POTENTIAL EXPLOITATION OF MODIFIED SURFACES TO MITIGATE FOULING IN THERMAL DESALINATION INDUSTRY

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ABSTRACT

The increased deterioration of existing groundwater resources and gradual decline in costs of freshwater water production, have given new impetus to the use of desalination plants in arid lands. Nonetheless, the formation of scale on heat transfer surfaces could profoundly reduce the efficiency of thermal desalination plants. The widely used practice to mitigate scale formation in such units is to use chemical inhibitors. However new environmental legislations restrict the widespread use of such chemicals. This paper highlights the potentially impact of surface treatment by changing surface properties or geometry as an environmentally-friendly mitigation techniques. Advantages and disadvantages of each surface modification technique will be discussed and a review of the previous investigations of fouling on various modified surfaces will be presented.

Keywords: Fouling, Scaling, Desalination, Surface treatment, Calcium sulphate, Calcium carbonate

1. INTRODUCTION

Thermally driven desalination units still constitute a large proportion of overall desalination units. In addition, the current trend of desalination industry does not project an immediate phase-out of the thermal units. Among numerous reasons for this are cheap, redundant fuel availability in some places, longer life-time and better quality of the produced potable water. Nevertheless the presence of deposits with low thermal conductivity is the prime obstacle among several other operational problems that prevent the optimum operation of these units [1]. Table 1 gives typical values of thermal conductivities for various incrustations that thermal desalination units may encounter in comparison with stainless steel. The presence of inverse-soluble salts such as calcium sulphate and calcium carbonate has been the main cause for the development of several desalination units among them was MSF where boiling occurs at sub-atmospheric pressure in order to prevent the supersaturation of calcium carbonate/sulphate salts above critical temperatures of 75-80^{o}C. However such operation requires massive and excessive amount of energy to sustain the required pressure drop. The present primary anti-fouling strategy is to use chemical inhibitors to mitigate fouling/scaling in thermal desalination units. However such approach is strictly under scrutiny as such chemicals involve materials which are harmful to the environment and consequently human health.

Table 1 Thermal conductivity of typical deposits in thermal desalination plants in comparison with stainless steel [9]

Calcium Carbonate	2.9 W/mK
Calcium Sulphate	2.3 W/mK
Biofilm	0.7 W/mK
Stainless steel	18 W/mK

Several other anti-fouling strategies are available with respect to the nature of fouling and operational characteristics of the process. One such method is the modification of heat transfer surfaces in terms of surface energy which was initiated by Müller-Steinahgen and co-workers [2] as well as surface texture. They showed some instances of which the crystallization fouling was reduced on surfaces with lower surface energies. Similar investigations for fouling of milk, crude oil and biofilms also showed tangible reduction of deposition rate on heat transfer surfaces [3, 4, 5]. The technique is generally based on the modification of energy and geometry related characteristics of the heat transfer surface to realize an increased duration of the induction period, the time that the deposit built-up is negligible. The application of surface modification in thermal desalination units is mainly limited to use high-grade anti-corrosive metallic substrates. However recent studies revealed while these substrates may reduce corrosion impacts, they may not necessarily prevent fouling too [6].

The present study highlights and briefs several surface modification techniques which can be utilised in thermal desalination industry. These approaches include surface coatings, change in surface texture and/or a combination of these two techniques. The paper firstly gives brief introduction of the each modification technique followed by some of the fouling results that have been reported so far. The advantages and disadvantages of each technique will also be discussed.

2. SURFACE MODIFICATION TECHNIQUES

From surface science stand point of view, the formation of a deposit on a metal surface may be considered as an interaction between the deposit and surface. As a result, all surface modification techniques either behave as turbulence promoter or endeavour to reduce the work of adhesion between the surface and deposit. In general, maximum adhesion occurs in systems undergoing a maximum decrease in surface energy thus poorest fouling adhesion should occur on materials that have low surface energies.

Figure 1 categorises different surface related techniques that can be utilised for fouling mitigation purposes. The first group is the change the surface physical properties. Müller-Steinhagen and Zhao [2] evaluated a number of such different techniques by measuring contact angle and surface energy of the coatings. They found that Ion Implantation, Unbalanced Magnetron Sputtering, Mixed Sputtering and Plasma Arc Deposition have the greatest potential for preparing low fouling surfaces. Unlike commonly used coatings, the additional heat transfer resistance of alloy layers is negligible because the alloy layer thickness is only about 1-3 μm. The other main advantages are that the alloy surface meets wear resistance and welding requirements.

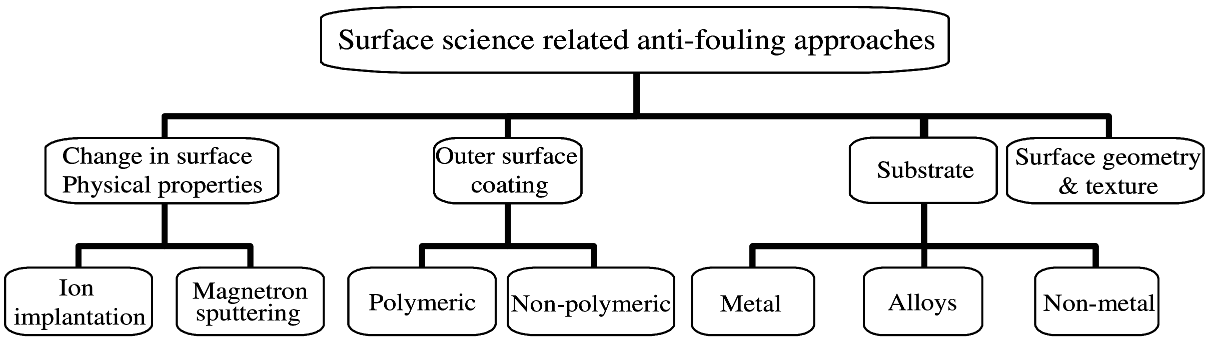

Fig. 1 Various surface related techniques for anti-fouling

The second measure is the technique that covers the surface with an outer coating like polymers such as Ni-P-PTFE and PFA or non-polymeric based like plasma sprayed coatings. In comparison with the first group, here, the layer of coating can be thicker but the stickability between the substrate and coating layer is usually weaker. The next category is to use high-grade materials such as metals e.g. titanium or alloys or non-metallic such as graphite or silicon carbide. These materials are frequently used in industry to reduce corrosion which may also influence the fouling propensity. The last group is to change surface geometry and texture. In what follows, some of these techniques are discussed briefly.

2.1. Ion Implantation

Ion implantation is the name given to a technology, which uses ion accelerators to direct beams of ions into materials. These ions are used to modify the target material, to create radiation damage and to sputter away surface atoms. Ion implantation is the major technology used to introduce impurities into solids in a uniform and reliable way. It is usually the technique of choice for the electrical doping of semiconductors. The introduction of atoms into the surface layer of a solid substrate by bombardment of the solid with ions can vary in the keV to MeV energy range. During ion implantation, a beam of dopant ions of fixed energy is swept across the target surface. The ions have a sufficiently high velocity, about 10^6 m/s, so that they penetrate through the surface and come to rest at a depth of 10 to 1,000 nm, depending on their energy and their mass, and on the mass of the atoms of the substrate material [2]. The technology has universal acceptance because of the accuracy of the number of implanted atoms, and the uniformity of the implantation across the surface [7].

When an energetic ion penetrates the substrate material, it will undergo a series of collisions with the target nuclei and electrons and lose its energy until it comes to rest. The major processes of energy loss are (i) direct collisions between the ion and a screened nucleus, (ii) excitation of electrons bound in the solid and there may be (iii) charge exchange processes between the ion and the atoms of the solid as well. All three processes are energy dependent and hence make different contributions to the energy loss along the path of the ion.

2.2. Ion Magnetron Sputtering

Sputtering is a process whereby material is dislodged and ejected from the surface of a solid due to the momentum exchange associated with surface bombardment by high-energy particles. In the sputtering process, the target (i.e. the source of coating material) is the negative pole or cathode. The substrate is usually the positive pole or anode, but it can be given an imposed negative bias in order to increase the energy of bombardment during deposition. When the electric field intensity produced between the two poles is above a certain value, it will ignite an electric discharge and ionise the working gas (e.g. Ar). Such a low-pressure electric discharge is called a glow discharge, and the ionised gas is called plasma. The target is negatively biased so that its surface is bombarded by positive ions from the plasma. When the atoms are dislodged and ejected from the target, they fly to the substrate and form a deposit on it. If the substrate is biased, it is subjected to positive ion bombardment to form a coating, see Fig. 2 [8].

Sputtering is a function of many variables including the masses of the ion and target atom, the ion energy, direction of incidence to the face of the target, the target temperature and the ion flux (current density). So far, only one coating type - diamond-like carbon (DLC) - was found to combine high hardness with a very low coefficient of friction. Because of the excellent physical properties of thin film diamond, there are many interesting applications of this material. Ion beam deposited carbon films are amorphous and exhibit properties such as optical transparency, high electrical resistivity, a high index of refraction, a high density and a hardness comparable with that of diamond.

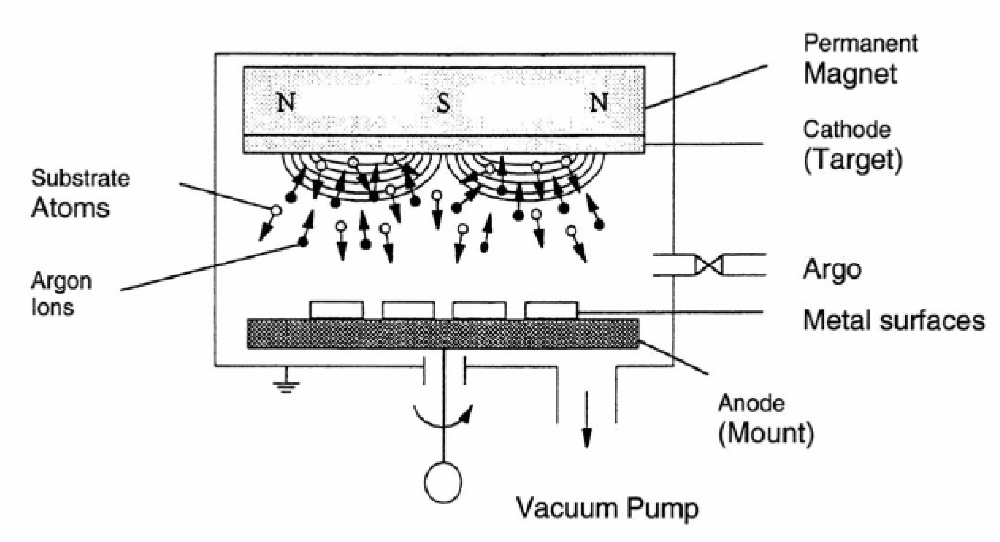

Fig. 2 Schematic diagram of a magnetron ion sputtering process [9]

2.3. Polymer Coating

Alternatively to the methods described above, a number of low-energy polymer coatings, for example, fluoropolymers and silicone polymers, have been developed. Fluoropolymers like Polytetrafluoroethylene (PTFE) and Perfluoroalcoxy-Copolymer (PFA) are of high interest for industrial coating applications because of their resistance to high temperatures, chemicals and organic solvents. They find wide applications as functional coatings with unique properties, such as reduction of wear due to low friction and abrasion and oil and water repellency, corrosion arid fatigue processes.

The unique surface properties of polymers containing fluorine atoms, compared to polymers containing hydrogen atoms, arise from the fact that electrons are held closely and tightly around the fluorine atom and can not be shared or easily polarised. Contrariwise the electron density around the hydrogen atom is mostly in a covalent bond, leaving the atom unshielded and able to induce weak bonds [10]. PTFE is a very inert material with a relatively high melting point (325 °C), and its coefficient of friction is lower than that of almost any other polymer (f = 0.1). The tribological properties of PTFE relate to the structure of the polymer molecule which allows the polymer chains to slide easily over each other when subjected to shear stresses. This behaviour readily facilitates the transfer of the polymer to the surface of the material sliding against it to form a thin lubricating film. Although these surfaces do accumulate fouling, due to their low surface energy (18.6 mJ/m^2), PTFE coatings have excellent non-sticking and antifouling properties therefore the attachment is more loosely adhered and quite easily detached.

Composite electroless nickel-phosporus-polytetrafluoroethylene (Ni-P-PTFE) coatings have become a major growth area within the electroless nickel market. These composite coatings meet a wide range of engineering specifications, providing wear resistance and lubricity. Processes that are easy to operate, and produce coatings of uniform composition on different substrates have been commercialised. A novel suggested application of the low-energy Ni-P-PTFE polymer coating is in heat exchanger fouling mitigation.

2.4. Change in Surface Geometry and Texture

Alteration of surface geometry in terms of surface texture of having grooves, fins or baffles could also influence the formation of deposit. The prime notion in applying such methods is to promote scale of turbulence. This causes fouling to deteriorate due to higher rate of shear force on the surface that may wash away the scale layer from the surface. It is relatively an old technique to enhance clean heat transmission which simultaneously could reduce fouling further. Perhaps the change from tubular to plate or spinal heat exchangers is the most spectacular example.

3. COMPARISON OF THE PREVIOUS RESULTS ON MITIGATION OF FOULING OF MODIFIED SURFACES

Fouling is a transient process that begins with a clean process surface and progresses until the surface no longer can probably be used effectively. The event sequence of the fouling process appears in general to be universal, beginning when fluid comes into contact with a process surface. During the induction period, the conditioning film forms with heat transfer efficiencies not changing significantly. The film development is followed by a rapid accumulation of deposit growth. It is during this growth phase that the heat transfer across the process surface starts to dramatically change. There are many parameters that influence the deposition process. It has long been speculated that surface properties may also have some impact on fouling mechanisms. However, due to lack of advanced equipment, such hypothesis remained unchecked. In the past decade, however, some studies were made on the effect of surface energy on the type and amount of crystallization deposit formed. As a result, presently a substantial number of studies is available in open literature in particular on precipitation fouling which is the core fouling problem in desalination industry.

Müller-Steinahgen and co-workers pioneered the idea in mid 1990's and patented several techniques that would to fouling rate reduction. Later on, other researchers followed the idea and some dark corners of such impact became clear. Förster and Bohnet [11] found a relation between surface energy and the induction period of calcium sulphate fouling, supporting the idea of the advantage of using low energy surfaces on heating elements. Later on, they also proved that the analysis of the interfacial energy between surface and calcium sulphate deposit can be used as a tool to predict the optimum surface energy to mitigate fouling [12]. They also showed that on DLC (Diamond Like Carbon) coating there was no deposit built-up. The effect of surface energy on the nucleation and deposit development of calcium phosphate was also studied by Liu et al. [13] and Wu et al. [14]. In both cases, it was found that nucleation and deposit development was higher for surfaces having high values of surface energy.

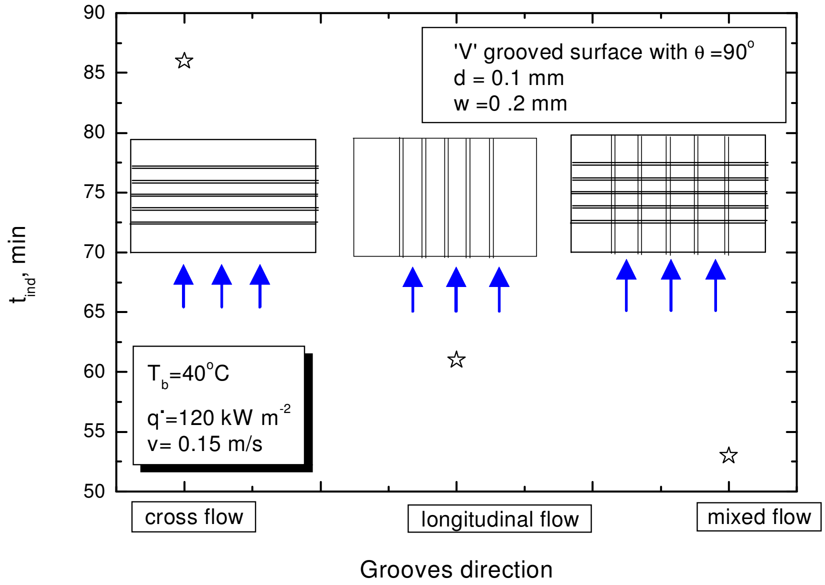

Fig. 3 Induction time as a function of groove direction [15]

In addition, the analysis of surface topography/texture showed that with respect to adhesion mechanisms since mechanical forces at the interface crystal/heat transfer surface are responsible for discrepancies between reality and theory [12]. From operating conditions point of view, Müller-Steinhagen and Zhao [2] showed that the difference between the performance of implanted and original surfaces increases with increasing heat flux and decreases with increasing bulk $CaSO_4$. Furthermore, the combination of different surface geometry as plate heat exchanger and Ni-P-PTFE coating could substantially fouling occurrence [4].

Most recently, Al-Janabi et al. [15] studied the impact of surface texture on the behaviour of $CaSO_4$ fouling on stainless steel surfaces. Different textures of grooved surfaces with respect to the direction of flow has been examined namely crossed, longitudinal and mixed grooves as shown in Fig. 3. In was aimed to discern the impact of these textures on the induction time of fouling curve. Figure 3 shows the induction time is a strong function of the groove direction with respect to the fluid flow. Longer induction times occurred over the crossed grooves in comparison with longitudinal and mixed grooves. Crossed grooves have a higher resistance to the flow than the other two surface textures, and hence provide a stronger inhibition to the formation of initial nuclei.

Perhaps the most spectacular example of change in surface geometry can be shown during pool boiling of foulants. In pool boiling the surface temperature is well above the saturation temperature which results in generation of bubbles on the surface.

Beneath the bubble, the concentration of foulant will increase due to steep temperature gradient. This gives rise to rapid formation of deposit beneath bubbles. Most recently, an ongoing research at ITW, the University of Stuttgart showed that the built-up of deposits can substantially be reduced when the surface texture is changed [16]. Figure 4 depicts some of the structured finned tubes from Wieland Company (Germany) that have been investigated. The finned shape of these tubes provides considerable additional nucleation sites that would generate more bubbles than smooth tubes.

Fig. 4 Pictures of finned tubes from Wieland company, Germany

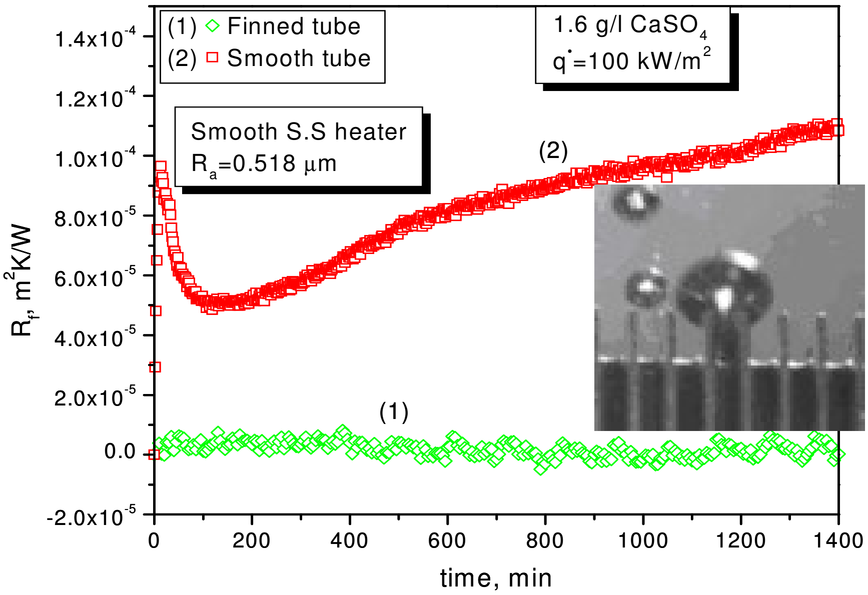

Fig. 5 Comparison of fouling resistance of smooth and finned tubes for the same operating conditions during pool boiling heat transfer [16]

Figure 5 demonstrates experimental results during pool boiling for a concentration of 1.6 g/L of $CaSO_4$. While on the smooth tubes the rapid formation of $CaSO_4$ deposits starts after 100 min, virtually no deposit is formed on the finned tubes. There are a number of speculations to explain these interesting results. Above all is the higher number of bubbles that are produced on finned tubes and higher scale of turbulence generated by these bubbles. The compact structure of finned tubes reduces the residence time of bubbles on the surface which in turn leads to lesser chance that foulant concentration increases beneath the bubble which is the case for smooth tubes. Furthermore, the detached bubbles generate higher degree of turbulence when they depart the surface which helps that any formed crystals can be washed away more easily.

4. CONCLUSIONS

Surface characteristics, mainly in terms of surface energy and texture, are important parameters which could significantly influence the propensity of scale formation on heat transfer surfaces. In particular the effect of change in surface physical properties in terms of surface energy has not been thoroughly investigated until the mid 1990's. In the past few years, however, several investigators demonstrated experimentally the significant effects of surface properties on fouling processes. In most, but certainly not all, cases lower surface energy resulted in reduced propensity of the surface to foul. While there have been some successful attempts at fouling mitigation with modified surfaces, many problems remain unanswered such as irreproducibility of results and degradation of surface performance. Better understanding of the interactive forces between deposits and surfaces could provide the required insights into the adhesion mechanisms on modified surfaces. Perhaps the impact of surface characteristics in terms of surface geometry and texture is more substantiated to influence fouling. The most promising results so far have been obtained during pool boiling of $CaSO_4$ solutions.

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