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Evaluation of remineralization performance of osmosis water on the calcite bed at a laboratory scale

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ABSTRACT

Sea and brackish water desalination is an alternative solution in arid zones. In the southern part of Morocco, the National Office of Electricity and Drinkable Water (ONEE) has installed many desalination plants which, however, produced water after desalination (osmozed water) with an unbalanced and aggressive character. Therefore, a post-treatment of remineralization is necessary to return the calco-carbonic balance of this water and to protect the distribution network from corrosion degradation. Following the obtained results in Daoura station, we further investigate the effect of many parameters on water quality at the laboratory scale by using the calcite bed pilot. Among others, we examine the effect of water debit, the residence time (Empty Bed Contact Time), the upward speed and bed length on the quality of the treated water. The knowledge and control of these parameters at the laboratory scale are indeed essential for the conception of optimal remineralization process. The results found here further support that the quality of the produced water depend on many parameters such as $CaCO_3$ type, time of residence E.B.C.T, height of bed, speed of water crossing bed, etc. Our results, as well as other economic considerations provide a way to optimize the necessary conditions for the remineralization operation using calcite bed in order to minimize its costs of sizing and extrapolation in the industrial field.

Keywords: Remineralization; Reverse osmosis; Calcite bed; Calco-carbonic equilibrium

1. Introduction

Water is a fundamental element of ecosystems and vital for people and their activities. Although it is abundant on our planet and represents a volume of 1.4 billion km, the saline water of seas and oceans represents more than 97% of the total water volume, while freshwater represents a little less than 3% of this volume [1]. Under the pressure of the considerable needs of modern civilization, we have passed from the use of source water and groundwater to the use of seawater and brackish water. By analogy, Morocco by its geographical location (arid and semi-arid zone) and its climatic conditions, does not escape the rule, its conventional water resources (surface and groundwater) are very limited. Therefore, to deal with this declared shortage of water,the national office of electricity (ONEE) and water has constructed many desalination plants in the southern cities of Morocco [2]. During the last two decades, ONEE

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has opted for desalination by reverse osmosis technique. The selection of this technique has essentially been dictated by the energy ratio required to produce one cubic meter of water per desalination which is much lower for reverse osmosis as compared to the other distillation techniques [3]. Reverse osmosis consists in obtaining fresh water using semi-permeable membranes, in which the pure water passes through the membranes by applying a high pressure to the salt water. The water produced after desalination (osmozed water) is unbalanced as it is characterized by low salinity, high aggressiveness and corrosivity. As a result, it can attack pipes and structures that can release undesirable substances that are detrimental to water quality [4,5]. Hence, the need for a remineralization post-treatment, to render osmozed water its calco-carbonic balance, and thus preserve the adduction and distribution network of drinkable water from corrosion degradation [6,7].

ONEE adopted three plants of reminalization techniques in the mentioned areas: (1) remineralization by hydrated lime with presence of CO_2 in Laâyoune desalination plant (SDL), remineralization by injection of calcium chloride $CaCl_2$ and Sodium bicarbonate $NaHCO_3$ in Sidi Elghazi plant (SDS), and remineralization by a passage of water through limestone bed in Daourade mineralization plant (SDD). The first plan (SDL) needs a high quantity of CO_2 to dissolve all of the hydrated lime $Ca(OH)_2$ but also the produced water has an aggressive character [8] and causes the clogging of the pipes by lime deposition during materials injection [9,10]. Thus, the addition of acid (to remove the clogging) results in an expensive exploitation of stainless pumps and other materials. Moreover, a poor control of hydrated lime addition with fresh water leads to undesirable pH changes due to the lime buffer properties absence [10,11].

After the remineralization, the final product water has to correspond to the following characteristics to be considered balanced [12]:

- TAC = 8°F
- Ca content = 8 °F
- 6.5 < pH = 8.5.

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

SDS is characterized by a simple addition and dissolution of products. This method has a low investment cost for the space required for its operation and certain chemicals used for this method particularly $NaHCO_3$, have a low solubility which requires large reservoirs for its dissolution. In major remineralization stations, this method requires supply of high quantity of reagents and availability of suitable spaces without moisture for their storage (case of $CaCl_2$) [13]. On the other hand, the calcium chloride has an advantage of being easier to implement due to its high solubility. It leads to chloride ions liberation in the water which, if they add (chloride ions) to content already noticeable, may counteract the effects of the remineralization treatment by their influence on the phenomena of corrosion [14].

SDD appears to be effective because it demands a minimum quantity of CO_2, almost a half that actually provided for SDL [10,11,14]. Therefore, the design of such cited project does not require the deployment of major efforts or precautions in its operation. We observed that remineralization by calcite bed (SDD) gives softer water compared to the others, while remineralization by chemical reagents (SDS) method leads to a significant increase in water conductivity due to ions dissolution in the water. The economic evaluation of chemicals cost used for the post-treatment shows that remineralization by calcite bed (SDD) is the least expensive [12]. In addition, the osmozed water remineralization by calcite bed gives promised results regarding water aggressiveness [14,15]. Knowledge and mastery of the optimal process of this technique are essential in order to confirm this proposition.

In this research we propose an experimental study at the laboratory scale. 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 osmozed water is T = 22.1°C and its pH is 5.1 (Fig. 1).

2. Experimental part

2.1. Calcium titration

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

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 (alkali metric tier) measures the content of free hydroxides (OH^-) and carbonates (CO_3^{2-})

The total alkalinity titer (TAC) measures the sum of free hydroxides, bicarbonates and carbonates.

We place in Erlenmeyer 100 ml of water to be analyzed, then we add 2–3 drops of phenolphtalaene solution.

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.

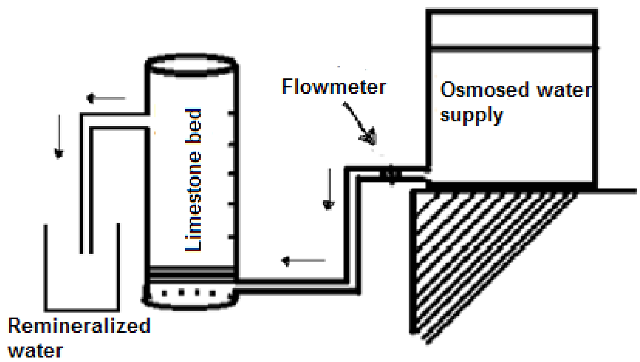

Fig. 1. Scheme of the limestone bed pilot.

If the solution becomes yellow, the TAC is determined in the same way as the TA. The turning zone is yellow-orange. The TAC is expressed in meq/L.

2.3. CO_2 titration

Aggressive CO_2 expresses the part of CO_2 that can dissolve $CaCO_3$, its content is calculated by the following relation:

$$CO_2\left(\frac{mg}{L}\right) = \left(TAC_s - TAC\right) \times 22 \quad (1)$$

TACs (total alkalimetric titre measured after the marble test) and TAC are expressed in meq/L.

3. Effect of osmozed water flowrate on water parameters

The water flow across limestone bed is an essential parameter influencing the treated water. Thus, the quality and the equilibrium of this water can be changed, that is why we have measured the physicochemical parameters of this water according to the water flow. The results are shown in Figs. 2–6. We define mc as mass of calcite stoked in the bed.

From Figs. 2–4, it is clear that pH, Ca content, and TAC (Complet alkalimetric Title) vary according to the flow rate of osmosis water crossing the calcite bed. The pH, Ca content and TAC decrease with water flow rate increasing. This is mainly due to the limestone dissolution ($CaCO_3$) in the water, which leads to a decrease of pH [3]. On the other hand, the quantity of $CaCO_3$ contained in the bed influences pH, Ca content and TAC value. In general, for the same flow rate, it is found that pH and TAC of the treated water are proportional to the $CaCO_3$ quantity (Figs. 2–4).It is therefore advisable to work on calcite bed with 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) makes it possible to determine whether or not the deposit of calcium carbonate will result from the following equation:

$$IL = pH - pH_s \quad (2)$$

pHs : pH of water measured after marble test.

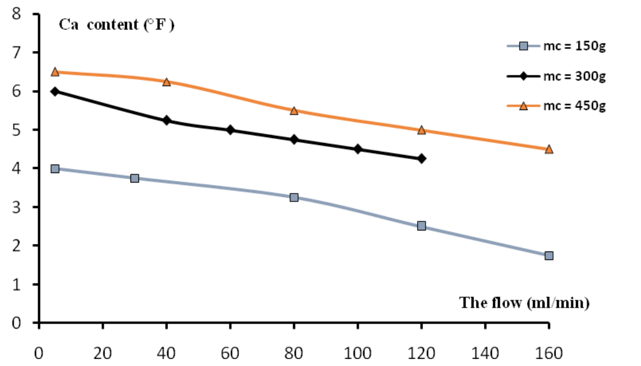

Fig. 4. Variation of Ca content according to the flow.

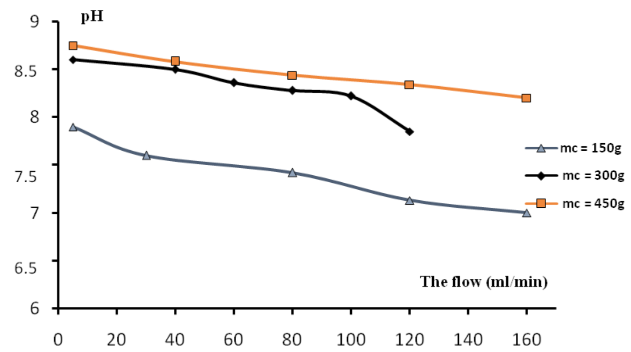

Fig. 2. Variation of pH according to the flow.

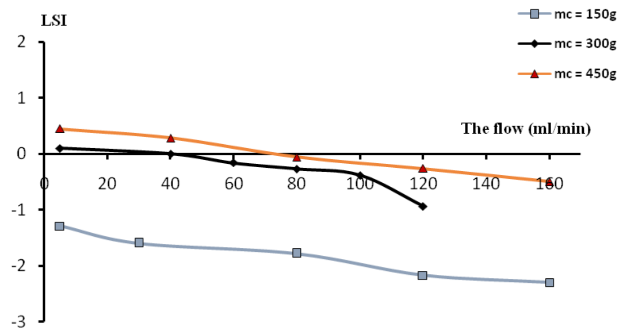

Fig. 5. Variation of Langelier saturation indice according to the flow.

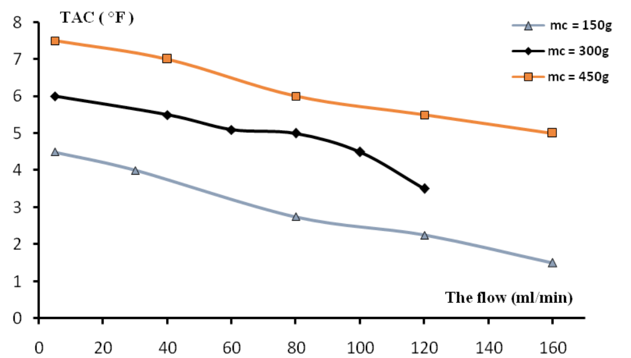

Fig. 3. Variation of alkalinity TAC according to the flow.

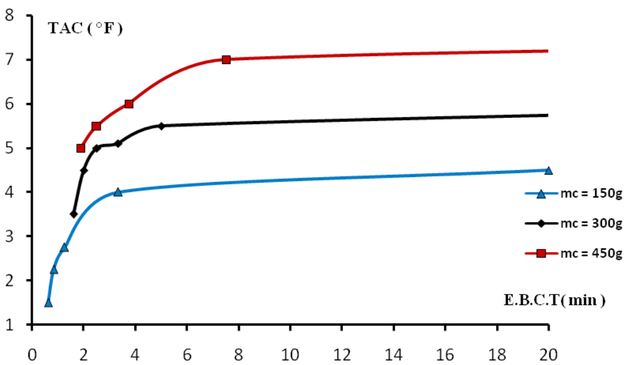

Fig. 6. Variation of CO_2 consumed according to the flow.

According to Fig. 5, 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.

In Fig. 6, the finding show that CO_2 consumption hinges on the amount of calcite mass and water flow rate. Neutralisation of aggressive water is total for the low flow rates, less than 60 mL/min. While this consumption begins to decrease markedly from a flow rate of 80 ml/min, thus justifying an excess of aggressive CO_2 in water, it will require neutralization.

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

The residence time E.B.C.T (Empty Bed Contact Time) is the measured contact time between support (limestone) and waterpassing the bed. It is expressed in minutes, and calculated using the following relation:

$$E.B.C.T = \frac{V_c}{Q} \tag{3}$$

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).

It is important to provide a sufficient contact time with calcite bed to achieve saturation of calcium carbonate. However, saturation depends on several parameters, including temperature, particle size of calcite, purity of calcite and alkalinity of feedwater. Figs. 7–9 show the evolution of pH, TAC and CO_2 consumption according to EBCT. The pH and TAC of the water reaches its equilibrium from a value of E.B.C.T equal to 7 min. In addition, 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, [16,17], 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. A consumption of 100% of dissolved CO_2 is achieved (Fig. 9) which is in agreement with the previous experiments (Figs. 7, 8).

According to Fig. 10, Langelier saturation index LSI increases also depending on residence time EBCT. For masses mc = 350 g and mc = 450 g, the produced water arrives its calco-carbonic equilibrium for a residence time greater than or equal to 7 min.

5. Effect of the calcite bed height on the water quality

A water re-mineralization system may generally comprise a calcite bed. The bed height makes it possible to ensure the contact time required for the calcite dissolution.

Figs. 11 and 12 show the pH and TAC evolution of remineralized water according to the bed height for different flow velocities. It is observed that pH and TAC increase slightly according to the bed height. Similarly, we observed that the velocity is inversely proportional to the pH and TAC of water.

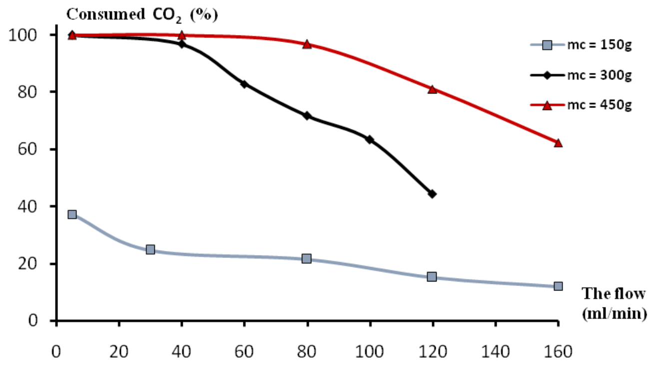

Fig. 7. Variation of TAC according to E.B.C.T.

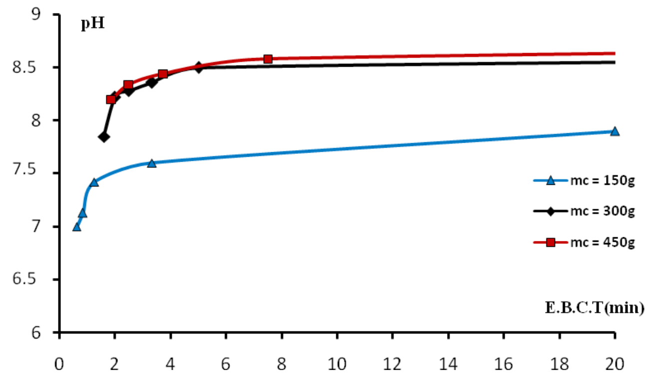

Fig. 8. Variation of pH according to E.B.C.T.

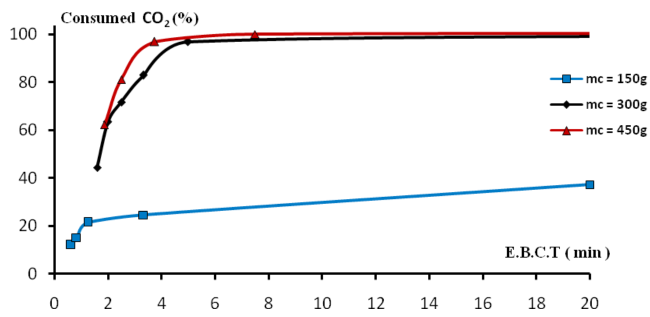

Fig. 9. Variation of CO_2 consumption according to E.B.C.T.

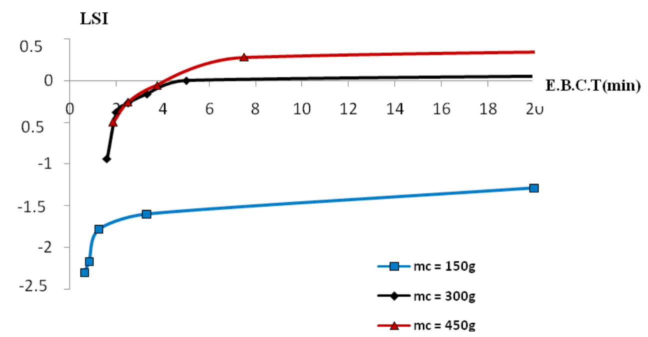

Fig. 10. Variation of LSI according to E.B.C.T.

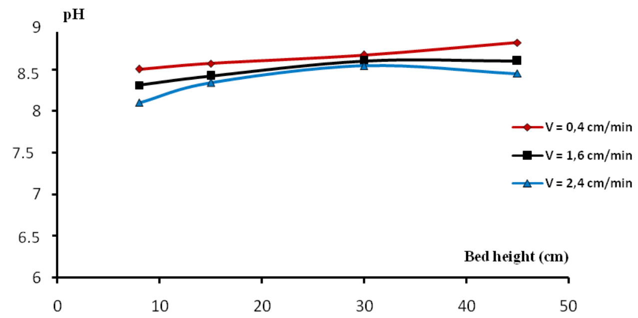

Fig. 11. Variation of pH according to the bed height.

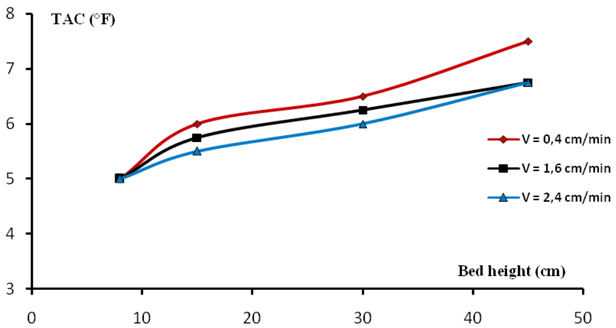

Fig. 12. Variation of TAC according to the bed height.

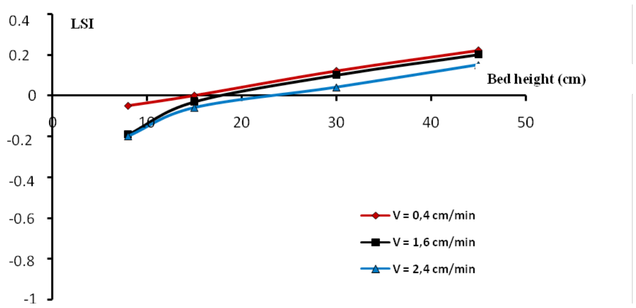

Fig. 13. Variation of LSI according to the bed height.

In connection with these results, S. Anushka [18] presented during her work the following relation:

$$H = E.B.C.T.V \quad (4)$$

H = bed height (m); v =water speed (m/min); E.B.C.T = contact time (min).

Fig. 13 graphically illustrates the data collected in this study. The water stability increases with bed height increasing, justifying the results found previously. Moreover, the same observations are found by Gao [19].

6. Conclusion

The treated water quality depends on several factors related to $CaCO_3$, residence time E.B.C.T (Empty Bed Contact Time), bed height and physico-chemical parameters of the osmozed water. A post-treatment of remineralization makes it possible for the water to gain back its calco-carbonic balance and thus to preserve the distribution network of degradation [20].

The pH and TAC of the treated water decrease with water flow increasing. It is therefore advisable to work with low flow rate in order to avoid pH adjusting of the produced water by the use of sodium hydroxide NaOH.

The $CaCO_3$ quantity initially introduced into the bed influences the water stability. In general, for the same flow rate, it is found that the pH of the treated water is proportional to the $CaCO_3$quantity.

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

The contact times are advantageously 7 min. Contact times less than 7 min generally give unsatisfactory results, whereas contact times greater than 7 min do not bring any significant improvement for the pH, Ca TAC and LSI parameters.

According to the results found above and in works, we confirmed that remineralization by filtration using calcite bed assures the correction of the osmozed water aggressiveness, and makes water render its equilibrium. The only drawback of this technique is that the impact of the bed sizing on the produced water parameters (bed height, grains size, etc.) [21,22,23]. Indeed, several studies have been recently conducted on the exploitation of calcite $CaCO_3$ powder (micronized) in suspension and in the presence of CO_2 as an alternative technique of the filtration on limestone $CaCO_3$ [24].

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