Investigating Pretreatment of Seawater using Precipitation agents to reduce Scale formation in distillers

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Abstract

The aim of this study is to treat the scale formation in multi stage flash distillers. The scale results from the precipitation of insoluble species notably calcium sulfate as well as calcium carbonate and hydroxide magnesium. The proposed solution involves a pretreatment of seawater before it is introduced into distillers. The pretreatment is based on the removal of the calcium and magnesium cations from seawater, using precipitating agents as: soda ash, potassium hydroxide, and mixture of soda ash with potassium hydroxide at different temperature of 25, 35, 50, and 100 °C. Pretreatment achieved by a mixture of potassium hydroxide and soda ash of seawater gave the best results. In addition, the results showed that by mixing soda ash (10g/L) and potassium hydroxide (3g/L) at temperature of 100 °C favor the precipitation of calcium and magnesium ions. The calcium and magnesium concentrations in seawater were completely reduced.

Keywords: desalination, scale, temperature, soda ash, potassium hydroxide.

1 Introduction

Desalination is a technique for producing pure water from salt water, there are two major processes commercially; thermal processes and membrane processes (El-Dessouky & Ettouney, 2002),(Khawaji & Kutubkhanah & Wie, 2008). Thermal processes are the most widely used methods in the world of desalination. Desalination provides water for domestic usages, and process industrials. Furthermore, the advantage of thermal desalination processes yields distillate water of a salts low concentration, in the range of few ppm, and low pH (AlDeffeeri, 2008), (Mizuno & Kansha & Kishimoto & Tsutsumi, 2013). The most common technique for thermal desalination is multi stage flash (MSF), found in many countries around the world. MSF process produces more than 60% of total world production capacity (El-Dessouky & Ettouney & Al-Roumi, 1999), (Al-Hengari & El-Bousiffi & El-Mudir, 2005). In Algeria country, kahrama desalination plant uses a MSF process, consists of three desalination units, each unit produces distillate water at a rate of 29.629m3/day. The MSF unit consists of evaporator, brine heater.

In MSF process, the production of pure water from seawater accompanied by the precipitation of organic and mineral salts present in seawater as process temperature is increased. Deposition of mineral salts is called scaling. Two types of scales can form in seawater evaporators, the alkaline scales calcium carbonate and hydroxide magnesium, and non alkaline scales such as calcium sulfate (Al-Sofi, 1999). The formation of scale on hot surfaces such as evaporators reduces heat transfer surface rates, decline flow rates and this lead to reduction of distillate water production.

Alkaline scales result from the interaction between the decomposition and hydrolysis products of bicarbonates ions of seawater with calcium and magnesium to produce calcium carbonate and hydroxide magnesium (Shams El Din & El-Dahshan & Mohammed, 2005). Deposition of calcium carbonate and hydroxide magnesium depends on temperature, pH, and the concentration of bicarbonate, carbonate, calcium, and magnesium ions (Al-Rawajfeh & Glade & Ulrich, 2005).

On the other hand, in MSF evaporators, the formation of non alkaline scales mainly calcium sulfate result from direct crystallization of anhydrite, hemihydrate, or gypsum from seawater. The higher amount of calcium sulfate is in form of hemihydrate (Sheikholeslami & Ong, 2003).

Langelier et al. spoke, if the temperature augment, the bicarbonate ions decomposes and yields carbonate ions, which precipitate in form of calcium carbonate. At still increased temperature, the carbonate ions hydrolyze to lead to the precipitation of hydroxide magnesium (Al-Sofi, 1999).

Many researchers have devoted to combat mineral salt precipitation on hot surfaces in the MSF system, scale prevention methods used: the addition of acid to prevent bicarbonate decomposition, and the addition of anti scale agents as a scale inhibitors (Ghani & AlDeffeeri, 2010), (Al-Hamzah & Fellows, 2015), (Gill, 1999). To remove scale, it is necessary to pretreat seawater, a decalcification pretreatment using a strong cationic resin, which removal the calcium ions in seawater before thermal desalination, will retard the scale formation (Hoffman & Martinola, 1988). Important strategy, seawater decalcification pretreatment using carbon dioxide as precipitator by alkalization to remove the calcium ions; Yingying et al. investigate mechanism of the pretreatment process by carbon dioxide injection with sodium hydroxide as alkali source; so, found that the calcium and magnesium rapidly removal with sufficient amount of alkali source (Zhao & Yuan, 2013), (Zhao & Cao, 2016).

Recently (Abdessemed & Nezzal, 2008), The softening pretreatment of seawater using lime, the resin and ultrafiltration, and coupling of the two technique softening ultrafiltration for removal scale formation in seawater desalination, it was concluded that the coupling treatment by ions exchange amberlite IR120 to ultrafiltration give de best result with considerable reduction of raw water total hardness, and 98% of decreased turbidity. In previous work (Ayoub & Zayyat & Al-Hindi, 2014), the use of a precipitation softening process as a pretreatment of seawater before desalination, the importance of the process is to eliminate the calcium and magnesium ions, under variable conditions of pH and temperature. And show that precipitation softening at a pH 11 leads to complete elimination of calcium and high removal of magnesium.

To remove calcium and magnesium from seawater, the present work aims to investigate a pretreatment of seawater before evaporator desalination using precipitator reagents such as soda ash (Na_2CO_3), potassium hydroxide (KOH) and mixture of soda ash with potassium hydroxide at different temperature.

2 Materials and Methods

2.1 Characteristics of Seawater

Table 1 gives the principal composition of the KAHRAMA plant seawater; we notice that the total hardness is strongly high 4600mg/L. For this purpose, it is required to find technique seawater pretreatment, before introduce to MSF evaporators. Consequently, removal of the seawater hardness demand the using precipitator reagents like as: soda ash, potassium hydroxide, and coupling soda ash- potassium hydroxide.

2.2 SEAWATER pretreatment: precipitation of Ca and Mg

The pretreatment process was studied by measured following parameters that: pH, total hardness TH (mg/L); calcium hardness Ca^{2+} (mg/L); and magnesium hardness Mg^{2+} (mg/L), HCO_3^-, CO_3^{2-}, and OH^- ion concentrations. The pH values of the filtered solutions were determined using an electrode in conjunction with a Starter type 210 pH meter. Calcium and magnesium ions were measured by an EDTA complexometric titration method; all analyses were run at a temperature of 25 °C.

first, in order to determine an optimal amount of soda ash a different amount ranging from 0.1 to 1.3 were poured into 100ml of seawater, then mixed for 5min at a speed of 250 rpm, at different temperature of 25, 35, 50, 100 °C.

Secondly, a different amount of potassium hydroxide were poured into 100 mL of seawater, and then mixed for 5min at 25 °C.

Finally, for study an optimal precipitation pretreatment, we poured a mixture of soda ash and potassium hydroxide into 100 mL of seawater, and then stirred for 5 min at a speed of 250 rpm, at temperature of 25, and 100 °C. All filtered solutions were analyzed at temperature of 25 °C.

Table 1 composition of the KAHRAMA plant seawater

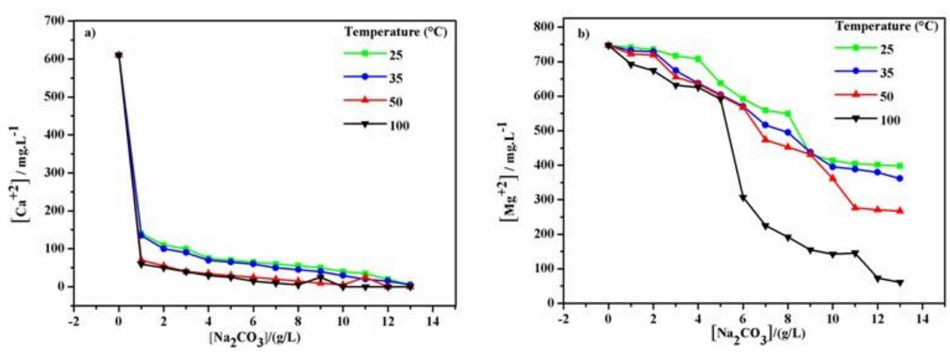
Parameters	Value
Total hardness, mg/L	4600
Ca^{2+}, mg/L	610
Mg^{2+}, mg/L	747,225
Cl^-, mg/L	20412,5
TA, mg/L	25
TAC, mg/L	85
TDS, at 180°C, mg/L	38942
Na^+, mg/L pH	13013
Temperature, °C	7,89
	25

3 Results and Discussion

3.1 Influence of Added Amount of Soda ash

In order to determine an optimal amount of soda ash (Na_2CO_3), Figure (1(a, b)) shows the variation in calcium and magnesium content as a function of the soda ash concentration at a contact times of 5minutes and at a different temperatures 25, 35, 50, 100 °C. The concentration of calcium and magnesium ions in filtered solution decreased after adding various amount of Na_2CO_3, as the concentration of Na_2CO_3 increased, the concentration of Ca^{2+} and Mg^{2+} in filtered solution declined. For instance, the concentration of Ca^{2+} and Mg^{2+} at temperature of 25°C were declined to near 5 mg/L and 379, 91 mg/L, respectively, after added 13 g/L of sodium carbonate. This result means that the soda ash is a promoter of calcium precipitation. Ricardo I. Jeldres et al. (2017) found that the sodium carbonate is useful to precipitate calcium, the calcium concentration falls to 0 mg/L after adding 0.05 M of Na_2CO_3 with mixing for 30 min at room temperature.

Fig. 1 Removal of calcium and magnesium by addition Na_2CO_3 in 25, 35, 50, 100°C: (a) calcium and (b) magnesium



At temperature of 100 °C, the concentration of calcium and magnesium ions declined to 2,5 mg/L and 142.76 mg/L, respectively, for an optimal amount of soda ash of 10 g/L. after this optimal concentration of soda ash in seawater, the concentration of calcium and magnesium remained constant in the filtered solution. Thus, the optimal soda ash concentration is 10 g/L at temperature of 100 °C. It can be concluded that temperature also favors the precipitation of calcium and magnesium ions, so to avoid falling to the scale problem during thermal desalination, calcium and magnesium ions must be removed at maximum.

Soda ash dissolves in seawater and produces two sodium ions $[Na^+]$, and one carbonate ion $[CO_3^{-2}]$ for each unit of soda ash (Equation 1). The carbonate of soda ash reacts with the calcium and magnesium ions existing in seawater to give the insoluble minerals of calcium carbonate $[CaCO_3]$, and magnesium carbonate $[MgCO_3]$, respectively (Equations 2 & 3).

$$Na_2CO_3 \longrightarrow 2\,Na^+ + CO_3^{2-} \qquad (1)$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3 \downarrow \qquad (2)$$

$$Mg^{2+} + CO_3^{2-} \longrightarrow MgCO_3 \downarrow \qquad (3)$$

$$HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O \qquad (4)$$

$$CO_3^{2-} + H_2O \longrightarrow OH^- + CO_2 \qquad (5)$$

The rise of temperature from 25 to 100 °C promotes the precipitation of calcium and magnesium. So, at moderate temperature the bicarbonates decompose to carbonates by the following reaction (equation 4). This will allow to the precipitation of calcium carbonate (AlSofi, 1999). As the temperature still more increase, the carbonate ions hydrolyze by the following cited reaction (equation 5). Therefore, production of the hydroxyl groups causing the precipitation of hydroxide magnesium ($Mg(OH)_2$).

Thus, the soda ash and higher temperature, removed more calcium and magnesium ions from seawater. At temperature of 25 °C and amount of 13g /L soda ash, remove 5mg/L and 397.91 mg/L of calcium and magnesium, respectively. The temperature of 100 °C and amount of 10 g/L soda ash gives the best result, precipitate the amount of 142.8 mg/L of magnesium and eliminate totally the calcium.

3.2 INFLUENCE of potassium hydroxide added on filtered seawater solution of soda ash at 25 and 100°C

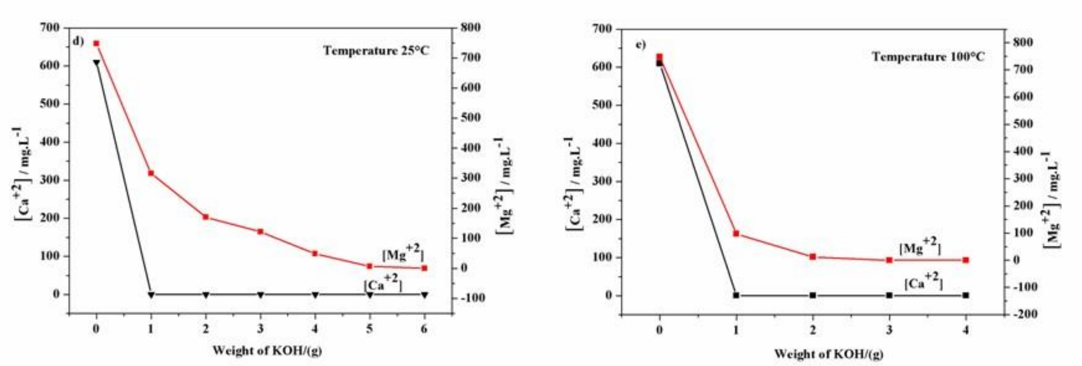
Soda ash provides the CO_3^{2-} ions to seawater solution, which react with calcium to precipitate in form of calcium carbonate, and sufficient amount of carbonate react with magnesium to form magnesium carbonate. At temperature of 25 °C display in Fig.2 (d) , the addition of KOH into filtered solution of soda ash, lead to increase in pH solution, this is increased the OH^- concentrations, which allow to decompose the bicarbonate ions in carbonate ions. pH solution at temperature of 25°C augment with KOH amount added into filtered solution of 10g/L soda ash, the concentration of calcium and magnesium ions decreased near to zero after added amount 1 and 6 g of KOH, respectively.

Soda ash and augment of pH solution, due to addition of KOH produce carbonate and hydroxide ions. Therefore, the two ions (CO_3^-, OH^-) react with calcium and magnesium to compose calcium carbonate and hydroxide magnesium.

At temperature of 100 °C showed in Fig.2 (e), there are two effects, the addition of soda ash-KOH and augment of temperature. The temperature continued the precipitation of magnesium, magnesium ions totally eliminate after added amount 3 g of KOH into filtered solution 10 g/L of soda ash. Thus, the amount 3 g of KOH added into 10 g/L gives the best results for completely remove the calcium and magnesium ions.

The seawater solution of soda ash-KOH heated at 100 °C; the temperature hydrolyzes the carbonate to form OH^- ions in solution. Therefore, hydroxide reacts with magnesium ions remained in filtered solution of soda ah -KOH and precipitate in form of magnesium hydroxide.

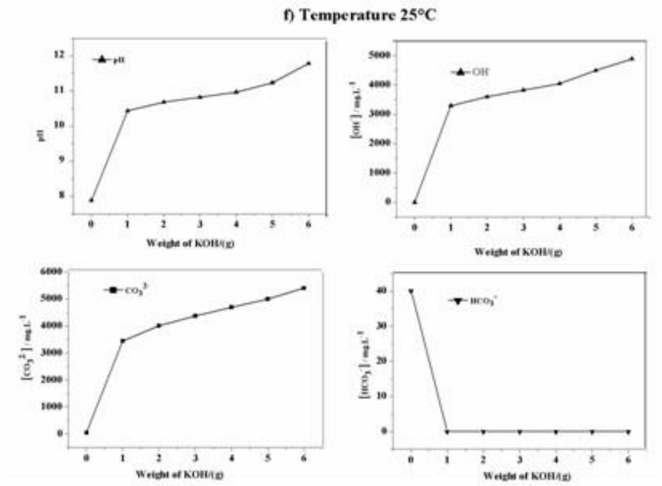
Fig. 2 The concentration of Ca^{2+}, Mg^{2+} in filtrated solution of 10 g/L soda ash after adding various amount of KOH at (d) 25 °C, (e) 100 °C.



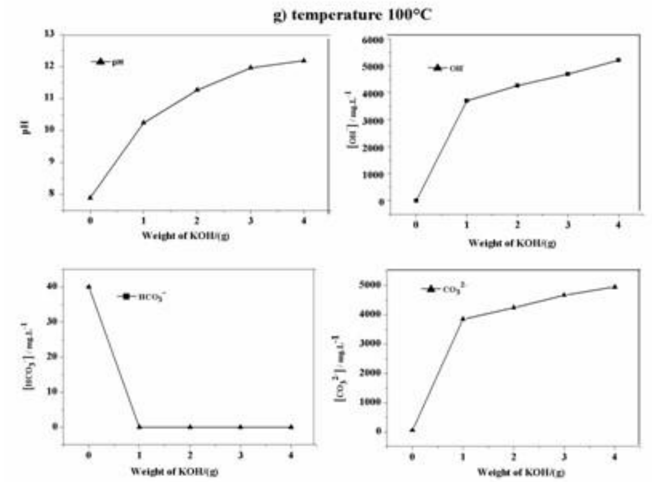
The pH and concentration of HCO_3^-, CO_3^{2-} , and OH^- in seawater solution and in filtered solution of 10 g/L of soda ash, after adding various amount of potassium hydroxide at temperature of 25, 100 °C and mixing for 5 min of 250 rpm were shown in Fig.3 (f, g).

Fig. 3 The pH and concentration of HCO_3^-, HCO_3^{2-} and OH^- in filtered solution after adding various amounts of potassium hydroxide (KOH) at a concentration of soda ash of 10 g/L at temperature f) 25°C

and g) 100 °



f) Temperature 25°C



g) temperature 100°C

At the both temperatures 25 and 100 °C, it can concluded that just added an amount 1 g of KOH in filtered solution of soda ash, the bicarbonate concentrations decline rapidly tends to zero. This concentration of bicarbonate rest constant with continuous added of KOH. But, the concentration of carbonate and hydroxide increased with increasing the amount of KOH added. The bicarbonate, carbonate and hydroxide concentrations in seawater are 40, 50 and 0 mg/L, respectively. The concentration of carbonate and hydroxide at temperature 25 °C reached to 5400, and 4900 mg/L, respectively, after added amount 6 g of KOH in filtered solution 10 g/L soda ash. But, at temperature of 100 °C, the concentrations of carbonate and hydroxide ions reached to value of 4670, 4680 mg/L, respectively, after added amount of 3 g KOH into filtered solution of 10 g/L soda ash.

The two curves of pH (Fig.3 (f, g)) showed that the pH value equal to 9.95 and 9.31 at temperature of 25 and 100 °C, respectively, before added any amount of KOH. These values of pH increase with the rise of temperature and added amount of KOH.

At temperature of 25 and 100 °C, The optimal pH value for the total elimination of calcium and magnesium ions is equal to 11.8; this pH value is obtained by addition of 6 and 3 g in filtered solution of 10 g/L soda ash, at temperature of 25 and 100 °C, respectively.

4 Conclusions

Precipitation pretreatment is a technique for removed the calcium and magnesium ions to combat scale formation in MSF evaporators, using precipitator agents such as soda ash, potassium hydroxide and coupling soda ash-potassium hydroxide. The precipitation technique using soda ash is useful for reducing calcium, more than magnesium. The using of soda ash reduces the content of the calcium and magnesium ions in seawater at 100 °C with the rates of 95.90 % and 80.89 %, respectively. At temperature of 25 °C, the use of KOH promotes the precipitation of magnesium, its rates has been reduced from 747.225 mg/L to 36.45 mg/L. The mixture of soda ash and potassium hydroxide at 100 °C reduced completely calcium and magnesium ions in seawater.

At temperature of 100 °C, Pretreatment by a mixture of soda ash (10 g/L) and potassium hydroxide (3 g/L) gave the best results. The calcium and magnesium ion concentrations in seawater were reduced completely.

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