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DETERMINING THE RATE OF CRYSTALLIZATION OF SODIUM CHLORIDE BY EVAPORATION OF SEAWATER



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Abstract

Seawater was collected from the Atlantic Ocean and boiled off bit by bit with time. The results were curve fitted with different models to reveal the behavior of salt crystallization from seawater. The results corresponded to normal forced crystallization. It also showed that crystallization cannot continue forever for a particular amount of seawater or as more saline solution is continuously added. At a steady temperature of 89 °C, 342.5g of NaCl crystallized in 1000mins with a peak rate of 1.956g/min in 103.3mins and a total of 4500g of evaporated water.

INTRODUCTION

Seawater contains a variety of salts, and when evaporated, these solids are left behind. Layers of salt occur naturally in the geologic record, comprising an abundant source of salt for human consumption worldwide. Today, some salt deposits are land derived as when salty water seeps from rock, evaporates and leaves a salty residue. Human beings have been aware of deposit of rock salt for centuries, and when salt was still quite rare, wars were sometimes waged over the control of such deposits, because salt is so critical to many human activities¹. Salt was controlled by governments and taxed as far back as 20th century in China². By the middle ages, caravans consisting as many as forty thousand camels traversed four hundred miles of the Sahara barring salt, sometimes trading it for slaves while other communities enriched themselves by trading salt and salted meats in the form of “trade by barter” for wine and other luxuries. Crystallization which is one of the most pristine unit processes has been thoroughly studied in more recent times by chemical industries so as to acquire more

knowledge on the dynamics of crystallization. Crystallization processes used in more recent times were into pigment manufacturing and sucrose production. Sometimes, these substances were produced by crystallizing the solutes of some more or less natural brine. This unit operation is now used in many industries where plenty of the products are very important as in the manufacture of drugs, sugar production, urea etc^{2,3}.

The aims of this work include to determine the crystallization rate of sodium chloride and evaporation of water from seawater and to establish model(s) of the rate of crystallization of sodium chloride and evaporation of water from seawater. Since the seas and oceans which are presently inexhaustible sources of sodium chloride are in abundance, this work will be a guide for any individual who wants to venture into its production from seawater. By the determination of the rate of formation of sodium chloride crystals and the establishment of the model which will tell the feasibility and profitability of sodium chloride production from seawater, the rate of crystallization can be easily predicted.

The scope of the project is limited to the determination of the rate of crystallization of sodium chloride and evaporation of seawater with the development of the sodium chloride crystallization model only.

An endorheic basin is a close drainage basin that retains water and allows no outflow to other bodies of water such as rivers or oceans. Normally, water that has occurred in a drainage basin eventually flow out through rivers or stream on earth's surface or by underground diffusion through permeable rock, ultimately ending up in the oceans. However, in an endorheic basin, rain (or other precipitations) that fall within it does not flow out but may only leave the drainage system by evaporation and seepage. The bottom of such a basin is typically occupied by a salt lake or salt pan. Endorheic basins are also called internal drainage systems [4]. Endorheic regions, in contrast to exorheic regions which flow to the ocean in geologically defined patterns, are closed by hydrologic systems. Their surface waters drain to inland terminal locations where the water evaporates or seeps into the ground, having no access to discharge into the sea. Endorheic water

bodies include some of the largest lakes in the world, such as Aral Sea and the Caspian Sea, the world's largest saline body of water cut off from the ocean^{4,5}.

Endortheic lakes (terminal or sink lakes) are usually in the interior of a body mass, far from an ocean. Their watersheds are often confined by natural geologic land formation such as a mountain range, cutting off water access to the ocean. The inland water flows into dry watersheds where the water evaporates, leaving a high concentration of minerals and other inflow erosion products. Over time this input of erosion product can cause endorheic lakes to become relatively saline (a salt lake). Since the main outflow pathways of this lakes are chiefly through evaporation and seepage, endorheic lakes are usually more sensitive to environmental pollutant inputs than water bodies that have access to oceans. An example of an endorheic lake is the Dead Sea⁴.

Australia has the highest percentage of endorheic regions at 21 percent while North America has the least at 5 percent. Approximately 18 percent of the earth land drains to endorheic lakes or seas, the

largest of these land areas being the interior of Asia⁵. Minerals leached to the surrounding rocks are deposited in the basin, and left behind when the water evaporates. Thus endorheic basins often contain extensive salt pans (also called salt flats, salt lakes, alkali flats, dry lake beds). These areas tend to be large, flat hardened surfaces and are sometimes used for aviation runways or land speed record attempts, because of their extensive areas of perfectly level terrain⁶. The Dead Sea whose water is nine times saltier than any of the oceans contains pillars of salt in it and has a salinity of 24%. It is so salty for living organism to live in. The Red Sea follows with a salinity of 4.0% and the Mediterranean Sea with a salinity of 3.8%. The lowest salinity is found in the upper reaches of the Baltic Sea which is 0.5% but most have a salinity of 3.5%. The saltiest ocean is the Atlantic Ocean⁷.

NUCLEATION

Crystal nucleation is the formation of an ordered solid phase from a liquid or amorphous phase. Nucleation sets the character of the crystallization process and it is therefore, the most critical component

in relating crystallizer design and operation. Total nucleation is the sum effects of two categories of nucleation; the primary nucleation (in the absence of crystal) and the secondary nucleation (in the presence of crystals)⁸. Before crystals can develop, there must exist in the solution a number of minute solid bodies, embryos, nuclei or seeds that acts as centers of crystallization. Nucleation may occur spontaneously or induced artificially. It can often be induced by agitation, mechanical shock, friction, and extreme pressures within solutions and melts^{9, 10}. Considering the energy involved in solid-phase formation and creation of the surface of an arbitrary spherical crystal of radius, r in a supersaturated fluid gives¹¹

$$\Delta G = 4\pi r^2\sigma + (4\pi/3) r^3 \Delta G_v \dots\dots\dots (1)$$

Where ΔG is the overall excess free energy associated with the formation of the crystalline body; σ is the interfacial tension between the crystal and its surrounding supersaturated fluid, and ΔG_v is the free energy change per unit volume associated with the phase change. The rate of nucleation is given in the form of an Arrhenius reaction rate equation^{11, 12}:

$$\eta = \frac{F \exp - 16\pi \sigma^3 v^2}{3k^3 T^3 (\ln S)^2} \dots\dots\dots (2)$$

Primary nucleation (both homogeneous and heterogeneous) has been modeled with the following¹³.

$$B = dN/dt = k_n (C - C^*)^n \dots\dots\dots (3)$$

Equation (3) equates the primary nucleation rate, B, to the super saturation

$$\Delta C = (C - C^*).$$

The following model is often used for secondary nucleation [13, 14],

$$B = dN/dt = K_1 M_T^j (C - C^*)^b \dots\dots\dots (4)$$

Crystal Growth

As soon as the stable nuclei, i.e. particles larger than the critical size, have been formed in a super saturated or super cooled system, they begin to grow into crystals of visible size. Once this smack crystal, the nucleus, forms, it acts as a convergence point (if unstable due to super saturation) for molecules of solid touching or adjacent to the crystal so that it increases its own dimension in most effective and common method for nucleation¹⁵.

Effect of Crystal Size

Experimental evidence shows that crystal growth rates are particles size dependent, possibly because the size depends on the surface deposition kinetics, and different crystals of the same size can also have different growth rates because of differences in surface structure or perfection. Also, small crystals of many substances grow much more slowly than larger crystals, and some do not grow at all [16]. Some impurities can suppress growth entirely; some may enhance growth while others may exert a highly selective effect, acting on only certain crystallographic faces and thus, modifying the crystal habit. Any substance other than the material being crystallized can be considered an impurity^{14, 15}.

Growth – Nucleation Interaction

Crystal nucleation and growth in a crystallizer cannot be considered independently because they interact with one another and with other system parameters in a complex manner. For a complete description of the crystal size distribution of the product in a continuously operated crystallizer, both the nucleation

and the growth process must be quantified and the laws of conservation of mass, energy and crystal population^{8,17}.

METHODOLOGY

The apparatus used in this work are stop watch, weighing balance, gas cylinder, wire gauze, thermometer, beaker, measuring cylinder, and sea water sample.

PROCEDURE

This experiment was carried out in the Industrial Chemistry laboratory of the Federal University of Technology, Owerri, Nigeria. The weight of an empty dry beaker, W_b , was obtained using a weighing balance. The seawater (27°C) sample was collected with a measuring cylinder and weighed. The weight of the beaker and seawater was $W_b + W_s$. The solution of seawater was evaporated with a constant heat supply using flame from a gas cylinder at an evaporation time, t . The crystal was weighed, and, evaporating/crystallizing time noted, using the stop watch. The time (t_c) it takes the crystal to cool to room temperature was, also recorded. The above procedure was carried out nine times with increasing volume of seawater each time,

and, constant heat supply. The weight of beaker, W_b , weight of solution W_s , weight of beaker and crystal $W_b + W_c$, weight of crystal, W_c , and evaporation time t , with crystal cooling time, t_c , were obtained for each of the runs.

RESULTS

The result obtained from the experiment is shown in Table 1.

DISCUSSION

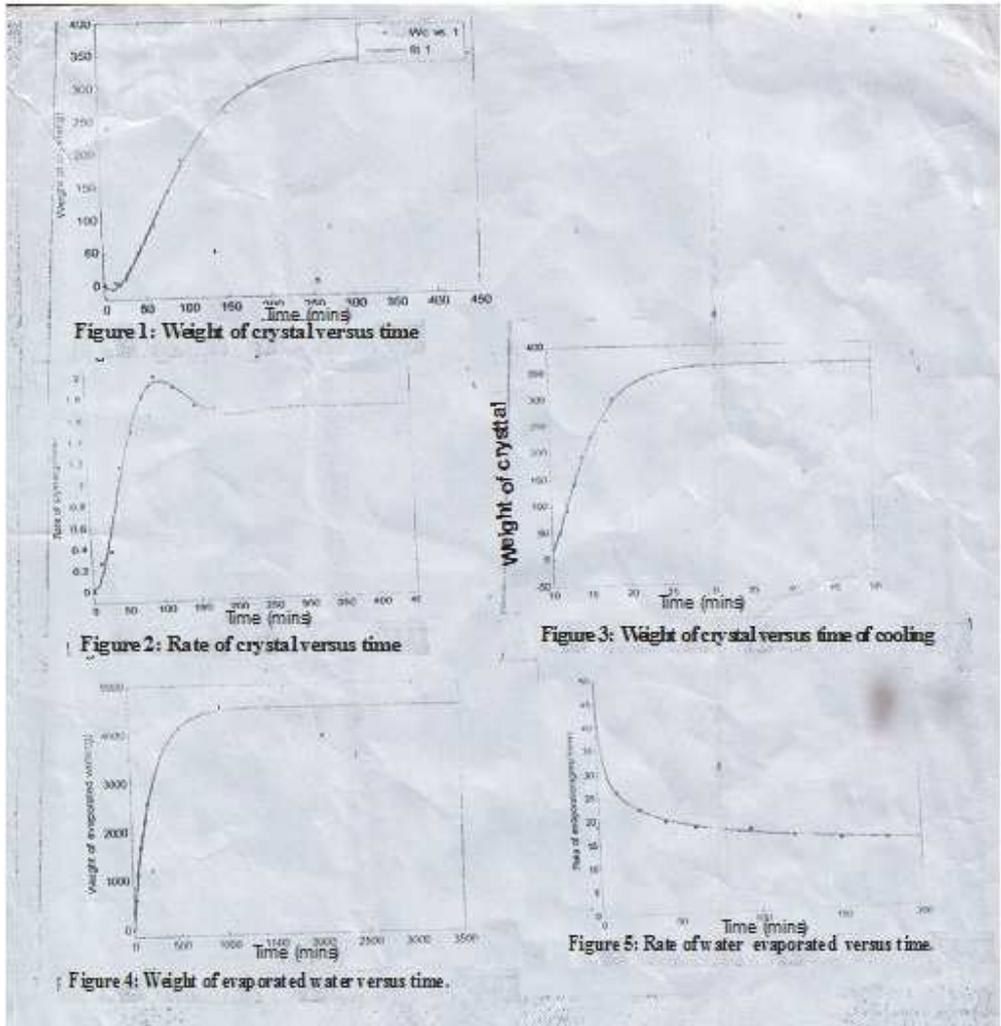
In Figure 1, the weight of crystal continues to increase with time as more solution was poured but not indefinitely. It gave an ultimate value of crystal of 324.46 grams at 1000 mins. The R-squared is 99.70%. In Figure 2, when rate of crystal formation was plotted against time, it gave a peak at 103.3 mins with a peak value of 1.956 g/min and later settled at an ultimate rate of 1.676g/min at 770mins. The R-squared is 98.78%. However, in Figure 3, the weight of crystal against time followed the sigmoid profile with ultimate crystal yield of 362.86 grams at 599 mins. The R-squared is 99.47%. From Figure 4, the weight of evaporated water continues to increase with time up to an ultimate value of 4,500

grams at 1000 minutes when the crystals have completely formed and all the water evaporated. The R-squared is 99.83%. But when the rate of these cooling crystals were plotted against time, the profile in Figure 5 was obtained, which showed a reality curve of cooling with R-squared of 99.16%.

CONCLUSION

Seawater was collected from the Atlantic Ocean and boiled off bit by bit with time. The results, put in scatter diagrams, were curve fitted with different models to reveal the behaviors of salt crystallization from seawater. The results showed that they behave normal as forced crystallization

would. It also showed that crystallization cannot continue forever for a particular amount of seawater, or, as more saline solution is continuously added during crystallization. At a steady temperature of 89°C, 342.5 g of NaCl crystallized in 1000 min with a peak rate of 1.956 g/min in 103 min and a total of 4500g of evaporated water. Salt production from seawater should be taken up as the primary source of salt, since it is medicinally better than salts from other sources. In the production of NaCl from seawater, provisions should be made for the removal of the impurities, from the crystal.



The curve fitting of the data are shown in Figures 1 to 5 and, Tables 2 to 6 respectively.

Table 1
Experimental Results

S/No	Weight of Beaker W_b (g)	Weight of Solution + Beaker $(W_b + W_s)$ (g)	Weight of Solution W_s (g)	Weight of Evaporated Water W_e (g)	Weight of Crystal W_c (g)	Time of Evaporation and Crystallization t (mins)	Rate of Crystallization W_c/t (g/min)	Rate of Evaporation (W_e/t) (g/min)	Time of Cooling t_c (mins)
1	590	933.5	343.5	340	3.5	13	0.27	26.15	9
2	590	1200	610	600	10	37	0.37	22.22	10
3	590	1490	900	850	50	43	1.16	19.78	11
4	590	1790	1200	1110	90	61	1.48	18.20	12
5	590	2120	1530	1390	140	78	1.79	17.82	13
6	590	2450	1860	1670	190	95	2.00	17.58	14
7	590	2750	2160	1930	230	122	1.89	15.82	15
8	590	3100	2510	2250	260	151	1.72	14.90	17
9	590	3400	2890	2590	300	179	1.68	14.47	18

Table 2
Coef. And Goodness of Fit for Fig. 1: $A*(1+b*x)*exp(-c*x)$

Coefs. (with 95% Confidence Bounds)		Goodness of Fit	
A:	= 342.5 (307.4, 377.5)	SSE:	= 348.6
B:	= 0.02482 (0.01758, 0.03205)	R ² :	= 0.997
C:	= 0.02055 (0.01694, 0.02416)	R ² -Adjusted:	= 0.9961
U: f(1000)	= 342.457	RMSE:	= 7.057

Table 3
Coef. And Goodness of Fit for Fig. 2: $A*(1-B*exp(-b*x))*Sin(c*x + D)$

Coefs. (with 95% Confidence Bounds)		Goodness of Fit	
A:	= 1.675 (1.469, 1.881)	SSE:	= 0.06152
B:	= 1.144 (0.7356, 1.552)	R ² :	= 0.9878
D:	= 1.032 (0.3447, 1.719)	R ² -Adjusted:	= 0.978
b:	= 0.01739 (0.003148, 0.03163)	RMSE:	= 0.1109
c:	= 0.03092 (0.02191, 0.03992)		
tpk:f(103.3)	= 1.95613		
U: f(770)	= 1.67519		

Table 4

Coef. And Goodness of Fit for Fig. 3: $k_p (1 - (1 + A^* ((x-9)^* \exp(-A^* (x-9)))) + b$

Coefs. (with 95% Confidence Bounds)			Goodness of Fit	
A:	=	0.425 (0.2729, 0.4121)	SSE:	= 510.5
Kp:	=	366.2 (316.7, 415.7)	R ²	= 0.9947
b:	=	-3.369 (-19.53, 12.79)	R ² -Adjusted:	= 0.993
U: f (59)	=	362.86	RMSE:	= 9.224

Table 5

Coef. And Goodness of Fit for Fig. 4: $A^*(1 - b^* \exp(-c^*x))$

Coefs. (with 95% Confidence Bounds)			Goodness of Fit	
A:	=	4,519 (3536, 5503)	SSE:	= 1.069e + 004
b:	=	0.9901 (0.9758, 1.004)	R ²	= 0.9983
c:	=	0.004598 (0.00313, 0.006067)	R ² -Adjusted:	= 0.9979
U: f (1000)	=	4500	RMSE:	= 39.08

Table 6

Coef. And Goodness of Fit for Fig. 5 $a^*x^b + c$

Coefs. (with 95% Confidence Bounds)			Goodness of Fit	
a:	=	46.7 (34.54, 58.87)	SSE:	= 0.9407
b:	=	-0.02067 (-0.4388, 0.02543)	R ²	= 0.9916
c:	=	-1.408 (-25.07, 22.25)	R ² -Adjusted:	= 0.9888
			RMSE:	= 0.396

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