Derivation of Relationships and Estimation of Thermal/Thermodynamic Parameters from Crystallization Data of Bittern

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During low temperature crystallization studies of magnesium sulphate from sea bittern, the time temperature plots have been found to be linear. This uncommon phenomenon in unsteady state operation has been explained through modified energy balance equation in terms of rate of overall heat changes associated with crystallization, characteristic properties of raw material, overall averages temperature drop and system constants. While explaining the linearity of the plots, the authors have not only deduced a law concerning low temperature crystallization and the conditions in which it is operative but also derived relationships for estimating heat of crystallization, heat transfer co-efficient and heat utilization co-efficient. It is observed that the composition of raw material (bittern) has a direct effect on specific heat and slope of temperature-time relationship, whereas heat of crystallization is governed by the type of sample used heated or normal.The numerical results have also established that it is rather the design of the cooling unit (chiller) which governs its efficiency whereas increase in chilling capacity enhances the output only (heat transfer co-efficient). Further, the statistical analysis of the numerical data revealed that in different situations it is not only normally distributed but also found substantiating the conclusions drawn from the observed data.

Key words: Low temperature crystallization, Heat transfer co-efficient, Sea bittern, Statistical analysis.

Introduction

An integrated process was described earlier for obtaining different chemicals from sea bittern (Beg *et al* 1986). Out of the several operational/processing steps, the one studied comprehensively was concerning low temperature crystallization of magnesium sulphate in chillers of different capacities and designs (Beg *et al* 1989). The parameters studied exhaustively comprised, drop in concentration of magnesium sulphate with respect to decrease in temperature at different time intervals along with change in the composition of other constituents namely chlorides of magnesium, sodium and potassium. Nevertheless, the work published earlier was related only to the temperature-concentration studies of magnesium sulphate during chilling and the detailed statistical analysis of the generated data (Beg *et al* 1989; Nayeemuddin and Mahmood 1991). The said efforts were also aimed at filling in the gap that existed in the work of previous researchers (Nikolaev and Frad kina 1946; Sugionohara 1953; Ilinskii *et al* 1956; Gadre *et al* 1958; Srinivasan 1958-59; Dixit 1960; Gadre *et al* 1962; Laddha 1965; Scherzerg *et al* 1985). The present investigation however, is an outcome of the investigations concerning the linearity of temperature-time plots which are ordinarily nonlinear for unsteady state batch operations

(Kern 1950). Simple mathematical treatment of energy balance equation, in conjunction with the linearity of relationships (Temperature time and concentration-temperature) led to the deduction of a law of low temperature crystallisation and evolving of other relationships for calculating parameters in terms of specific heat, a characteristic property of the raw material, system constants (namely mass of raw material, effective cooling area and the rated heat removal capacity of the chiller), performance parameters (namely overall average temperature drop between crystallizing slurry and evaporating refrigerant) and slopes of the said plots.

Mathematical formulation/derivation of relationship. Energy balance equation (16) in respect to low temperature crystallization, because of the involvement of time, has been suitably modified for the rate of enthalpy changes over a batch crystallizer. Hence, q the rate of heat removal (by external means) could be equated both sensible heat and heat of crystallization, while ignoring the radiation losses and latent heat of vaporization of solvent (water). Rate of energy balance equation may therefore, be represented as follows:

$$q = \frac{m}{(\theta_f - \theta_i)} \times \bar{C}p\,(t_i - t_f) + \frac{m}{(\theta_f - \theta_i)}\,(C_i - C_f) \times H_c \,\ldots\ldots\ldots (1)$$

The above equation may also be represented in general form in terms of the involved variables as follows:

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$$q = \frac{m\overline{C}p\,(t - t^1)}{\theta} + \frac{m\,(C - C^1) \times H_c}{\theta} \quad\quad \text{......................} \quad (2)$$

Equation 2, apparently appears to consist of three variables namely time, temperature and concentration. Slight cosiderations would reveal that the portion of eq. 2 namely $(C-C') \times H_c$ that represents heat changes with 100 kg of solution should be a constant quantity. In such situation during subsequent steps of treatment, the expression $(\Delta_c \times H_c)$ should be treated as single quantity, and hence should not be separated till the completion of the treatment, if any.

Therefore, eq 2 could be re-arranged as follows in terms of two variables namely time 'θ' and temperature 't' to represent a straight line.

In eq 2 intercept 'b' is represented by the denominator of temperature axis (y-axis) as given below:

$$b = \frac{\overline{Cp} \times t^1 - H_c\,(C-C^1)}{\overline{C}_p}$$

At the initiation of crystallization, 'b' represents initial temperature t_i, hence $C = C_i$

Thus we have: $t_i = b = \dfrac{\overline{C}_p\,t^1 - H_c\,(C_i-C^1)}{\overline{C}_p}$ which leads to the following relationship

$$H_c = \frac{\Delta t}{\Delta C} \times \overline{C}p = \frac{\overline{C}p}{\Delta C / \Delta t} = \frac{\overline{C}p}{m^\circ_{c\text{-}t}} \quad\quad \text{...................} \quad (4)$$

Re-arranging eq 4

$$\overline{C}_p \times \Delta t = |H_c| \times \Delta C \quad\quad \text{............................} \quad (4.a)$$

$$m\overline{C}_p\,\Delta t = m\,|H_c| \times \Delta C \quad\quad \text{..........................} \quad (4.b)$$

Equation 4b leads to conclusion that in low temperature crystallization process, sensible heat lost by liquid is numerically equal to heat released during crystallization. On the other hand the basic energy balance equation tells that total heat changes associated with the process is the numerical sum of sensible heat lost by the liquid and heat released during crystallization.

Thus $Q = m\overline{C}_p\,\Delta t + mH_c\,\Delta C = m\overline{C}_p\,\Delta t + m\overline{C}_p\,\Delta =$
$$\hspace{3cm} 2\,m\overline{C}_p\,\Delta t \quad\quad \text{......................} \quad (4.c)$$

Thus eqs 4b and 4c lead to a law that may be called "law of low temperature crystallization," while the linearity of temperature-time concentration-temperature plots, and negligilibility of heat losses as radiation and solvent vaporization provides necessary conditionalities. The said law may be stated as follows:

If low temperature crystallization is taking place in such a fashion that the temperature drop is proportional to time differential (or rate of cooling is constant) and the drop in concentration of the active component in the mother liquor is proportional to temperature drop, the overall heat changes are equally partitioned into sensible heat and heat released due to crystallization; the condition being that there are no radiation and vaporization losses (of solvent). The rate of heat flow may be estimated as follows:

$$q = \frac{Q}{\Delta\theta} = 2m\overline{C}_p\,\frac{\Delta t}{\Delta\theta} = 2\,m\overline{C}_p\,m^\circ_{t\text{-}t} \quad\quad \text{...................} \quad (4.d)$$

The rate of heat removal 'q' may also be equated to the term $U_i A_i\,\Delta t_{ave}$ which enables to calculate heat transfer co-efficient. In the present conditions, overall average temperature drop may be calculated as follows (Bird *et al* 1960):

$$\Delta t_{ave} = \frac{\Delta t_i + \Delta_f}{2} = \frac{(t_i - t_s) + (t_f - t_s)}{2} = (t_{ave} - t_s) \quad \text{..........} \quad (4.e)$$

Another important physical quantity, which enables to compare the performance (efficiency) of different chillers on corresponding basis, may be termed as co-efficient of heat utilization. It is estimated as ratio of rate of heat removal from the system to the rated heat capacity of the chiller in consistent units and is given as follows:

$$\overline{C}_u = \frac{q}{\overline{q}} = \frac{2\,m\,\overline{C}_p \times m^\circ_{t\text{-}t}}{\overline{q}} \quad\quad \text{...........................} \quad (5)$$

Materials and Methods

The materials, methods, and sampling procedure were exactly the same as reported earlier (Beg *et al* 1989). The raw material consisted of normal heated sea bittern whose density ranged from 31 to 33° Be. Experiments were carried out in two chillers of different capacities and design, each complete with standard stirring and appropriate cooling arrangement. The cooling coils were fitted externally in small chiller, whereas in the large one, the coils were immersed in liquid.

The nomenclature adopted previously (Nayeemuddin and Mahmood 1991) was strictly adhered to namely (i) Block 'A' 25 litre experiments with normal bittern, (ii) Block 'B' 25 litre experiments with heated bittern and (iii) Block 'C' 400 litre experiments with normal bittern. The composition of raw material (bittern) was uniform in Block 'C' because it was transported in big tanker in a single lot, whereas abrupt variations occurred in its composition (Block 'A' & 'B') mainly because the samples were procured on several occasions in small cans of 40 litre capacity. Further, 400 litre experiments were arranged in summer when bittern is noted for high concentration of magnesium sulphate ((Beg *et al* 1989) and 25 litre experiments were carried out in winter when it is characterized by the lower concentration of the said salt. Therefore, in order to enhance the percentage magnesium

sulphate in winter season, a series of experiments were arranged in which the sea bittern samples were heated (110°C to 114°C) and designated as 'heated bittern'. Experiments were initiated by charging aliquot volume of normal/heated bittern of known composition. Samples were taken out at different time intervals during chilling and the corresponding temperature recorded. The collected samples were immediately filtered off and analyzed for magnesium sulphate and other salts.

Data retrieval/representation. The required data has been taken from previous investigations as detailed below: (I) The mass of sea bittern, (II) the slope of concentration temperature plots (III), specific heat of raw material estimated from its overall composition (unpublished part) and conventional relationship using heat capacity data of individual constituents (Perry 1950; Wannacott and Womnacott 1976; Miller and Miller 1986), and (IV) the average value of slope of temperature time data (estimated both from the respective graphs and by linear regression). The data so collected along with design and performance data of chilliers is recorded in various tables as detailed below:

The system constants and the design features in respect of two chillers appended in Table 1a and the data in respect of chillers performance are shown in Table 1b. Whereas the temperature-time plots for different sets are presented in Figs. (1a to 1c). The parameters, namely specific heat, heat of crystallization, overall heat transfer co-efficient have been estimated from appropriate relationships (Spiegel 1981; Beg *et al* 1982, & 1984; Galindo *et al* 1986) derived in the preceeding section and indicated in Table 2. Primary statistical parameters calculated from pertinent relationships are shown in Table 3; whereas Table 4 indicates the results of tests of significance (F-test and T-test).

Results and Discussion

The modified energy balance equation, while explaining the linearity of temperature-time plots, has been instrumental in evolving relationships for estimating variables like heat of crystallization, rate of heat removal from the system and heat transfer/utilization co-efficients and also paved way for deducing a law concerning low temperature crystallization and its operative conditions.

Examination of different relationships reveals that various variables involved may be catergorized into property and non-property groups. The former includes specific heat, heat of crystallization and slope of concentration-temperature plot (being the characteristic of raw materials). The second category may be further sub-divided into: system constants (namely mass of sea bittern, effective cooling area and the

rated heat removal capacity of the chiller), system variables like heat transfer/utilization co-efficients and rate of heat removal from the system) and performance parameters such as the slope of temperature-time plot, overall average temperature drop between crystallising slurry and evaporating refrigerant.

The data (Tables 1a and 1b) is instrumental in estimating various parameters detailed above, whereas temperature-time plots (Figs. 1a to 1c) in each set of experiment is represented by characteristic line with high order of correlation co-efficient (0.993 to 0.998). The intercept on ordinate of these plots represents average crystallization temperature which is characteristic of percent magnesium

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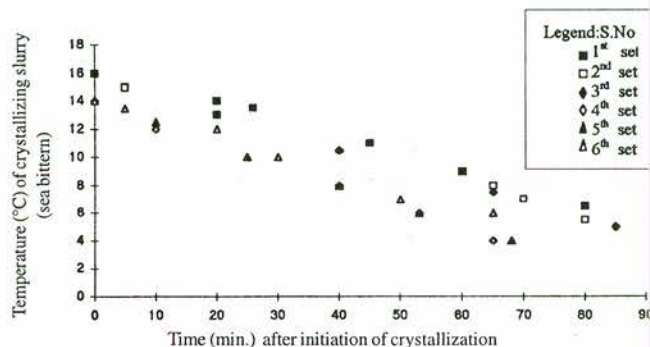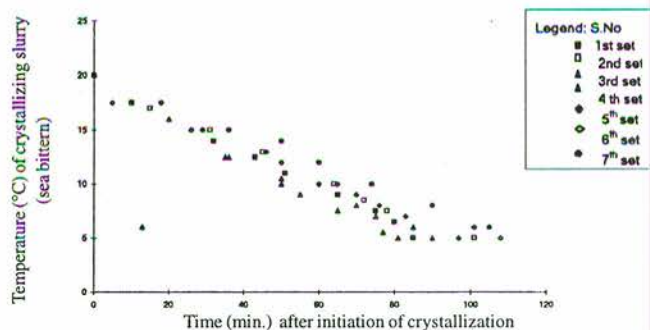

Fig 1b Different sets of experiments on crystallization of magnesium sulphate during chilling of sea bittern (25 litre heated bittern).
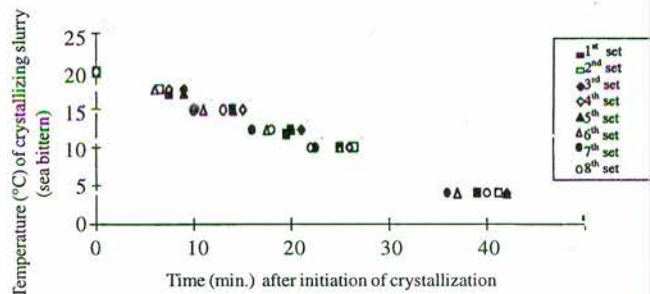

Fig 1c Different sets of experiments on crystallization of magnesium sulphate during chilling of sea bittern (400 litre normal bittern).
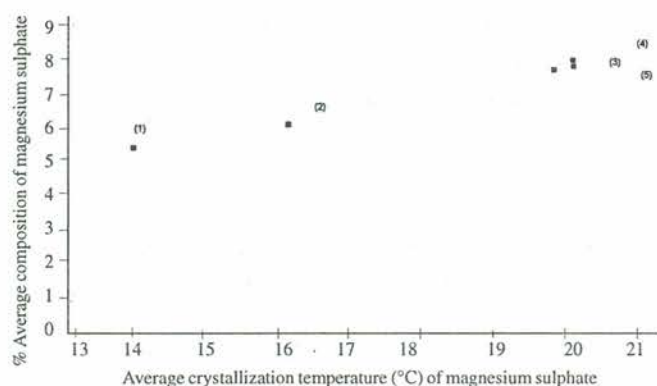
Fig 2 Showing relationship between average crystallization temperature and corresponding average composition of magnesium sulphate in sea bittern samples.

sulphate in sea bittern. The examination of the plots reveals that the composition has direct bearing on the slope, because its irregular changes (Block 'A' and 'B') bring about corresponding abrupt changes in respective slopes and vice versa.

Obviously, bittern being a mixture, its specefic heat is a function of its composition which (Beg *et al* 1982 & 1984) is influenced by seasonal variations. Therefore, depending on crystallization patterns in a particular weather, specific heat should also have seasonal values, which indeed is substantiated by the different values of the parameters (Table 2) for normal bittern samples in winter and summer seasons. On the other hand, prima facia, the low but close values of specific heat of normal and heated bittern samples in winter (Table 2) suggest that perhaps heating only slighly affects the parameter. If these conclusions are analyzed in the light of the fact that slope of temperature-concentration plot (which depends on the type of bittern whether heated or normal and not the seasonal condition, Table 2), it comes to surface that heating has much more dominating effect on heat of crystallization although specific heat values in the two situations differ (Block 'A' & 'C', Table 2). Therefore, it is thus established that weather changes do not influence the heat of crystallization as heating of bittern does. Review of the results of heat transfer/utilization co-efficient (Table 2, Blocks A & B) reveals that although increase in cooling capacity of smaller chiller (0.20 to 0.25 Hp) increase the output or heat transfer coefficient, it does not affect the efficiency or heat utilization coefficient. Rather it is the design of chiller which influences the parameter (efficiency) as is obvious from its higher values in case of bigger chiller in which the coils were immersed in liquid (Table 2, Block C).

The plot of average crystallization temperature against average percent magnesium sulphate (in bittern) is incidentally found to be linear (Fig 3) with high order of correlation co-efficient (0.996).

Statistical analysis. Critical review of the statistical param-

Table 1 a
System constants and design features of chiller

	A	B	C
Net capacity (lit)	25	25	400
Type of bittern	Normal	Heated	Normal
Ave mass (kg)	32.4	32.46	515.16
Cooling areas (Beg *et al* 1989)	0.383	0.383	2.23
Compressor rating (H.P)	0.20	0.25	7.5
Refregerant	Freon-12	Freon-12	Freon-22
Evaporation temperature (°C)	-15	-15	-15
Suction pressure (PSI)	12	12	28.3

Maximum/rate of heat removal capacities in various units (King 1971)

KJ h^{-1}	3150	2520	96000
KJ min^{-1}	42	52.5	1600
KJ h^{-1} kg^{-1}	77.6	97.6	186.3

Table 1 b
Performance data

Temperature range for linear portion	A	B	C
Initial temp (t_i) °C	12	14	18
Final temp (t_f)°C	4	4	12
Average temp (t_{ave})°C	8	9	15
Cooling range $(t_i - t_f)$°C	8	10	6
Overall average temperature drop (Δt_{ave})	23	24	30
Slopes:			
Concentration-temperature $(m°_{c-t})$	0.316	0.41	0.3146
Temperature-time $(m°_{t-\theta})$	For various trials and blocks		
1.	0.162	0.162	0.4090
2.	0.125	0.150	0.3654
3.	0.127	0.153	0.396
4.	0.1495	0.1275	0.387
5.	0.145	0.164	0.3895
6.	0.133	0.1595	0.422
7.	---	0.1324	0.4202
8.	---	---	0.424

eters (Table 3) suggests that: (i) the observed data in different instances is normally distributed, (ii) systematic error is absent and (iii) the error allowance is tenable. Further, the values of co-efficients of variation in respect of system variable viz. heat transfer/utilization co-efficients concerning smaller chiller indicates more relative dispersion and hence are suggestive more variations in its performance.

Review of the data in respect of the tests of significance (Table 4) brings the following to the surface:

F-tests. In case of the properties (sp.heat and heat of crystallization), the test suggests that the compositions of normal bittern used in different sets of 400 litre (Block-C) are more consistent and precise than those used in 25 litre experiments (Block A & B) which is obviously caused by the respective method of procurement. However, the samples of heated and normal bittern in the later case (Block A & B) are found to be of simillar consistency amongst themselves. Inspite of the

change in rated capacity of smaller chiller, similarity in the consitency is noted in its output, efficiency and rate of heat removal from the system. The variability in the efficiency of bigger chiller (400 lit), as suggested by one tailed F-Test is more precise, which may be attributed to its design.

T-Tests. The test in respect of specific heat indicates that change in weather conditions causes significant differennce in the mean value of parameter whereas the effect of heating is insignificant. Both seasonal variations and heating of bittern cause statistically significant difference in the mean values of heat of crystallization. The test in respect of system variables indicates that increase in chilling capacity of smaller chiller does not affect output and efficiency significantly. However, significant increase in the performance of bigger chiller may be attributed to both design and increase in capacity in terms of $KJ\ h^{-1}\ kg^{-1}$.

Conclusions

While explaining the linearity of time temperature plots, the modified energy balance equation has been catalytic in arriving at a law concerning low temperature crystallization which states that if temperature-time plots are linear and the drop in concentration of active component in mother liquor is also proportional to temperature drop, the overall enthalpy changes are equally divided into sensible heat and heat of crystallization. In addition, the manipulations have also been instrumental in driving appropriate relationships for estimating heat of crystallization, heat transfer/utilization coefficient and rate of heat removal from the system in terms of average specific heat of solution, mass of raw material, effective cooling area, overall average temperature drop between crystallizing slurry and evaporating refrigerant and slopes of temperature-time plots. It has been established through

Table 2
Estimated values of different parameters

Block	A					B					C				
	(25 lit normal bittern)					(25 lit heated bittern)					(400 lit normal bittern)				
S.No.	$\overline{Cp}$	|-Hc|	Ui	q	$\overline{Co}$	$\overline{Cp}$	|-Hc|	Ui	q	$\overline{Co}$	$\overline{Cp}$	|-Hc|	Ui	q	$\overline{Co}$
1.	2.843	899.6	2.57	22.64	0.539	2.005	704.20	3.32	30.51	0.581	3.137	992.27	19.78	1324.00	0.8275
2.	2.843	899.6	2.61	23.02	0.548	2.930	710.30	3.10	28.50	0.543	3.157	999.05	17.73	1184.50	0.7403
3.	2.850	901.9	2.66	23.45	0.558	2.825	684.85	3.07	28.25	0.538	3.144	994.90	19.31	1291.89	0.8074
4.	2.888	913.9	3.17	27.84	0.663	2.825	684.85	2.54	23.30	0.444	3.160	1000.0	18.81	1258.19	0.7860
5.	2.915	922.5	3.11	27.36	0.6515	2.916	706.91	3.39	31.18	0.394	3.145	995.25	18.85	1260.74	0.78.79
6.	2.920	924.1	2.84	25.10	0.597	2.899	702.79	3.26	30.05	0.572	3.154	999.68	20.52	1372.55	0.8580
7.	--	--	--	--	--	2.811	681.45	2.62	23.99	0.572	3.159	999.68	20.25	1354.92	0.8468
8.	--	--	--	--	--	--	--	--	--	--	3.157	999.05	20.71	1385.60	0.8660

Table 3
Statistical parameters

Block:	A					B					C				
	(25 lit. Normal bittern)					(25 lit. Heated bittern)					(400 lit. Normal bittern)				
S.No.	$\overline{Cp}$	|-Hc|	Ui	q	$\overline{Co}$	$\overline{Cp}$	|-Hc|	Ui	q	$\overline{Co}$	$\overline{Cp}$	|-Hc|	Ui	q	$\overline{Co}$
No. of trials (N)															
	6	6	6	6	6	7	7	7	7	7	8	8	8	8	8
Degrees of feedom															
	5	5	5	5	5	6	6	6	6	6	7	7	7	7	7
Measures of central tendency															
Ave. $\overline{x}$	2.892	915.0	2.84	24.90	0.596	2.874	696.48	3.04	27.97	0.5327	3.152	977.54	19.49	1304.00	0.8150
*Median (M.D)															
	2.869	907.9	2.75	24.275	0.5775	2.825	702.79	3.10	28.50	0.543	3.155	999.05	19.55	1307.945	0.817
Standard deviation (S.D.)															
	0.0652	20.46	0.261	2.757	0.055	0.0488	12.22	0.336	31.38	0.0597	0.078	2.813	1.015	68.40	0.043
Variance (S²)															
	0.0043	418.61	0.0697	5.025	0.003	0.0024	149.33	0.113	9.85	0.0036	0.001	8.07	1.03	4678.56	0.00185
Coefficient of variation (S²)															
	2.25	2.236	9.26	9.06	9.23	1.68	1.754	11.03	11.29	11.207	2.474	0.282	5.210	5.20	5.245

* Means are close to medians

Table 4
Results of tests of significance

Parameters	Type of Test	Within 25 lit. between heated and normal (Between A&B difference)	Between two scales of operation, normal to heated bittern. (Between B&C difference)	Between normal bitterns. (Between C&A difference)
Specific heat, $\overline{C}p$	F-Test			
	Two tailed	Insignificant	Significant	Significant
	One tailed	"	"	"
	T-test	Insignificant	Significant	Significant
Heat of crystallization, |Hc|	F-Test			
	Two tailed	Insignificant	Significant	Significant
	One tailed	"	"	"
	T-Test	Significant	"	"
Heat transfer coefficient, Ui	F-Test			
	Two tailed	Insignificant	**	**
	One tailed	"	"	"
	T-test	"	"	"
Rate of heat flow, q	F-Test			
	Two tailed	Insignificant	**	**
	One tailed	"		
	T-test	"		
Heat utilization coefficient, $\overline{C}$o	T-Test			
	Two tailed	Insignificant	Insignificant	Insignificant
	One tailed	"	"	"
	T-test	"	Significant	Significant

** Difference is already significant because of capacity difference; Values of statistical test (F&T) were considered significant $P<0.05$.

numerical results that composition of sea bittern which is very sensitive at seasonal variations, affect directely the specific heat of crystallization and slope (temperature-time plot) whose intercept represents crystallization temperature which in turn is characteristic of magnesium sulphate in sea bittern. The properties (specific heat and heat of crystallization) do possess seasonal values and the difference is statistically significant. Heating does not affect the specific heat but it influences significantly the heat of crystallization.

Further, increase in the chiller capacity enhances the output but does not affect efficiency which mainly depends on the design of chiller. The statistical analysis of the results apart from indicating the normalcy of data, tenability of error allowances and absence of systematic errors have also substantiated the above conclusions.

The studies have also been helpful indicating that the relationship between the average crystallization temperature and the average percent of magnesium sulphate in sea bittern is linear within the close working range of 12°C to 20°C.

Notations

$A =$ Area of heat transfer, meter square.

$b =$ Intercept on Y-axis.

Ave $=$ Average

$C =$ Concentration variable.

$C_i =$ Initial concentration or weight percent of magnesium sulphate in solution, $\dfrac{\text{kg of magnesium sulphate}}{100 \text{ kg solution}}$

$C_f =$ Final concentration of weight fraction of magnesium sulphate in solution $\dfrac{\text{kg of magnesium sulphate}}{100 \text{ kg solution}}$

$C' =$ Any concentration during chilling.

$\overline{C}_p =$ Ave sp. heat of the liquid bulk $\dfrac{KJ}{kg \ °C}$

$\Delta C =$ Drop in percent concentration during chilling $(C_i - C_f)$

$\overline{C} =$ Heat utilization co-efficient.

ΔH_c or $|Hc| =$ Numerical Value of Heat of crystallization

$= \dfrac{KJ}{\text{kg magnesium sulphate crystallized.}}$

$q =$ Rate of heat removal from the system
$KJ\ h^{-1}$ or $KJ\ min^{-1}$

$\bar{q} =$ Rated heat capacity of chilling unit in $KJ\ h^{-1}$ or $KJ\ min^{-1}$

$Q =$ Total heat changes associated with crystallization

$m^{\circ}_{c,t} =$ Slope of temperature time plots (ΔC) - Drop percent concentration. per $^{\circ}C$. Δt

$m^{\circ}_{t,\theta} =$ Slope of temperature plots (Δt) - Drop in temperature $^{\circ}C$ per min. Δt_c

$m =$ Mass of solution, kg.

$t =$ Temperature variable.

$t_{c(ave)} =$ Ave. crystallization temperature.

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

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

$t' =$ Any temperature during chilling $^{\circ}C$.

$t_s =$ Evaporating temperature of refrigerant $^{\circ}C$.

$t_{ave} =$ Average temperature of crystallizing slurry $^{\circ}C = (t_i + t_f)/2$

$\Delta t_{ave} =$ Overall average temperature drop between crystallizing slurry and evaporating refrigerant $(t_{ave} - t_s)$.

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

$\bar{U}_i =$ Average overall heat transfer co-efficient based on inside area of reactor $KJ\ min^{-1}\ m^2 {}^{\circ}C$.

$\theta =$ Time variable

$\theta_i =$ Initial time of chilling in min.

$\theta_f =$ Final time of chilling in min.

$\theta_c =$ Temperature duration of crystallization, $^{\circ}C$.

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