Analytics and Kinetics of Crystallization of Magnesium Sulphate from Sea Bittern, Through Supersaturation

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Experimental part of the studies consist of change in concentration of magnesium sulphate against time of its crystallization from sea bittern during chilling. The said data is represented by characteristic straight lines, the slopes(s) of which give the numerical value of kinetics of reaction (Kinetic constant) suggesting that the reaction is of zero order. It is observed that in case of normal bittern the kinetic constant is influenced by the % magnesium sulphate which in turn depends on quality of raw material/weather conditions. Nevertheless, in case of any treatment such as heating and reconstitution of sea bittern, the kinetics constant indicated to depend on the ratio of magnesium sulphate to magnesium chloride. Statistically, the data found to be normally distributed, consistent and free from systematic errors. The calculated values of (i) intercepts have been observed to be very close to actual values. In case of verification factor, the change in calculated values found to be +8% to -11% of ideal values. The theoretical portion comprises of comprehensive treatment of energy balance/overall energy balance equations(s), their transformation to different standard straight lines consisting of bivariates, namely concentration/temperature, concentration/time and temperature/time. Subsequent manipulated of the intercepts/slopes of the lines led to derive important relationships such as heat of crystallization and overall heat requirement of the process. Further, the significance of the parameters/terminology involved in the process, have also been appropriately elaborated. Furthermore, the relationship amongst the slopes of three combinations of variables has led to conceive a new term being called 'verification factor', which under ideal conditions should be unity and the departure from which would be the indication of different types of errors.

Key words: Sea bittern, Supersaturation, Verifaction factor.

Introduction

The present work mainly concerns with the kinetics of magnesium sulphate from sea bittern through chilling. However, it also deals with the comprehensive treatment of energy balance / overall energy balance equations, considering all the three combinations of variable, namely concentration / temperature, concentration / time and temperature / time.

i). The data regarding concentration of $Mg\,SO_4$ / time of crystallization, obtained from earlier work (Beg *et al* 1986,1989; Nayeemuddin *et al* 2000b) is presented through (Fig. 1a - 1d) and linear regression of the said plots comprising (a) slopes in respective cases (b) intercept that corresponds to initial concentration alongwith its actual values determined analytically (c) verification factors have been appended in (Tables 1a -1d), whereas (d) the statistical data in respect of slopes and verification factors are shown in the Table 2.

ii). Comprehensive treatment of energy balance/over-all energy balance equations, and their treatment/transformations to the three bivariate alongwith detailed manipulation of the respective intercepts/slopes are discussed in the following paragraphs.

Mathematical formulation of energy balance/Overall energy balance equations. During low temperature crystallization (ignoring the radiation and vaporization losses) total heat to be removed from a batch crystallizer may be given by the following equation (Perry 1950):

$$Q = m\,\overline{C}_p\,(t_i - t_f) + mH_c\,(C_i - C_f) \quad \text{......................................}(1)$$

The heat that could be removed(during crystallization through cooling) from any system by external means may be estimated by the following relationship:

$$Q' = U_i A_i \Delta t_{ave}\,(\theta_b) \quad \text{...}(2)$$

When the thermal equilibrium is attained, Q and Q' become identical, and thus we would have:

$$m\,\overline{C}_p\,(t_i - t_f) + mH_c\,(C_i - C_f) = U_i A_i \Delta t_{ave}\,(\theta_b) \quad \text{.................}(3)$$

The above equations (1) and (3) have been reported in terms of terminal conditions, whereas, in order to facilitate their further treatment as an analytical equation, it would be imperative to express the same in terms of variables involved, as given below:

$$m\,\overline{C}_p\,(t - t') + mH_c\,(C - C') = Q \quad \text{......................................}(4)$$

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$$m\bar{C}_p\,(t - t') + mH_c\,(C - C') = U_iA_i\Delta t_{ave}\,\theta \dots\dots\dots\dots\dots(5)$$

With a view to manipulate slopes/intercepts to arrive at useful relationships, it would be essential to transform above equations to standard straight line form. As for the energy balance equation (4), it already consists of two variables namely temperature and concentration which could be conveniently transformed to the desired form. Nevertheless, the overall energy balance equation (5), comprising three variables cannot as such be transformed to straight line unless reduced to bivariate form. This could be conveniently accomplished by taking either component, that is, sensible heat or heat released during crystallization as constant by expressing the basic relationship in terms of terminal conditions. Accordingly, treatment of the above equations has been effected as detailed in the following paragraphs.

Transformation to standard straight line. i) Concentration / Temperature: Energy balance equation (4) could be readily transformed to standard straight line, as shown below:

$$C = \left[\frac{-\bar{C}_p}{H_c}\right]t + \frac{Q/m + H_cC' + \bar{C}_p\,t'}{H_c}\dots\dots\dots\dots\dots(4a)$$

In the above equation;

$$\text{Slope} = m^{\circ}_{(c/t)} = \frac{-\bar{C}_p}{H_c} \text{ or } H_c = \frac{\bar{C}_p}{m^{\circ}_{(c/t)}}\dots\dots\dots\dots(4a\text{-}1)$$

Since intercept is represented by the initial concentration, therefore;

$$\text{Intercept } C_i = \frac{Q/m + H_cC' + \bar{C}_p\,t'}{H_c}\dots\dots\dots\dots(4a\text{-}2)$$

Putting the value Q/m from equation (4) and solving for H_c, we would have:

$$H_c = \frac{\bar{C}_p}{\dfrac{(C_i - C)}{t}}$$

Now assuming final temperature to be zero $^{\circ}$C, drop in temperature = $(0-t) = -\Delta t$ and the corresponding drop in concentration $(C_i - C) = \Delta C$.

$$\text{Therefore, } [H_c] = \frac{\bar{C}_p}{\Delta c/\Delta t} = \frac{\bar{C}_p}{m^{\circ}_{(c/t)}}\dots\dots\dots\dots(4a\text{-}3)$$

Thus manipulation of slope and intercept yielded the same relationship.

ii) Concentration / Time: Taking sensible heat of solution $[m\bar{C}_p(t_i - t_f)]$ to be constant, the equation (5) in bivariate form may be written as follows:

$$C = \left[\left(\frac{U_iA_i\Delta t_{ave}}{m\bar{C}_p}\right)\theta\right] + \left[\frac{mH_cC_f - m\bar{C}_p\,(t_i - t_f)}{mH_c}\right]\dots\dots(5a)$$

$$\text{Slope} = m^{\circ}_{(c/\theta)} = \left[\left(\frac{U_iA_i\Delta t_{ave}}{m\bar{C}_p}\right)\theta\right] \text{ or } U_i = m^{\circ}_{(c/\theta)}\left(\frac{m\bar{C}_p}{A_i\Delta t_{ave}}\right)\dots(5a\text{-}1)$$

Since, intercept in this situation is represented by initial crystallization temperature, therefore,

$$t_i = \frac{mH_cC_f - m\bar{C}_p\,(t_i - t_f)}{mH_c}\dots\dots\dots\dots\dots\dots(5a\text{-}2)$$

Taking $C' = C_f$, rearrangement of the above equation yield:

$$m\bar{C}_p\,(t_i - t_f) + mH_c\,(C_i - C_f)\dots\dots\dots\dots\dots(5a\text{-}3)$$

iii) Temperature/Time: Taking heat released due to crystallization as constant and expressing it in terminal conditions, that is; $[mH_c\,(C_i - C_f)]$ the equation (5) may be expressed in bivariate form as follows:

$$t = \frac{(U_iA_i\Delta t_{ave})\theta}{m\bar{C}_p} + \frac{m\bar{C}_p\,t' - mH_c\,(C_i - C_f)}{mH_c}\dots\dots(5b)$$

$$\text{Slope} = m^{\circ}_{(t/\theta)} = \left[\left(\frac{U_iA_i\Delta t_{ave}}{m\bar{C}_p}\right)\theta\right] \text{ or } U_i = m^{\circ}_{(t/\theta)}\left(\frac{m\bar{C}_p}{A_i\Delta t_{ave}}\right)\dots(5b\text{-}1)$$

Value of 'U_i' calculated from either of two the formulae (Eqs 5a-1 or 5b-1) is just half the actual value obtained from energy balance equation. It is most probable that erroneous relationship is obtained because of taking constant either of the two components, namely heat released during crystallization or sensible heat lost. However, a correct relationship for determining this parameter has already been derived and the numerical values calculated previously (Nayeemuddin *et al* 2000a).

Since, intercept in this situation is represented by initial crystallization temperature , 'C_i' therefore,

$$C_i = \frac{mH_cC_f - m\bar{C}_p\,(t_i - t_f)}{mH_c}\dots\dots\dots\dots\dots(5b\text{-}2)$$

Taking $t' = t_f$, rearrangement of the above equation yields:

$$m\bar{C}_p\,(t_i - t_f) + mH_c\,(C_i - C_f)\dots\dots\dots\dots\dots(5b\text{-}3)$$

Verification factor: It is worthnoting that the slopes of the three combinations of bivariates are related through following simple relationship as given below:

$$\left[\frac{\Delta C}{\Delta\theta} = \frac{\Delta C}{\Delta t} \times \frac{\Delta t}{\Delta\theta}\right]\dots\dots\dots\dots\dots\dots\dots(6)$$

or

$$[m^{\circ}_{(c/\theta)}] = [m^{\circ}_{(c/t)}] \, [m^{\circ}_{(c/\theta)}] ....(6a)$$

According to the above equation, the slope of concentration/ time plot, should be equal to the product of remaining two slopes, namely concentration/ temperature and temperature / time. The L.H.S of the above equation (6) is indeed actual slope whereas the R.H.S., if designated as its calculated value, the ratio of the two, in ideal conditions should be unity. This ratio leads to a novel concept that may be called 'Verification Factor' of overall data as given below:

$$Vf = \frac{\text{Actual value of } m^{\circ}_{(c/\theta)}}{\text{Calculated valfue of } m^{\circ}_{(c/\theta)}} ....(6b)$$

The above relationship thus permits overall verification of the results of different sets of data collected during low temperature crystallization of a compound (salt).

However, because of various types of errors in measurements of physical parameters like concentration and temperature etc in actual practice, the two values often happen to be unequal and consequently the ratio shall not be unity

Materials and Methods

The raw material(s), consist of three types / quality of sea bittern. In summer, magnesium sulphate content of sea bittern is around 8% to 8.5% and the samples are used as such without any treatment are known as 'normal sea bittern'. However, during winter season the percentage of magnesium sulphate drops down to 5% to 6% which could enhanced by heating normal bittern and such samples are referred as 'heated sea bittern'. Still another type of samples are called 'lean bittern' comprising of the one from which magnesium sulphate has already been recovered by chilling and residual samples are solar evaporated to raise the percentage of magnesium sulphate. Yet another method known as reconstitution of sea bittern has been adopted in the present situation comprises of dissolving of magnesium sulphate in normal bittern around 50°C and filtering the resulting slurry.

For equipment stirrers of standard design (McCabe and Smith 1985) viz 6 curved or 3 straight blades were used at three different rpm levels namely 370, 218 and 165. As for the size of batches, the experiment mainly carried out with 25 litre capacity vessel complete with suitable stirring / cooling arrangement. Nevertheless in only one situation studies were carried out with 400 litre capacity chiller using normal bittern.

The method as described earlier (Beg *et al* 1989*;* Nayeemuddin and Mahmood 1991; Neyeemuddin *et al* 2000 a,b) consists of cooling an aliquot amount of different quality sea bittern in batch crystallizers / stirred tank vessels of varying designs/ sizes. As for data, it comprised of noting down the temperature of crystallizing slurry at different time intervals and simultaneously taking out samples for determination of concentration of active component $(MgSO_4)$ and other constituents (if so desired), through standard analytical techniques (Vogel 1961).

Results and Discussion

The data of each set of experiment (Fig 1a to 1d) is presented by characteristic straight lines which alongwith statistical results suggested the following:

a) Critical review of the (Fig 1a-1d) suggested that in each instance slope represents the kinetic constant thus suggesting that the reaction is of zero order. Preliminary examination of data (Tables 1a-1d) revealed that the slopes (or the kinetics constants) observed to be influenced by the initial concentration of active-component-magnesium sulphate which in turn depend on the quality of raw material. It maybe pointed out that in summer whence the sea bittern is characterized by higher magnesium sulphate content, (Beg *et al* 1989), the values of slopes were found also higher (Table 1c), whereas, in the winter the raw material gets depleted in magnesium sulphate content and the values of the parameter are also lower (Table 1a). However, due to any type treatment, although concentration of magnesium sulphate improves but in context with over all results (Tables 1a-1d) the slope no more remains proportional to the concentration of active component. When the problem is analyzed in the light of the salvation property of magnesium chloride, (Nayeemuddin *et al* 2002a) it is suggested that the parameter (slope) should be change of with the ratio of magnesium sulphate to magnesium chloride, and actual situation the idea was substantiated by the actual results (Tables 1b and 1d).

b) The data found to be consistent, and the calculated values of slopes (by linear regression) were very close to the corresponding graphical values.

c) The calculated values of initial concentration of active component given by intercept on ordinate lie within ± 5% of actual values. On the other hand, verification factor varies within the limits of + 8% to -11% of ideal values.

d) Statistical parameters are suggestive of normal distribution, absence of systematic error and tenability of error allowance in respect of data (Tables 1a to 1c).

Significance of parameters. i) Initial concentration / Crystallization temperature: Correct knowledge of these parameters is highly desirable for the estimation of other

variables. Dependable values for initial concentration could be conveniently determined analytically, however, alternatively (Nayeemuddin and Mahmood 1991) the values may also be estimated as intercept of linear regression of concentration/ time data which found to have errors around $\pm 5\%$ (Tables 2a to 2c). As for initial crystallization temperature, its measurement in batch crystallizers yields mislead results, because of the deposition of the layer of active component all along the cooling surface. Most probably, its dependable values could findout both (i) as intercept of linear regression of temperature/ time data (Nayeemuddin *et al* 2000 a,b) and (ii) through extrapolation of percent recovery / temperature plots to zero percent recovery *(*Beg *et al* 1989*)*.

ii*) Heat of crystallization*: In the scenarios of process of low temperature crystallization (POLTEC), heat of crystallization is of special significance. Unfortunately, as yet no direct relationship is at hand to estimate the variable parameter and on the top of it scant data is available in literature concerning this very important parameter. A simple and direct method is explained for the determination of this property (Perry 1950), without giving any formula; a simple relationship is also mentioned (Othermer 1965) according to which H_c or $\Delta H_c = -\Delta H_{sol}^{\infty} + \Delta H_{dil}$, where $-\Delta H_{sol}^{\infty}$ has been recorded for several compounds (Perry 1950; Othemer 1965) whereas, data is lacking in respect of ΔH_{dil} which being in smaller quantity is usually ignored in practical situations. Therefore, after
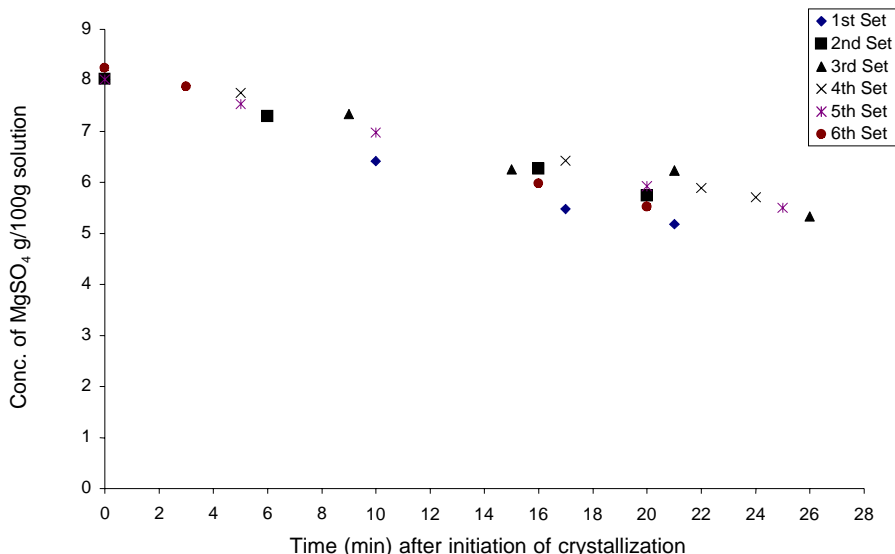

Fig 1a. Different sets of experiments on crystallization of magnesium sulphate during chilling of sea bittern (400 liter normal bittern)
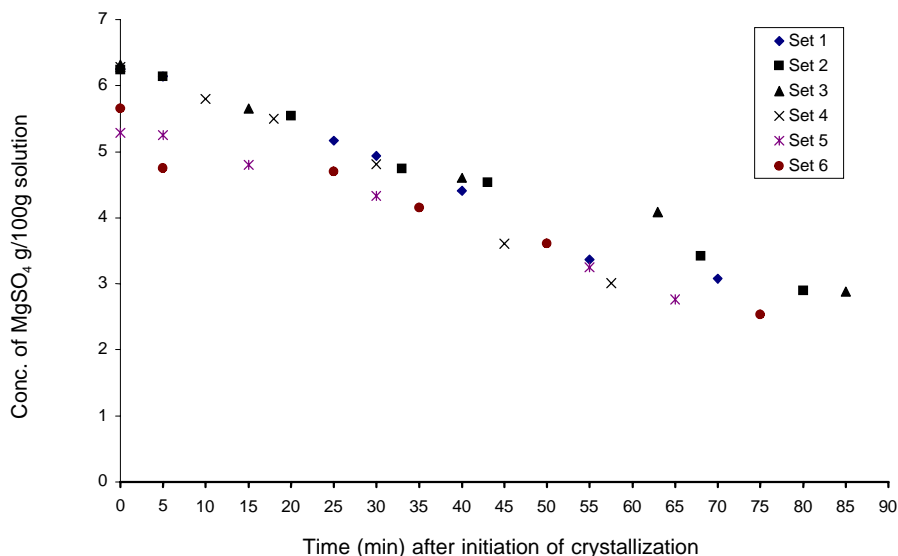

Fig 1b. Different sets of experiments on crystallization of magnesium sulphate during chilling of sea bittern (25 liter normal bittern)

dropping ΔH_{dil}, relationship reduces to $\Delta H_c \approx \Delta H_{sol}^{\infty}$, which evidently is based on approximation. The distinctive feature of present studies is that a very simple formula for estimating this parameter is derived from the manipulation of both slope and intercept of concentration / temperature plot obtained from the rearrangement of energy balance equation. In view of non availability of direct relationship and marked absence of pertinent data in respect of this important parameter, a precise

formula, in terms of already known and conveniently determinable quantities would be quite satisfactory.

iii) Identity of two heat components. The phenomenon of partioning of heat into two equal components – sensible heat lost by the liquid and heat released by crystallization-probably occurs in each globule (Nayeemuddin *et al* 2002 b)which in turn is facilitated by the dispersion of supersaturated layer in the main liquid bulk. Further
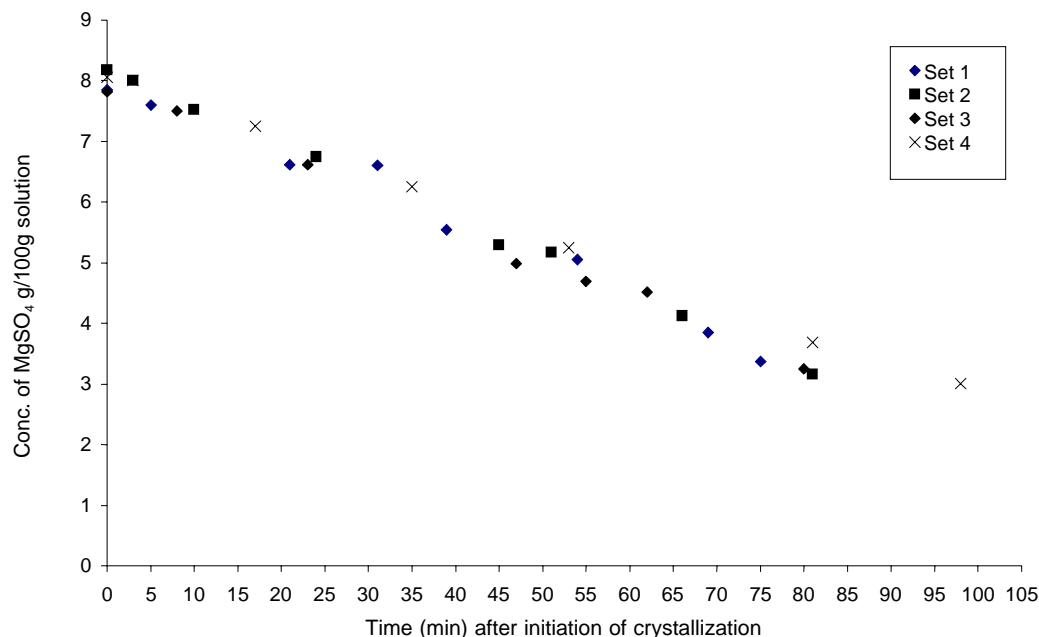

Fig 1c. Different sets of experiments on crystallization of magnesium sulphate during chilling of sea bittern (25 liter normal bittern)
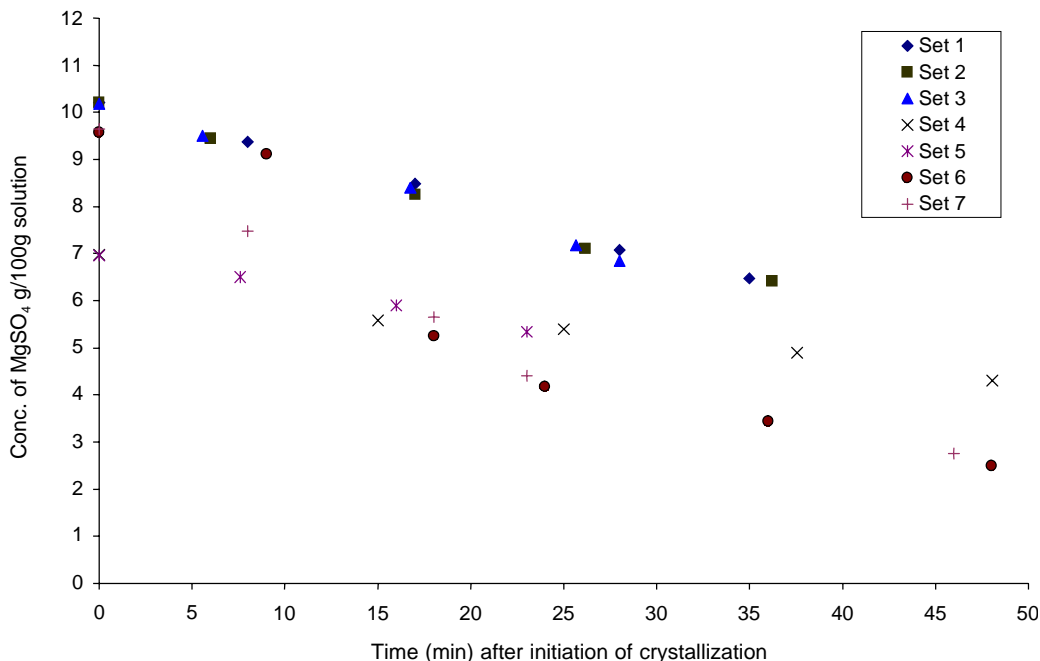

Fig 1c. Different sets of experiments on crystallization of magnesium sulphate during chilling of sea bittern (using normal/treated samples)

Table 1a

Regression and other results, in respect of actual slope and verification factors for various batches.
25 liters normal bittern batches(144 rpm)

Initial concentration $MgSO_4$ (%)		Conc/time slope ($m°_{c/\theta}$)		Verification factor	Ratio of
Actual	Caltd.	*Ave (actual)	Caltd.	*V_f	$MgSO_4$/ $MgCl_2$
6.25	6.35	0.047	0.052	0.918	0.265
6.24	6.33	0.0435	0.0395	1.0760	0.270
6.34	6.24	0.040	0.041	0.997	0.271
6.14	6.23	0.0475	0.472	1.005	0.255
5.29	5.40	0.041	0.0458	0.895	0.223
5.67	5.67	0.0425	0.04203	1.011	0.232

Table 1b

Regression and other results, in respect of actual slope and verification factors for various batches.
25 liters heated bittern batches(144 rpm)

Initial concentration $MgSO_4$ (%)		Conc/time slope ($m°_{c/\theta}$)		Verification factor	Ratio of
Actual	Caltd.	*Ave (actual)	Caltd.	*V_f	$MgSO_4$/ $MgCl_2$
7.85	7.85	0.0613	0.0672	0.897	0.398
7.85	7.9	0.0613	0.06225	0.980	0.427
8.18	8.18	0.0615	0.0635	0.980	0.492
8.06	8.15	0.056	0.0529	1.059	0.374
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Table 1c

Regression and other results, in respect of actual slope and verification factors for various batches.
400 liters normal bittern batches(144 rpm)

Initial concentration $MgSO_4$ (%)		Conc/time slope ($m°_{c/\theta}$)		Verification factor	Ratio of
Actual	Caltd.	*Ave (actual)	Caltd.	*V_f	$MgSO_4$/ $MgCl_2$
8.02	7.96	0.136	0.1286	1.057	0.471
8.03	7.99	0.116	0.1149	1.009	0.529
8.03	8.11	0.111	0.125	0.891	0.534
8.02	8.11	0.114	0.1218	0.936	0.529
8.02	8.00	0.108	0.1225	0.881	0.471
7.88	8.23	0.142	0.1326	1.0695	0.549

Table 1d

Regression and other results, in respect of actual slope and verification factors for various batches
using normal/treated bittern samples

RPM	Type of bittern	Initial conc. of $MgSO_4$ (%)		Conc/time slope ($m°_{c/\theta}$)		Verification factory	Ratio of $MgSO_4$ /$MgCl_2$
		Actual	Caltd.	*Ave (actual)	Caltd.	*V_f	
370	Normal	10.2	10.28	0.116	0.1262	0.919	0.59
370	Normal	10.2	10.19	0.121	0.1242	0.974	0.59
370	Normal	10.18	10.21	0.12	0.1239	0.968	0.50
218	Lean	6.98	6.6	0.0482	0.0492	0.98	0.355
218	Lean	6.96	6.73	0.0495	0.0494	1.00	0.354
165	Reconstituted	9.58	9.58	0.228	0.2551	0.894	0.6
165	Reconstituted	6.38	6.38	0.0805	0.079	0.019	--

The statistical perimeters of physical quantities marked (*) are place in Table 2.

Table 2
Statistical parameters

Type of raw material / batch size	25 Liters normal sea bittern		25 Liters heated sea bittern		400 Liters normal sea bittern	
Statistical parameters	Actual (Ave) slope ($m°_{c/\theta}$)	Verification factor V_f	Actual (Ave) slope ($m°_{c/\theta}$)	Verification factor V_f	Actual (Ave) slope ($m°_{c/\theta}$)	Verification factor V_f
Number of trials (n)	6	6	4	4	6	6
Degrees of freedom (d.f)	5	5	3	3	5	5
Measure of central tendency:						
Average / mean ($\bar{X}$)	0.0434	0.984	0.0597	0.976	0.121	0.974
Median	0.0425	1.0005	0.0605	0.975	0.115	0.967
Measure of dispersion:						
Range	0.007	0.22	0.060	0.162	0.034	0.19
Standard deviation (S)	2.85×10^{-3}	0.0607	2.178×10^{-3}	0.0574	0.1297	0.0755
Variance (S^2)	8.12×10^{-6}	3.68×10^{-3}	4.744×10^{-6}	3.3×10^{-3}	0.01681	5.702×10^{-3}
Coefficient of variation [$S/\bar{X}$]	0.0656	0.0617	0.0365	0.0588	1.07	0.0775
Limits of standard deviation:						
$\bar{X} + 2S$	0.0491	1.105	0.0640	1.091	0.3804	1.125
$\bar{X} - 2S$	0.0377	0.8626	0.0553	0.861	- 0.138	0.823
Limits of standard error of mean for 95% confidence level:						
$\bar{X} + t\sqrt{s}/n$	0.0994	1.242	0.1339	1.3569	0.4988	1.2622
$\bar{X} - t\sqrt{s}/n$	-0.0126	0.725	0.0145	0.5951	0.2568	0.685

considerations reveal that the linearity of bivariate systems, (i.e, concentration/ temperature and temperature/time) and the identity of two heat components are interrelated and reciprocate each other. If one is true, the other should be follow as a logical consequence. The phenomenon has provided basis for the law of low temperature crystallization which clearly describes the analytics of the process (Nayeemuddin *et al* 2000b).The deduction of the same relationship from the intercepts of both temperature / time and concentration/ time further validates its use.

Conclusions

Numerical and statistical data has revealed that.
a) The reaction namely, crystallization of magnesium sulphate from sea bittern through cooling, found to be of zero order. The slope of concentration against time represents the kinetic constant which under normal conditions depends on the concentration of magnesium sulphate, that in turn is found to be influenced by seasonal variations. Further, incase of any treatment of sea bittern, the overall data of slopes found to be proportional to the ratio of magnesium sulphate/magnesium chloride.

b) i) Statistically, both primary and derived data is consistent and distributed normally. ii) Manipulation of intercepts/ slopes of energy / over all energy balance equations in all situations yielded relationships for (a) heat of crystallization and (b) the relationship comprising of two components namely sensible heat and heat released due to crystallization.

Nomenclature

A_i = Area of contact m^2.

C = Concentration variable.

C_i = Initial concentration of active component
$$= \frac{\text{Kg of magnesium sulphate}}{100\,\text{Kg solution}}$$

C_f = Final concentration of active component
$$= \frac{\text{Kg of magnesium sulphate}}{100\,\text{Kg solution}}$$

C ' = Any concentration during chilling.

$\bar{C}_p$ = Average specific heat of the liquid bulk $\dfrac{K.J}{Kg\,°C}$

ΔC = Drop in concentration during chilling ($C_i - C_f$)

H_c or ΔH_c = Heat of crystallization
$$= \frac{K.J}{\text{Kg magnesium sulphate crystallized}}$$

ΔH_{sol}^{∞} = Heats of solution (of solute) at infinite dilution

$$= \frac{K.J}{Kg \text{ magnesium sulphate crystallized}}$$

ΔH_{dil} = Heat of dilution = $\dfrac{K.J}{Kg \text{ magnesium sulphate crystallized}}$

Q = Rate of heat removal from the system   K.J/hr or K.J/min

Q' = Total heat to be removed from a batch

$\bar{Q}$ = Rated heat capacity of chilling unit in K.J/hr or K.J/min.

$m^{\circ}_{(c/\theta)}$ = Slope of concentration-time plots [$\Delta C/\Delta\theta$], drop in percent concentration per min.

$m^{\circ}_{(t/\theta)}$ = Slope of temperature - time plots [$\Delta t/\Delta\theta$] - drop in temperature $^{\circ}$C per min.

$m^{\circ}_{(c/t)}$ = Slope of concentration -temperature plots [$\Delta C/\Delta t$] - drop in percent concentration per $^{\circ}$C

m = Mass of solution Kg.

t = Temperature variable.

$\Delta t_{(ave)}$ = Overall average temperature gradient.

t_i = Initial temperature $^{\circ}$C.

t_f = Final temperature $^{\circ}$C.

t' = Any temperature during chilling.

Δt = (t_i - t_f) temperature drop during chilling $^{\circ}$C.

U_i = Average, overall heat transfer co-efficient based on inside area of reactor KJ/min m $^{\circ}$C.

V_f = Verification Factor

θ = Time variable- also represents duration of chilling.

θ_b = Time of cooling of a batch, h or min

References

Beg M A A, Nayeemuddin, Mahmood S N, Khan W B, Iqbal Z 1989 Production of marine chemicals in Pakistan, Part II. Studies on manufacture of chemicals from seawater bittern. *Pak J Sci Ind Res* **29**(5)389 - 396.

Beg M A A, Mahmood S N, Nayeemuddin 1989 Production of marine chemicals in Pakistan, part III. Studies on recovery of magnesium sulphate by chilling. *Pak J Sci Ind Res* **32**(2) 126 - 132.

Nayeemuddin, Mahmood S N 1991, Statistical analysis of results of chilling of sea bittern. *Pak J Sci Ind Res* **34** (2/3)106 - 110.

Nayeemuddin, Mahmood S N 2000a Derivation of relationships and estimation of thermal/thermodynamic parameters from crystallization of sea bittern. *Pak J Sci Ind Res* **43**(3)155 - 161.

Nayeemuddin, Mahmood S N, Farzana Azmat, Mohsin Ali 2000b Effects of agitation and bittern quality on recovery of magnesium sulphate. *Pak J Sci Ind Res* **43**(5)275 - 282.

Nayeemuddin, Mahmood S N, Farzana Azmat 2002a Solvation property effect on crystallization through cooling. *Pak J Sci Ind Res* **45**(1) 27 - 28.

Nayeemuddin, Mahmood S N, Farzana Azmat 2002b Mechanics of low temperature crystallization. *Pak J Sci Ind Res* **45**(4) 237 - 242.

Othermer K 1965 *Crystallization Crystal Yield and Heat Effects*. Mc Grew Hill publications **6**ed, pp 509-510.

Perry J H 1950 *Theory of Crystallization Heat Effects/ Heat of Crystallization* Mc Grew Hill, New York, USA, p 1052.

Vogel A I 1961 *Quantitative Inorganic Analysis. Analysis of Magnesium and Sulphate Ion.* London, England, 3rd ed, p 434.