TWO MODELS OF INDUSTRIAL OSLO CRYSTALLYSER

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SALT PRODUCTION

Keywords: Sodium chloride, Oslo crystallizers, models

SUMMARY

The design of an industrial OSLO crystallizer is based on experiments in lab, small scale pilot plant, semi-industrial plant and industrial plant that has been operating for 20 years .The objective was to produce spherical particle size of salt of about 5 mm; the known state of the art allowed only to produce a particle size of about 2mm maximum. A development was made for 2 years in lab and small-pilot scale; an industrial plant was started in 1987.

During the development, two mathematical models have been developed in order to better understand the particularities of OSLO Crystallizers, in particular with regards of the seeding and some aspects of segregations in fluidized bed of crystals.

A **first model** of OSLO crystallizer ideal, perfectly classified is described .The model takes into account the possibility of natural nucleation or external seeding with crystal of already good size.

A **second model** try to integrate some degree of classification of the particles in the fluidized bed: in fact the fluidized bed is divided in three well-mixed reactors where the super-saturated brine is moving upwards and the external seeding is moving counter-currently downwards.

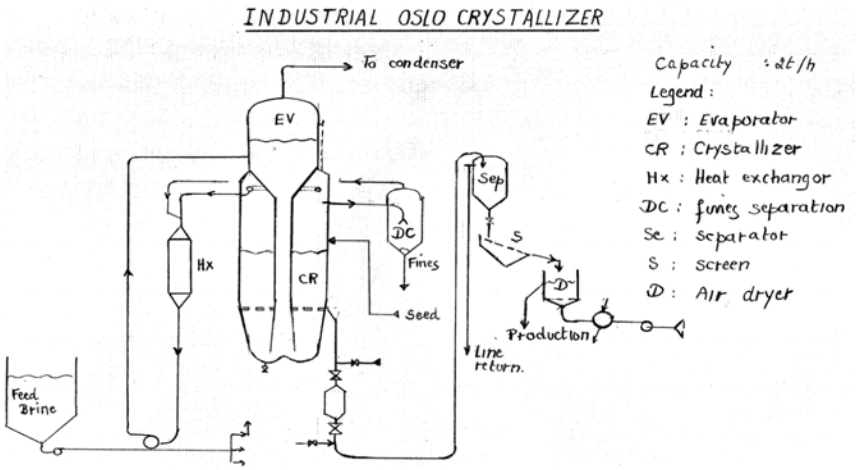
INTRODUCTION

Production of large spherical particle size of sodium chloride has been requested for market applications: a size of 5mm diameter is desirable

Known technology tells us that a maximum size of 2 mm diameter can be reached (1).

An industrial plant was built and has been operating for 20 years (1987 to 2007).

The drawing of the process is shown below and has been described extensively in another paper.



The elaboration of theoretical models of the operations of these crystallizers allows us to analyze the results of pilot operations and facilitates the scale-up to industrial size of results collected in pilot.

TYPES OF MODELS

1. IDEAL OSLO CRYSTALLIZERS

An OSLO crystallizer is considered ideal when all crystals moves in piston flow from the top of fluid bed to the bottom where they are drawn as production and when brine moves upward piston flow.

Crystals are well classified: the smallest sizes are introduced in the bed (external seeding) or appear spontaneously (natural seeding).

Fines are confined to the top of fluidized bed .Larger crystals are drawn at the bottom.

The brine progress in piston flow and counter-currently of crystals; during the progression, super saturation decreases regularly from the inlet (bottom) to the outlet (top); it is circulated outside the crystallizer in order to create new super saturation.

Several reason can cause the crystallizer to deviate from ideal piston flow models:

- Crystal bed may be partially or totally mixed, depending on the quality of fluidization and distribution of brine .This mixing is not desirable: model 2 has been designed to consider several mixed reactors
- To correct this problem, an external classification device can be adapted to the drawing of production
- A perfect classifying fluid bed is an abstraction: depending on the choice of fluidization velocity, very small particles resulting from uncontrolled nucleation is

entrained out of the bed and circulates in the external loop; they can accelerate the process of nucleation and they grow on their own until a critical size is reached when they can be captured by the bed; the OSLO crystallizer is a mixed crystallizer for very fine particle and piston flow for larger size

2. MODEL OF IDEAL FLUID BED OSLO CRYSTALLIZER

This type of model has been described in literature by MULLIN (1); it has been modified to include an external seeding by particle of intermediate size.

ASSUMPTIONS

- Nucleation is perfectly controlled; special cares are taken to avoid any germination from impurities, breakage or cold spots
- The fluid bed is seeded by a constant flow of small particles perfectly calibrated of diameter D_0
- The crystal fluid bed is perfectly segregated and can be divided in layers of crystals of similar diameter; all same diameter crystal have the same residence time in the bed
- The rate of growth of crystal, r , kg/h.m^2 is given by measurement in lab fluid bed (2)

$$r = k.C \qquad (1)$$

- Crystals are almost spherical; a factor of form can be adapted for near spherical crystal
- Symbols are at the end

RELATION DIAMETER-RESIDENCE TIME OF PARTICLES

Relation diameter-residence time given in literature neglects the initial diameter of seed; this assumption leads to results difficult to apply in very common case where nuclei of very small size are eliminated and where seeding with intermediate size particles is applied.

Mathematical Relations

Mass balance between bottom of crystallizer and intermediate layer: mass given by brine equals weight gain of particles:

$$Q.(Ce-C) = \alpha.No.\rho_c.(Dp^3-D^3), \quad kg/h \qquad (2)$$

Net production of crystallizer is established in two ways:

- From solid: $P = \alpha.\rho.No.(Dp^3-Do^3)$, kg/h (3)
- From liquid: $P = Q.(Ce-Cs)$, kg/h (4)

Rearranging (2) and (3) we obtain:

- $C = Ce - P/Q.[1 - \{(D/Do)^3-1/(Dp/Do)^3-1\}]$ (5)

Rate of growth of crystal diameter: in an intermediate element of volume, weight of crystal is dW and particles stay a time dτ

Number of particles in this element of volume is:

- $dM = N_0.d\tau$

Surface offered to crystallization is:

- $dA = N_o.\ d\tau.\beta.D^2$

Increase of weight

- $dW = N_0.d\tau.\beta.D^2.kC$ (6)

The increase of weight of crystal by differentiation of formula (2) is:

- $dW = 3\alpha.\rho_c.N_o.D^2d(D)$ (7)

Combining (6) and (7) we obtain:

- $dD/d\tau = (\beta/3\alpha)*kC$ with $\beta/3\alpha = 2$ for sphere (8)

Combining (5) and (8) , we obtain the general relation

$$\frac{dD}{dT} = \frac{\beta}{3\alpha}\frac{kCe}{\rho}\left[1 - \frac{P}{QCe}\{1 - ((D/Do)^3 - 1)/((Dp/Do)^3 - 1)\}\right] \quad (9)$$

From (4), $\frac{P}{QCe} = 1 - Cs/Ce = \gamma$, is a relative de super saturation

Setting $gp = (\beta/\alpha 3)*(kCe/\rho)*$ is the maximum rate of growth for crystal , and $\varepsilon = Do/Dp$

The general relation (9) is written after integration.

$$\tau = \frac{Dp}{gp} * \int_{\varepsilon}^{1} dx/[1 - \gamma\{1 - (x^3 - \varepsilon^3)/(1 - \varepsilon^3)\}] \quad (10)$$

A similar relation can be drawn with the time T of mass renewal of mass crystal in the bed

$$T = \frac{Dp}{gp} * \int_{\epsilon}^{1} x^3\ dx/[1 - \gamma\{1 - (x^3 - \varepsilon^3)/(1 - \varepsilon^3)\}]$$

NUMERICAL EXEMPLE

For sodium chloride, crystallized in large particles of 5 mm in OSLO crystallizer, the following numerical values are typical:

r = 1.25 m/h $(\beta/\alpha 3) = 2$ (spheres) $\rho = 2150\ kg/m^3$

Dp = 0.005 m Ce = 0.4 kg/m^3 $^{g}_{p}$ = 4.65 .10^{-4} m/h

Result of numerical integration of relation (10) is given in at the figure 2

There is a strong relationship residence time and relative de super saturation: if γ tends to 1, residence time τ tends to ∞: this a case that is impossible without a very large height of crystal.

To obtain particles sizes of 5 mm starting with seeds of 1 mm, a residence time of 30 h is necessary for γ = 0.9 and 55 h for γ = 0.95

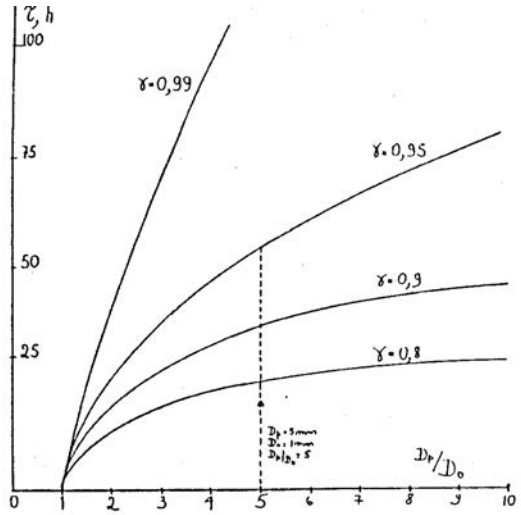


Figure 2 Residence time of particles

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3. MODEL OF CASCADE OF 3 WELL MIXED REACTORS

An OSLO crystallizer can be modeled by a cascade of continuous crystallizers connected counter-current.

Super saturation change from stage to stage; seeding is external like in the other model.

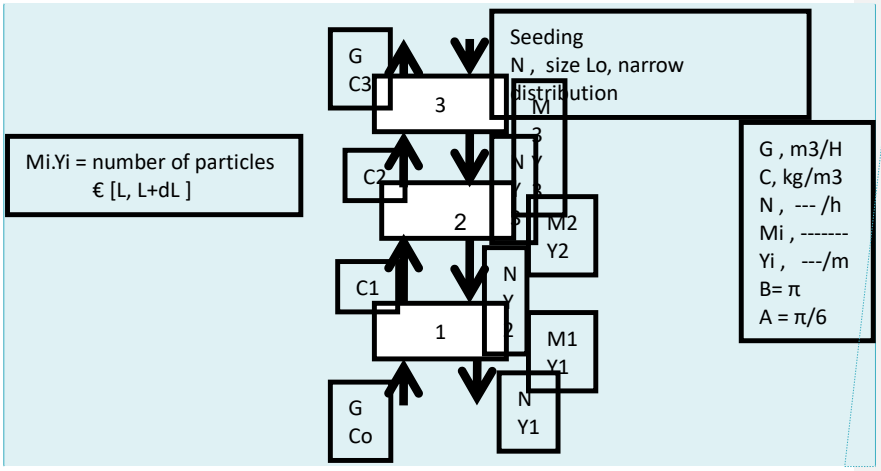
ASSUMPTIONS

- Crystallizers are well mixed reactors
- The rate of growth of crystal , r , kg/h.m^2 is given by measurement in lab fluid bed (2)

r = k.C C is a super saturation (11)

- Distribution of residence time are identical for solid and liquid in each reactor
- Flow rate of brine is the same all the way in the cascade
- Each crystallizer is characterized by:
  - Mi , total number of particles
  - Yi , proportion of particles with diameter between L and L+dL
  - Y = Y(L)
  - $\int_0^\infty Y(L).dL = 1$
- The assumption of Mi number of particle is a weakness of this type of model because, today , segregation of particles in several smaller reactors is not known in practice
- The cascade of reactor is fed by a constant number of particles in each reactors

MASS BALANCE AND POPULATION BALANCE



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MASS BALANCE AND POPULATION BALANCE FOR REACTOR i

Mass Balance

Total weight solid lost by liquid

$W = G.(C_{i-1} - C_{i)}$ kg/h (12)

Total weight solid gained by crystals in reactor

$W = K.Ci.\int_0^\infty \beta L^{2.}.Mi.Yi.dL$ (13)

From (12) and (13) we obtain the super saturation leaving the reactor i

Ci = $\frac{G.C_{i-1}}{G+K.\int_0^{\infty} \beta L^2\, MiYidL}$ (14)

This relation is important because it allows to compute the residual super saturation in the liquid leaving reactor I and to compare it , when analysis are accurate enough, with results of measures.

POPULATION BALANCE

Balance of particles of size interval [L , L + dL]

Accumulation = inlet - outlet + creation – disappearance

- Linear rate of growth of particles : $\frac{dL}{d\tau} = \frac{\beta}{3\alpha}\frac{KCi}{\rho} = \lambda$ (15)

With $\lambda = \frac{\beta}{3\alpha}\frac{KCi}{\rho}$

- Creation – disappearance of particles in interval L , L+dL: $-\lambda.\frac{d(Mi.Yi\lambda)}{dL}$dL
- Inlet – outlet : NY_{i+1}-NY
- In steady state, accumulation =0

The general equation for reactor i :

$$\frac{dYi}{dL} = \frac{N}{\lambda.Mi}(Yi+1 - Yi) \quad (16)$$

N/Mi = λ_i , residence time of particle in reactor I (16) is rearranged in

$$\frac{dYi}{dL} + \frac{Yi}{\lambda\tau i} = \frac{Yi+1}{\lambda\tau i} \quad (17)$$

Note:

For reactor 3, seeding is made with narrow particle size distribution Lo

Y_{3+1} = Dirac function δ(Lo)

SET OF EQUATIONS FOR 3 REACTORS

Reactor 1 : $\frac{dY1}{DL} = \frac{1}{\lambda\tau}(Y2 - Y1)$

Reactor 2 : $\frac{dY2}{DL} = \frac{1}{\lambda\tau}(Y3 - Y2)$

Reactor 3 : $\frac{dY3}{DL} = \frac{1}{\lambda\tau}(\delta(\text{Lo}) - Y3)$

This set of equations can be solved analytically by Laplace Transforms.

By example, if $\lambda 1 = \lambda 2 = \lambda 3$, the solution for Y1 is very simple:

After transform of Laplace and elimination, we obtain a solution in term of p Laplace transform:

Y1(p) = $(\frac{1}{\lambda\tau})^3 \frac{e^{-pLo}}{\left(p+\frac{1}{\lambda\tau}\right)3}$

The inverse transform is:

Y1(L) = $(\frac{1}{\lambda.\tau})^3 \frac{1}{2}\ (L - Lo)^2 e^{-(L-Lo)/\lambda\tau}$

With this expression , a computer program can easily compute the total surface of crystallization , the total mass in the crystallizer and the particle size distribution in each reactor and in particular at the outlet of the crystallizer.

Total surface Ai = $\int_{Lo}^{\infty} \pi x^2 Y1(x)dx$

Total mass Mt= $\frac{(\rho\pi)}{6} \int_{Lo}^{\infty} x^3 Y1(x)dx$

Numerical example

For sodium chloride, we adopt the following data:

Individual residence time: τi =10 h Total residence time: τ =30 h

Individual number of particles: Mi =250.10^6 Total number = 750.10^6

Lo = 0,001 m Ce = 0,5 kg/m^3 G = 4000 m3/H

Results of this example:

For Ce = 0,5 kg/m3 Cs= C3 = 0,0354 k/m3

AT = 15906 m2 Total surface of crystallization

Mt = 24212 kg Total mass of crystal

Pr = 1935 kg/h Hourly production

De = 28, 1 kg/h Mass flow rate of seeding particle 1 mm

From particle size distribution results, average mass diameter = 5.5 mm

List of symbols

Q = m3/h	flow rate of brine
W = kg	total mass of crystal
P = kg/h	net production of crystallizer
No = h^{-1}	number of seed per h
k = m/h	kinetic constant of growth rate
r = kC, kg/h.m2	increase of weight of crystal
gp = m/h	linear growth rate of diameter
D, L, m	diameter of crystal
Do, Lo m	diameter of seed
Dp, m	diameter of crystal production
C, kg/m3	super saturation
Ce, kg/m3	super saturation inlet
Cs, kg/m3	super saturation outlet
ϱ , $\frac{kg}{m3}$	specific mass of crystal
α ,	form factor
β,	form factor
γ,	relative de super saturation
τ, h	residence time of particles
ε ,	ratio of diameter = Do/Dp

ACKNOWLEDGEMENT

Keywords: Sodium chloride, Oslo crystallizers, large particle size

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