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Study on thermal desalination effect on the solids' precipitation variation

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ABSTRACT

The topic of this paper is the thermal impact desalination in the fouling and corrosion phenomena as an auxiliary and rejection waters on the environment in the western littoral of Ghazaouet site—Tlemcen (Algeria). The methodology we used consists of taking samples from different qualities of water used in the distillation process in multiple effects (MED): auxiliary water, brine water, and undrinkable water production. They have been characterized by physical–chemical analysis such as pH, temperature, conductivity, salinity, dissolved solids (TSD), turbidity, calcic hydrotimetric title, alkalimetric title, and organoleptic parameters. We also carried out a study on the influence of the distillation parameters on calco-carbonic balance and furring solid's precipitations of forming carbonates, hydroxides, and sulfates. The results showed that the rejected brine water in the sea contains a considerable quantity of dissolved chemical bodies in suspension where salinity reached 49 g/l, containing also effluents acid coming from the correcting operations of the auxiliary water. The saturation index of this water determined by different methods that showed the furring and corrosive character of the seawater.

Keywords: Thermal desalination; Auxiliary water; Brine water; Scaling and corrosion; Calco-carbonic balance; Solid's precipitation; Marine environment

1. Introduction

Water supply by unconventional means in order to produce water at reduced cost is the solution which has been planned to safeguard the drinking water and the industrial water supplies as in Algeria [1]. They became a major economic and strategic stake permitting the increase in the hydrous resources. According to this program, several stations are already functional and others under development using two processes: evaporation and condensation such as the multiple effects of distillation (MED), or multi-stage flash distillation and membranous process such as reverse osmosis, nanofiltration, and electrodialysis.

One was interested in this study of the influence of thermal desalination parameters on the solids' precipitation; the furring and corrosion properties of the auxiliary water, the chemical composition variables in

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seawater charged with ions in consequence of an uninterrupted rejection of brine water, concentrated in salt and chemical products resulting from the correcting operations of the auxiliary water, and the reduction in the content of dissolved oxygen [2].

These phenomena are preoccupying where the thermal transfers decreased and influence the industrial water quantity produced by a MED processes such as the industrial water production by sea's desalination as an electrolytic unit of Ghazaouet ALZINC company in Algeria. One will be interested particularly to study the influenced parameters of distillation such as temperature, pH, and concentration on calco-carbonic balance and furring solid's precipitations of carbonates, hydroxides, and sulfates formed in thermodynamic conditions where the solubility limit is exceeded in oversaturation water and the kinetic conditions where the deposit rate is sufficiently high.

The characterization methods used various kinds of water in desalination such as the auxiliary water, the brine water, and the undrinkable water production (industrial water), the furring and corrosive effects of auxiliary water, the effects of the rejected brine water on the environment, and the influence of dissolved gas concentration will be discussed.

2. Materials and methods

In this study, the methodology that we used consists of taking the appropriate water samples from different chemical compositions used in the thermal desalination process such as auxiliary water, rejected brine water, and the industrial water production. Samples have been analyzed by different characterization methods in order to determine the physical–chemical parameters: temperature, pH, conductivity, salinity, dissolved solids, turbidity, and calcic hardness or hydrometric calcic title, HCT, expressed in mg/l of $CaCO_3$, and organoleptic parameters.

2.1. Sampling mode

The representative water sample analysis before and after the desalination was carried out in order to avoid any contamination or external pollution using clean bottles in polyethylene of 1.5 l previously disinfected and rinsed several times with distilled water. They have been filled to overflowing to avoid any air bubbles penetration and closed again with a label where are noted some information about the water sample such as time of sampling, type of water, pH, temperature, and turbidity.

2.2. Characterization method

The taking samples have been analyzed by volumetric and gravimetric dosages, spectrophotometry UV/Visible analysis-type Jasco V-500, range 190–2,500 NM, and atomic absorption spectrophotometry of flame air/acetylene-type Perkin Elmer, models Analyst 300, controlled by a microcomputer.

2.3. Analysis results

Analysis results different kinds of water from the thermal desalination process are summarized as the following table. The sampling brine water has been chosen on the littoral site near the rejections (see Tables 1 and 2).

3. Results and discussions

The study in this project was focused on the influence of thermal desalination parameters and solids' precipitation of scaling and corrosive properties of the auxiliary seawater. We considerer many influence parameters which negatively affects the environment and the ecosystem balance such as: the chemical composition change of seawater as results of stress release concentrated brines in salt and chemicals from the auxiliary water operations correcting, the products derived from marine pollution such as hydrogen sulfide, ammonia compounds and fuel products, the decrease in dissolved oxygen.

Ionic concentrations of the elements in the auxiliary water are determined by absorption spectrophotometry (Tables 3 and 4) have shown a high content

Table 1
Physical–chemical characteristics of the auxiliary water

	Measured values				Measured values		
Parameters	1	2	3	Parameters	1	2	3
Temperature (°C)	20.5	21.3	20.5	TDS at 20.7°C mg/l	51,300	51,300	51,400
pH	8.21	8.16	8.2	Turbidity in NTU	0.82	0.83	0.82
Conductivity At 20°C (μS/cm)	52.6	53.4	54.5	Salinity at 20.7°C, mg/l	36.5	36.5	36.6

Table 2
Hardness and alkalinity values of auxiliary water (°F) (1°F corresponds to 10 mg/l of $CaCO_3$)

Water hardness (°F)	Values
Total Hydrotimetric hardness (TH)	760
Carbonated hardness	15
Permanent hardness	635
Calcic hardness	140
Magnesium hardness	620
Full alkalimetric title	15

of hydrogen carbonate ions 129.32 mg/l, chloride 19 880 mg/l and sulfate 2,740 mg/l. The contents of positive ions: $Ca^{2+} = 560$ mg/l, $Mg^{2+} = 1{,}315$ mg/l and $Na^{+} = 11{,}040$ mg/l promote the precipitation of $CaCO_3$ and $MgCO_3$.

The furring effect was verified by the characterization indices of auxiliary water expressed by the value of the saturation index (SI). They were determined by the index of Stiff and Davis based on the Langelier approach [3,4] for fresh water, considering the salinity of auxiliary water is higher than 10.000 mg/l.

$$\mathrm{SI} = \mathrm{pH} - \mathrm{pHs} \tag{1}$$

$$\mathrm{pHS} = K_{cc} - \log\left[\mathrm{Ca}^{2+}\right] - \log\left[\mathrm{HCO}_3^- + 2\mathrm{CO}_3^{2-}\right] \tag{2}$$

pHS—water saturated with calcium carbonate.

K_{cc}—Coefficient, which depends on the ionic force and temperature.

The results were given a SI = 1.394 shows that a furring character of the auxiliary water.

Table 3
Concentrations of dissolved salts in auxiliary water

Salts	mg/l per degree	Salts	mg/l per degree
CO_3^-	26.40	HCO_3	129.32
$MgCO_3$	36.00	$Ca(HCO_3)_2$	171.72
$CaCO_3$	44.00	$Mg(HCO_3)_2$	154.76
$NaCO_3$	46.64	$NaHCO_3$	178.08
Dissolved salts		36,030 mg/l	

Table 4
Values of dissolved gas concentrations in the auxiliary water (mg/l)

Dissolved gas	Concentration (mg/l)
CO_2	24.64
O_2	7.77

3.1. Scaling and corrosive effect of auxiliary water

The characterization methods per direct measurement of physical–chemical parameters: pH, temperature, conductivity, salinity, dissolved solids, turbidity, and calcium hardness obtained from measurements of the taken samples or by Stiff and Davis indices [3] according to the selected high salinity of Mediterranean seawater which showed that the auxiliary seawater presents a scaling and corrosive character. The salinity at ambient temperature is about 36.5 mg/l, while the pH is 8.2 (Table 1).

Scaling is a major technological limit to heat exchange and corrosion is the degradative material resulting from chemical and electrochemical interactions with the environment [4,5]. Seawater from its physical–chemical properties: high conductivity due to a significant salinity, high content in chloride ions and dissolved salt, oxygen gas, activity of micro-organisms (bacteria, microalgae, etc.) constitute a favorable mean to scaling and corrosion [6]. Also energy parameters such as vapor and water flow, pressure, and temperature were selected to avoid any scaling salt precipitations as vacuum distillation with a temperature of 52 and 62°C relatively lower than the boiling point of water, in which corrosion and scaling problems were observed. Vacuum distillation by adjusting the pressure provides these relatively lower temperatures than the boiling point of water, which will spray water and avoid problems of scaling and corrosion that raise with the increasing temperature.

The furring effect is based on the calco-carbonic balance of water [7,8] where the carbon dioxide (CO_2) is partially ionic form in water characterized by the dissolution or the precipitation of calcareous in water governed by a series of equilibrium reactions.

$$\mathrm{CO_2 + H_2O \leftrightharpoons H_2CO_3 \leftrightharpoons H^+ + HCO_3^-} \tag{3}$$

$$\mathrm{HCO_3^- \leftrightharpoons H^+ + CO_3^{2-}} \tag{4}$$

$$\mathrm{CaCO_3 \leftrightharpoons Ca^{2+} + CO_3^{2-}} \tag{5}$$

Under the usual conditions, CO_3^{2-} reacts almost entirely to form HCO_3^- which explains one finds significant quantities of dissolved calcareous in water in the form of $Ca(HCO_3)_2$ which precipitates in the pipes:

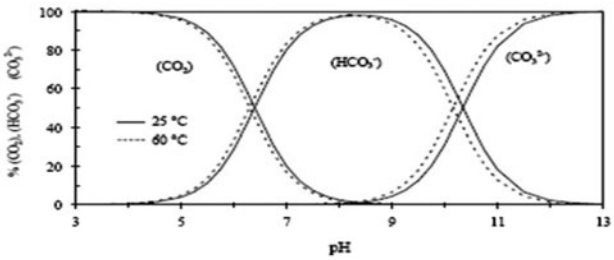

Fig. 1. Diagram of carbonate species distribution according to the pH.

$$CO_2 + H_2O + CaCO_{3\downarrow} \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad (6)$$

Calco-carbonic balance is related to several parameters which tend to form furring deposits such as temperature, pH, water hardness, and concentration of dissolved salt [9,10].

The presence of calcium bicarbonate content requires a dissolved gas called balancing CO_2. If dissolved or free CO_2 content is higher than balancing CO_2, the reaction is the dissolution of $CaCO_3$ in this case, water is called aggressive by calcareous formation. If dissolved or free CO_2 is lower than balancing CO_2, the reaction is the formation of $CaCO_3$ in this case, water is called scale-forming water. If dissolved or free CO_2 content is equivalent to balancing CO_2, the reaction is in pH balance or saturation pHs (see Fig. 1).

The corrosive effects appear by a degradation of material as pitting due to a chemical interaction with surrounding means characterized by mass loss when the protection fails [11,12]. The results of the physical–chemical auxiliary water characterization (Table 1) showed that conductivity raised about 54.5 μS/cm at 20˚C, content in chloride ions 19.88 g/l, content of dissolved salt concentration of carbonate and hydrogen carbonate ions, dissolved oxygen only 7.77 mg/l, micro-organisms, dissolved salt from pollution constitutes a favourable mean of corrosion development which most often appears as a mechanism in electrochemical or microbiological mode where water constitutes the electrolyte of corrosion current, and the material is altered by anodic dissolution. Degradation by corrosion pitting is frequently observed in thermal desalination plants.

3.2. Releases effects of brine water on the marine environment

Brine water after thermal desalination from its physical–chemical characteristics: salinity, dissolved solids, conductivity, pH, temperature, turbidity, dissolved gas is unsuitable to any use in agriculture or industry and far from being drinkable, and constitutes a threat for the marine environment by releases. The results in Table 5 showed that salinity reached to 49.5 mg/l, and conductivity of 72.2 μS/cm at 20˚C, pH 8.5, dissolved salts, etc. These values compared to standard values are raised and influence negatively on the marine environment and the ecosystem.

The Mediterranean Sea salinity varies between 36 and 38 g/l. It is naturally controlled by regulatory elements that are marine micro-organisms (consuming minerals), the currents between the seas and oceans which tend to balance the concentration differences, in part against constant inputs of minerals transported by rivers to the sea. The differences caused by heavy rains (lower rate) or high evaporation during the peak summer heat are only temporary and quickly compensated. But when water is loaded with salt from industrial discharges such as desalination process, the salinity of the sea increases with a negative effect on marine species (Table 5).

3.3. Influence of dissolved gas concentration

Dissolved gases in seawater have several origins whose principal one is mainly the atmospheric gases: nitrogen, oxygen, and carbon dioxide [13] (see Fig. 2).

Nitrogen is considered chemically and biologically inert. Its concentration's variations are only due to seasonal variations in atmospheric pressure, temperature, and salinity. carbon dioxide equilibrium varies calco-carbonic balance of water, so the initial concentration

Table 5
Physical–chemical characteristics of the brine water

	Measured values				Measured values		
Parameters	1	2	3	Parameters	1	2	3
Temperature (˚C)	40.2	42.0	43.2	TDS at 20.7˚C, mg/l	71,200	71,000	71,300
pH	8.50	8.3	8.44	Turbidity in NTU	0.91	0.89	0.92
Conductivity At 20˚C, in μS/cm	64.9	64	72.2	Salinity at 20.7˚C, mg/l	49.0	48.2	49.5

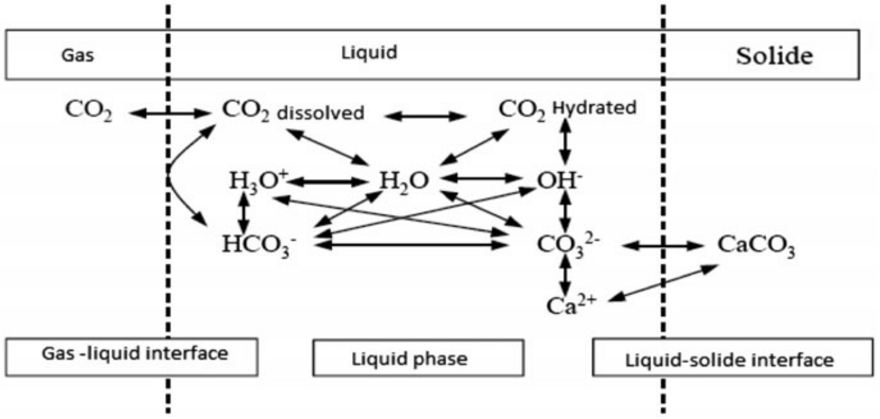

Fig. 2. Schematic representation of the exchanges of materials interfaces and liquid-phase reactions of calco-carbon system [13].

Table 6
Concentrations of dissolved salts in brine water

Salts	mg/l per degree	Salts	mg/l per degree
OH^-	0	$MgCO_3$	36
Ca	0	$CaCO_3$	44
Ca $(OH)_2$	0	$NaCO_3$	46.64
Mg $(OH)_2$	0	HCO_3	129.32
MgO	0	$Ca(HCO_3)_2$	171.72
Na (OH)	0	$Mg(HCO_3)_2$	154.76
CO_3^-	26.4	$NaHCO_3$	178.08
Dissolved salts			49,000 mg/l

Table 7
Hardness and alkalinity values of brine water (˚F)

Water hardness (˚F)	Measured values
Total hydrotimetric hardness (TH)	820
Carbonated hardness	20
Permanent hardness	800
Calcic hardness	120
Magnesium hardness	700
Full alkalimetric title	20

Table 8
Values of dissolved gas concentrations in the brine water (COD: chemical oxygen demand)

Dissolved gas	Concentration (mg/l)
CO_2	35.2
COD	4.58

was 24.64 mg/l and passed to 35.2 mg/l promoted by the increasing temperature. Oxygen gas affects many chemical and biological phenomena. The results showed a reduction in oxygen concentration from 7.77 to 4.58 mg/l which influences negatively on the ecosystem balance and the life of marine species. The decrease in marine oxygen, as the results show, a discharge of salt-laden water from desalination plants that affects marine species. A biological study is needed to confirm our results and to complete this investigation (Tables 6–8).

4. Conclusions

Desalination processes have been developed to achieve lower costs and higher flow rates. Thermal desalination is a competitive solution to mitigate the water scarcity characterized by limitations such as scaling and corrosion. Scaling is a major technological limit to heat exchange. Seawater from its physical–chemical properties: high conductivity due to a significant salinity, high content in chloride ions and dissolved salt, oxygen gas, activity of micro-organisms (bacteria, microalgae, etc.) constitute a favorable medium to scaling and corrosion. The scaling effect is based on the calco-carbonic balance of water where the CO_2 is partially ionic form of water characterized by the dissolution or the precipitation of calcareous in water. The corrosive effect appears by a degradation of material as pitting resulting from a chemical interaction with the surrounding medium characterized by mass loss when the protection fails. The characterization of the physical–chemical auxiliary water showed that the raise of conductivity constitutes a favourable medium of corrosion development which most often appears by a mechanism in electrochemical or microbiological mode. Brine water from its physical–chemical characteristics is unsuitable to any use and constitutes a threat for the marine environment by releases. Oxygen gas affects many chemical and biological phenomena. The results showed a reduction in oxygen which influences negatively on the ecosystem balance and the life of marine species. Existing management through the establishment of two separate networks, the first one for the collection and the treatment of wastewater and the second for rain water which is the solution to consider before desalination.

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References

[1] N. Ghaffour, MEDREC (Middle East Desalination Research Centre) role in desalination, 4-day intensive course on R.O process of sea and salt water desalination, Bejaia, 2008. pp. 20–25.

[2] Y. Lefebvre, Seawater Circuits, Treatments and Materials, Technip Edition, 1993.

[3] H.A. Stiff Jr., L.E. Davis, A method for predicting the tendency of oil field water to deposit calcium carbonate, Pet. Trans. AIME 195 (1952) 213–216.

[4] W.F. Langelier, The analytical control of anti-corrosion water treatment, J. Am. Water Works Assn. 28 (1936) 1500–1521.

[5] P. Bandelier, J.C. Deranzier, Thermal desalination processes in high performance GRETH, Grenoble, Research group CLEFS CEA N° 44, 2000.

[6] F. Bailer, Study of the Different Mechanisms of Particulate Deposits Leading to Fouling of the Gas Phase Heat Exchanger Tubes, Thesis, polytechnic institute of Grenoble, 1998.

[7] H. Elfil, Reconsidering water scaling tendency assessment, AIChE J. 52(10) (2006) 3583–3591. Wiley Interscience.

[8] <http://www.ipeiem.rnu.tn/Elfil.pdf>.

[9] Dembele, Study on MED Process by Thermodistillation Solar of Brackish Water, PFE engineers project, Tlemcen university, 2006.

[10] <http://www.techniques-ingenieur.fr/base-documentaire/environnement-securite-th5/gestion-de-l-eau-par-les-industriels-42447210/inhibiteurs-de-corrosion-et-d-entartrage-biocides-w9010/>.

[11] <http://media.xpair.com/pdf/qualite-air/causes-consequences-calcaire-corrosion-embouage.pdf>.

[12] <http://www.planethorizons.com/fr/application-domains/buildings-homes/scaling-corrosion.html>.

[13] <http://www.ipeiem.rnu.tn/Elfil.pdf>.