40	143	130
1.4539	220	520	35	157	137
1.4462	460	640	25	240	210
1.4547	300	650	40	205	187
1.4410	530	730	20	300	267

1) Will not be included in EN until 2005. There is, however, an ASME code case, case 2418.

The duplex grades have approximately or close to twice the strength of the corresponding (PRE-number) austenitic grades. This can for certain applications imply a considerable reduction in gauge, weight and cost.

### 2.2 Corrosion resistance

The corrosion resistance in chloride containing environments, e.g. seawater or brine, is often measured as critical pitting and critical crevice corrosion temperatures, CPT and CCT respectively, in standardised chloride solutions mainly to get a ranking between

different grades, Table 3. Such critical temperatures can normally not be regarded as engineering data, but they can still be valuable instruments when combined with reliable service experience.

Table 3. Critical pitting and crevice corrosion temperatures for some stainless steels.

Grade	CPT (°C) <sup>1)</sup>	CCT (°C) <sup>2)</sup>	CCT (°C) <sup>3)</sup>
1.4404	20	-	20
LDX 2101	20	-	45
904L	55	10	-
2205	52	20	60
254 SMO	85	35	-
SAF 2507	82	35	-

1) According to ASTM G 150 (the Avesta Cell).

2) ASTM G 48-D (6 % FeCl<sub>3</sub>).

3) ASTM G 48-D modified (5 % FeCl<sub>3</sub> + 1 % NaNO<sub>3</sub>).

The grades 1.4404 and LDX 2101 are not resistant enough to be tested in the normal G 48-D environment and it is necessary to modify the test solution to establish a reliable ranking. Also 2205 was included in the modified test as reference. The ranking achieved by comparing the PRE-numbers is in good agreement with actual test data for CPT while some deviations can be found for CCT, i.e. some duplex grades are better than expected.

### 2.3 Evaluation of candidate grades

Different candidate grades have been evaluated and commented considering also the future importance of other grades still not commonly used within the desalination industry.

#### *1.4404 (316L)*

An old well known grade with acceptable resistance to product water and it normally also resists atmospheric conditions in hot and humid climates, but it does not resist seawater containing oxygen on ppm level. It has been extensively used in old SWRO plants with poor success while the experience from distillation plants is much depending on leakage of air into the evaporators.

It can in most cases be replaced by a duplex grade of type LDX 2101 or 2205.

#### *LDX 2101 (EN 1.4162/ASTM S32101)*

This is a new duplex grade, which has a resistance to pitting and crevice corrosion that is very close to the resistance of 1.4404. Available test data indicate an even superior resistance in several cases. The high strength should imply possibilities to reduce the gauge with up to 50 % in comparison with austenitic 300 series grades for components where the design is based of the proof strength although restrictions in design codes limits the real savings to around 35-40 % [1].

LDX 2101 has already attracted engineering companies within e.g. civil engineering and the pulp and paper industry for the building of bridges and large storage tanks

respectively. One such application is illustrated in Figure 1.



Figure 1. A white liquor tank made of LDX 2101 for the cellulose industry.

The white liquor tank is for a Finnish pulp mill and the weight and cost saving is around 40 % when compared with 304 material, which has been commonly used in the past for such tanks.

LDX 2101 should consequently imply considerable cost savings for large product water storage tanks in desalination plants and it should also be an ideal material for roofs/ceilings in MSF plant evaporators, i.e. parts that are not directly exposed to splashes from the flashing seawater.

#### *1.4438 and 1.4439 (317L and 317LMN)*

Austenitic grades, which have better corrosion resistance than 316L. They have good resistance to marine atmospheric conditions and product water but they do not resist seawater unless it is deaerated. Both these grades could be regarded as alternatives to 316L for lining of MSF evaporators and have as such been used for some plants.

However, they are in general slightly old-fashioned in comparison with duplex grades of type 2205.

#### *904L (1.4539/N08904)*

An old austenitic grade that was developed during the 1930's to resist dilute sulphuric acid. The high contents of chromium and molybdenum contribute to rather good resistance to pitting and crevice corrosion, but lack of nitrogen still implies a less optimised grade for the handling of halide containing environments. It has been used to solve bromide induced stress corrosion cracking problems in Ras Abu Fontas MSF plant in Qatar [2,3,4], Figure 2.



Figure 2. Severe bromide induced stress corrosion cracking of 316L in the vent system of Ras Abu Fontas (left) and the remedy, the installation of 904L drain legs (right).

It has also been used with mixed success for the high-pressure piping of SWRO plants.

Can in most situations be replaced by the less costly duplex grade 2205.

#### *2205 (1.4462/S32205)*

This is an austenitic-ferritic or duplex stainless steel with high strength in combination with a corrosion resistance on approximately the same level as 904L. It has become the dominating construction material for several industrial sectors outside the desalination industry, one of particular interest being the pulp industry since the material selection philosophy for pulp digesters has undergone approximately the same development stages as for desalination MSF plant evaporators.

It started during the late 19<sup>th</sup> century with unprotected mild steel, followed by stainless steel lining, stainless steel clad plate and solid austenitic stainless steel with enhanced mechanical properties. Today every single pulp digester built is made of solid duplex stainless steel, grade 2205.

It has far better resistance than 316L and 317L to pitting and crevice corrosion, it is more on the level of 904L, but it does still not resist air-saturated seawater and the experience from SWRO plants is rather poor.

It should, however, be an ideal grade for MSF and especially MED evaporator shells where the high strength enables a more cost effective design, which, in combination with a resistance to pitting and crevice corrosion far better than that of 316L, will result in a generally better and less costly plant than if 316L is being used. It has been used for one MSF plant, Melittah in Libya [5], Figure 3, and it has been ordered for a second plant, still under construction.



Figure 3. Melittah MSF recycling plant with solid duplex stainless steel evaporator shells.

Other suitable applications for 2205 can be found amongst different auxiliary systems, e.g. deaerators, CO<sub>2</sub>-filters and CO<sub>2</sub>-adsorbers, Figure 4.

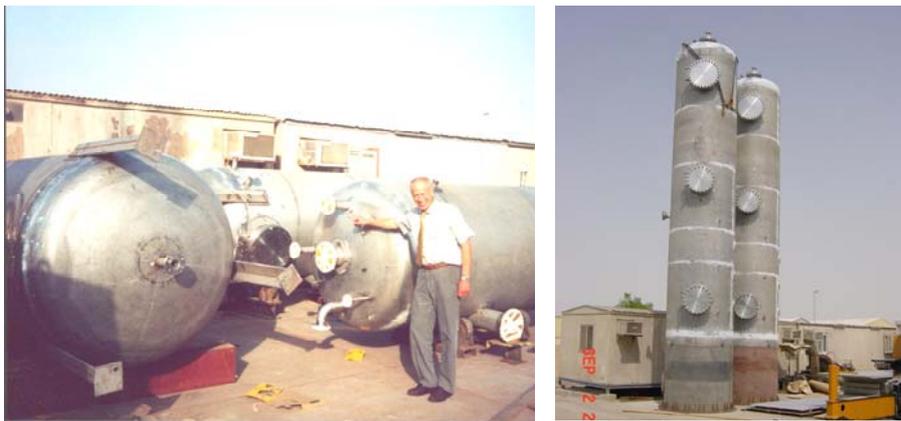


Figure 4. CO<sub>2</sub>-filters and CO<sub>2</sub>-adsorbers made of duplex 2205 stainless steel.

*254 SMO and SAF 2507 (1.4547/ S31254 and 1.4410/S32750 respectively)*

One superaustenitic and one superduplex grade having approximately the same high resistance to pitting, crevice corrosion and stress corrosion cracking.

Both these grades will resist crevice corrosion in air-saturated seawater up to around 35°C, unless the seawater is chlorinated, and the experience reported from installations of 254 SMO high-pressure piping in more than 30 SWRO plants is excellent.

SAF 2507 has not been used to the same extent, but it should be just as good as 254 SMO. The advantage of SAF 2507 is the higher strength, which should enable a considerable reduction of gauge for large diameter piping. SAF 2507 has been installed in some plants for high-pressure piping and energy recovery systems.

Grade 254 SMO has successfully been used for evaporators in MSF once-through plants and also LT-MED plants [6], Figure 5.



Figure 5. Evaporator shells made of solid 254 SMO for an MSF once-through plant (left) and an LT-MED plant (right).

### 3 DESALINATION PROCESSES

#### 3.1 Multi Stage Flash (MSF)

As described above, the materials used for the evaporators have passed through different development stages ranging from mild steel to solid stainless steel, but still only touching upon the future, i.e. solid duplex stainless steel.

The use of unprotected mild steel, which should be satisfactory in an air free environment, has not worked well due to leakage of air into the system either during shutdowns or through un-tight flanges at manholes etc. Neither lining with stainless steel 316L nor clad plate with the same cladding material has solved the problem of corrosion.

Solid stainless steel has been proposed as a more cost effective alternative than clad steel [7] but the grade used so far has been 316L, which has inadequate corrosion resistance, shown by superficial pitting and crevice corrosion in the evaporators of Hidd after a few years of service, commissioned in early 2000 [8].

An even more cost effective alternative was proposed at the EDS conference in Yokohama in 1993 and later also at the corresponding conference in Bahamas in 2003, i.e. the use solid duplex stainless steel of type 2205 instead of clad steel for the evaporators [9,10]. By using solid 2205 it is according to the study by FISIA possible to save millions of US-dollars at the construction of the evaporators, the exact number depending on the current price of stainless steel and also the capacity of the plant [10].

There is one plant built with evaporators made of solid stainless steel 2205, Melittah in Libya, which started producing water in May 2004, Figure 3. By using solid 2205 instead of solid 316L it was possible to reduce the weight from 400 to 280 tons implying a cost reduction of some 100,000 €. The extra benefit is the far higher safety against pitting and

crevice corrosion and also external stress corrosion cracking.

This discussion has covered the most common MSF concept, recycling plants, while the situation for once-through plants is different. In such a case the feed entering the brine heater has not undergone any deaeration and more corrosion resistant stainless steel is demanded. In-plant testing, confirmed by service experience, has shown that austenitic 6Mo grades such as 254 SMO fulfils the requirements for the first flash chambers where some oxygen and residual chlorine may be present while the duplex 2205 should be used for down-stream stages [6]. Also a superduplex grade such as SAF 2507 could be an option for the first non-deaerated stages although there is no experience reported for this concept.

Another area of concern in MSF plants is the vent systems, i.e. where vacuum is created. Type 316L has suffered severe pitting and even stress corrosion cracking due to chlorides and bromides in such systems, Figure 2, and more highly alloyed grades should be used. One remedy could be the use of 904L as described above (figure 2), but considering the less optimised chemical composition of this grade, 254 SMO should be an even better alternative.

The latter grade has a significantly better resistance to not only pitting and crevice corrosion as described in table 3, but also to chloride induced SCC [11] and SCC can also be caused by caused by chlorides, Figure 6.

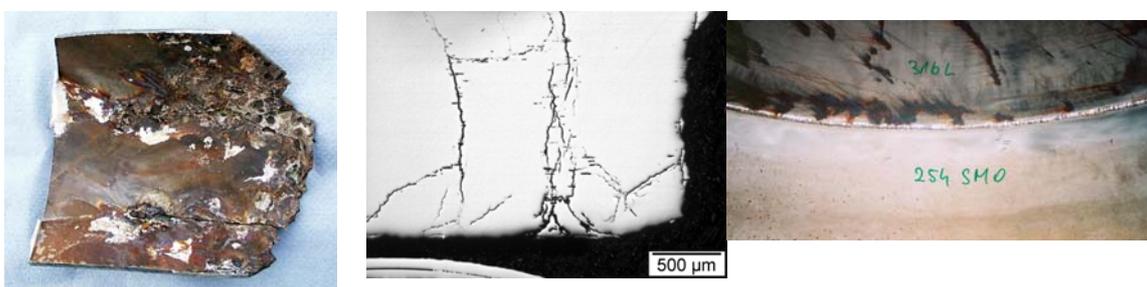


Figure 6. Chloride induced SCC in a 316L vent system (left and centre) and a combination of 254 SMO and 316L in another vent system (right) in Arabian Gulf MSF plants.

### 3.2 Low Temperature Multi Effect Distillation, LT-MED

Compared to MSF this is a more recently developed process and the selection of material for the evaporators has not yet been fully established. The most common material for large plants is solid stainless steel of type 316L, but also the highly alloyed 254 SMO has been used for several plants in Saudi Arabia, Figure 5.

However, the possibility to utilise the strength of a duplex grade such as 2205, or even SAF 2507, should enable an even higher cost saving possibility since the cylindrical cross section of the evaporators is more advantageous from design point of view.

### 3.3 Seawater Reverse Osmosis, SWRO

The fastest growing process for large-scale desalination plants is SWRO, mainly due to the development of better and less costly membranes.

The high pressure in such plants, often in the range of 60-80 bars, requires metallic materials and stainless steel has been the predominantly material used. The first such plant was the old Jeddah with high-pressure piping made of 316L, which suffered extensive crevice corrosion under the Victualic couplings, Figure 7, and the same problem has later been experienced in a series of large plants in the Arabian Gulf region and the Mediterranean Sea, not only for grade 316L, but also higher alloyed grades such as 317L, 2205 and also 904L, [12,13,14].



Figure 7. Crevice corrosion under Victualic couplings in high-pressure piping made of 316L (Jeddah-left) and 904L (Spain-right).

The consequence was that the more resistant grade 254 SMO was installed in several plants on Mediterranean Sea islands, e.g. Malta and Cyprus, and later also on the Canary Islands and in the Middle East [14,15]. Grade 254 SMO and similar 6Mo grades has since been the dominating grade for SWRO high-pressure piping and later also used, together with superduplex grades such as SAF 2507, for energy recovering systems. Also 904L has, due to lower cost, been installed in some recent large SWRO plants, with corrosion problems in at least one of these, Figure 6.

The low-pressure part of an SWRO plant, i.e. upstream the high-pressure pumps, where pre-treatment of the feed takes place, is facing even more corrosive conditions due to presence of residual chlorine and severe corrosion has been reported for different kinds of filters made of 316L [12]. Despite the lower pressure, it is necessary to select grades of type 254 SMO or SAF 2507 for these parts if stainless steels are being used.

## 4. CONCLUSIONS

- Traditionally used austenitic stainless steels of the ASTM 300-series can for critical components be replaced by more modern stainless steel grades, either highly alloyed austenitic grades or from the family of duplex stainless steel.
- Duplex stainless steels of type 2205 imply far more cost effective design concepts for evaporator shells in distillation plants and can be combined with other duplex grades to optimise the demands for corrosion resistance and costs.

**REFERENCES**

1. Ericsson C, Utilizing high strength for lower weight and cost in structural applications using the new low nickel duplex grade LDX 2101<sup>®</sup> (S32101). Proc. *Stainless Steel America 2004* (Stainless Steel World, Houston 2004).
2. Lee W.S.W., Oldfield J.W. and Todd B. Corrosion problems caused by bromine formation in additive dosed MSF desalination plants. Proc. *First world congress on desalination and water re-use* (DECHEMA, Florence, 1983).
3. Nordin S. Studies of stainless steels for service in desalination plants. Ibid.
4. Bertuzzi M., D'Angelo G. and Moretti E. Experience with 4 x 5 m<sup>2</sup> MSF plant in Qatar: Report on construction material performance. Ibid.
5. Olsson J., Jägerström V. and Resini I. MSF chambers of solid duplex stainless steel. Proc. *IDA World congress on desalination and water re-use* (Bahamas 2003).
6. Olsson J. and Minnich K. Solid stainless steel for MSF once-through plants. Proc. *Desalination and water reuse* (EDS, Las Palmas, 1999).
7. Sommariva C., Pincioli D., Tolle E. and Adinolfi R. Optimization of material selection for evaporative desalination plants in order to achieve the highest cost-benefit ration. Ibid.
8. Private communication.
9. Olsson J. and Groth. Evaporators made of duplex stainless steel. A new approach to reduced costs. Proc. *IDA and WRPC World conference on desalination and water treatment* (Yokohama, 1993).
10. Ghiazza E. and Peluffo P. A new design approach to reduce water cost in MSF evaporators. Proc. *IDA World congress on desalination and water re-use* (Bahamas 2003).
11. Andersen H., Arnvig P-E., Wasielewska W., Wegrelius L. and Wolffe C. SCC of stainless steel under evaporative conditions. *NACE/ Corrosion '98*, paper No 251 (USA 1998).
12. Hassan A.M., Al-Jarrah S., Al-Lohibi T., Al-Hamdan A., Bakheet L.M. and I-Amri A. Performance evaluation of SWCC SWRO plants. Proc. *Fourth world congress on desalination and water re-use* (IDA, Kuwait, 1989).
13. Carew J., Abdel-Jawad M., Julka A. and Al-Wazzan Y. Performance of materials used in seawater reverse osmosis. Proc. Ibid.

14. Lamendola M.F. and Tua A. Desalination of seawater by reverse osmosis, the Malta experience. *Desalination & Water reuse* 1995, 5(1), 18-22.
15. Olsson J., Cosic K. Stainless steels for SWRO plants high-pressure piping, properties and experience. Proc. *IDA World congress on desalination and water re-use* (Bahamas 2003).