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Water quality depends on remineralization's method in the desalination plant

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Abstract: Desalination of seawater is an alternative solution in arid zones to provide potable water. In south Morocco, the National Office of Electricity and Water (ONEE) has built many desalination factories. However, the osmosis water (permeate) is unbalanced and has a corrosive character. Therefore, a post-treatment of remineralization is necessary to return to water its calcio-carbonic equilibrium and to protect the distribution pipelines from corrosion degradation. Following the performance on limestone bed remineralization in Daoura plant in comparison with other methods, this article evaluates this technique, by checking the effect of parameters on water quality on the laboratory scale using a calcite bed pilot. We tested E.B.C.T (Empty Bed Contact Time), the upward speed, the bed length, the effect of water debit and the residence time on the treated water quality. Monitoring these parameters on the laboratory scale is indeed essential for optimal remineralization process. With the results of this study as well as economic consideration, it is possible to optimize the choice of the conditions needed for remineralization operation through limestone bed to minimize its costs with sizing and extrapolating to the industrial scale.

Keywords: Aggressive water, Remineralization, Pipe corrosion, Calcio-carbonic equilibrium, Desalination.

1. Introduction

Water has become a major concern in the regions of the Moroccan South. The conventional water resources (surface and subterranean) are minimal [1-2]. The scarcity of water resources and their poor quality, along with increasing urbanization, may induce significant future effects on the socio-economic sectors in these regions, particularly agro-business and tourism. Indeed, to face this predicted shortage of water, the National Office of Electricity and Water (ONEE) in Morocco made a commitment in the realization of a vast and ambitious program aiming at the construction of several stations of desalination of seawater in Southern Morocco [3-4]. It is thus particularly important to note that during these last three decades, the ONEE follows the progress of the new technologies of desalination to increase gradually the production capacities of stations in drinking water [5-8].

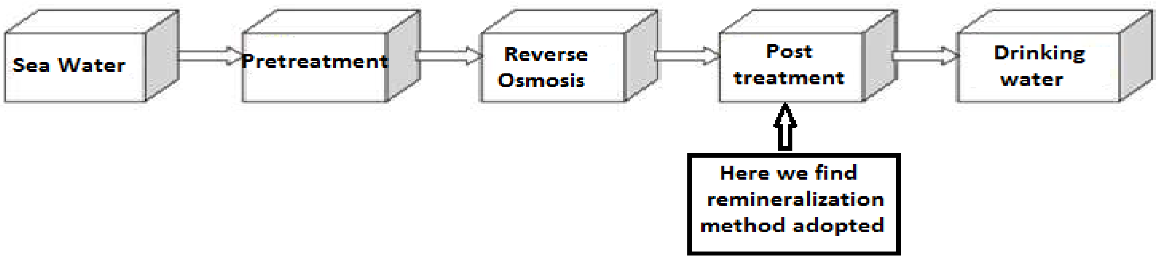

Figure 1. Different steps followed for the production of drinking water

The first experiment of the ONEE regarding desalination of the water in the southern regions goes back to 1976, when the Office created a unit of demineralization by electrodialysis, reaching production capacity 75 m^3/day to supply the city of Tarfaya with drinking water. The produced in the

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reverse osmosis unit after desalination (desalinated water) is unbalanced as it is characterized by high aggressiveness, high corrosively and low salinity. As a result, it can attack networks and structures that can introduce harmful substances that are detrimental to water quality [9-11]. Hence, the necessity for a remineralization posts treatment, to return to osmosis water its calcio-carbonic equilibrium, and thus preserve and protect the pipelines of drinkable water from corrosion degradation [14-17] (Figure 1).

There are many remineralization techniques of desalinated water [12,13,18]. ONEE adopted three remineralization techniques in plants of the mentioned areas: (1) remineralization by hydrated lime in presence of CO_2 in Laâyoune desalination plant (SDL), (2) remineralization by a passage of water through limestone bed in Daoura demineralization plant (SDD) and (3) remineralization by injection of calcium chloride $CaCl_2$ and sodium bicarbonate $NaHCO_3$ in Sidi Elghazi (or Agti Elghazi) plant (SDS) (Figure 2).

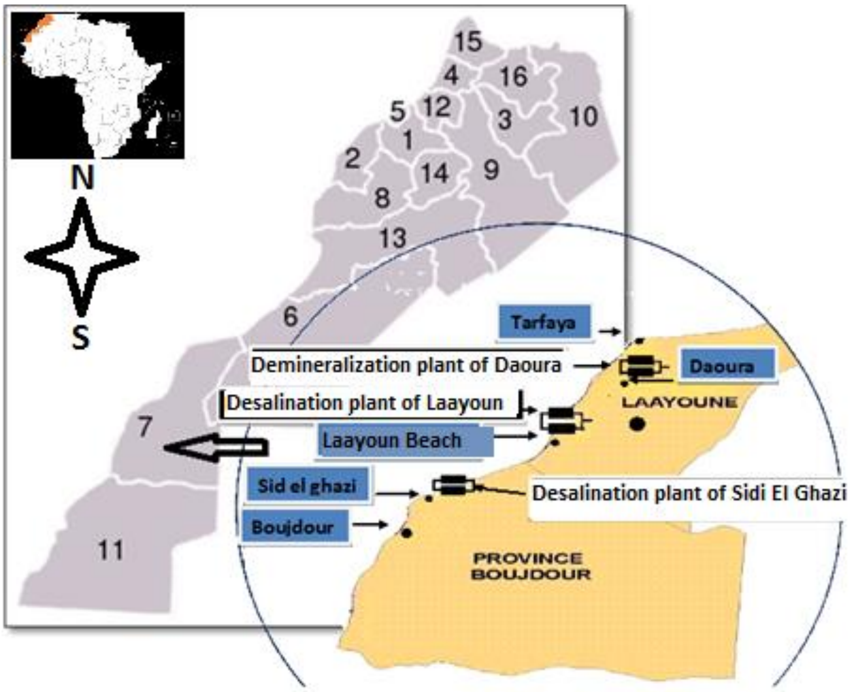

Figure 2. Geographic situation of different plants in Sakia Elhamra Laayoune region [19]

Remineralized water must correspond to these characteristics to be considered as balanced water [17]:

- ✓ $8 < pH \leq 8{,}5$
- ✓ $Ca^{2+} = 8$ °F
- ✓ TAC ≥ 8 °F

We defined the French degree (°F) as 1°F=10 mg/L of $CaCO_3$.

For example, in the first plant (SDL), poor control of hydrated lime addition with freshwater led to undesirable pH changes due to the disappearance of lime buffering properties [15,16].

This article contains a comparative study between these three processes of remineralization, using the above parameters. The measures are made for the same period to assess the best technique adopted.

2. Materials and methods

2.1. Calcium titration

At V = 100 mL of water, we add 5 mL of NaOH 2 M (buffer solution), and small spatula of indicator (calcon), then titrated by EDTA solution (C = 0,02M) until the end point of titration.

2.2. TAC and TA titration

Alkalinity titration is measured by the neutralization of ions (OH^-, HCO_3^- and CO_3^{2-}) in a certain volume of water by a dilute solution of a strong acid. The TA (alkalimetric titration) measures the content of free hydroxides (OH^-) and carbonates (CO_3^{2-}). The total alkalinity titration (TAC) measures the sum of free hydroxides, bicarbonates and carbonates. 100 mL of water to be analyzed is placed in an Erlenmeyer, and then 2–3 drops of phenolphthalein solution were added.

If the solution does not turn pink: the TA is: 0.

If the solution becomes pink, we use a burette to add hydrochloric acid (0.1 M). The equivalence point corresponds to a colorless turn. The value found on the burette corresponds to the TA (meq/L). Do not readjust the burette. In the above sample, add 3 drops of helianthine. If the solution turns red or orange: TA = TAC.

2.3. CO_2 titration

Aggressive CO_2 expresses the part of CO_2 that can dissolve $CaCO_3$, is calculated by the following relation [23]:

$CO_2 = (TACs - TAC) * 22$ (mg/L)

Such that TAC (total alkalinity titer of the water) and TAC_S (the total alkalinity titration of the water measured after the marble test) is expressed by meq /L.

3. Results and discussion

3.1. Remineralization by the hydrated lime $Ca(OH)_2$ in presence of CO_2 in the SDL

This station (SDL) is installed since 1995, assuring production of 7000 m^3/day. Then, in 2005, an extension allowed it to produce 13000 m^3/day. Now, the production reaches 26000 m^3/day. The permeate water is remineralized by the injection of $Ca(OH)_2$ prepared in a saturator of lime to obtain water balanced in the presence of CO_2 according to the reaction:

$2CO_2 + Ca(OH)_2 \rightarrow Ca^{2+} + 2\ HCO_3^-$

The necessary quantity of $Ca(OH)_2$ to balance the water is 59,2 g/m^3; by taking into account a rate of 8 % impurities in our case, the quantity of the $Ca(OH)_2$ added is of the order 64 g/m^3.

3.1.1. The evolution of treated water parameters

To study and examine the performance of the method exploited for the remineralization in the SDL, we suggest following some indicators: pH, Ca^{2+}, TH and TAC so as to maintain the quality of the produced water. Figure 3 collects the evolution of the characteristics of the water treated during 18 months, from 04/01/2012 till 15/05/2013.

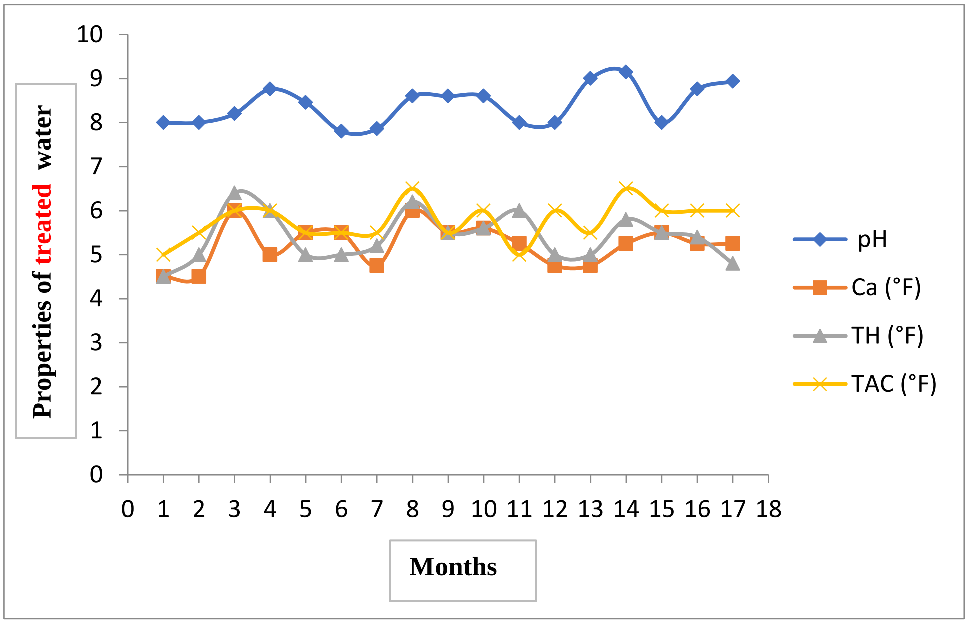

Figure 3. Variation of the SDL water characteristics

Table 1. Physico-chemicals Parameters of sea water and guidelines of Morocco regulations.

	pH	TAC Meq/L	Cond µs/cm	Ca^{2+} mg/L	Turb (NTU)	NO_3 mg/L	NO_2 mg/L	SO_4 mg/L
Sea water	7,57	300	10100	426	0,73	1,3	0,002	2809
Guidelines as per Morocco regulations	6,5 -8,5	< 200	< 2700	< 500	≤ 5	50	0,5	400

According to Figure 3, it seems that during all the period, the characteristics of the water are not in check. Most of the time, the values of the TAC and of Ca^{2+} concentration stay lower than 8°F despite the addition of the 'theoretically sufficient' quantity of lime $Ca(OH)_2$ equal to 64 g/m3 for the remineralization.

In conclusion, the remineralization by the lime within the SDL is submitted to significant limitations because of the deficiency of the quantity of CO_2 corresponding to the calcio-carbonic balance.

It is thus desirable to introduce a sufficient quantity of sulfuric acid to provide sufficient content in CO_2

in the permeate water [19]. As a result of that, the operating cost will increase [20].

3.2. Remineralization by addition of the $CaCl_2$ and $NaHCO_3$

The station of desalination AGTI ELGHAZI is installed in 2009. Its daily production is 90 m^3/j, for a population estimated at 2500 inhabitants. The method adopted for remineralization within this station consists essentially in adding directly the solutions of bicarbonates of sodium ($NaHCO_3$) and chlorides of calcium ($CaCl_2$) in the permeate water with exact doses to normalize the TAC, pH and the TH according to the reactions:

$$CaCl_2 + H_2O \rightarrow Ca^{2+} + 2Cl^- + H_2O$$

$$NaHCO_3 + H_2O \rightarrow HCO_3^- + Na^+ + H_2O$$

$NaHCO_3$ and $CaCl_2$ solutions require large reservoirs. $CaCl_2$ solution is prepared by dissolving 10 kg of $CaCl_2$ of 70% purity in 100 L of water. The injection is carried out using an injection pump with a flow rate Q = 6 impulses/minute. $NaHCO_3$ solution is injected into osmosis water proportionally until pH increase to 8.

3.2.1. Monitoring of treated water parameters

In this paragraph, we suggest following the characteristics of the water produced by the station of AGTI ELGHAZI during 19 months from 24/02/2012 till 27/08/2013. Figure 4 describes the evolution of treated water properties. According to this figure, remineralization by the injection of $NaHCO_3$ and $CaCl_2$ corrects the pH between 7,8 and 8,3. Other parameters, TH and TAC are unstable. They vary between 7°F and 9°F, while the ion Ca^{2+} does not overtake 7,5°F.

This method of remineralization is characterized by an easy addition and a simple dissolution of products. Besides, it presents a low cost of investment for the space required for its exploitation. On the other hand, certain chemicals and in particular, $NaHCO_3$ has low solubility and require large reservoirs to dissolve them.

In the large stations of remineralization, this method asks for a large number of expensive reactive, that imposes the presence of reactive supply away from moisture and availability of the suitable spaces for their storages and to avoid any break in this operation.

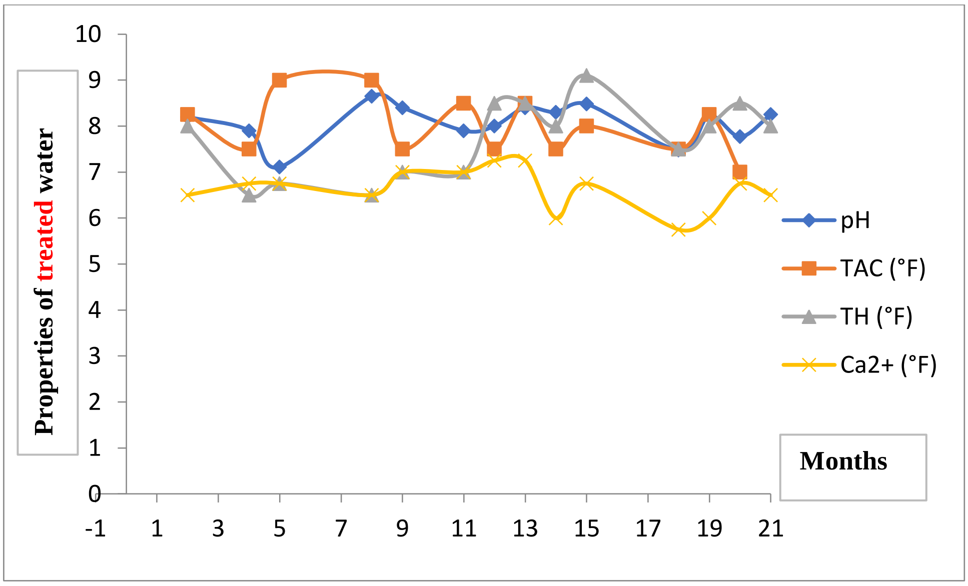

Figure 4. Variation of water characteristics of the station Agti Elghazi

3.3. Remineralization by passage through a bed of calcite

Daoura is a small town situated in the North of Laâyoune city. Since 2009, The ONEE has built a demineralization station in this village, from brackish water, for production a drinking water, to feed a population of more than 8000 inhabitants by a daily production of 240 m3/day. Our study is especially interested in the remineralization adopted within this station. It consists inflowing the permeate water through a bed of calcite from the bottom upward by a debit of 10 L/h so that the outgoing water is remineralized. We are interested in pH, TAC and Ca^{2+} of treated water which gives an idea of the performance of the adopted method.

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2\,HCO_3^-$$

3.3.1. Monitoring of treated water parameters

We follow the various characteristics of the water produced after the remineralization through a bed of calcite. The results are shown in Figure 5.

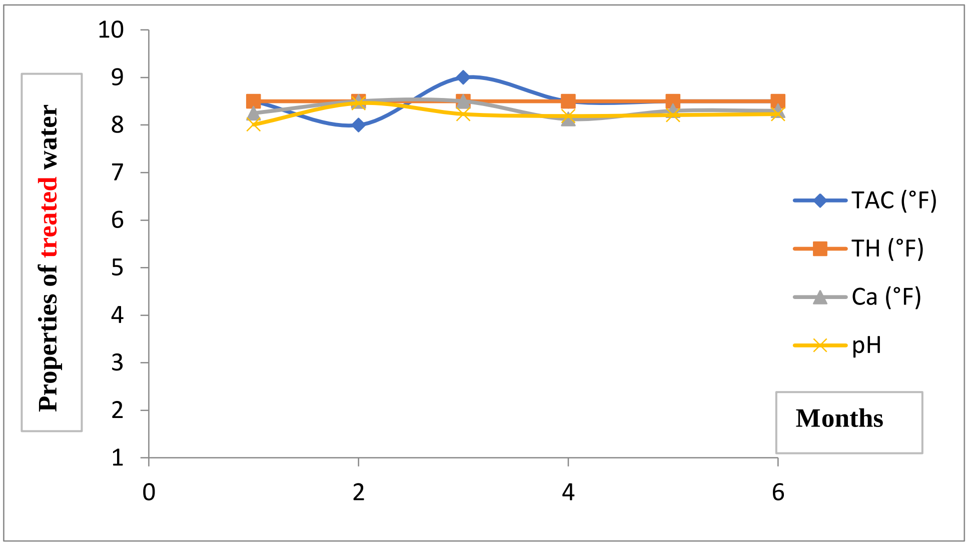

Figure 5. Variation of water characteristics of Daoura station with acidification

The process allows adjusting the physicochemical parameters of the permeate water shown in Figure 5.

Remineralization through a bed of calcite is efficient and straightforward [25]. It requires a minimal quantity in CO_2, almost half of that demanded by the method using the lime. It does not require significant efforts or precautions in its exploitation. Besides, this method allows taking all the necessary measures to assure the security and protect the health of the operators [25]. In addition, the remineralization by the bed calcite is the easiest and the least expensive compared with other techniques [20].

According to the remineralization reaction's stoichiometry:

- $NaHCO_3$ and $CaCl_2$ requires 135 g/m^3 of $NaHCO_3$ and 88,8 g/m^3 of $CaCl_2$.

- Lime in the presence of CO_2 requires 64 g/m^3 of $Ca(OH)_2$ and 120 g/m^3 of H_2SO_4.

- Calcite bed requires 80 g/m^3 of $CaCO_3$ and 60 g/m^3 of H_2SO_4.

Table 2: the cost in (€/m^3) for each method. Among these three adopted processes, it is clear that the remineralization by the $NaHCO_3$ and $CaCl_2$ is the most expensive, while the remineralization by the bed calcite is the least expensive

Table 2. Costs in (€ /m^3) of remineralization for every process adopted.

Chemicals	Remineralization by lime	Remineralization by Chemical reactives	Remineralization by calcite bed
$NaHCO_3$	--------	0,0122	--------
$CaCl_2$	--------	0,0691	--------
$Ca(OH)_2$	0,0132	--------	--------
H_2SO_4	0,0145	--------	0,0079
$CaCO_3$	--------	--------	0,005
Total (€/m^3)	0,0278	0,0814	0,0129

4. Evaluation of remineralization water on the calcite bed at a laboratory scale

Due to the results presented before, remineralisation by limestone bed appears the best method of remineralisation in comparison with others, that is why in this research we propose an experimental study at the laboratory scale on calcite bed. During this experiment, we examined the effect of water flow, contact time, velocity and bed height, on the treated water parameters. This study was carried out on calcite bed pilot with height L = 15 cm and radius R = 4 cm. The temperature of the water produced from the RO plant is T = 22,1°C, and its pH is 5,1 (Fig. 6).

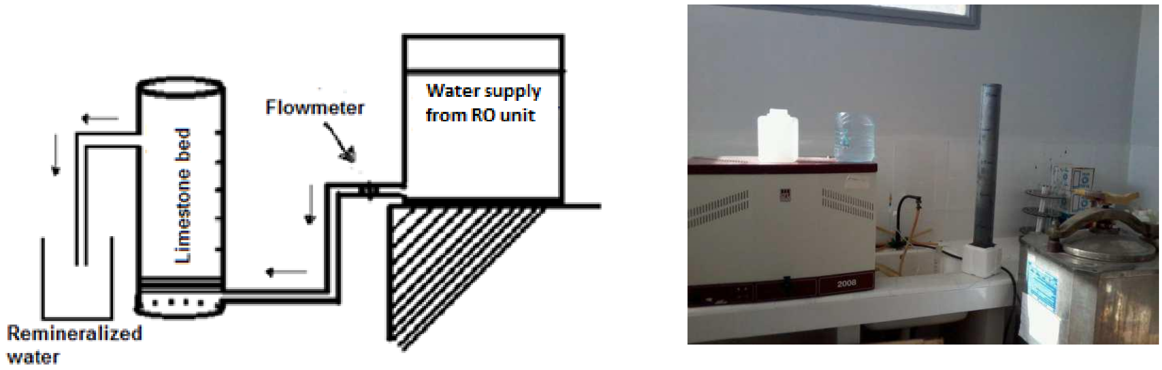

Figure 6. Scheme of the limestone pilot

4.1. Effect of desalinated water flow rate on water parameters

The water flow rate across the limestone bed is an essential parameter influencing the treated water. That is why we have measured the physicochemical parameters of this water according to the water flow. The results are shown in Figs. 7–10. We define mc as a mass of calcite present in the bed.

From Figs.6–9, it is clear that pH, Ca content, and TAC (Complet Alkalimetric Titration) vary according to the flow rate of desalinated water crossing the calcite bed. While the water flow rate is increasing, the pH Ca content and TAC decrease. This is mostly due to the limestone dissolution ($CaCO_3$) in water, which causes a decrease of pH [21].

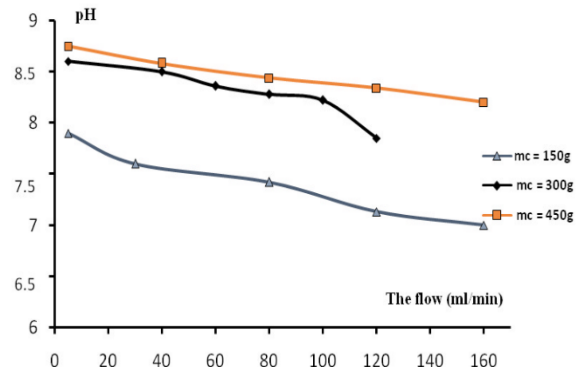

Figure 7. Variation of pH

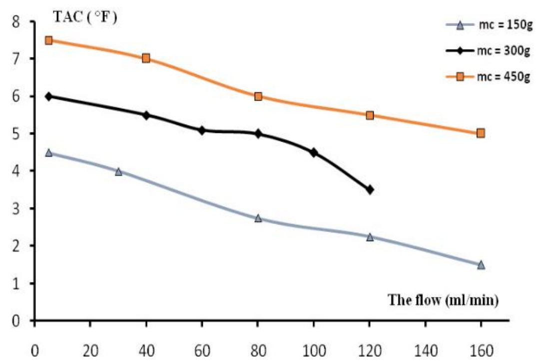

Figure 8. Variation of alkalinity TAC

However, the $CaCO_3$ quantity contained in the bed affects pH, Ca content and TAC value. In general, for the same flow. It is therefore advisable to work on calcite bed with a low flow rate in order to avoid pH adjusting of the produced water by the use of sodium hydroxide NaOH after calcite remineralization. The Langelier Index (IL or LSI) makes it possible to determine whether or not the deposit of calcium carbonate will result from the following equation [26]:

$$LSI = pH - pHs$$

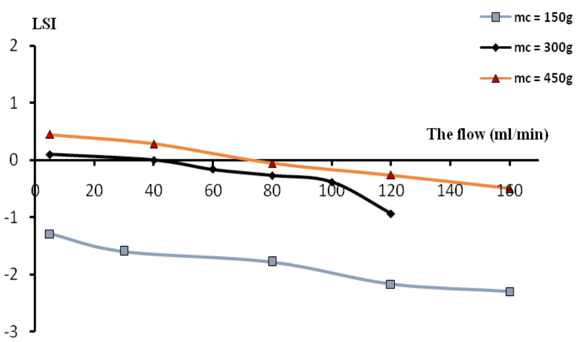

Figure 9. Variation of Langelier saturation indice

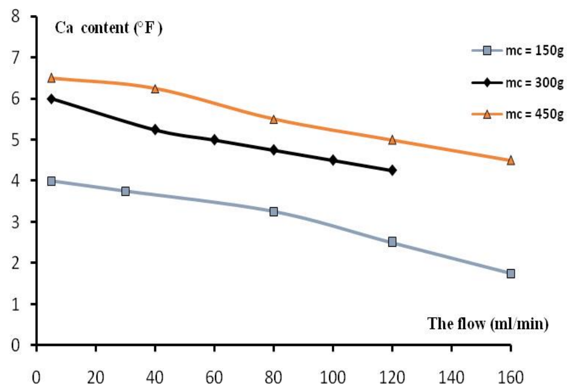

Figure 10. Variation of Ca content

According to Fig. 9, the Langelier index decreases with water flow increasing. The stability of the produced water is closely related to the flow of the rising water. The water balance is obtained for the low flow rates, less than 60 mL/min.

4.2. Effect of desalinated water residence time (E.B.C.T) on the treated water quality

(Empty Bed Contact Time) or E.B.C.T is the residence time, it measures contact time between support (limestone) and water passing the bed. It is expressed in minutes and calculated using the following relation:

$$\mathrm{E.B.C.T} = \frac{\mathrm{Vc}}{\mathrm{Q}}$$

Q is the flow rate of the water to be remineralized passing through the bed; *V*c is the volume of the calcite in the contactor (m^3).

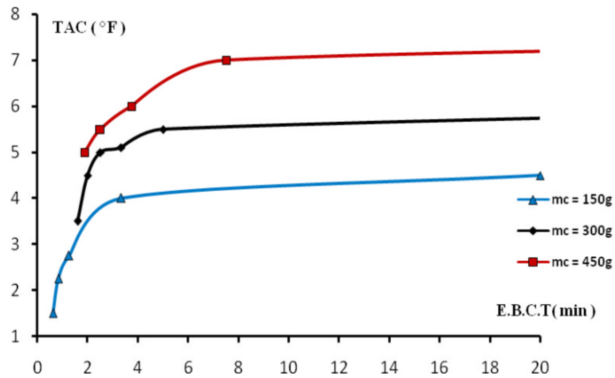

Figure 11. Variation of TAC according to E.B.C.T.

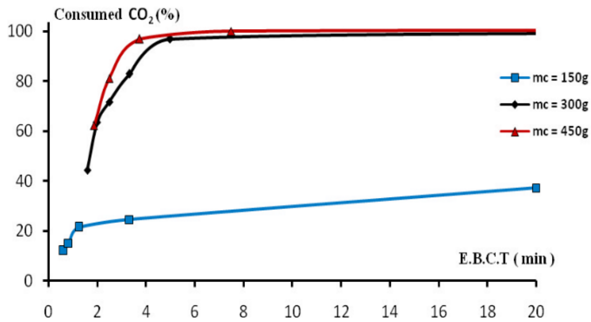

Figure 12. Variation of CO_2 according to E.B.C.T

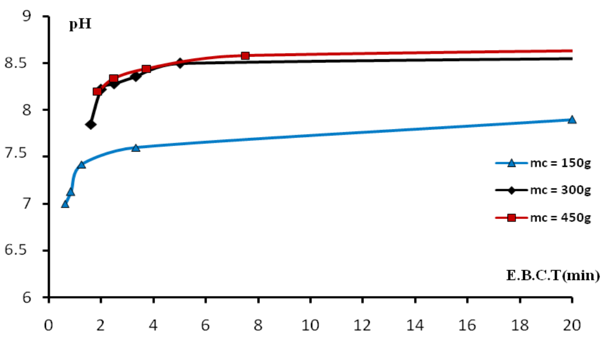

Figure 13. Variation of pH according to E.B.C. T

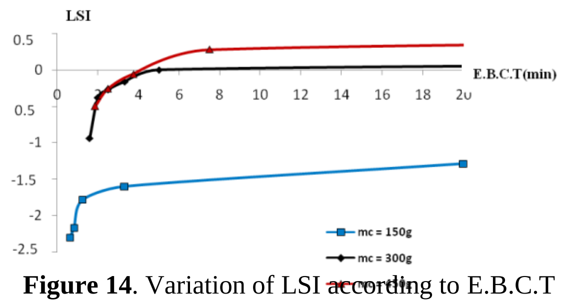

Figure 14. Variation of LSI according to E.B.C.T

It is essential to provide a sufficient contact time with calcite bed to achieve saturation of calcium carbonate. However, saturation depends on several parameters, including temperature, the particle size of calcite, purity of calcite and alkalinity of feed water. Figs.11–14 show the evolution of CO_2 consumption, TAC and pH according to EBCT.

The pH and TAC of the water reach its equilibrium from a value of E.B.C.T equal to 7 min. Also, for large calcite masses, the change in pH as a function of E.B.C.T is identical. According to the results found by Tillmans and Anderlohr [24,27], the reaction rate is also influenced by grain diameter and water temperature. The CO_2 consumption increases according to EBCT. For the tests carried out with $CaCO_3$ quantity equal mc= 300 g and m = 450 g; the dissolution reaction of $CaCO_3$ends at 7 min of E.B.C.T. Consumption of 100% of dissolved CO_2 is achieved (Fig. 12) which is in agreement with the previous experiments (Figs. 11, 12).

According to the results found above in other works, we confirmed that remineralization by calcite bed ensures the correction of the desalinated water aggressiveness, and returns to the water its equilibrium. The apparent limitation of this technique is the necessity of adapting the bed sizing to the water flow (height, grains size, etc.), because of its impact on the produced water parameters [17,22,23].

5. Conclusion

The ONEE has adopted the technique of reverse osmosis to desalinate the seawater in Laâyoune and Agti Elghazi, as well as to demineralize brackish waters in Daoura. The produced water after the reverse osmosis (osmosis water) is unstable and unbalanced because it is characterized by low salinity and high aggressiveness and corrosivity.

A post-treatment in desalination plant is necessary to return to the water its calcio-carbonic balance and to protect the distribution network from degradation by corrosion. This treatment is realized by various methods.

Remineralization through calcite bed gives softer water, while remineralization by methods using chemicals engenders a significant increase of the conductivity of the produced water. The remineralization through calcite bed is efficient and straightforward.

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