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Brine Treatment by Solar Energy: Case Study in Tor-Sinai – Egypt

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THE absence of scalable, low energy requirement for brine treatment present a real threat and coming disaster for future generations targeting RO desalination. Brine with a certain concentration was evaporated with different solar concentrators and the effect of evaporation time on liquid concentration by variation in concentrator's volume. The effect of different concentrator's volume on the recovered condensate fresh water and weight of precipitated salts was showed. The thermal solar efficiency was found to exceed 90% for the different applied capacities. The concentrator volume was largely affecting the rate of evaporation in the closed and exposed ones. The excellent morphology and purity of precipitated salts with full characterization with the designed closed solar concentrator when compared with the exposed ones was shown. This morphology as spherical, agglomerated particle having a variety of particle size distribution, i.e., distinguished crystals for solar concentrator compared with continuous distribution for solar ponds. The ease of concentrator's design and the adverse effect of volume enlargement on operability for incident solar energy 300 W/m^2, makes the implementation of multilayer small capacity solar concentrator is an alternative.

Keywords: RO desalination brines, Solar energy, Salt recovery, Brine disposal.

Introduction

Membrane desalination and high recovery-thermal desalting are currently the most promising, well-established and cost effective desalination technologies, especially for brackish water. Together with the stringent governmental directions for Sinai development in Egypt nowadays, the search for cost effective development techniques in reverse osmosis-brackish desalination pre- and post-treatment steps which will decrease the cost of desalinated water for integrated sustainable development of such remote areas [1]. For better brine management and more fresh water production from RO concentrate, advance methods of temperature driven membranes are needed. The application of such systems will increase fixed and working capital of the system with the increase in efficiency in operation at larger scale [2].

Due to the lack of adequate methods for the disposal of waste brine produced during membrane desalination processes especially for brackish water units, the use of desalination systems is still limited. Recently, some processes and technologies have been proposed and studied to accomplish higher water recovery through brine treatment. These processes include the use of pressure-driven and electrical potential-driven membranes, thermal-based technologies and other technologies [3]. Zero liquid discharge (ZLD) or close-to-ZLD schemes are undergoing investigations in order to minimize reject brine volume and recover water as well. High purity distillate reaching 95–99% recovery can be obtained from the waste brine streams [4].

The most common methods to treat concentrates include: disposal to evaporation ponds [5] with the great losses in pure water, discharge in deep

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disused gold mines or run-off oil wells [6] or using digging deep discharge pipes to reach saline layer equivalent to concentrate salinity. However, all previous techniques present bad alternatives from environmental and economic point of view. Formerly, it was suggested that the treatment of waste brine by engineering out the source of brine and so reducing the dissolved solids in the brine by implementing chemical or engineering changes in the production process [7]. Or by converting brine into useful chemicals by means of recycling, or recovering chemicals or salts from the waste brine. There are several basic techniques that can remove dissolved solids from water; distillation (evaporation and cooling), membrane separation, electro-dialysis which requires high power consumption, ion exchange, eutectic freezing, and chemical processes (e.g. calcinations)[8].

From various routes to provide fresh water for remote arid villages or places, solar stills may be potentially applicable for brine treatment. Preferred design guidelines are recommended for various climate conditions and inlet brine salinity [9]. Some researchers [10–13] have reviewed the studies and developments of solar stills for brine treatments. Kabeel and El-Agouz [10], Velmurugan and Srithar [11] highlighted structure modifications and their effects on the productivity and the efficiency. Kaushal and Varun [12] divided solar stills based on the shape of each device and presented some energy transfer equations of distillation process. Sampath kumar et al. [13] provided a detailed and specialized review on active solar distillation. Tayeb [14] reported the experimental results of four basin solar stills with different glass covers installed in El-Minia–Egypt with 14.6MJ /m^2/ d, giving 1.3 kg/m^2/d yield of distilled water. Using a basin still with a semi-sphere covers with a solar radiation absorption area of 0.24 m^2 and a condensation area of 0.267 m^2, on sunny days, and the thermal efficiency was 21.8%. These results indicate that the inclined flat glass cover would be preferred.

In this work, a comparison of two solar based-prototype units for reverse osmosis desalination concentrate (brine) treatment for the unit located in Tor Sinai -South Sinai Governorate, Egypt will be presented. The aim of this work is system implementation and evaluation of these units utilizing solar energy and their performance evaluation to produce valuable salt produced from waste concentrate stream. The production of pure permeate water was only feasible from solar concentrator, which makes the comparison in this point can't be covered. This means that the main goal here is to judge the quality and quantity of produced salts from both units at constant solar intensity of an average winter day. Together with including the concept of "zero liquid discharge (ZLD)" with desalination concentrate which entails further concentration stages of the brine to complete dryness by various integrated processes and so water losses will reach its minimum.

Materials and Methods

Concentrate brine solution was subjected to full chemical analysis according to standard analytical methods [15] and shown in table 1. Concentrate solution full analysis was fulfilled by means of flame photometer (Jenway PFP7), UV double beam spectrophotometer Agilent cary 100 and Solar Meter Model 776, KBE 610 weiterstadt2.

TABLE 1. Physico chemical characteristics of Beer Abo-Kalam desalination concentrate

Parameters		Concentrate brine (Concentrate)
pH	---	7.8
TDS	mg/l (ppm)	11208
EC	dSm-1	14.01
Calcium	mg /l	61.5
Magnesium	mg/l	168
Sodium	mg/l	3606
Potassium	mg/l	10.53
HCO_3^-	mg/l	398.35
Cl^-	mg/l	4790
SO_4^{--}	mg/l	1824.8
Iron	mg/l	0.8
Manganese	mg/l	0.17

RO desalination brine analysis which was shown in table 1 indicates the absence of such interfering ions, which won't require further processing techniques for profitable salt production plant. The work proposed and reached findings in this article to solve such environmental problem from RO brines is shown in figure 1, and deals with RO concentrate by means of open solar pond or closed system evaporators. This will secure a way to get benefit from precipitated salts and recycled again fresh water.

It was obvious from table1 that various types of salts, including $CaSO_4$, NaCl, $Mg(OH)_2$, $CaCl_2$, $CaCO_3$ and Na_2SO_4, which can be produced from Tor-Sinai RO desalination concentrate.

An exposed solar pond with shown dimensions and capacity of 50 liters as shown in figure 2 was fabricated from stainless steel 316 as corrosion resistant for concentrated salt solution. A smaller capacity solar ponds 5, 20 and 30 liters; were also fabricated for smaller capacities experiments to be processed.

A small scale batch solar concentrator, 5 liters capacity with a scaled-up capacity till 50 liters were fabricated from glass lined by mirrors with the illustrated dimensions in figure 2 as optimized in previous work [16,17].The design stages was only based on preliminary experimental small scale units with different parameters which was then optimized and scaled up with the installed and applied solar concentrator.

The dimensions of the solar concentrator (figure 3 a) were designed to be 100cm *50 cm *50 cm from the back side with and only 18 cm from the front side with an about from 32.5-35inclination angle of the reflecting surface. The simple solar concentrator design was built upon so simple facts based on calculated fixed tilt angle selected for maximum solar absorbance in low solar energy intensity in winter days. The application of black nano-coatings (STC -10) for the outer glass surface to increase its surface absorptivity and decreases its emissivity as a solar collective surface. The internal condensate coils were painted with black nano-coatings (STC -10) and the inner walls was linned with mirrors for minimum heat dissipation as shown in (figure 3b). This design was examined to measure the efficiency of such solar concentrator based on produced salt quality, yield that will be reflected on overall efficiency of brackish RO desalination unit. This solar concentrator was implemented as a pilot unit for initial process -proof concept. The engineering designed unit depends on the sealed isolated coil in the bottom of the black tank as efficient vapor condensation closed cycle to get pure permeates together with precipitated

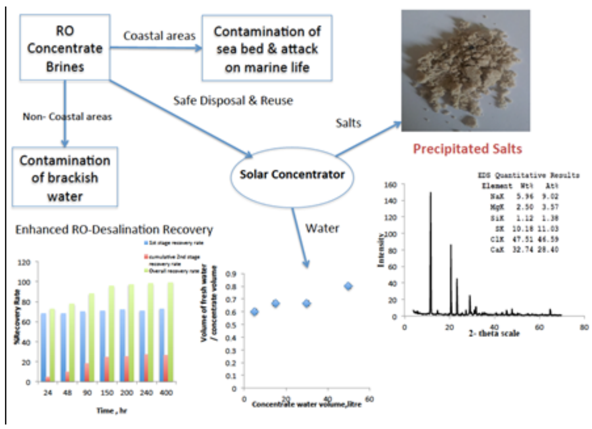

Fig. 1. RO Concentrate problems and summary of reached findings.

Fig. 2. 50 litres exposed stainlesssteel 316 solar pond.

(a) **(b)**

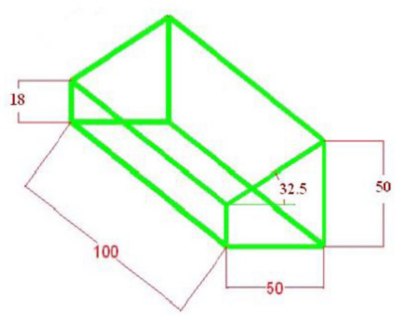

Fig. 3. 5-liters(100cm*50cm*50cm) batch closed solar concentrator with reflecting surfaces and insulated coil for condensate.

blended salts.

The feed concentrate was held in a solar ponds and solar concentrators with varied capacities according to experiment-studied parameters. For example, generally concentrate stream salinity varied over a range from 8500 to 15000 ppm according to feed water salinity; but this study was performed on a minimum salinity of 15,000 ppm and for concentrate with decreased salinity, it will be increased thermally first.

The decrease in concentrate water volume was recorded with time as a measure of solar heating efficiency inside the concentrator. The blank experiment for this concentrator will be a set of exposed solar evaporative ponds for yield comparison of precipitated salts and gained heating efficiency of aforementioned design and so pave the road for ZLD concept for desalination concentrate treatment compared with the reduced fixed capital of designed solar concentrator. Different operating parameters will be varied to express and present their effect on precipitated salts, and yield"Yield of precipitated salts", calculated as the mass of dried filtered salts was recorded at different concentrator volume showing the productivity of different solar stills towards improving their applicability. The rate of formation and product final characteristics was also presented. The reached optimized operating parameters will be compared with international norms for solar evaporators and concentrator together with our previously designed solar concentrator [16-17]. The temperature of the brine in the concentrator increased by means of convection and the greenhouse effect both caused by transmission of the solar radiation. The glass cover on the other hand was cooled by the wind, thus causing condensation of the vapours inside to form small droplets at the underside side of the cover. Under the influence of gravity, these droplets ran down the underside of the glass cover into drainage and were evacuated from the unit by gravity flow [18,19].

The most important factor that causes the energy usage for recovering water from this brine via evaporative techniques to be significantly greater than that normally seen when recovering water from brackish or seawater is the high total salt concentration. The boiling temperature of brines generally increases with increasing salt concentration. That factor results in the energy efficiency of water evaporation processes being lower as they treat higher concentration brines. Solar evaporation is considered one of the emerging techniques that play an important role in increasing RO overall efficiency. The thermal solar efficiency [9-12] can be calculated as follows:

$$\eta = \frac{\sum m * \gamma}{3.6 * \sum A * G} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

m is the hourly distilled water production Kg/hr, γ is the vapor latent heat, kJ/kg; A is the total area of an absorber, m^2; and G is the solar radiation intensity over the area of A, W/m^2.

The uncertainty in calculated solar thermal efficiency (equation1) was diminished to minimum by means of fixed experimental place where the solar intensity was almost taken as a minimum value of 300 W/m2 in winter months. The fixed dimensions of the solar concentrator applied and so its absorber surface area also decreases data uncertainty.

The overall recovery efficiency of RO desalination unit [9,10] will be highlighted by the following equations:

$$\%R = PF/FF*100 \quad \text{.....................2}$$

Where % R is recovery rate percent, for each stage, PF is the permeate water, and FF is the feed water at a certain operation time.

The same reproducibility and repeatedly for recovery rate (equation2) and overall recovery rate (equation3), which was based on the amounts of permeate and feed water over different stages.

$$\%\ OR = (PF\ 1 + PF2)/(FF\ )*100 \quad \text{......................3}$$

Where %OR is the overall recovery, PF1 is the permeate flow rate from the first stage, PF2 is the permeate flow rate from the second solar stage.

Based on previous evaluation data published by Shalaby et al. [19], the overall efficiency can be calculated according to equation 3 with data of %R1 in the first 20 days only which is the time where the solar concentrator data were collected until dryness. By means of equation 2, the solar evaporators recovery rate will be presented.

Results and Discussions

The increase in fresh water condensate with the increase in concentrate volume with the same starting salinity was a good indication of coil insulation techniques (shown in figures 4a & 4b). The process solar heat efficiency was found to reach 80 % recovery as fresh water recovery from concentrate with the increase in concentrate water volume. The weight of precipitated salts was showing a maximum with the decrease in concentrate volume [20]. The increase in solar concentrator's volume shows increase in extracted fresh water condensate from 60% for the 5 litres volume to reach 80% for the 50 litres volume. Together with the increase in blend salt weight, showing an acceptable design parameter for applied solar concentrator. All data was collected when solar intensity was about 300W/m^2 as a selected maximum through winter months in Egypt and not to be compared with weather in Gulf countries and Saudi Arabia [21].

The rate of concentrate evaporation was measured by recording the decrease in

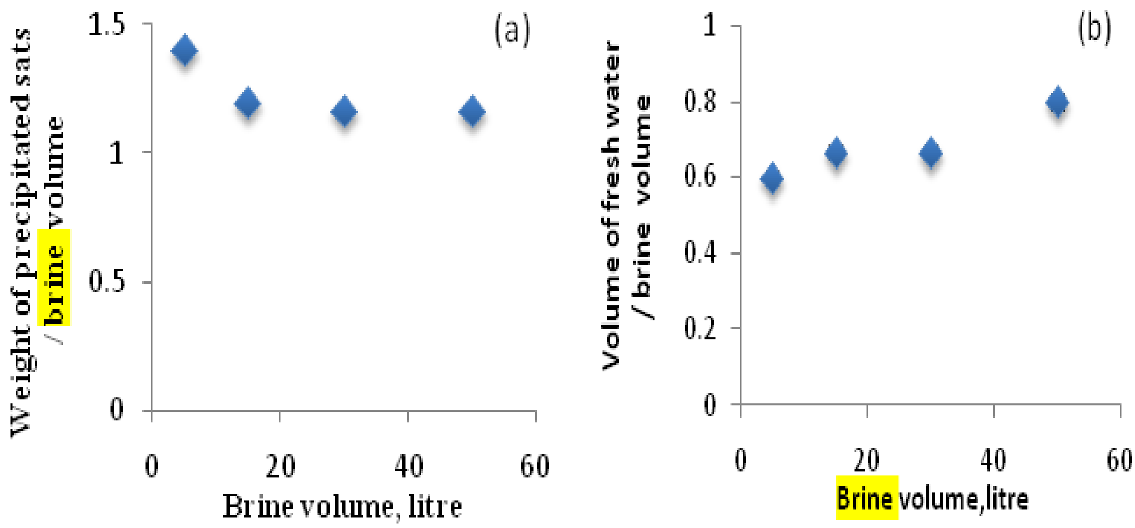

Fig. 4. The weight of precipitated salts/brine volume (a) , and the volume of fresh water / brine volume(b) at different brine volume in solar concentrator.

concentrate volume and then referred as a % of the initial concentrate volume. The mass of dried filtered salts was recorded at different concentrator volume showing the productivity of different solar stills towards improving their applicability.

The decrease in concentrate volume shows a fast decrease in the first 5-days to lose about 77%, 65%, 51%, and 45% of concentrate volume for 5, 15, 30, and 50 litres solar concentrator as shown in figure 5. And then this can be compared with the reached evaporation rate for exposed evaporation ponds in the first 5- days for the same initial concentrate volume as shown in figure 6. The concentrate % volume shows a slow evaporation rate when compared with that of solar concentrator at the same initial concentrate volume, for example; during the first 5-days period , only 34%, 24%, 20% and 16% are lost from concentrate volume used in 5, 15, 30, and 50 litres exposed solar ponds. The precipitated blend salts were subjected to X-Ray Diffraction (XRD), Energy Dispersive X-ray Fluorescence (EDX), and Scan Electron Microscope (SEM) to show the effect of solar evaporation design parameters, closed or open cycle on salts concentration, crystallography, and crystal arrangement with salts elemental analysis.

The differences between blend salts-crystallography were presented in figures 7, and 8 extremely larger precipitation period was required for same concentrate volume in solar pond when compared with solar concentrators which have an adverse effect on crystallized salts that increases the concentration of sodium chloride with gypsum as shown in figure 7 when compared with figure 8 which shows a major occurrence of gypsum with lower concentration of sodium chloride as minor noise fluctuations together with lower concentrations of other salts. The data collected were recorded through three

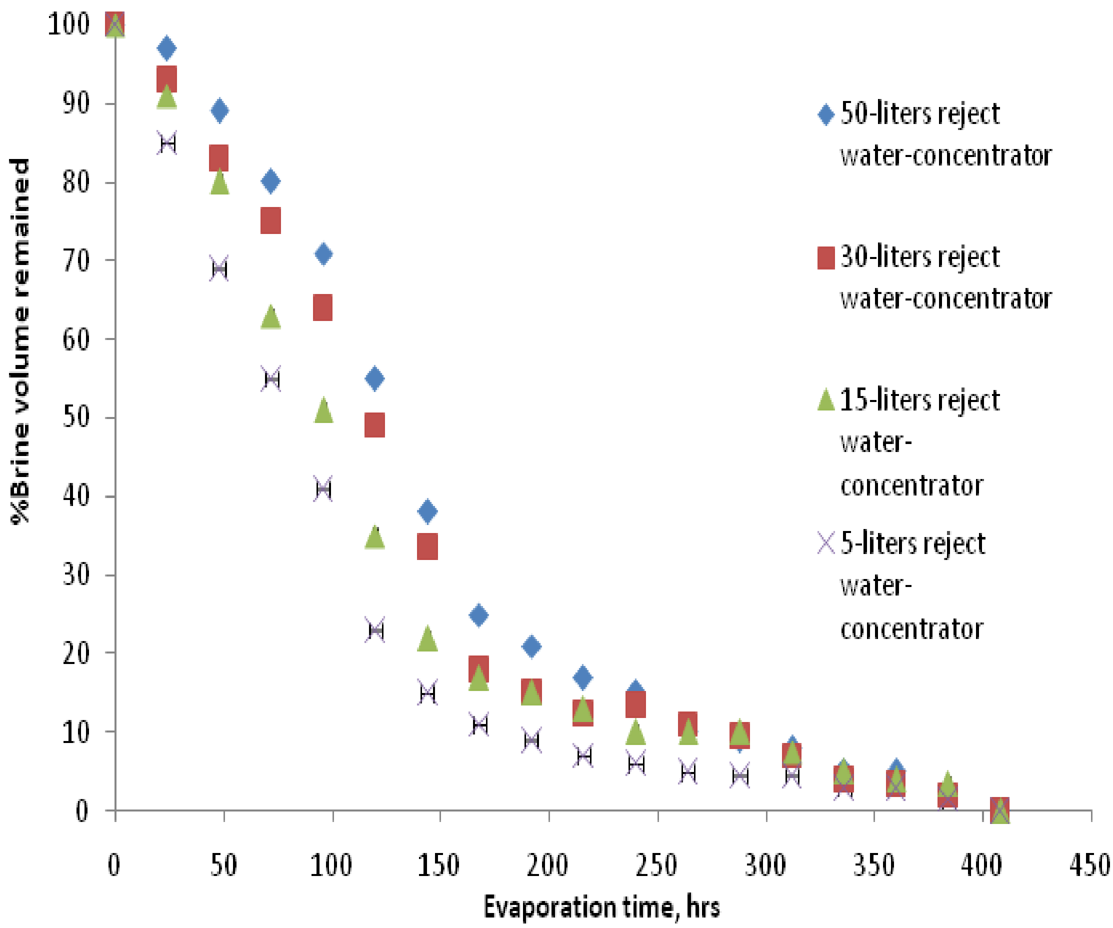

Fig. 5. The effect of evaporation time on % concentrate volume with different volume of solar concentrator.

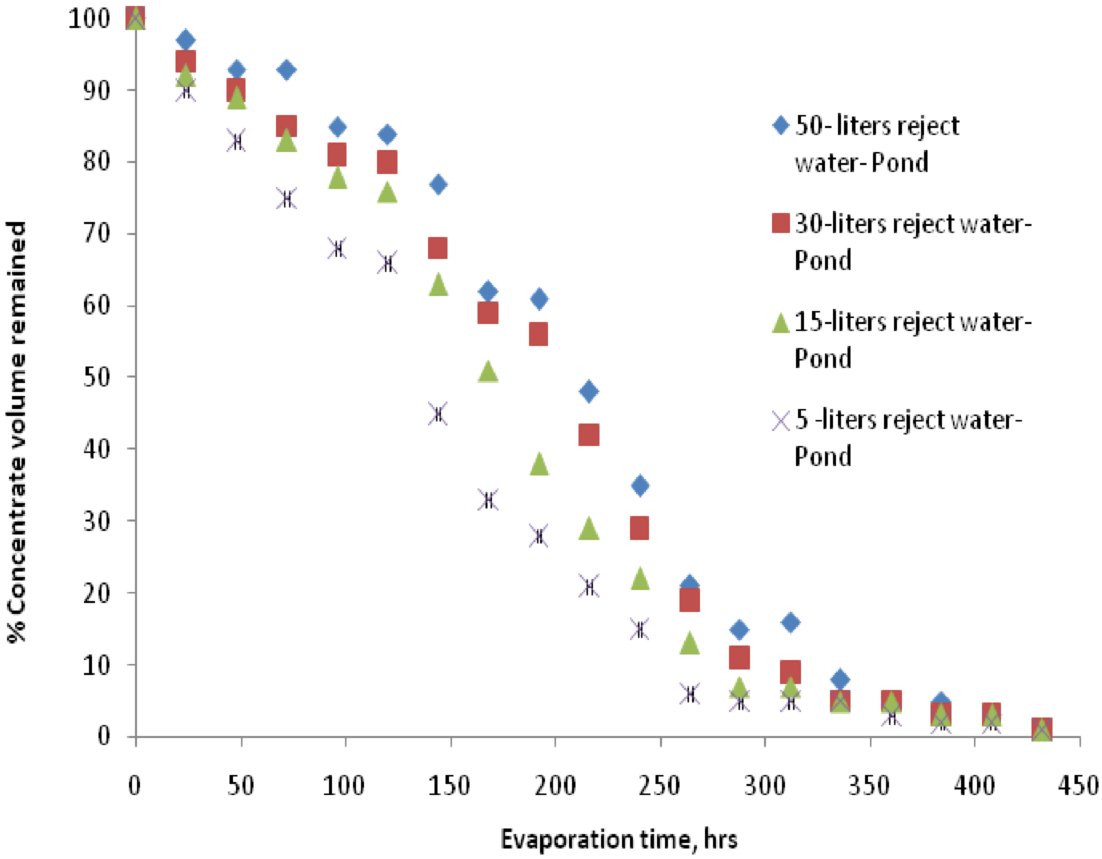

Fig. 6. The effect of evaporation time on % concentrate volume with different volume of solar pond.

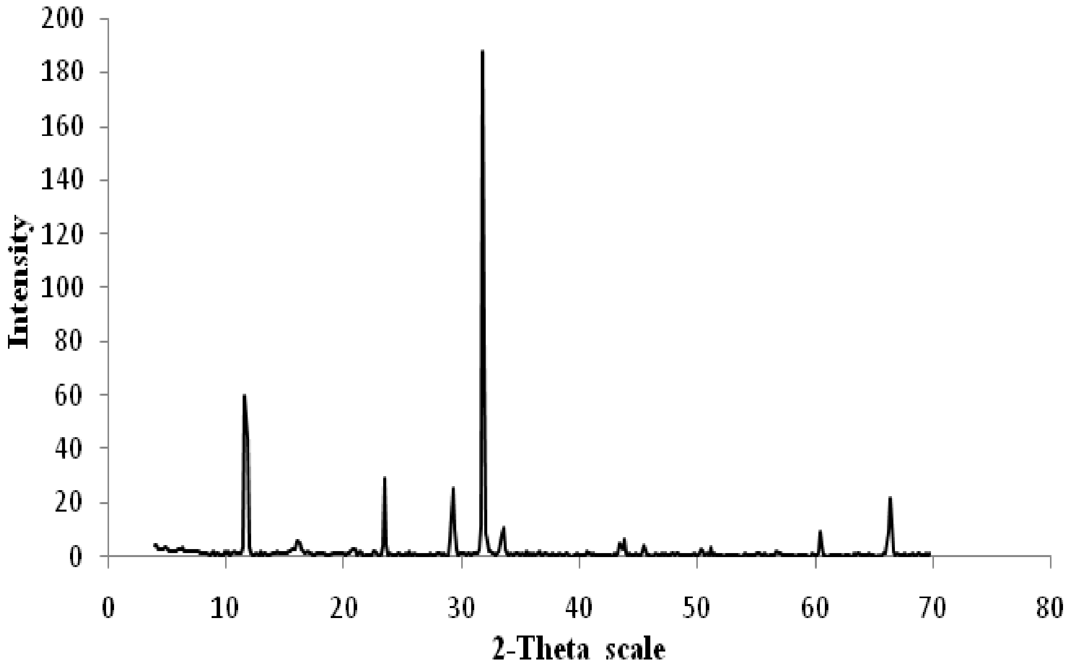

Fig.7. X-Ray Diffraction for precipitated blend salts from solar pond.

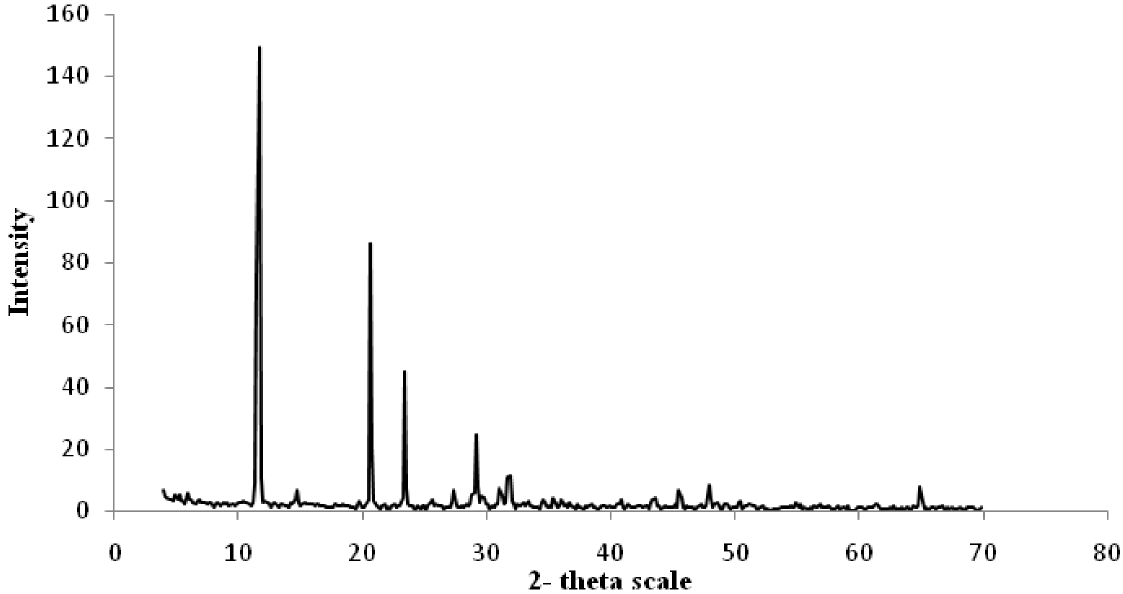

Fig. 8. X Ray Diffraction for precipitated blend salts from solar concentrator.

TABLE 2. Coefficients of thermal solar efficiency for different concentrators.

m, Kg/hr	γ ,kJ/kg	A, m2	G, W/m2	η
0.025	2264.76	0.25	300	0.904438652
0.042	2264.76	0.15	300	
0.065	2264.76	0.09995	300	
0.098	2264.76	0.03332	300	

successive samples and then their average were plotted in figures from 4 to 6.

The thermal solar efficiency for the solar concentrator shown in figure 3 was calculated according to equation 1 and based on experimental and estimated data as shown in table 2.

According to previously illustrated data shown in figures 4 to 6, and their corresponding X-ray diffraction, the ease of design and application of solar concentrator and so its efficiency have to be highlighted. It was found; that the reached thermal solar efficiency shown above in table 2 of about 0.9, which means that the preliminary design of this concentrator needs a further development which will enhance the reached efficiency. The solar radiation was stabilized as the minimum value found through days of winter months in Egypt as a worst scenario evaluating the design. Highlighting the differences between different solar concentrators published in literature will be given, but it is not with the same design parameters together with the difference in testing basis. Different solar stills (concentrators) have been proposed and studied based yield per day, which have efficiencies within the range of (30–40) % and a yield of (4–5) - kg/day [10]. Another thermal model for a basin solar still with an external reflector was evaluated experimentally, the accumulated distilled water was found to be 4300 mL/day with efficiency of 44% in the afternoon [22].

Results indicated that the use of an energy storage material led to a larger productivity of distilled water and that the larger the concentration of the saline water the lower the productivity of the still. Also higher flow rate and high inlet saline water temperature improved the still efficiency. The maximum productivity of energy storage material still was 4.536 L/min, 6 h daytime operation plus overnight distillation due to stored energy, when the saline water flow rate was 40 ml/min, equivalent to a still efficiency of 36.2 percent [23]. The above mentioned previous designed concentrators of different parameters will not give clear comparative view due to probable experimental variations. As in our work, we use the starting volume of feed concentrate water for both concentrator and ponds with their variety in capacities and then the permeate water was recorded over experiment time with almost stabilized solar intensity.

On the other hand, the reached overall recovery rate for the two stages desalination unit by means RO desalination and followed by solar treatment of concentrate water by means of 50 liters concentrator. It can be showed clearly in figure 9 where the previous evaluation of RO desalination unit with the calculated recovery rate was compared with the solar concentrator recovery rate according to equation 2 together with the ORR (overall recovery rate).

It was clear that the recovery rate with reverse osmosis unit seems to be stabilized over the evaluation period unlike the solar concentrator recovery rate which was greatly influenced by time and by cumulative decrease in concentrate water. The overall recovery rate (ORR) was showing a gradual increase due to increase in solar evaporative condensation cycle. The applied small scale (5-litres) was validated till 50 litters but not guaranteed on large scale and the recorded efficiency tending to reach 99% was based on 50 litres with minimal heat and water losses.

The photos of precipitated salts from solar ponds and solar concentrators are shown below, one can notice clearly hygroscopic nature of solar pond (p) precipitated salts shown in figure 10 (b) when compared with solar concentrator (S) salts in figure 10(a). This was attributed to difficulty in reaching complete dryness on ambient conditions.

The morphology of precipitated salts blend with their elemental quantitative concentrations was shown in figures from 11 to 14 using SEM (scan electron microscope) and EDX (energy dispersive x-ray fluorscence) analysis for both solar concentrator and solar pond. These figures were in conformity with the discussed results found by XRD (X-Ray Diffraction) but it increases on it that the formed calcium salts were found as chlorides as well as sulphates as in figures 12 and 14.

Figures 10 and 12 show a number of morphological differences between solar concentrator and exposed solar ponds in crystal

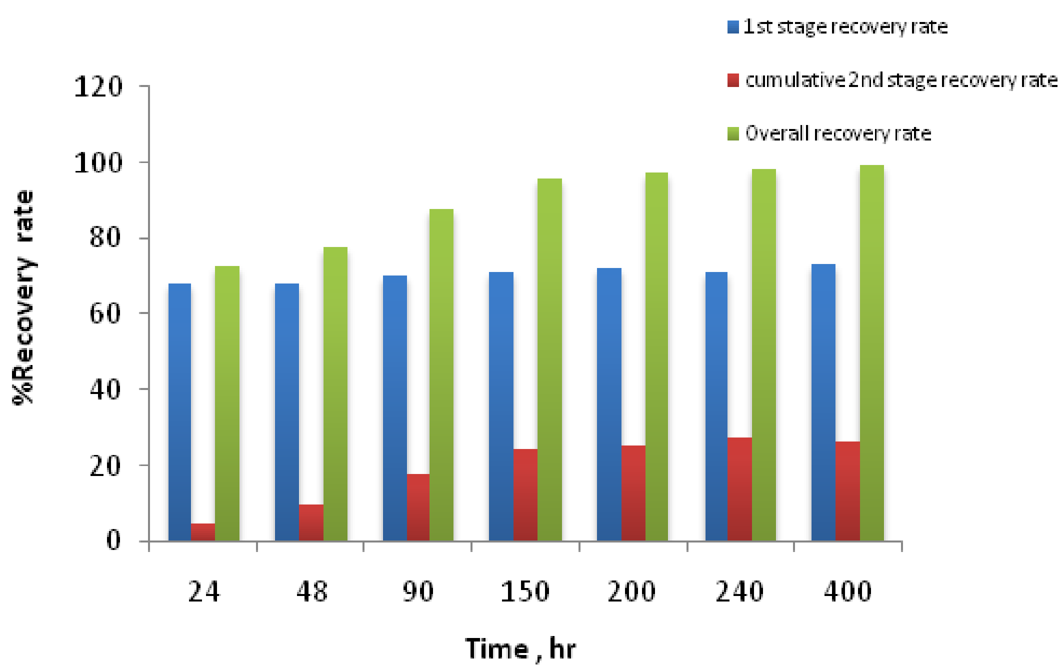

Fig. 9. Overall recovery rate (RO desalination) compared with that of stages.

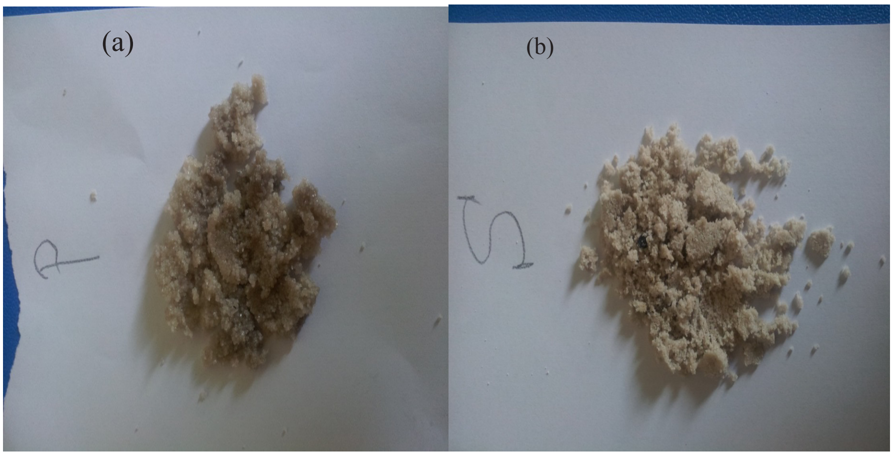

Fig. 10. Photos of precipitated salts from solar concentrator (a) and solar pond (b).

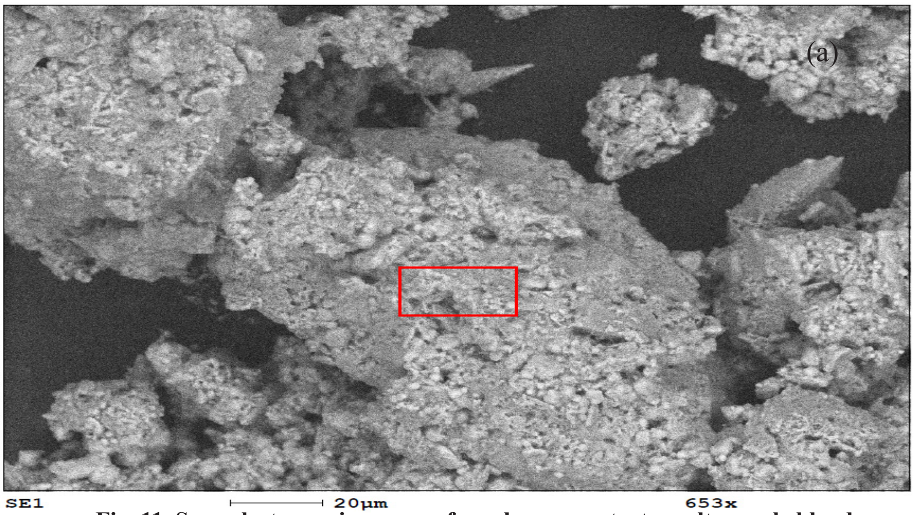

Fig. 11. Scan electron microscope for solar concentrator salt sample blend.

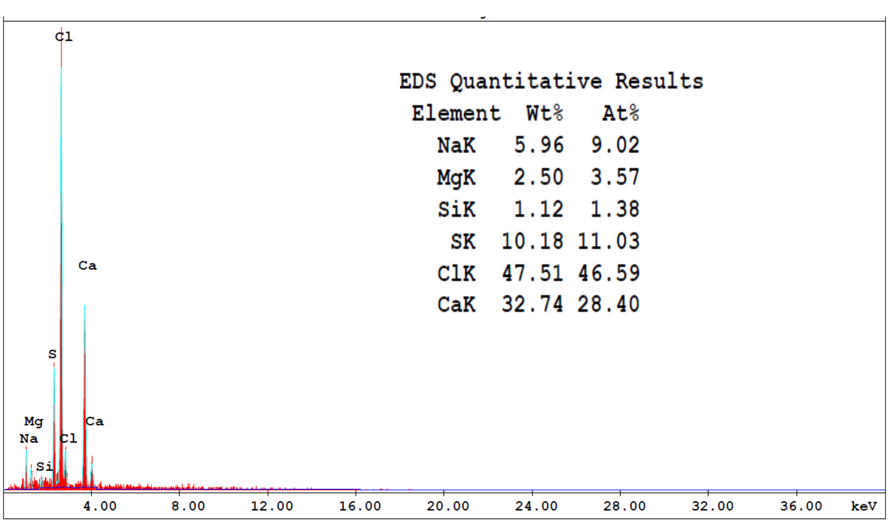

Fig. 12. Energy dispersive x-ray fluorescence chart and elemental quantitative analysis for solar concentrator salt sample blend.

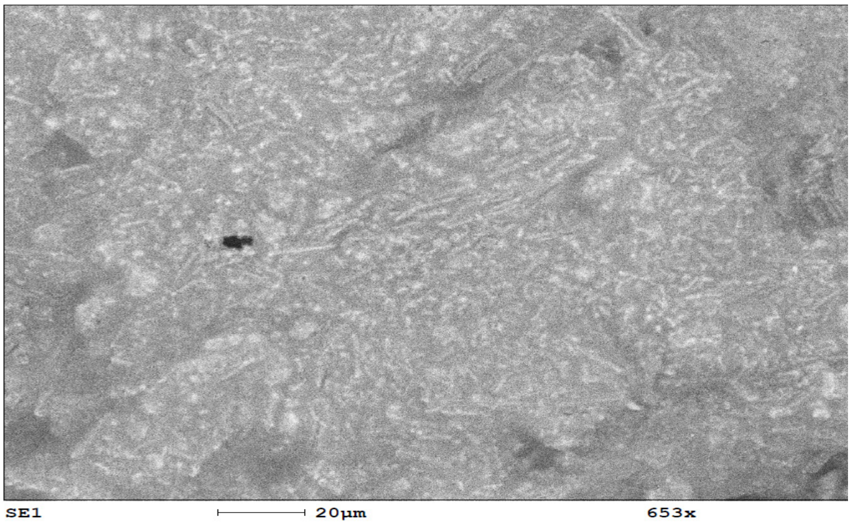

Fig. 13. Scan electron microscope for solar pond salt .

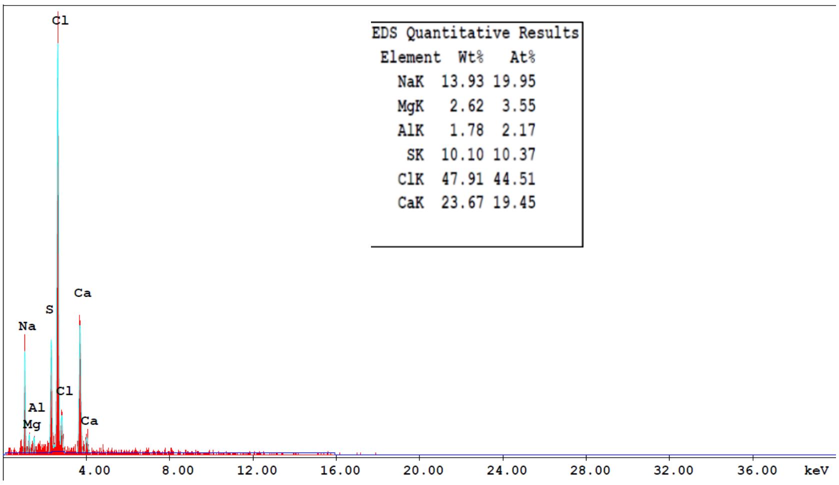

Fig. 14. Energy dispersive x-ray fluorescence chart and elemental quantitative analysis for solar pond salt

growth, a higher super imposition was clear for calcium and sodium salts in figure 10 for solar concentrator. By comparing this by figure 12 for solar exposed ponds which takes a certain extended precipitation period which shows adverse effect on crystal growth giving powder salt blend. The same was clear in figures 11and 13 for ions concentrations in solar concentrators and ponds respectively.

Conclusions

The concentrate water was fed to a low cost salt recovery designed and implemented closed solar concentrator with a compared solar evaporation pond at stabilized solar intensity of 300 w/m^2 as maximum stablized intenisty level in winter months. The thermal efficiency of designed solar concentrator was found to exceed 90% in the range of data collected for different capacities from 5 to 50 litres. The reached recovery from solar concentrator single stage exceeds 90% recovery, which then will give an overall recovery percentage for succesive reverse osmosis with solar concentrator from 72-99%. The simple-designed solar concentrator shows many excellence points over exposed solar ponds for salt concentration, morphology, sample dryness and purity. The increase in solar concentrator volume has an adverse effect on recovery percentage and required precipitation period in the first 8-days period for solar pond and the first 5-days period for solar concentrator and so this study recommend multi- levels solar concentrator with lower capacity. This study was examined as a pilot study where the results prove the validation with the recommended design for practical applications that was shown clearly with the recorded efficiency through studied lab scale but with the up scaling the efficiency and recovery rates were predicted to show a certain decrease.

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معالجة محلول الرجيع الملحي باستخدام الطاقة الشمسية : دراسة حالة جنوب سيناء- مصر

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تمثل مشكله التكلفه العاليه و كذا استهلاك الطاقه و صعوبه الوصول الي الاستدامه في تفاقم مشاكل السائل الرجيع من محطات تحليه مياه الآبار باستخدام اغشيه الضغط الاسموزي و التي تمثل تهديدا خطيرا علي الاجيال القادمه لما تمثله من تلوث للمياه الجوفيه. و تعتبر مشكله السائل الرجيع من اهم العوائق التي تقف امام انتشار تحليه مياه الابار بالاغشيه. كان لاستخدام الطاقه الشمسيه لتبخير هذا السائل دراسات عديده. و الهدف من هذا العمل هو دراسه كفاءه المبخر الشمسي و حجمه مع زمن التبخير و حجم السائل الذي يتم تبخيره و ذلك لاسترجاع مياه نقيه وكذا ملح كمنتج ثانوي. و لقد وجد انه وصلت نسبه كفاءه الحراريه الشمسيه الي ما يزيد عن ٩٠٪ لمعظم الاحجام المنفذه لهذه المبخرات الشمسيه. و لقد وجد ان حجم المبخر المغلق او المعرض لاشعه الشمس يؤثر تأثيرا مباشرا علي معدلات التبخير للسائل الرجيع. درجه نقاء بلورات الملح و كذا ترتيب هذه البلورات تم عرضها بالتوصيف الكامل للمبخر المعرض للشمس و كذا المغلق.و بالتالي سهوله التصميم و الاعتماد علي الطاقه الشمسيه يجعل هذه المبخرات وسيله لزياده معدلات استخلاص المياه من تحليه مياه الابار(٢٠٠٠٠ جزء لكل مليون جزء) بالأغشية لتصل الي حوالي ٨٧-٩٠٪ و ذلك باستخدام طاقه للشعاع الشمسي الساقط حوالي ٣٠٠وات/م٢ ، و هذا ادي الي وضع تصور للوصول الي المستوي الصناعي عن طريق تصميم مبخرات متعدده الطوابق رأسيه الشكل.