

## **HISTORY AND CURRENT STATUS OF MATERIAL SELECTION IN THERMAL DESALINATION PROCESSES**

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### **Summary**

Material selection in thermal desalination project is a very important component of the design basis of the plant. Since the design of the first thermal desalination units there has been a significant development in the material selection in desalination projects. This has been the cause of a continuous improvement driven both by the development in the science of material, reduction of costs and the necessity of more robust reliable and having longer life desalination units.

The aim of the chapter is to present the historical development of the material selection in thermal desalination processes since the 1050s of industry development. The chapter will therefore provide a rationale explaining the reasons for the innovations introduced both from a technical and an economical perspective.

### **1. Introduction**

Material selection for thermal desalination plants is of great importance for both the influence that the material selection has on the plant capital costs as well as on the reliability and lifetime of the plant.

The operational experience on the first generation of large MSF desalination plant has demonstrated that the original expected life of these units has been largely exceeded. Several plants installed for an initial industrial life forecast of 10 to 15 years have been found to be in reasonable condition for their age after 30 years of operation. Some of the very old thermal desalination plants were showing signs of tube corrosion to the extent that tube failures warranted a program of monitoring and replacement generally in the hotter sections of the plant. Although these thermal desalination plants had been designed with a significant corrosion allowance, operational experience indicated that corrosion over several years of operation has taken its share.

In this respect rehabilitation and upgrading projects have been regularly implemented in order to set up measures to stop further material loss by, for example, retro fitting of stainless steel lining, repairing excessive wall thinning etc.

In particular several contracts for the rehabilitation and upgrading of desalination units installed in the early seventies have been awarded after twenty to thirty years of operation with the aim of extending the industrial life of these units by a further fifteen years.

Developments in materials technology and a progressive decrease in the stainless steel and duplex steel costs versus carbon steel have resulted in the adoption of nobler materials and it is expected that the generation of large thermal desalination plant installed between the nineties and the early 2000 will last for more than 30 years with minimum maintenance and minor overhauling.

On this basis it is assumed that forty to fifty years design life is a reasonable target which can be obtained if the material selection is optimized in respect of the operating conditions.

The gradual emergence of the MED process in the market portion previously belonging to MSF technology suggests that an evaluation of the operating conditions and material selection for MED plant can also grant an expected life of fifty years. However despite the core of the thermal desalination plant – the evaporator – generally was found in acceptable working conditions after several years of operation the majority of the desalination plants in the Middle East reported major problems related to the main process pumps for seawater and brine.

In these pumping applications NiResist has been extensively used for the casing and rising main of the pump and has been consistently failing due to stress corrosion cracking. This problem was even faced on the younger plants. Many end user have undertaken a long term replacement program using duplex stainless steel will be necessary to overcome this problem. Other subsystems such as ejector/condenser, ball tube cleaning and chemical dosing were found to need either complete replacement or major renovation on the older units. Material upgrades and replacements were identified for carbon steel rubber lined pipe and concrete pipe carrying seawater/brine to GRP.

Other balance of plant items such as electro-chlorination, CO<sub>2</sub> production and fire water systems showed the need for replacement, major reworking or updating even at 15 years age.

Several papers [1] [2] have already demonstrated the sharp influence of material selection on the plant cost; therefore the choice of the plant components that request the contractor and end user to invest in upgrading materials and the evaluation of the financial revenue, in term of extension of plant life and reduction of maintenance are key technical aspects for the future of desalination.

By comparing the various operating conditions occurring in the desalination units and the impact on corrosion/erosion of the materials employed, this paper aims at giving guidelines that will allow material selection to be optimized with respect to the plant costs.

## 2. Historical Review

The first generation of desalination plants installed in the Gulf in the 1960 till 1980 largely employed carbon steel as a material for the evaporator shell and internals. Carbon steel is relatively inexpensive, readily available and possesses engineering properties that have been understood and used for decades. Another feature of carbon steel that is largely understood is its tendency to corrode and allowance has been made for this in the past by increasing the thickness and hence the weight of the components that are subject to a corrosive environment.

Some significant changes have occurred in the material selection specified for the second generation of desalination plants designed and constructed one decade later due to the deeper understanding of the operating conditions occurring inside the evaporator and their consequences on the material selected.

Some of the most significant changes are summarized in Table 1 below:

Component	First generation specification	Second generation specification	Reasons	third generation specification
Vent baffles	Carbon steel	Stainless steel typically AISI 316L sometime 304	Understanding of corrosion induced by high concentration of CO <sub>2</sub> , O <sub>2</sub> bromamine and non-condensable gases	Duplex steel DIN 1.4462 or equivalent i.e. SAF 2205

Support plates	Carbon steel	Stainless steel typical AISI 316L sometime 304	Ditto	Duplex steel DIN 1.4462 or equivalent i.e. SAF 2205
De-aerator	Carbon steel + rubber lining	Stainless steel Typical AISI 317 LN	Understanding of corrosion induced by high oxygen and chloramine concentration	Duplex steel DIN 1.4462 or equivalent i.e. SAF 2205
Shell	Carbon steel painted	Stainless steel AISI 316L sometime CS clad	Maintenance reduction cost effect	Duplex steel DIN 1.4462 or equivalent i.e. SAF 2205
Internals	carbon steel Painted	Stainless steel AISI 316L	Ditto	Duplex steel DIN 1.4462 or equivalent i.e. SAF 2205
Make up spray pipe	carbon steel stainless steel	Duplex steel DIN 1.4462	Understanding of the erosion phenomena induced by flashing inside the pipe	Duplex steel DIN 1.4462 or equivalent i.e. SAF 2205

Table 1. Material selection development for MSF plant desalination

The development of stainless steels in thermal desalination continues as an understanding of corrosion mechanisms and the associated kinetics is gained and this has resulted in a wide range of alloys under the umbrella title of “stainless steels” being readily available for the technology.

Specific grades of stainless steel may now be applied to counter particular types of corrosion and / or erosion.

Development of corrosion resistant materials however is not confined to stainless steel, a notable material finding application, particularly for tubing, being titanium. The erosion and corrosion resistance of titanium is well known in the power industry and its application to desalination has resulted in significant reduction in tube weights as thinner wall thickness is used for what is already a lighter material than steel.

The corrosion mechanism for carbon steel that is most often encountered in desalination plants is that of general corrosion, whereby metal is removed from the surface of the exposed material, resulting in a general thinning. This is not the case with stainless steel, where corrosion usually takes the form of pitting. This results in very little metal loss but raise the possibility of localized penetration. Much of the development of stainless steel is associated with establishing resistance to pitting in high chloride environments.

The adoption of stainless steel instead of carbon steel for evaporator and de-aerator shell has caused, along with a general upgrading of the material, also a reduction in the weights of the evaporator, which is indicated in Figure 1 below [1].

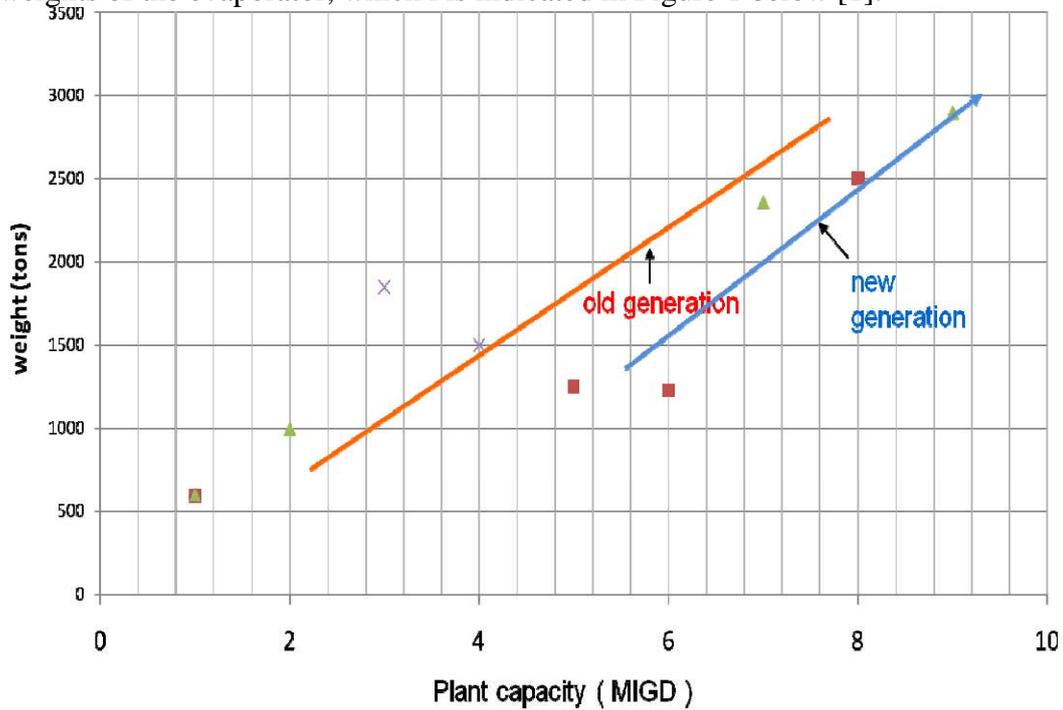


FIGURE 1: overall weight against capacity MSF plant

Figure 1. overall weight against capacity MSF plant

However the gradual decrease in the evaporator overall weight both due to the elimination of corrosion allowances and the refinement in the structural design which permits lower thickness as well as further thermodynamic design optimization that has allowed an overall reduction of the heat transfer surface.

The trend in modern thermal desalination is towards Duplex stainless steel as they combine a very high tensile strength that in turn allow to reduce the thickness of the shell plate and at the same time ensure a better performance against corrosion and erosion.

### 3. MSF Technology

#### 3.1. Heat Transfer Tubes

The material selection for heat transfer tubes represents one of the most important technical choices in the design of thermal desalination plant.

In particular the Tube bundle represent a very large component of the overall desalination plant costs furthermore the tube bundle is generally made of copper nickel alloys or titanium and both materials are extremely sensitive to market price variations. The main copper alloys used in desalination plants for the heat transfer tubes are basically the following:

- UNS C68700 Aluminum Brass (Traded as Cubral)
- UNS C70600 Copper-Nickel 90/10 (Traded as Niton 10)
- UNS C71500 Copper-Nickel 70/30 (Traded as Niton 30)
- UNS C71640 Copper-Nickel 66/30/2/2 (Traded as Iper Niton)

The nominal composition of these alloys is schematically indicated in the table below:

	Niton 10	Niton 30	IperNiton	Cubral
Copper -Cu	90%	70%	66%	76%
Nickel -Ni	10%	30%	30%	-
Zinc -Zn	-	-	-	22%
Aluminium -Al	-	-	-	2%
Iron			2%	
Manganese			2%	

Table 2. Nominal composition of STM alloys

The most important feature that a copper alloy tube should have is to have a good resistance to corrosion. The tube inner surface status plays a crucial role in eliminating the tube reactivity to surface agents and in getting its natural bent to achieve the best protective self-coating during the start up of the tube bundle.

The copper alloys owe their corrosion resistance in oxygenated environments to corrosion products layers which form during initial exposure. The kinetics of corrosion layer growth are determined by the oxygen reduction at the tube inner surface.

It is therefore extremely important that the alloy surface be homogeneous with respect to oxygen overvoltage to avoid differentiation into cathodic and anodic areas.

General the operational experience with Copper alloys tubes has been quite successful but there have been cases where some substantial failures were observed immediately after commissioning of the plant. These failures were not attributable to any shortfall in the material application but in the manufacturing process and in the original quality of the metal that is used for the tube.

In general the manufacturing factory receives the individual constituents of the tubes in sheets of copper, nickel, aluminum etc. The relevant raw material components are melted, and mixed in the required ratio at the factory site furnace. This melt is then formed into billets which in turn are heated, and punched by hot extrusion process to make the basic tube form.

The basic tube is further cold drawn in a number of stages to produce the required end product dimensions. Annealing is done at various intermediate stages. Generally different mandrels were used for each different material.

Manufacturing standards call for clean, smooth surfaces, free from grease and especially from graphitic carbon films. Graphitic carbon films, which derive from the cracking of lubricants during the final heat treatment of the tubes, are well known as strong depolarisers of oxygen reduction and as a cause of pitting attack. Modern factories have taken steps to remove any lubricant before heat treating while in some cases the old and obsolete method of sand blasting to obtain a carbon free surface is applied. Sand blasting, however, also remove the thermal oxide layer which is formed on the inner surface of tubes during the final heat treatment, thus leaving a rather “live metal” sensitive surface.

The increased sensitivity of the alloy surface results in lower stability of the initially formed protective layers while a thin thermal oxide film ensures better, long term stability by reducing the layer growth.

### 3.1.1. Typical Material Selection for Heat Transfer Tubes

The material selection for the MSF plants tube bundle could vary according to the Client design. There are specifications that are considered more sophisticated and demanding than other specifications but generally the material selection has not been subject to great changes in the development of MSF technology.

A typical material selection can be indicated in the table below:

	<b>Frequent</b>	<b>Occasional</b>	<b>Rare</b>
Brine heater	CuNi 70/30 or CuNi 66/30	CuNi 90/10	Titanium ASTM B338 -2 (with titanium tubeplate)
Heat Transfer Tube Heat Recovery section			
High Temperature Stage 112°-70°	CuNi 70/30 or CuNi 66/30	CuNi 90/10	Al Brass

Low Temperature stage Below 70°	CuNi 90/10 Al Brass	CuNi 90/10 Titanium ASTM B338 -2	CuNi 70/30
Heat Transfer Tube Heat Reject section	CuNi 70/30 Titanium	CuNi 90/10	Al Brass

Table 3. material selection for heat transfer tubes

As it can be seen from the table above the adoption of CuNi 90-10 (typical specification BS 2871 CN 102) is prevailing for the major MSF desalination plants. The application of copper nickel 90-10 is predominant in the heat recovery section of the MSF distiller while this material was in general replaced in the heat rejection section by the CuNi 66-30 (typical specification BS 2871 CN 108) or CuNi 66 20 Fe2Mn. Due to the higher nickel content, CuNi 66 20 Fe2Mn, ensures a better resistance to the corrosion phenomena at high temperature for this reason it has been employed instead of CuNi 90-10 in brine heater and high temperature stages of the distiller.

However the cost per unit weight of the CuNi 66-30 tubes is in general 30 % to 40% higher than the CuNi 90-10, in addition the thermal conductivity of this material is lower ( $0.293 \text{ Joule cm} / (\text{cm}^2 \text{ sec } ^\circ\text{C})$ ) compared to 90-10  $0.502 \text{ Joule cm} / (\text{cm}^2 \text{ sec } ^\circ\text{C})$ . This implies the requirement of larger heat exchange surface if CuNi 66-30 tubes are adopted. In view of the high costs, the adoption of Copper Nickel 66-30 alloy for heat exchange tubes is limited to the high temperature stages as an alternative to Copper nickel 90 –10. Despite the material selection has not been subject to many changes the operational experience with MSF plant has gradually allowed to reduce the thickness of the heat transfer tubes. A typical thickness value adopted in the 1980s was 1.2 mm whereas nowadays the tube thickness does not generally exceed 1.00 mm and often reaches 0.89.

Table 4 below shows the prevailing thickness adopted in the MSF plant during their historical development. Operational experience has shown that the adoption of copper nickel tubes of 1.2 mm thickness, seems to be un-necessary, since records exist of plant lasting more than 20 years constructed with Copper nickel 90-10 and Aluminum brass tube operating successfully with limited re-tubing, a possible further reduction to 0.9 mm may be possible as a result of the optimization studies.

Material	Prevalent Thickness Adopted (mm)		
	Until 2000	Last ten Years	Last 4 years-future
CuNi 90/10	1.2	1	0.9 -0.8

CuNi 66/30	1.2	1	0.9 – 0.8
Al brass	1.2	1	1-0.9
Titanium	0.7	0.7-0.5	0.4

Table 4. Prevalent Thickness Adopted for MSF Plants for Titanium and Competing Alloys: Heat Recovery Section

This reduction in thickness has allowed a substantial optimization in the heat transfer areas and in the cost of the evaporator.

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### **Biographical Sketch**

**Dr. Sommariva** has a PhD in Chemical engineering from Genoa University and a diploma in management from Leicester University Dr. Sommariva is presently the Managing Director of ILF

Consulting Engineers Middle East and the head of the worldwide desalination activities of ILF. Dr Sommariva joined ILF in 2009 after working 9 years with Mott MacDonald where he has been leading the desalination and water treatment group as Managing Director of generation Middle East. A member of the International Desalination Association Board of Directors, Dr Sommariva has been the President of the European Desalination Society (EDS) from 2004-2006 and Vice President of the international desalination Association (IDA) between 2002-2004. He served as chairman of WHO committee for the establishment of safe drinking water from desalination,

He is the technical Chairman of the 2009 IDA world conference in Dubai and he is an honorary Professor at Genoa and L'Aquila Universities where he holds regular courses on desalination and water re-use related matters.

Dr Sommariva published over 50 papers on desalination leading edge research and economics and published two books on Desalination management and economics.

In his early career Dr Sommariva worked in Ansaldo Energia and Italmimpianti in various roles in the Middle East