MECHANICS OF LOW TEMPERATURE CRYSTALLIZATION AND RELATED CONSIDERATIONS

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Miers theory, although elucidated satisfactorily the phenomenon of supersaturation and consequent crystallization, nevertheless, failed to explain mechanics of POLTEC (process[†] of low temperature crystallization) in a batch crystallizer; which has been evolved based on observations made during earlier investigations/logic. It is proposed that because of cooling, the layer in contact with the vessel's wall gets supersaturated and is dispersed in solution and spontaneous adiabatic crystallization occurs in each element of dispersed phase. Subsequent to sprouting of salt from each globule, mixing of the liquid residuals causes smooth cooling of solution. Miers idea of required degree of supersaturation, its mechanics and that of POLTEC in context with fluid dynamics/hydrodynamic of batch crystallizer (stirred tank vessel), has been found instrumental in explaining reasons lying behind the pattern of changes in overall heat transfer coefficient and recovery with agitation observed earlier.

Key words: Supersaturation and spontaneous crystallization, Mechanics of low temperature crystallization, Hydrodynamic/thermodynamics of batch crystallizer.

Introduction

The earlier work (Nayeemuddin *et al* 2000a), presented derivation of the formulae and their satisfactory application to the previous data (Beg *et al* 1986 and 1989) in respect of crystallization of magnesium sulfate during cooling of sea bittern. The said efforts were, however, lacking in appropriate explanation concerning theoretical issues like (i) the underlying reason of the linearity of unsteady state data namely concentration of magnesium sulphate against temperature of crystallizing slurry (Beg *et al* 1989) and (ii) basis and mechanics of POLTEC. Since the former aspect has already been dealt with Nayeemuddin *et al* (2002), this conceptual paper, therefore attempts to present the following aspects:

(i) It reviews briefly Miers theory (Perry 1950a and b; Buckley 1958) and elucidates related transport phenomena.

(ii) Proposed concept 'The mechanics of low temperature crystallization through cooling/supersaturation in a batch crystallizer and its reliability evaluated suitably.

(iii) The unexplained reasons underlying the earlier investigations concerning changes in overall heat transfer coefficient and recovery of active component against agitation (Nayeemuddin *et al* 2000b) in low temperature c.ystallization have now been elucidated appropriately.

(iv) The related issues such as probable path followed during POLTEC and type of crystallization have also been discussed briefly.

Basic theoretical considerations. (i) Miers concept reviewe and scope. Miers and co-workers, in the light of Oswald's idea (Perry 1950a; Buckely 1958) and their own extensive experimental work, conceptualized the phenomenon of spontaneous crystallization in an initially unseeded, supersaturated solution (Perry 1950b). It was Buckley (1958), who objectively reviewed Miers work and also described subsequent investigations. In his opinion Miers critics "failed to appreciate his concept of supersolubility curve and objected too rigid use of the term metastable, since they considered it a less defined entity". Further, the part of Miers theory, which provided necessary basis to POLTEC and could be more relevant to it is that "There is minimum degree of supersaturation which acts as driving force for spontaneous crystallization; greater the degree of supersaturation, the greater would be the capability to crystallize more spontaneously". The other parts of his concept or its corollaries which are of lesser importance are placed as Appendix. It is worth noting that Miers work is given in terms of concentration/temperature, changes, whereas in POLTEC, in addition, enthalpy/temperature and enthalpy/concentration would perhaps be more pertinent.

(ii) Transport phenomena: In POLTEC, basic interrelated and the most important transport processes involved are heat and momentum transfer, whereas mass-heat transfer (exothermic crystallization) follows as natural consequence.

Therefore the essential features of the two former concerned transport processes are being described below:

(a) Heat transfer/thermodynamics: In case of out side cooling, heat transfer initiates because of evaporating refrigerant in tubes wound around the batch crystallizer-an externally cooled stirred tank vessel, which in turn extracts heat through conduction (i) from tubes walls, (ii) vessels walls, (iii) layer of salt which gets deposited *in situ* on cooling surface, (iv) stagnant liquid and laminar layers (which are conventionally expressed as a combined equivalent film or resistance) and (v) finally through forced convection from the main liquid bulk. Each of the said step/medium offers a definite amount of resistance to the heat flow and the overall thermal resistance is made-up of (sum of) all the said resistances. In a given situation, the first two resistances mentioned above are comparatively lower than the remaining three which constitute system constant and could be taken care of at the design/fabrication stage. In view of this, during operation overall thermal resistance could be reduced both by scraping salt layer from time to time and also by increasing agitation level/Reynolds number which, however, has a limit. Further, while starting the process, if solution is unsaturated and not at its concentration/temperature equilibrium, first the same shall be attained and then the layer of the liquid passing past the vessel's surface (wall) would start getting supersaturated. As soon as the required degree of supersaturation is attained crystallization initiates and consequently the concentration of active component, the temperature of liquid and that of the supersaturated layer also start falling (Fig 1). The process would thus continue either till the complete removal of the active component or the system attaining some sort of equilibrium.

(b) Momentum transport/hydrodynamics: Agitation plays an important role in the hydrodynamics of low temperature batch crystallizer (LTBCR) since the convective currents help in maintaining uniform conditions of concentration/temperature. Further it facilitates the heat removal process and thereby also helps in achieving the desired degree of supersaturation; suggesting that the thermodynamics of the process depends on hydrodynamics of crystallizer.

Conceptualization of the phenomenon of process mechanics. The main limitation of Miers work is that, being confined to a narrow field of the physics of supersaturation and consequent spontaneous crystallization, the thermodynamics and particularly the mechanics of low temperature batch crystallization are out of its scope. Consequently, it does not offer any guideline concerning the behaviour of the supersaturated layer in the subsequent stages, particularly the manner in which it enters the main liquid bulk. The problem therefore, needs necessary conceptualization. In this connection, the observations made during original experimental work (Beg *et al* 1989, Nayeemuddin *et al;* 2000b) as summarized below have provided some useful clues.

(a) Laboratory scale experiments consisted of cooling of an aliquot amount of sea bittern in a beaker fitted with stirrer. At the end of process, the whole product along with the crystallized salt looked like an opaque colloidal mass which after some time got separated into two distinct layers.

(b) In pilot scale experiments, which were carried out in an externally cooled stirred tank vessel, in spite of agitation, it was noticed on quite a few locations that as if salt was sprouting out of some sort of enclaves. Further appearance of crystal rain like conditions strongly suggested that the said phenomenon probably occurred throughout the main body of solution but because of agitation could not be seen everywhere.

The above observations led to conclude that most probably supersaturated layer form a separate phase. In laboratory scale experiments, perhaps due to uncontrolled fast cooling and vigorous agitation, the contents temporarily assumed appearance of opaque colloidal mass. On the contrary, in a batch crystallizer, controlled cooling/agitation along with suitable geometry of the vessel provided favourable conditions to obtain a layer appropriately supersaturated and uniformly dispersed. It appears that probably spontaneous crystallization occurs in dispersed phase. However, in order to comprehend mechanism of the phenomenon clearly, it would need the support of few assumptions which are being mentioned in the following paragraphs in sequence and manner that also forms the structure of the concept of process mechanics. Later on, during discussions the assumptions have been appropriately evaluated.

Assumptions

* Properly supersaturated layer on being struck against baffles gets disintegrated into infinite tiny globules of spherical shape-comprising a certain size range-which are evenly distributed into main liquid bulk.
* A supersaturated layer of very small width that gets dispersed within a very short time interval, comprises a crop of globules, possessing uniform degree of supersaturation, which irrespective of size variations has the same life span.
* During the life span of globules which, however, is very short, there occurs no mass or heat transfer across their

respective surfaces.

* The dispersion is immediately followed by adiabatic crystallization within each globule.
* Instantaneously after spontaneous crystallization, salt sprouts from individual entities of the dispersed phase and the liquid residuals (the remnants left after sprouting of salt) quickly get mixed with solution and cool it.
* In ideal conditions, cooling of solution should entirely take place through liquid residuals.

Results & Discussion

Validity of assumptions/reliability of proposed concept.

* In the light of observations made during original studies (Beg *et al;* 1989) and review of Mier's concept (Perry 1950; Buckley 1958), it appears highly probable that the cooling so changes the physical characteristics of supersaturated layer that it becomes a different phase and hence is rendered dispersible in solution. Further, it is well known phenomenon that during atomization and similar two phase operations, the dispersed phase most commonly assumes spherical shape which inherently possesses self supporting configuration. Thus the globules formed are able to withstand convective currents.

* Concentration/Temperature gradient existing in a supersaturated layer of very small width gets homogenized and thus a crop of globules of even composition is formed. Therefore, because of the uniformity of driving force in terms of degree of supersaturation, the globules of the same crops, in spite of irregularity of sizes, would have the same life span and crystallize simultaneously.

* Since dispersed phase is immediately picked up by convective currents therefore, there could be no momentum transfer and mass or heat transfer either, across the surfaces of respective gloubles during their short life span. Further more, dispersion is immediately followed by simultaneous crystallization within each element of dispersed phase of the same crop. Evidently under prevailing conditions the process should be adiabatic one; in turn suggesting that each entity of dispersed phase during its life span acts as a system in itself.

* Alternatively, the phenomenon of adiabatic crystallization may also be explained through simple logic. Since in case if the dispersed phase (or supersaturated layer entering main liquid stream) happens to exchange heat with the solution prior to crystallization, it is bound to loose a proportionate capability to crystallize spontaneously. This in turn would start resulting into decreased process efficiency/recovery and unproductive over cooling which should ultimately suppress crystallization (Buckley 1958) and would disturb the process. Conversely, if some process is running smoothly with reference to its concentration temperature changes without causing any over cooling, as was factually observed in the past (Beg *et al* 1989, Nayeemuddin *et al* 2000b), it may be concluded that adiabatic crystallization is taking place in supersaturated layer which most probably would be in dispersed form.

* It may be recalled that during crystallization through supersaturation/cooling, the total heat required to be removed from the system comprises (i) heat of crystallization and (ii) sensible heat lost during supersaturation (Perry 1950c). At the end of adiabatic crystallization, heat released stands dissipated by the portion of heat lost due to supersaturation which obviously is accompanied by proportional rise in temperature in each element of dispersed phase, as indicated by M_1M (Fig.1). The other component namely fall in sensible heat being still retained in each element, as also evident from derivations (Nayeemuddin *et al* 2000a) evidently be having temperature lower than liquid bulk.

* Spontaneous crystallization makes the globules swell, hence salt would instantaneously sprout out of them and their residuals, quickly get mixed with the solution and cool it.

Application of hydrodynamics/Thermodynamics. During earlier studies following came to surface:

(i) In the increasing scenarios of Reynolds number/ agitation level (Nayeemuddin *et al* 2000b), overall heat transfer coefficient which has increasing trend, attained a constant value at certain critical rpm, whereas change in recovery with agitation rate was found to be anomalous.

(ii) When a batch crystallizer operated at some higher constant agitation level beyond certain critical limit, recovery - which initially changes linearly with temperature - after some time, starts showing diminishing trend (Beg *et al* 1989).

The above aspects were indeed remained unexplained because of the lack of knowledge of hydrodynamics of stirred tank vessel and its influence on degree of supersaturation. The said phenomena have now been appropriately explained as follows:

a) In the increasing scenarios of Reynold's number/agitation level: In an stirred tank vessel, as Reynold's number/ rpm keep increasing, the thickness of combined film which has decreasing trend attains a constant thickness at certain

rpm. Consequently overall heat transfer coefficient initially shows increasing tendency and ultimately attains a constant value. As for the degree of supersaturation, like overall heat transfer coefficient, it also first increases with rpm, nevertheless, its behaviour beyond the critical value of Reynold's number/agitation level needs some considerations. In this connection, a couple of points may be of interest to note. Firstly, in stirred tank vessel, rpm is just a nominal or apparent parameter, while it is time of contact/residence time of the layer passing past the vessel's wall and getting supersaturated plays key role in the process of supersaturation. Secondly, time of contact bears an inverse relationship with rpm. So long as overall heat transfer coefficient keeps increasing with Reynold's number/agitation level, the decreasing values of residence time do not appear affecting the process and consequently the degree of supersaturation/recovery also keeps increasing with the said variables. The moment overall heat transfer coefficient attains a constant value, it ceases to be a factor and no more effects the process. In its place most probably residence time becomes a dominating parameter, whose decreasing values eventually result into diminishing values of degree of supersaturation and hence recoveries. It is therefore unfolded that in the increasing scenarios of Reynold's number/agitation level, fluid dynamics first causes recovery to attain an optimum value at certain rpm, beyond which it starts decreasing because of hydrodynamics of stirred tank vessel. The above elaboration thus explains the basic logic of heat transfer coefficient attaining a constant value and an anomalous change in recovery with the increasing Reynold's number/agitation level in LTBCR.

(b) Performance of LTBCR when operated at constant higher rpm: The dilution of active component starts increasing from the very inception of the process. On the other hand recovery initially changes linearly with temperature, which beyond certain lower dilution becomes nonlinear, showing diminishing trend end eventually attains a constant value (Beg *et al* 1989). This, most probably occurs since in the increasing dilution scenarios, a critical level is reached at which residence time of layer passing past the surface becomes just insufficient to let the liquid attain the desired degree of supersaturation. Consequently, further processing would result into diminishing values of the degree of supersaturation and hence recoveries. Eventually, a dilution level arrives, at which further increase in supersaturation and consequent spontaneous crystallization/recovery ceases. At this stage the solution starts behaving as unsaturated one (which may also be called 'Quasi Permanent Unsaturation') and the process of supersaturation stops and perhaps also becomes independent of time of contact/residence time. In view of

this, if processing is continued any further, it would merely result into unproductive over cooling. It is worth noting that depending on the marginal increase in rpm beyond critical one, recovery attains corresponding low constant value (Nayeemuddin *et al* 2000b). This finding therefore, invalidates the earlier view concerning redissolving of active component and attaining *pseudo* equilibrium at higher agitation level in low concentration/temperature regions (Beg *et al* 1989).

Some related considerations. Presentation of covert and overt changes. The main impediment in the graphical presentation of different steps of the process is that concentration/temperature variations involved from degree of supersaturation up to mixing of liquid residuals cannot be determined quantitatively and accordingly these changes may be classified as covert ones. Nevertheless, in order to obtain an overall picture of changes at a galance, it has been attempted in the light of proposed concept of POLTEC to indicate different steps diagrammatically as detailed in the following paragraph.

Fig. 1, $AA_iA_oA_y$, shows concentration/temperature equilibrium curve, the conditions below which are unsaturated one. $BB_iB_oB_y$ indicates the supersaturated curve, the area above which is known as **labile region**. The space between the two curves is called **metastable zone**, within which the solution, although supersaturated but unable to crystallize spontaneously. A_oA_x and B_oB_x are linear extrapolated portions of the two curves.

Let A_iB_iB', (Fig.1) be homogenized degree of supersaturation attained by a layer of supersaturated liquid of very small width which got dispersed during very short time period. Second assumption is that the different steps being mentioned just now are cumulative effects of all the globules formed out of the said layer in which crystallization occurs simultaneously.
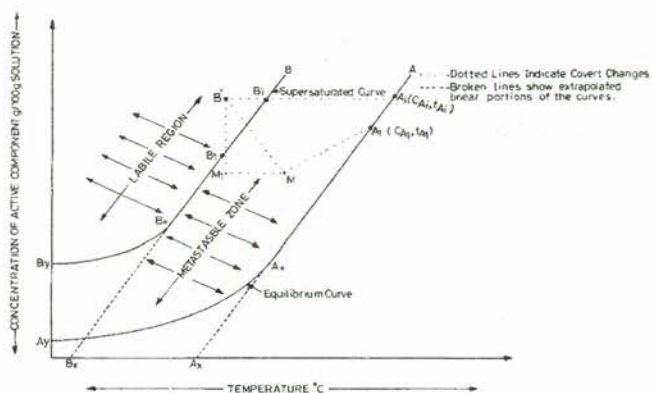

Fig 1. Diagram showing concentration temperature changes (In batch crystallization through supersaturation).

At B′spontaneous crystallization initiates and ends at M_1. $B′B_1M_1$ represents the drop in concentration of the active component, M_1M shows corresponding adiabatic temperature rise (within globules.) B′M represents path of adiabatic changes, while MA_1 being the mixing path of liquid residuals with the main liquid bulk. The path of overall changes taking place in one step then may be indicated by $A_1B_1B′B_1M_1MA_1$. The process would thus be comprising inconveniently large number of very small steps. Therefore, a pragmatic solution would be to choose a layer of reasonable width in which concentration variations are just small, and the average degree of supersaturation remains reasonably constant.

A_1 (Fig.1), concerns with the overt changes and its position is governed by the degree of supersaturation attained, the amount of liquid getting supersaturated in unit time and the fulfillment of assumptions already described. The location of A_1 at given moment presents average concentration/temperature of liquid bulk that could be conveniently recorded as function of time and represented graphically. The data so collected doesn't precisely represent equilibrium values but for all practical purposes could be considered so.

Type of crystallization. In LTBCR, deposition of a layer of active component on cooling surface from the very start of the process, is just unavoidable. Consequently, the liquid layer while getting supersaturated and passing past the vessel's wall sweeps away nuclei/crystals and thus there is presence of seeds from the very inception of the process, which indeed is contrary to the Miers idea. Therefore, this particular portion of Miers concept may be considered inapplicable to batch crystallization (through supersaturation). As far the type of crystallization, evidently the spontaneous one taking place within each element of dispersed phase should definitely unseeded, since time would be too short to permit the inoculating affects of nuclei/crystals to be of any consequence. However, as noted by Perry (1950a), presence of seed could catalyze the process and inoculating affects might be effective and seeded crystallization may occur in the corner of baffles and bottom of the vessel wherein, a portion of solution supersaturated to lesser degree gets in and has good chances of being there in contact with nuclei/crystals for quite some time.

Conclusions

(1) Mechanics of POLTEC and evaluation of its concept suggested the following:

    a) No mass/heat transfer takes place across individual elements of dispersed supersaturated phase and within each globule spontaneous crystallization occurs adiabatically.

    b) Normally, cooling of solution should entirely take place through liquid residuals-remnants left after crystallization.

    c) Abnormal/non-ideal conditions if allowed to persist, shall eventually inhibit spontaneous crystallization.

    d) From its generation to destruction, each element of dispersed phase acts as a system in itself.

(2) POLTEC, like any other chemical engineering process, is an independent one by itself, having its own mechanics and thermodynamics.

(3) In the increasing scenarios of Reynold's number/agitation level, following emerged out of the analysis of LTBCR:

    a) attaining a constant value by overall heat transfer coefficient and optimum one by recovery is basically a fluid dynamic phenomenon. However, the decreasing values of recovery - above a certain critical rpm - revealed it to be hydrodynamics of stirred tank vessel, suggesting that anomalous change in recovery is caused by both fluid dynamics and hydrodynamics of stirrer tank.

    b) When a unit is operated at higher constant rpm beyond critical one, increasing values of dilution, beyond certain limit result into decreasing degrees of supersaturation/recoveries. Eventually, spontaneous crystallization would stop and depending on the marginal increase in rpm above critical one, recovery attains a corresponding low constant value whence time of contact no more remains a factor. The system at this juncture may be considered as 'quasi permanent unsaturated solution' and as such further processing shall be counter productive.

    c) Contrary to Miers idea, there is a *defacto* presence of seeds well ahead of spontaneous crystallization. Further, there occurs mixed type of crystallization in which unseeded type predominates.

Nomenclature

C   Concentration of active component, $g100g^{-1}$solution.

C_{Aj}, C_{A1} Respective concentrations of active components at points A_j and A_1.

t   Temperature °C (may be +ve or -ve).

t_{Aj}, t_{A1} Respective temperatures of solution at points A_j and A_1.

Appendix

Principles/Corollaries deduced in the light of Miers theory and Buckley's review (Perry 1950a and b; Buckley 1958).

1) There exists a supersaturated curve, running parallel to concentration/temperature equilibrium curve.
2) Both, an improperly supersaturated layer and a super-saturated layer, which for some reason loses its heat energy to the surrounding liquid, result into unproductive overcooling.

References

Beg M A A, Nayeemuddin, Mahmood S N, Khan W A, Iqbal Z 1985 Production of marine chemicals in Pakistan, Part-II, Studies on manufacture of chemicals from seawater bittern. *Pak J Sci Ind Res* **29** 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 of sea bittern. *Pak J Sci Ind Res* **32** 126-132.

Buckley H C 1958 *Solubility and Supersolubility in Crystal Growth*. New York *John Willey and Sons, Inc.* pp 7-23.

Nayeemuddin, Mahmood S N, Farzana Azmat, Razia Begum 2000a Derivation of relationships and estimation of thermal/thermodynamic parameters from crystallization data of sea bittern. *Pak J Sci Ind Res* **43** 155-161.

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

Perry J H 1950 The Chemical Engineers Hand Book. In: *(a) Crystal Formation-Miers Theory* pp 1055. *(b) Crystal Formation-Supersaturation* pp 1054. *(c) Heat Effects in Crystallization Process* pp 1052, McGraw Hill Book Company, New York, USA.

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