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Study of the vapour pressure of saturated salt solutions and their influence on evaporation rate at room temperature

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ABSTRACT

Brine disposal is an important problem in desalination facilities, especially in inland plants. Nowadays, the management alternatives to treat these brines are focused on reducing brine volume to solid state. There are different treatments to reduce brine volume such as evaporation ponds, brine evaporators, evaporation with extended surfaces and zero liquid discharge technologies. With reference to the treatments based on evaporation, vapour pressure of brines is a relevant factor. In this work, vapour pressure of salt solutions containing the major ions present in brines has been studied in order to estimate its influence on the evaporation rate at room temperature. To this aim, vapour pressure has been studied by means of an experimental setup equipped with a hygrometer. Solutions studied included the following ions: Na^+, Cl^-, CO_3^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+} and SO_4^{2-}. Experiments were performed in the temperature range of 25–40°C, with saturated, unsaturated solutions and their mixtures. Moreover, additional experiments were performed to relate vapour pressure with natural evaporation of different salts under typical Mediterranean climate conditions. The obtained results are useful for design of evaporation treatments at room temperature.

Keywords: Vapour pressure; Evaporation; Salt; Brine

1. Introduction

Water scarcity, deterioration of freshwater resources and present legal framework have increased the application of membrane technologies to produce drinking water and to reuse wastewater.

Brine disposal is an important problem in desalination facilities. Desalination plants located near to the coastline dump these brines into the sea usually after dilution. However, in inland plants and in industrial plants, surface disposal methods are not usually feasible.

Nowadays, the different alternatives to manage brines in inland plants are deep well injection, land application, evaporation ponds, brine concentrators and zero liquid discharge [1].

Vapour pressure is an important parameter in desalination processes and in other technologies like absorption heat pumps [2]. Evaporation rates from large freshwater bodies depend on many factors such as wind speed, temperature, and vapour pressure [3].

Some researchers have studied vapour pressure of seawater concentrates. Apelblat and Korin [4,5] studied the vapour pressure of several saturated solutions, as nitrates, chlorides, sulphates, etc. Foote et al. [6] also studied vapour pressure of aqueous solution of certain salts, but their studies are more than half a century old. Robinson [7] found that the vapour pressure of natural sea

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water is higher than that of a sodium chloride solution of equal density. Patil et al. [2] in 1991, studied the vapour pressure of binary solutions, and fitted experimental data to the Antoine type equation.

In this work, the vapour pressure of salt solutions containing the major ions present in brines has been studied in order to estimate its influence on evaporation rate at room temperature.

First, the vapour pressure of unsaturated salt solutions for the binary system NaCl–H_2O was analyzed. Second, the vapour pressure of saturated salt solutions of NaCl, Na_2CO_3, $NaHCO_3$, $CaCl_2$, $MgSO_4$ and Na_2SO_4 were studied. Afterwards, several ternary systems of NaCl with Na_2CO_3, $CaCl_2$, $MgSO_4$ and Na_2SO_4 were studied.

Finally, with the purpose of studying evaporation rate, an experiment with saturated salt solutions of NaCl, Na_2CO_3, $NaHCO_3$, $CaCl_2$, $MgSO_4$ and Na_2SO_4 was carried out.

2. Experimental procedures

2.1. Vapour pressure experiments

Vapour pressure experiments were performed by means of relative humidity measures at different temperatures in an experimental setup equipped with a hygrometer DELTA OHM. The performance of this device was checked by measuring vapour pressure of certain solutions and comparing it with bibliography.

Salt solutions studied in this work were produced using analytical reagent grade and anhydrous of NaCl, Na_2CO_3, $NaHCO_3$, $CaCl_2$, $MgSO_4$ and Na_2SO_4. Salts samples were dried out in a vacuum oven during 12 h. The solutions were prepared by using deionized water.

Measurements of relative humidity were made with a hygrometer in the experimental setup shown in Fig. 1. Temperature was controlled by a thermostat bath. All experiments were performed in the temperature range from 25°C to 40°C. Measures were taken after system stabilization was observed.

Vapour pressure of unsaturated solutions of NaCl were analysed. We decided study this solution, because of sodium chloride is the main salt presents in brines. The concentrations studied were prepared in the range of 5–300 $g{\cdot}L^{-1}$ (0.08–5.75 molal).

Secondly, vapour pressure of saturated salt solutions of NaCl, Na2CO3, NaHCO3, CaCl2, MgSO4 and Na2SO4 were studied in the temperature range of 24–40°C. In this case, the molality of solutions was chosen according to the solubility at different temperatures.

Finally, experiments to determinate the influence of several salts in vapour pressure of sodium chloride solutions were carried out. These experiments were performed with ternary solutions composed of sodium chloride, pure water and each of the salts previously studied. The molality ratios (m_{NaCl}/m_{salt}) studied for different salts were 0.2 and 0.5, where m_{salt} is the molality of salt solution of Na_2CO_3, $CaCl_2$, $MgSO_4$ and Na_2SO_4. For Na_2CO_3, $MgSO_4$ and Na_2SO_4 a saturated salt solution was employed, but for $CaCl_2$ solutions with 3 and 4 molal were used. In this case, temperatures studied were 25 and 30°C.

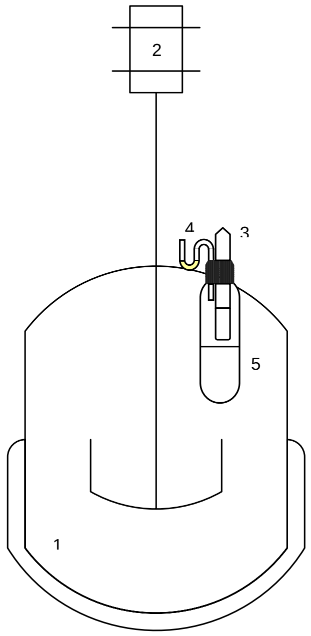


Fig. 1. Experimental device to study vapour pressure. 1 – thermostatic bath, 2 – agitator, 3 – hygrometer probe, 4 – U-tube, 5 – sample.

2.2. Evaporation experiment

The aim of this experiment was to study evaporation rates of saturated salt solutions. In evaporation tests, saturated salt solutions at 25°C of NaCl, Na_2CO_3, $NaHCO_3$, $CaCl_2$, $MgSO_4$ and Na_2SO_4 were used. These solutions were placed into circular vessels with a solution depth of 1 cm. The contact surface between the solutions and the air was 0.0065 m^2. Table 1 shows the characteristics of different solutions. Moreover, pure water was evaporated at the same time that the salt solutions.

Experiments were carried out under typical Mediterranean climate conditions, throughout month of May.

Table 1
Saturation properties of studied salts

Salt	Solubility (% weight)	Molality ($mole{\cdot}kg^{-1}$)
NaCl	26.45	6.44
Na_2CO_3	23.50	2.46
$NaHCO_3$	9.32	1.46
$CaCl_2$	44.83	7.88
$MgSO_4$	26.30	3.12
Na_2SO_4	21.94	2.87

During the tests, temperature fluctuated between 21–27°C and air relative humidity between 28–60%. Mass losses along the time, temperature and relative humidity were registered.

3. Results and discussion

3.1. Vapour pressure of unsaturated NaCl solutions

Measurements of vapour pressures were carried out in the temperature range of 24–34°C and concentration range of 0.08–5.75 molal with the binary system NaCl–H_2O. The results are shown in Table 2.

Vapour pressure was higher for the less concentrated solutions of NaCl. However, the influence of concentration on vapour pressure was lower at temperatures near 34°C for the most unsaturated solutions (Fig. 2).

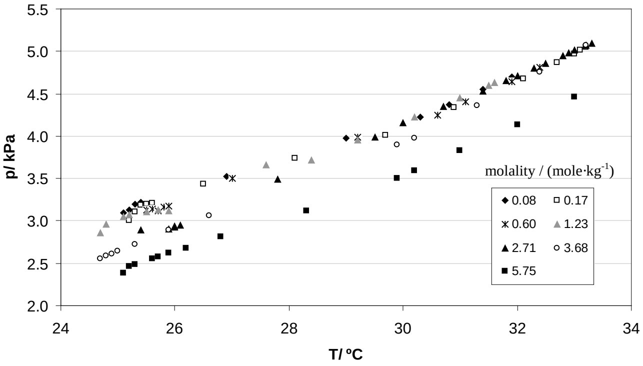


Fig. 2. Vapour pressure of unsaturated NaCl solutions at different molalities.

3.2. Vapour pressure of saturated salt solutions

Figs. 3–7 show the vapour pressure of the saturated salt solutions. Results were checked with literature. Vapour pressure measurements did not significantly differ from those of the literature [2,4,6,8]. Only, there

Table 2
Experimental vapour pressure of unsaturated NaCl solutions

Molality (mole·kg^{-1})	*T* (°C)	*p* (kPa)	*T* (°C)	*p* (kPa)	*T* (°C)	*p* (kPa)
0.08	25.1	3.084	26.9	3.529	30.8	4.387
0.08	25.2	3.115	29.0	3.989	31.4	4.563
0.08	25.3	3.182	30.3	4.234	31.9	4.708
0.17	25.2	2.997	28.1	3.751	32.7	4.891
0.17	25.3	3.098	29.7	4.020	33.0	4.989
0.17	25.5	3.181	30.9	4.354	33.1	5.032
0.17	26.5	3.416	32.1	4.695	33.2	5.066
0.60	25.5	3.125	27.0	3.505	31.1	4.422
0.60	25.6	3.134	29.2	3.984	31.9	4.661
0.60	25.8	3.155	30.6	4.259	32.4	4.828
1.23	24.7	2.866	25.7	3.140	30.2	4.218
1.23	24.8	2.970	25.9	3.124	31.0	4.451
1.23	25.2	3.076	28.4	3.713	31.5	4.598
1.23	25.5	3.119	29.2	3.954	31.6	4.629
2.71	25.4	2.903	30.0	4.149	32.5	4.851
2.71	25.9	2.914	30.7	4.345	32.8	4.938
2.71	26.0	2.935	31.4	4.531	32.9	4.976
2.71	26.1	2.945	31.8	4.653	33.0	5.009
2.71	26.2	2.952	32.0	4.706	33.2	5.066
2.71	29.5	3.982	32.3	4.796	33.3	5.094
3.68	24.7	2.554	25.3	2.728	30.2	3.977
3.68	24.8	2.585	25.9	2.891	31.3	4.362
3.68	24.9	2.610	26.6	3.065	32.4	4.760
3.68	25.0	2.638	29.9	3.892	33.2	5.072
5.75	25.2	2.466	26.2	2.682	30.2	3.598
5.75	25.3	2.490	26.8	2.814	31.0	3.833
5.75	25.7	2.577	28.3	3.123	32.0	4.135
5.75	25.9	2.618	29.9	3.507	33.0	4.461

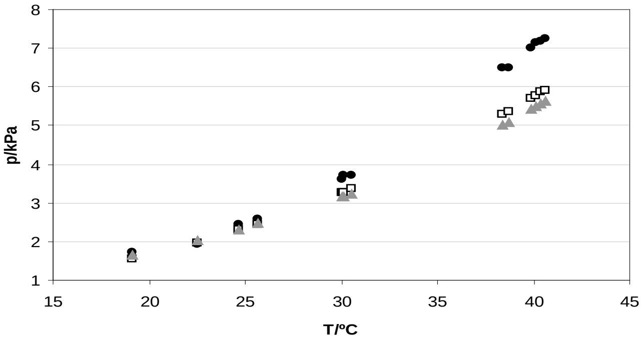


Fig. 3. Vapour pressure of saturated NaCl solution: ● experimental, □ [4], ▲ [6].

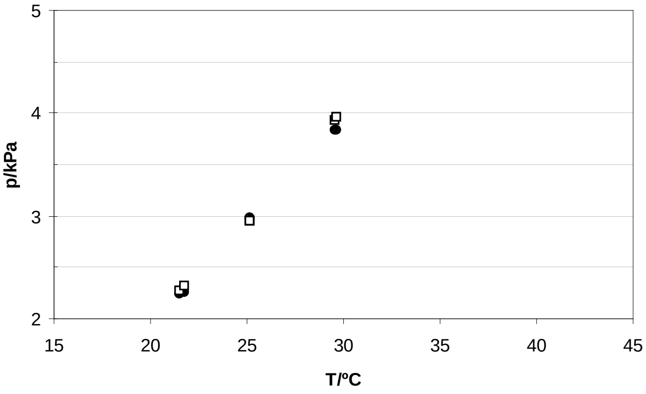


Fig. 4. Vapour pressure of saturated Na_2CO_3 solution: ● experimental, □ [8].

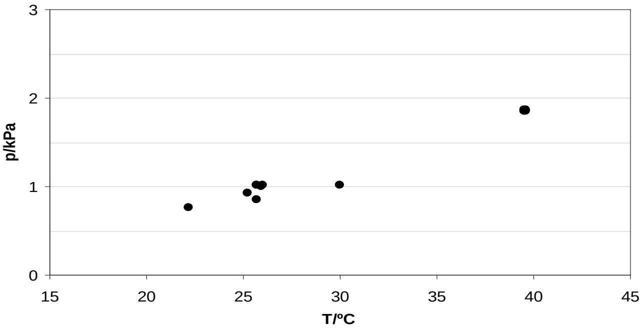


Fig. 5. Vapour pressure of saturated $CaCl_2$ solution: ● experimental.

was an important difference for vapour pressure of NaCl at 40°C. Regarding sodium hydrogen sulphate, vapour pressure measurements were practically equal to water vapour pressure. Moreover, for calcium chloride no literature data has been found at the concentration range. Patil [2] studied the vapour pressure of $CaCl_2$ solutions from 1.002 to 7.885 molal in the temperature range of 303.15–343.15 K, and fitted experimental data to the Antoine type equation.

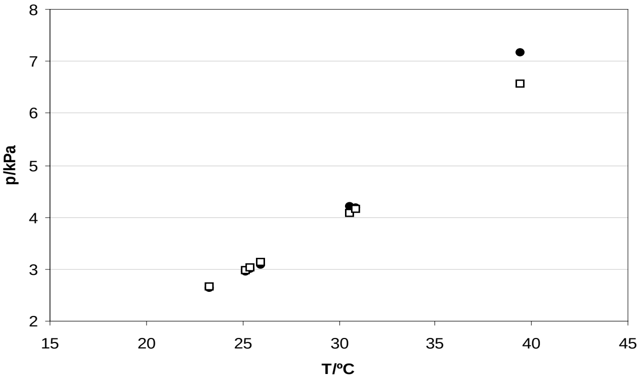


Fig. 6. Vapour pressure of saturated $MgSO_4$ solution: ● experimental, □ [8].

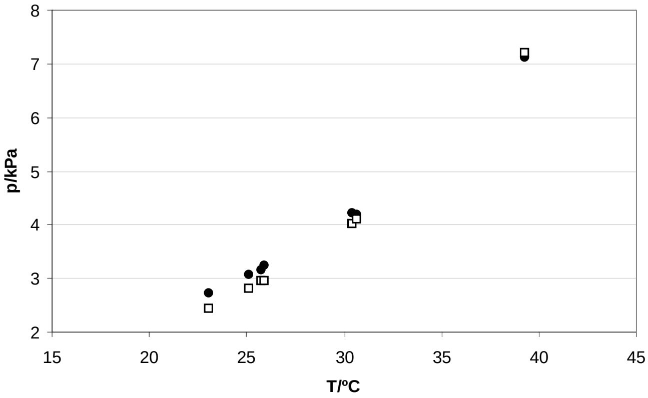


Fig. 7. Vapour pressure of saturated Na_2SO_4 solution: ● experimental, □ [6].

The obtained data were fitted to an Antoine like Eq. (1). Table 3 shows the parameters A, B and C for the salt solutions, as well as the average error of the fitting.

$$\ln[P(kPa)] = A - \frac{B}{T(K)+C} \tag{1}$$

3.3. *Vapour pressure of ternary solutions*

In Tables 4–7, vapour pressure of ternary solutions are shown. Moreover, vapour pressure of binary solutions ($NaCl/H_2O$) with the same molality are detailed in order to compare the influence of salt mixtures.

Table 3
Parameters of Antoine equation for the different salts.

Salt	*A*	*B*	*C*	*R*^{2}
NaCl	19.0740	4506.63	–49.9228	0.9959
Na_2CO_3	16.8754	3768.68	–59.9345	0.9912
Ca_2Cl_2	20.3571	8364.03	111.0100	0.9654
$MgSO_4$	17.6782	4200.91	–45.2567	0.9990
Na_2SO_4	17.3280	4254.97	–35.7714	0.9981

Table 4
Vapour pressure of ternary solution NaCl/Na_2CO_3/H_2O

T (°C)	Molality ratio m_{NaCl}/m_{salt}	mole·kg^{-1}			$p_{mixture}$ (kPa)	p_{NaCl} (kPa)
		NaCl	Na_2CO_3	Total		
25	0.0	0.00	3.3	3.30	2.87	2.72
25	0.2	0.66	3.3	3.96	2.53	2.62
25	0.5	1.65	3.3	4.95	2.27	2.44
30	0.0	0.00	4.0	4.00	3.98	3.90
30	0.2	0.80	4.0	4.80	3.69	3.68
30	0.5	2.00	4.0	6.00	3.40	3.54

Table 5
Vapour pressure of ternary solution NaCl/$CaCl_2$/H_2O

T (°C)	Molality ratio m_{NaCl}/m_{salt}	mole·kg^{-1}			$p_{mixture}$ (kPa)	p_{NaCl} (kPa)
		NaCl	$CaCl_2$	Total		
25	0.0	0.00	3.0	3.00	2.36	2.75
25	0.2	0.60	3.0	3.60	2.15	2.67
25	0.5	1.75	3.0	4.75	2.12	2.47
30	0.0	0.00	4.0	4.00	3.15	3.90
30	0.2	0.80	4.0	4.80	2.62	3.95
30	0.5	2.00	4.0	6.00	2.58	3.54

Table 6
Vapour pressure of ternary solution NaCl/$MgSO_4$/H_2O

T (°C)	Molality ratio m_{NaCl}/m_{salt}	mole·kg^{-1}			$p_{mixture}$ (kPa)	p_{NaCl} (kPa)
		NaCl	$MgSO_4$	Total		
25	0.0	0.00	3.03	3.03	2.91	2.75
25	0.2	0.61	3.03	3.64	2.62	2.67
25	0.5	1.52	3.03	4.55	2.29	2.50
30	0.0	0.00	3.34	3.34	4.01	4.03
30	0.2	0.67	3.34	4.01	3.77	3.90
30	0.5	1.67	3.34	5.01	3.60	3.62

Table 7
Vapour pressure of ternary solution NaCl/Na_2SO_4/H_2O

T (°C)	Molality ratio m_{NaCl}/m_{salt}	mole·kg^{-1}			$p_{mixture}$ (kPa)	p_{NaCl} (kPa)
		NaCl	Na_2SO_4	Total		
25	0.0	0.00	2.12	2.12	3.04	2.81
25	0.2	0.42	2.12	2.54	2.80	2.78
25	0.5	1.06	2.12	3.18	2.55	2.73
30	0.0	0.00	3.00	3.00	4.11	4.06
30	0.2	0.60	3.00	3.60	3.97	3.99
30	0.5	1.50	3.00	4.50	3.90	3.76

In all the experiments carried out, the addition of NaCl to the others saturated salts meant a decrease in vapour pressure. Therefore, ternary systems presented minor vapour pressure than binary system with the same concentration. Besides, the more NaCl was added the more decreased the vapour pressure. The vapour pressure for system with a molality ratio of 0.2 was higher than for the system with 0.5 molality ratio. For that reason, in mixtures of salt solutions, the concentration is a more relevant factor on vapour pressure than the own vapour pressure of simple salt solution.

Fig. 8 shows that at 25°C, for the same molality, vapour pressure of Na_2SO_4, $MgSO_4$ and Na_2CO_3 is higher than NaCl pure solution, and the $CaCl_2$ presents a lower value ($m_{NaCl}/m_{salt} = 0$). With regard to ternary solutions (0.2 and 0.5), these solutions have a lower vapour pressure than the correspondent NaCl solution with the same molality. The differences between the vapour pressure values of ternary solutions and the correspondent NaCl solution with the same molality were slightly smaller at 30°C than at 25°C. Therefore, natural evaporation of brines composed of these salts will be smaller than that of an equivalent NaCl solution with the same molality.

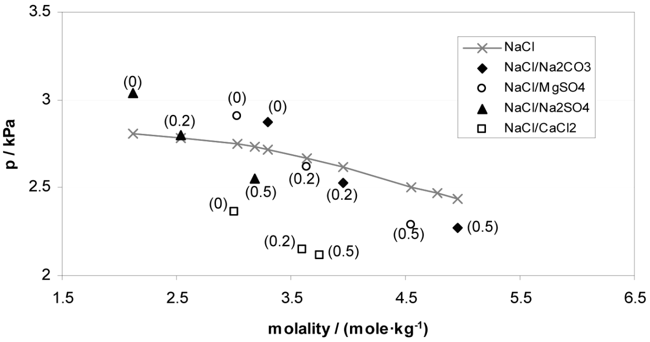


Fig. 8. Comparison between the vapour pressures of ternary solutions with NaCl solutions at 25°C.

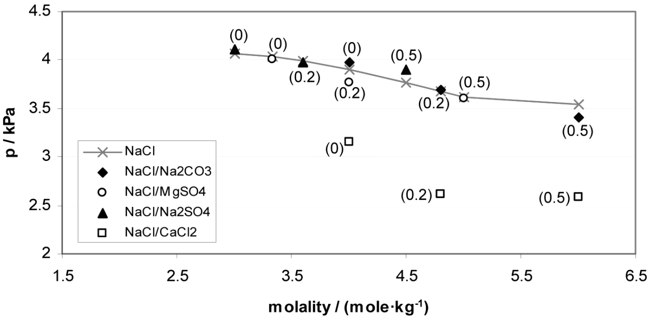


Fig. 9. Comparison between the vapour pressures of ternary solutions with NaCl solutions at 30°C.

3.4. Evaporation experiments

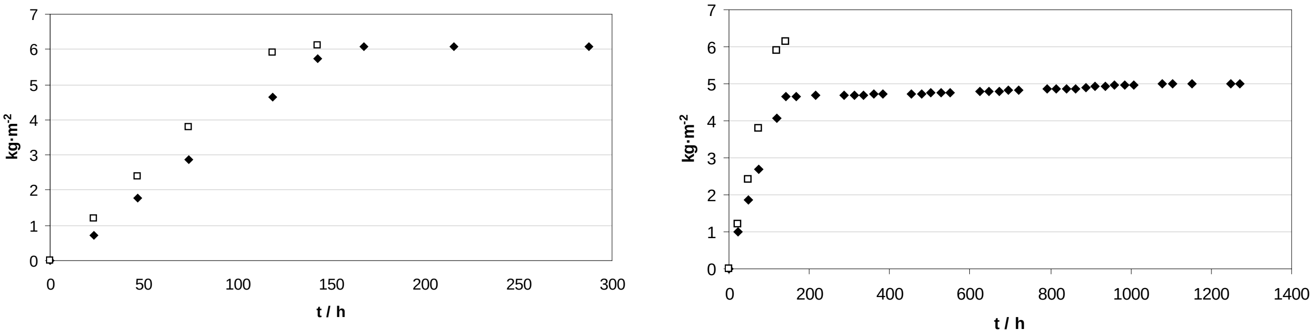
In the evaporation experiments, for the tests conditions, the order of crystallization was: $NaHCO_3$, NaCl, Na_2SO_4, Na_2CO_3, $MgSO_4$ and $CaCl_2$. Fig. 10 shows the evaporation rate of the different salts. At the beginning of the test, $NaHCO_3$, NaCl, Na_2SO_4, Na_2CO_3 and $MgSO_4$ presented higher evaporation rate. $CaCl_2$ solutions due to their hygroscopic character absorbed water from the environment for relative humidity above 50%. However, once first crystals were formed, evaporation rates dropped for all salts.

In Table 8, vapour pressure of solutions and evaporation rates are shown in crystallization order. Average evaporation rate values correspond to average evaporation at the moment that the vessel of water was completely dried. Vapour pressure is inversely proportional to solubility. Salt solutions with higher vapour pressure evaporated faster. However, sodium chloride solution reached solid state before than the other salt solutions with higher vapour pressure. This situation happened, owing to the fact that temperature changed along the tests. While solubility of Na_2SO_4, Na_2CO_3, $MgSO_4$, $CaCl_2$ change considerably with temperature, NaCl has practically the same solubility in the temperature range 20–40°C. In this way, for a temperature around 30°C NaCl is less soluble than Na_2SO_4, Na_2CO_3, $MgSO_4$ and $CaCl_2$.

Table 8
Data of evaporation test at 25°C

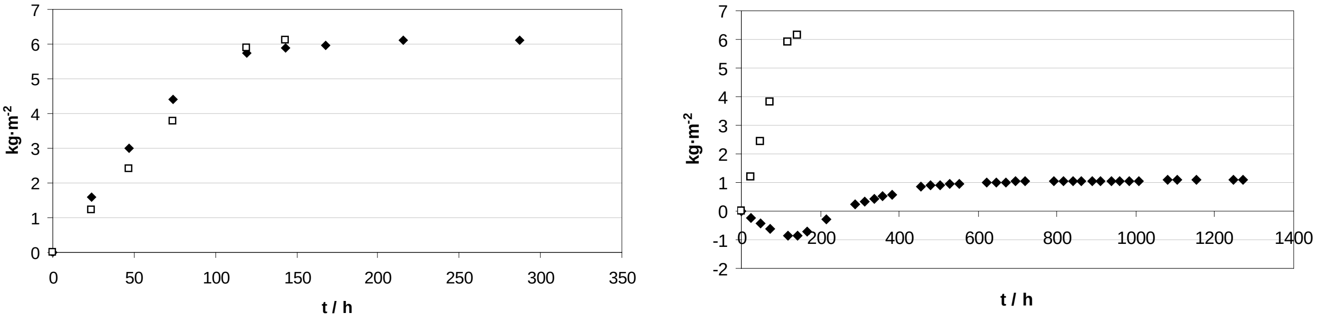
Crystallization order	Solution	Solubility (%)	p (kPa)	Average evaporation rate ($kg·m^{-2}·h^{-1}$)
1	H_2O	—	3.19	0.0495
2	$NaHCO_3/H_2O$	9.32	3.18	0.0483
3	$NaCl / H_2O$	26.45	2.48	0.0391
4	Na_2SO_4 / H_2O	21.94	3.08	0.0383
5	Na_2CO_3 / H_2O	23.50	2.94	0.0342
6	$MgSO_4 / H_2O$	26.30	2.97	0.0148
7	$CaCl_2 / H_2O$	44.83	0.92	–0.0073*

* $CaCl_2$ solutions due to their hygroscopic character absorbed water from the environment



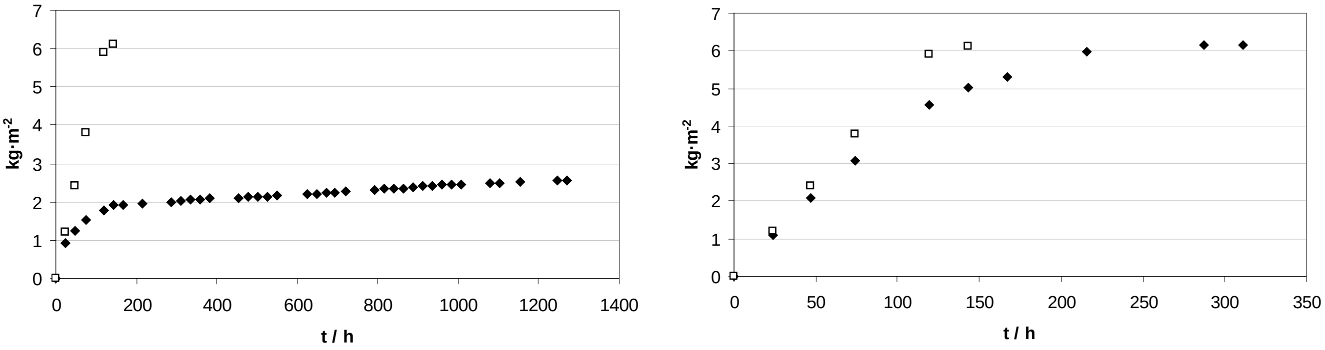
(a) ◆ NaCl □ H_2O

(b) ◆ Na_2CO_3 □ H_2O



(c) ◆ $NaHCO_3$ □ H_2O

(d) ◆ $CaCl_2$ □ H_2O



(e) ◆ $MgSO_4$ □ H_2O

(f) ◆ Na_2SO_4 □ H_2O

Fig. 10. Evaporation rates of saturated salt solutions.

$NaCl$ $NaHCO_3$ Na_2CO_3

Na_2SO_4 $MgSO_4$ $CaCl_2$

Fig. 11. Saturated salt solutions crystallized.

In Fig. 11, crystallization of salt saturated solutions is shown. Sodium chloride, sodium hydrogen carbonate and sodium sulphated were dried completely, whereas sodium carbonate, sodium sulphate and magnesium sulphate crystallized with occlused drops of water between crystals.

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