Applications and prospects of titanium and its alloys in seawater desalination industry

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Abstract. Seawater desalination (SD) is an effective method to solve the shortage of human water resources. Because of the excellent corrosion resistance of metallic materials in natural waters, as well as the best corrosion resistant, low density, high strength and good heat resistance in seawater, titanium and its alloys are considered the desirable marine material, including in SD equipment. This review introduces material characteristics of titanium and its alloys, and three currently most widely used commercial SD technologies: multiple effect desalination (MED), multi-stage flash (MSF) and reverse osmosis (RO). The applications and prospect of titanium and its alloys in SD industry are overviewed and analysed. This paper can be a reference for the future material selection of SD equipment.

1. Introduction
With the change of the world environment, increase of population, improvement of living standards and rapid development of industry, the whole world today is facing a serious shortage of fresh water resources. According to the international organizations concerned, the population living in water-scarce countries will increase from 1.06 billion to 2.43 billion by 2050 [1]. Seawater desalination (SD) is an important way for human to solve the water resources crisis. After more than half a century of development, SD technology has been relatively mature, and widely used in water-deficient countries. Due to the corrosive nature of seawater, the design and manufacture of SD equipment must consider the materials resistant to seawater corrosion [2]. The titanium and titanium alloys have good corrosion resistance to chloride ions, and titanium known as "marine metal" is an ideal material for SD devices. The depth and breadth of titanium and titanium alloys application will increase with the development of social economy and the increasing demand for SD [3].

2. Characteristics of titanium and titanium alloys
Pure titanium has the characteristics of small density, high strength compared with ordinary steel and stainless steel. The physical properties of metals commonly used in SD engineering are listed in Table 1 [3]. As can be seen from the table, the density of titanium is 4.5g cm⁻³, 57% of ordinary steel. High specific strength of titanium and titanium alloys can promote the miniaturization and lightweight of SD equipment.
Titanium and titanium alloys have good plasticity and toughness, and can process and form plates, tubes, forgings and castings through the traditional processing technology. In addition, the use of ordinary tungsten gas protection welding of titanium and titanium alloys can meet the standard of good weldability, and the weld strength and plasticity are close to the base material [4].

The comprehensive assessment of retired titanium equipment can be based on the specific corrosion situation and the status of equipment materials. The downgrade and/or recycled use of corresponding design norms implements for titanium and titanium alloy equipment after a long period of use. It can reduce the overall cost of equipment throughout the service period. Therefore, the selection of titanium alloys is a trend from the point of view of sustainability and environmental protection [5].

| Physical properties          | Pure titanium (TA2) | Ordinary steel (SPCC) | Stainless steel (SUS304) |
|-----------------------------|---------------------|-----------------------|--------------------------|
| Density (g cm\(^{-3}\))     | 4.5                 | 7.9                   | 7.9                      |
| Specific strength (N m kg\(^{-1}\)) | 29                  | 23                    | 23                       |
| Thermal conductivity (W mK\(^{-1}\)) | 17                  | 63                    | 16                       |
| Specific heat (J kgK\(^{-1}\)) | 519                 | 460                   | 502                      |
| Conductivity (% to Cu)      | 3.1                 | 18                    | 2.4                      |
| Elastic modulus (Gpa)       | 106.3               | 205.8                 | 199.9                    |

3. Application of titanium and titanium alloys in SD

3.1. SD Methods

The definition of SD is the process of removing salt from seawater in order to obtain fresh water [1]. The main SD methods are divided into thermal method and membrane method. The former mainly includes multistage flash evaporation (MSF) and multi-effect distillation (MED). The reverse osmosis (RO) method and electric osmosis method are definitely the latter. In the course of the development of SD, three mainstream technologies: MSF, MED and RO have gradually formed mainstream desalination technology since the 1980s [6]. They are also the main SD methods widely used in industrial market at present.

3.1.1. MSF method. MSF method is to heat the raw seawater, and then introduce the flash chamber to flash evaporation. The pressure of flash chamber controls in the feed seawater temperature corresponding to the saturated vapor pressure. The fresh water is obtained from the steam condensation when the temperature of the seawater is reduced due to the overheating and rapid partial gasification during the hot seawater into the flash chamber. Figure 1 shows the schematic diagram of MSF. In turn, the concentrated seawater is introduced into the multiple grade flash steam chambers. The number of flash chambers has 20~30 grades, even more than 40 grades. MSF is more suitable for large-scale SD projects and has a high market share in the Middle East.

3.1.2. MED method. The main principle of MED is to heat the next effective solution by two steams produced by distillation. This method can fully reuse the heat energy consumed by evaporation in order to reduce energy consumption. However, there is a serious scaling problem in MED which solved by the low-temperature multi-effect distillation (LTMED) technology in the 1970s. The schematic diagram of three effects of LTMED is shown in Figure 2. This novel LTMED method restores the mainstream position in the field of SD. At present, it has become a very promising SD technology.
3.1.3. **RO method.** RO is one of mainstream SD technologies, mainly using the selective transmittance of RO membranes, which separates fresh water from seawater under a certain pressure. Figure 3 schematically illustrates the principle of osmosis and RO. RO generally does not need heating in the whole process, and has the advantages of simple process, low energy consumption, easy operation and control. The international heat method still dominates about 60% of the world's market. However, the development rate of heat method lags behind the RO method.

3.2. **Application of titanium and titanium alloys in SD**

Titanium welded pipe, mainly used in heaters, condensers, distillers, evaporators and heat exchangers, etc. is the important components of SD equipment. For the grade of titanium, the most widely used are
industrial pure titanium TA1 (Gr1), TA2 (Gr2), high temperature seawater heater using TA9 (Gr7, Ti-Pd), TA10 (Or12, Ti-0.3Mo-0.7Ni), two grades with better corrosion resistance [4].

3.2.1. Application in MSF. In MSF equipment, the spray of hot seawater and the erosion of hot salt mist are main considerations. In the course of service of heat exchanger group, the thermal conductivity and corrosion resistance is the first factor of the material selection, and the strength is the secondary factor [7]. Therefore, for choosing a heat exchanger material, the material service conditions (temperature, corrosive medium, and flow rate), the material properties and material cost need to be considered in a comprehensive manner. At present, three main kinds of materials are titanium and titanium alloy, copper alloy and aluminum alloy. Table 2 lists the thermal conductivity, corrosion resistance and cost of three materials, respectively. The corrosion resistance of titanium alloy is excellent, the heat transfer efficiency is lower than copper alloy, and the cost is higher in contrast with other materials. The oxygen and carbon dioxide contained in seawater can cause harm to copper and have no adverse effect on titanium at all [7]. Therefore, most top of the heat exchanger group uses titanium alloy using its antispay erosion effect, which can make the pipe group to achieve maintenance-free reliability level. It is necessary to use titanium tubes to remove bacteria from seawater by injecting oxidizing fungicides in MSF equipment. In addition, flash steam and heater tube plate can also be selected titanium steel of composite material, not only to ensure good resistance to seawater corrosion, but also to ensure good rigidity [8].

The thermal recovery part and the refrigerant radiator are made of industrial pure titanium in MSF components of heat release parts. The quantity 6 000 and 100 thousand ton of titanium welded pipe was used in the exothermic and heating parts of MSF welding device made by Japan Tsurumi, and the specifications were φ16 mm×0.3 mm, φ16 mm×0.4 mm and 19mm×0.4 mm [9].

Table 2. Performance and cost of common materials used in heat exchange pipe sets [10]

| Materials              | Thermal conductivity (W m K⁻¹) | Corrosion resistance | Density (g cm⁻³) | Price ($10000 t⁻¹) |
|------------------------|-------------------------------|----------------------|------------------|-------------------|
| Titanium alloy (TA2)   | 17                            | Excellent            | 4.5              | 2.8               |
| Copper alloy (Aluminum brass) | 29~100                       | Good                 | 8.4~8.9          | 0.8               |
| Aluminum alloy (5052)  | 140~160                       | Average              | 2.66             | 0.21              |

3.2.2. Application in MED. Titanium tubes are mainly used in heaters and distillers of SD devices. In the MED distillation unit, titanium is mostly used in the first drain pipe of evaporator and the condensing tube of condenser [7]. LTMED SD device is mainly composed of evaporator, condenser, vacuum injection system and piping system. Like MSF evaporation, low temperature and multi-effect common corrosion includes chloride ion corrosion, heavy metal corrosion and electrochemical corrosion, all contact with seawater heat exchanger using titanium pipe is the most reliable choice, but material selection should take into account both functional needs and price factors. Therefore, the heat exchanger pipe in contact with seawater uses titanium tubes to ensure the service life of the entire unit, such as the condenser bundles in the SD plant manufactured and the upper three row bundles of the evaporator are used titanium tubes by the French Sidem company and the United States WDI Company.

Titanium welded pipe is the best pipe for SD project from the material point of view [3]. In LT MED equipment, the components directly affected by seawater scour position (top three row) and the final process of deoxygenation, degasification condenser equipment are used titanium pipe. The use of titanium pipe is about 10% of the number of main tubes. Taking the SD device of daily production of fresh water quantity of 10 000 ton as an example, it is necessary to use titanium pipe about 8~10 ton. A distiller is a multi-tube heat exchanger that uses a large number of titanium tubes. A daily production 13600 m³ desalination plant requires 1200~1500 ton titanium tubes if all thin-walled welded titanium tubes are used for heat transfer [11].
3.2.3. Application in RO. Titanium welded pipe can be used not only as the heat pipe (also known as heat exchanger) for evaporator and condenser in SD equipment, but also as the pipeline that require frequent contact with seawater [7]. For titanium tubes, the critical flow rate of corrosion is 20~30/s in clean flowing seawater, 6~8/s in the high sand flow of seawater, and 2~3/s in the general material design. Titanium tubes are largely unaffected at the flow rate above. Titanium alloy is mainly used in high-pressure pump and some parts of energy recovery device of RO system besides the pipe fittings. The application of titanium alloy in RO SD is less than that of thermal SD. It is necessary to further improve the overall performance of the capacity recovery device and the high pressure pump to improve the energy efficiency of RO performance.

4. Advantages and shortages of using titanium and titanium alloys in SD plants

4.1. Advantages
Titanium is the best material to resist the corrosion performance of seawater at room temperature, and it has excellent corrosion resistance even in polluted seawater, hot seawater (less than 120 °C), sea mud and flowing seawater. Its excellent corrosion resistance is ascribed to the good self-passivation. The surface oxide film or passivation film can quickly repair and restore itself when titanium is subjected to some degree of damage. Table 3 shows the comparison table of seawater corrosion rates of titanium and other metals [3]. Titanium surface can form a strong adhesion and tough oxide film in marine media. So its corrosion resistance is more than other metals [4]. According to the existing desalination project, even if the flow rate of water is 10 m³/s, the titanium tube will not appear any denudation, cavitation or impact corrosion. In addition, in titanium SD equipment with the flow rate of water 3~5 m s⁻¹, the phenomenon of biological fouling is the slightest [3]. It is well proven to be reliable that the world's millions meters of titanium tubes are used in desalination projects.

Titanium tubes have a longer service life in usage performance [7]. The seawater is often mixed with sediment and sea creatures, which easily attach to the heat transfer tube and the end of the pipe. This will erode the copper alloy pipe. However, titanium pipe will not appear this problem. In particular, when oxygen has to be injected to kill bacteria in seawater, it is necessary to use titanium tubes with good corrosion resistance.

Although the thermal conductivity of titanium is not high, the type of heat transfer between surface and steam is droplet condensation. The heat transfer pipe is a small-calibre circular tube. The copper alloy pipe and other wall thickness is generally 0.9~1.2 mm under the premise of satisfying the strength. By reducing the thickness of thin wall of pipe, the thermal resistance can be reduced. The wall thickness of titanium pipe is much thinner, and has higher thermal conductivity compared to B30 copper [7]. For the titanium pipe, it can not only save costs, but also improve the heat exchange coefficient. At the same time, because the heat transfer mode of titanium pipe surface and steam is drip condensation, the thermal resistance is reduced, and the heat transfer performance of titanium is significantly improved.

Table 3. Seawater corrosion rates comparison table of titanium and other metals [3]

| Project       | Titanium | Carbon steel | Cu-Ni alloy | 316L stainless steel | Duplex stainless steel |
|---------------|----------|--------------|-------------|----------------------|-----------------------|
| Annual corrosion rate (mm/a) | 0.00078  | 0.05         | 0.0025      | 0.0029               | 0.001                 |

In terms of economy, titanium has a more cost-effective advantage than copper. The density of titanium is 4.51 g cm⁻³, and B30 copper is 8.94 g cm⁻³. When the wall thickness of titanium pipe is half of the copper tube, the weight of same heat transfer area of titanium tube is only one-fourth of the copper tube. That is to say that the cost of titanium pipe will not exceed the cost of copper unit price, if titanium pipe does not exceed four times the copper tube. According to the current price level, the unit price of thin-walled titanium tubes is about 1.2 times that of B30 tubes and 1.8 times that of B10 tubes, which is much lower than 4 times of the level. It shows that titanium tubes are far more competitive than copper tubes in terms of cost performance.
4.2. Shortages
Although titanium has many advantages. It is also necessary to pay attention to some special cases of corrosion phenomenon in the application of titanium, such as electrochemical corrosion, gap corrosion and so on. The potential of titanium is negative. The acceleration corrosion of other materials is easy to occur when in contact with other materials, and the cathodic protection method of sacrificial anode is generally used. At the same time, the connection between the titanium pipe and the pipe plate is prone to gap corrosion in seawater with the temperature of 100 °C and the PH value of 8, and the gap can be eliminated by the method of pipe section sealing welding.

In addition, the electric potential of titanium in more than 80 ℃ seawater is lower than other materials. There is the possibility of hydrogen absorption phenomenon, and the production of hydrogen embrittlement. If hydrogen absorption occurs when titanium comes into contacting with metals such as iron and zinc, it needs to be protected by sacrificial anode method [12]. Titanium has the necessary erosion resistance and impact resistance, and is not affected by chlorine, nitrogen and hydrogen sulfide and its compounds. Titanium has a good corrosion resistance capacity of oxidation and acid, is the first choice for the production of such pipes materials. Hydrogen absorption does not occur when titanium is in contact with copper alloys and stainless steel [7].

In addition, titanium materials are used on the surface of equipment that contacts with high-speed flowing seawater [13]. However, titanium welded pipe for a variety of reasons, mainly includes the cost, is not part of the main tube of equipment at present. In the world, the main tube of the use of materials are mainly two types, one for the aluminum brass tube HAL77-2, one for the emerging aluminum alloy tube 5052 (the most used in Israel IDE Company). The evaporator and the heat exchanger in the condenser are made of aluminum brass tube or aluminum tube in the SD device, and the corresponding supporting process is required to prevent the corrosion of aluminum pipe when the aluminum tube is used [7].

5. Prospect of titanium and titanium alloys in the field of SD
The lack of drinking water in many countries requires the use of SD to solve household water problems, and industrial production and power generation also continue to grow water consumption for desalination. According to the national coastal urban planning, the future demand for desalination capacity will reach 200~260 million t d⁻¹. With the increasing demand for fresh water in coastal areas, SD industry is bound to become a new industry. Titanium has excellent corrosion resistance, even in the environment of the high salt content of seawater, the high water temperature and the serious water pollution, the amount of titanium will greatly improve.

Titanium welded pipe in the field of SD is the useful supplement and alternative material for copper pipe and stainless steel pipe. With the reduction of production technology and cost control, the future development of titanium welded pipe technology is mainly in the development of ultra-thin-walled tubes and cost control.

Therefore, the welded pipe production enterprises must fully master the production technology as soon as possible. The performance and surface quality of cold rolled pure titanium belt coil for SD has extremely demanding requirements. The control range of process is very narrow, and the equipment process operation has strict requirements. The process equipment operation of titanium belt production should be carried out more in-depth research. It is necessary to enhance the quality of titanium welded pipe, improve production capacity and efficiency, reduce production costs, to meet the market needs of SD industry applications.

It is expected that in the next few years, titanium welded pipe will become much thinner in the field of SD. The titanium welded pipe with the wall thick 0.3 mm appears. The overall price is stable and slowly reduced trend. The weight of using titanium welded pipe in SD project is also decreasing, and the comprehensive cost of the project greatly reduces due to the appearance of ultra-thin-walled tubes.

The price of titanium has fallen sharply in recent years. The proportion of titanium material cost in the whole SD device has also declined greatly, so the application of titanium in SD industry will have a broad market prospect.
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