

Potash Crystallization

Lynn Batten¹, Colin Carbo², Peter Letkeman³, Tim Myers⁴, Michael Tsatsomeros⁵, Sam Yam⁶

Problem presented by Graeme Strathdee, Potash Corporation of Saskatchewan

Report prepared by Tim Myers & Michael Tsatsomeros
with the assistance of Lynn Batten

1 Introduction

1.1 Statement of the problem and objectives

The potash crystallization problem considered at the workshop, as stated by the Potash Corporation of Saskatchewan (PCS), is as follows. PCS recrystallizes potassium chloride, a primary fertilizer and industrial chemical, from saturated brines. Typically, hot brine at about 100° C is cooled by vacuum evaporation in agitated vessels in 2-4 stages to a final temperature of about 40° C. Suspended, growing KCl crystals and agglomerates are typically 40 to 1000 microns in size.

On a macroscopic scale, knowledge of the spatial distribution of the chemical supersaturation state of the brine would help to improve the process control objectives:

- Define conditions for crystal growth
- Minimize occluded brine contaminants trapped in crystals
- Reduce nucleation rate of KCl and increase growth on fluidized solids

KCl supersaturation of brine is a function of these general factors:

- Crystallizer vessel design and controlled temperature setpoint
- Flow rate and temperature of hot feed brine
- Internal circulation rate of the fluidized slurry of crystals
- Particle size distribution and solids density of the slurry
- Heat transfer and mixing characteristics within the crystallizer

Models exist for crystal growth, but not for mapping of the physical supersaturation condition and crystal growth that depends on the overall system fluid dynamics and heat transfer. Modeling an industrial crystallizer operation for interpretation and visualization of 3-D distribution of crystal growth would be a useful engineering accomplishment, for this industry and others.

On a microscopic scale, we observe that fine crystals appear to agglomerate during crystallization to form aggregates. This process increases the particle size distribution above that predicted by surface area dependent

¹Deakin University

²Saskatchewan Telecommunications

³Brandon University

⁴Cranfield University

⁵University of Regina

⁶Brandon University

growth of independent free particles. If this particle growth mechanism and rate could be stimulated by modification of fluidized slurry hydrodynamic conditions, e.g., by increased turbulence to enhance interparticle collisions, then the performance of crystallizers would be improved for potash industry applications.

Modeling of crystallization at the macroscopic or microscopic scales would help to improve experimental investigations and process equipment designs.

1.2 Operating conditions of the crystallizer

The following describes the operating conditions and the process at the first stage crystallizer vessel at PCS, which are depicted in Figure 1.

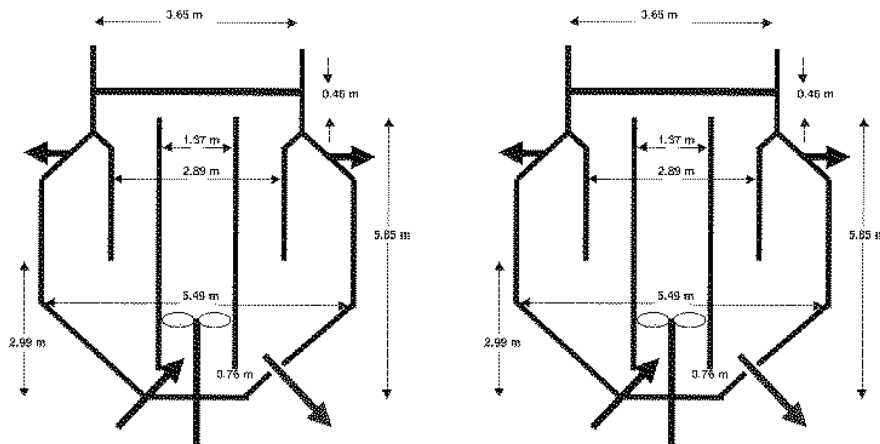


Figure 1: Crystallizer dimensions and operating conditions

The total vessel volume is 96,000 L. A brine solution (slurry) at 96° C and density 1.24 kg/L containing NaCl and KCl is fed to the crystallizer at 455 kg/s. The brine solution is near, but under saturation. The solution is then propelled upward through the inner pipe by an impeller at a rate of 4550 kg/s, resulting in turbulent flow. As the brine solution exits the inner pipe near the top of the vessel, vacuum evaporation (cooling) takes place at 4.4 kg/s. Then the brine flows to a quiet zone where part of it, having density 1.24 kg/L, runs off at 404 kg/s and is fed to the second stage crystallizer. The product, namely sufficiently large KCl crystals, settle and are removed. The typical crystal size distribution observed is displayed in Figure 2. The crystals removed constitute 30% of the mixture. The remaining brine solution (which by now is at 84° C) mixes with incoming brine and recirculates through the impeller and the inner pipe.

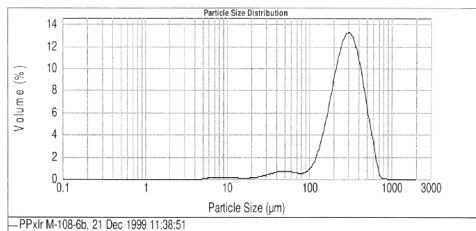


Figure 2: Typical crystal size distribution of KCl

c	Heat capacity	J/kg/K
g	Gravity	m/s ²
H	Heat transfer coefficient from vessel walls	W/m ²
L_c	Latent heat of crystallization	J/kg
L_e	Latent heat of evaporation	J/kg
\dot{m}, \dot{M}	Mass flow rates	kg/s
T	Temperature	K
u	Velocity	m/s
μ	Dynamic viscosity	N s/m ²
ρ	Density	kg/m ³

Subscripts

a	Average
c	Crystal
e	Entrained
f	Feed
k	KCl in solution
N	NaCl and water solution
s	Slurry

2.2 Useful parameter values

The parameter values defined in this section are required for the calculations of §??.

2.2.1 Sodium chloride solution properties

The viscosity of sodium chloride solution is given in [??, pp. 6-250]. Assuming a linear variation between 10 and 20% concentration gives

$$\mu_N = 1.428 \times 10^{-3} \text{ N s m}^{-2} ,$$

at 17%.

The solution density may be inferred from [?]. If the feed solution is saturated with NaCl the density at 96°C is obtained from [??, pp. 6-13]

$$\begin{aligned} \frac{1}{\rho_N} &= 0.886 + \frac{96 - 90}{100 - 90} (0.891 - 0.886) \\ \rho_N &= 1125 \text{ kg/m}^3 . \end{aligned}$$

2.2.2 Potassium properties

Potassium chloride crystals are typically cubic, with a density

$$\rho_c = 1988 \text{ kg/m}^3 ,$$

[??, pp. 4-77]. The feed solution has a density 1240kg/m³. This comprises 25% KCl (in solution), 17% NaCl and 58% water. The potassium density in solution is therefore

$$\rho_k = \frac{1240 - 0.75 \times 1125}{0.25} \approx 1585 \text{ kg/m}^3 .$$

2.2.3 Heat capacity

The heat capacity of water is 4200 J/kg/K. The feed brine has a heat capacity of 3100 J/kg/K. In the absence of information on the heat capacity of NaCl and KCl in solution it will be assumed that they take the same value. In which case,

$$0.25c_K + 0.17c_N + 0.58 \times 4200 = 3100 , \quad (1)$$

$$\Rightarrow c_K = c_N = 1581 \text{ J/kg/K} . \quad (2)$$

The heat capacity of potassium chloride crystals is given in [??, pp. 12-171]. Assuming a linear variation between 350 and 400 K, it has a value of $c_K = 52.6 \text{ J/mol K}$ at 370K (or 96°). A mole of KCl weighs 74.55g therefore

$$c_c = 705.8 \text{ J/kg/K} .$$

2.2.4 Average velocities

The mass flux in the central pipe is 4550 kg/s. This fluid comprises 10% feed brine and 90% recycled solution. The feed brine has density $\rho_f = 1240\text{kg/m}^3$. Since the re-entrained fluid enters below the position of the slurry pipe, it seems likely that the density of the re-entrained fluid is the same as that of the slurry. In which case the density of the re-entrained fluid $\rho_s = 1470\text{kg/m}^3$. The average density of the fluid in the pipe is given by

$$\rho_a = 0.1\rho_N + 0.9\rho_s = 1447\text{kg/m}^3 . \quad (3)$$

The cross-sectional area of the pipe $A = \pi \times 1.37^2/4 = 1.47 \text{ m}^2$. The average velocity in the central pipe is therefore $u_p = Q/(\rho_a A) = 2.14 \text{ m/s}$.

The outer body has the same mass flux and average density. The area is $A = \pi \times (2.89^2 - 1.37^2)/4 = 5.08\text{m}^2$. The average velocity in the outer section is therefore $u_o = 0.61 \text{ m/s}$.

3 Mathematical analysis

3.1 What size crystals drop out?

Using a standard analysis for Stokes flow around a sphere provides the force experienced by a spherical crystal due to the flow:

$$F = 6\pi r \mu_b u . \quad (4)$$

If the Stokes force is larger than the gravitational force, then the crystal is likely to follow the fluid; if it is smaller, then the crystal is likely to drop to the bottom of the tank. This means that spherical crystals are likely to drop to the bottom when

$$6\pi r \mu_b u \sim \frac{4}{3}\pi r^3 (\rho_c - \rho_N) g , \quad (5)$$

see [??]. Using the viscosity and density values defined in §??, ?? and $u = u_o \approx 0.61\text{m/s}$, gives a critical crystal radius of

$$r_{crit} = \sqrt{\frac{9\mu_b u_o}{2(\rho_c - \rho_b)g}} = 681\mu\text{m} . \quad (6)$$

The above analysis relates to the motion of a spherical object, for which analytical solutions are available. A spherical crystal of radius r will have the same mass as a cubic crystal of width l when

$$l = \sqrt[3]{\frac{4\pi}{3}}r . \quad (7)$$

The critical size of cubic crystal is therefore

$$l_{crit} = \sqrt[3]{\frac{4\pi}{3}}r_c \approx 1096\mu\text{m} . \quad (8)$$

All crystals above this critical size will be too heavy to follow the flow. The size distribution diagram provided (Figure 2) shows that very few crystals above $1000\mu\text{m}$ are produced. This is to be expected from the above analysis, which refers to the fastest flow region. In reality, the flow must turn round near the re-entrainment region. The vertical velocity here will be significantly slower than u_0 , so allowing much smaller crystals to drop out.

3.2 Growth rate

The crystal growth rate will depend primarily on the level of supersaturation, temperature above saturation level and surface area. The mass accretion rate may therefore be expressed as

$$\frac{dm}{dt} = c'(SA)^\alpha(\Delta C)^\beta(\Delta T)^\gamma , \quad (9)$$

where SA represents the surface area, ΔC and ΔT represent the supersaturation level. The phase diagram (Figure 3) allows us to relate the temperature to the level of supersaturation, so $\Delta T = f(\Delta C)$ and either ΔT or ΔC may be removed from the above equation. KCl may come out of a supersaturated solution whenever there is a nucleation site or sufficient turbulence to provide the necessary energy. In the central pipe there is a high level of turbulence and existing crystals (from the re-entrained flow). Hence, whenever the concentration moves above the saturation level new crystals or existing crystals may grow immediately. Effectively this means that the concentration will always equilibrate to a value close to the saturation level. In which case, $\Delta C \approx \text{constant}$ and the accretion rate equation becomes

$$\frac{dm}{dt} = c(SA)^\alpha . \quad (10)$$

The mass growth rate therefore depends on the surface area only. This relation involves two unknown constants, which may be determined by comparison with experiments.

As a simple example, assume the crystal is approximately cubic and the growth rate is linear ($\alpha = 1$). If the width of the crystal is denoted by l , equation (10) becomes

$$3\rho_c l^2 \frac{\partial l}{\partial t} = 6cl^2 \quad \Rightarrow \quad l = \frac{2c}{\rho_c}t . \quad (11)$$

The width therefore increases proportionally to time. To determine the growth rate c consider the current experimental results, which give a peak in crystal size distribution with a radius of $300\mu\text{m}$. These crystals are most likely formed at the impeller and have dropped out of the flow at the first opportunity, i.e., they have not been re-entrained and passed through the impeller a second time.

The distance from the impeller to the top of the central pipe is approximately 4.2m. The distance from the top of the pipe to the slurry outlet is approximately 4.85m. Using the average velocities calculated in §??, the transit time from the impeller to the outlet is therefore $t \approx 4.2/2.14 + 4.85/0.61 = 9.9\text{s}$. This gives a value $c = 0.03\text{m/s}$. The crystal size distribution tails off with a maximum crystal size just below $1000\mu\text{m}$. Substituting this value and the value for c in (11) shows that these crystals take $t \approx 30\text{s}$ to form. The largest crystals must therefore travel three times round the system before falling out.

3.3 Diffusion and heat flow

The fluid may be basically treated as having two components, water with NaCl and KCl. These may come from the feed brine or the slurry. We can write down coupled diffusion equations for the mass density of each component. The equations may be written in 1D since the turbulent mixing averages all variables across the region:

$$u \frac{\partial \rho_i}{\partial z} = \frac{\partial}{\partial z} \left(\rho D \frac{\partial}{\partial z} \left(\frac{\rho_i}{\rho} \right) \right), \quad (12)$$

where ρ_i is the mass density of NaCl solution or KCl. The sum of the densities is $\rho = \rho_N + \rho_k$. Flow of a binary mixture is discussed in detail in [??, chapter 18]. Since the flow is turbulent the average velocity field resembles plug flow, so u is constant. This will hold except in boundary layers near the container walls. It will be assumed that this does not have a significant effect on the bulk flow and so u will be taken as constant in each region (i.e., the central pipe and the outer container). The appropriate values are given in §??.

Conservation of mass implies ρ is constant and so (??) may be solved exactly:

$$\rho_i = A_i \exp(uz/D) + B_i. \quad (13)$$

Assuming the mass densities are known above the impeller and with the given value of water removal at the free surface provides three boundary conditions:

$$\rho_i = \rho_{i0} \Big|_{z=0} \quad \frac{\partial \rho_N}{\partial z} = E \rho_N \Big|_{z=L}, \quad (14)$$

where E represents the evaporation rate. From §??,

$$\rho_{N0} = 1125 \quad \rho_{b0} = 1585.$$

The final condition comes from conservation of mass:

$$\rho_k \Big|_{z=L} = (\rho_{N0} + \rho_{k0}) - \rho_b \Big|_{z=L}. \quad (15)$$

A typical value for the turbulent diffusion coefficient D is 0.5 (or lower). With all physically sensible values of E the density profiles specified by equation (??) subject to (??) – (??) show a constant density throughout the length of the pipe. Near the free surface a boundary layer exists where the density quickly adjusts to a new value, depending on the choice of E . Since temperature satisfies the same equation as density, the temperature will also be constant throughout the pipe except for in the vicinity of the free surface boundary layer. Physically this means that convection dominates the temperature and density distribution. Turbulent diffusion is negligible. Temperature and density changes in the central pipe only occur at the impeller and at the free surface. A similar argument will hold in the outer regions of the vessel.

4 Temperature calculation

There are two regions where large temperature changes occur: across the impeller and at the free surface. The analysis of the previous section indicates that convection is the dominant method of heat transfer hence, to estimate the temperature throughout the vessel we need only consider these two regions. For simplicity we will assume that the dominant phase change mechanism at the impeller is crystallization, and at the free surface it is evaporation.

4.1 Mass and energy balances across the impeller

The fluid fed into the inner region of the vessel, below the impeller, is at temperature T_f . This fluid may be considered as consisting of two components, water with dissolved NaCl, and water with dissolved KCl. These enter at rates \dot{m}_N and \dot{m}_K respectively. Fluid from the outer region is also entrained into the inner region. This enters at temperature T_e . The fluid comprises water with dissolved NaCl, dissolved KCl and crystallized KCl. It will be assumed that existing crystals do not re-dissolve. The mass flow rate of re-entrained water and NaCl is denoted by \dot{M}_N , the dissolved KCl by \dot{M}_K and crystal KCl by \dot{M}_c . Above the impeller the solution is well-mixed and all the constituents have the same temperature, T_i . The amount of water-NaCl is unchanged. A proportion of the dissolved KCl has crystallized releasing latent heat, L_c . An energy balance across the impeller gives

$$(\dot{m}_N c_N + \dot{m}_K c_K)T_f + (\dot{M}_N c_N + \dot{M}_K c_K + \dot{M}_c c_c)T_e = [(\dot{m}_N + \dot{M}_N)c_N + \dot{M}'_K c_K + \dot{M}'_c c_c]T_i + L_c(\dot{M}'_c - \dot{M}_c) . \quad (16)$$

A KCl mass balance gives

$$\dot{m}_K + \dot{M}_K + \dot{M}_c = \dot{M}'_K + \dot{M}'_c . \quad (17)$$

Primes denote the new values above the impeller.

The fluid traveling from the impeller region loses little energy and so reaches the free surface at temperature T_i . At the free surface evaporation occurs and water is lost (at a known rate). Energy may also be lost from the side surface of the vessel. The phase change and surface cooling act to reduce the mixture temperature to T_e , which is the entrainment temperature used in equation (??). An energy balance for the remainder of the vessel takes the form

$$[(\dot{m}_N + \dot{M}_N)c_N + \dot{M}'_K c_K + \dot{M}'_c c_c]T_i = [\dot{M}'_N c_N + \dot{M}'_K c_K + \dot{M}'_c c_c]T_e + L_e \dot{M}_e + A_T H(T_e - T_{amb}) . \quad (18)$$

The water-NaCl mass balance is

$$\dot{m}_N + \dot{M}_N = \dot{M}'_N + \dot{M}_e . \quad (19)$$

The feed fluid is at a temperature of 96° C and has a flow rate of 455 kg/s. According to the phase diagram, at this temperature, it is composed 75% water with NaCl, 25% KCl. The entrained fluid is at a temperature of 84° C, with a flow rate of 4095 kg/s. Assuming its composition is the same as the slurry, it contains 70% fluid and 30% crystals. The phase diagram (Figure 3) indicates that at this temperature the fluid is composed of 77% water with NaCl, 23% KCl. The necessary mass flow rates for equation (??) are therefore

$$\begin{aligned} \dot{m}_N &= 0.75 \times 455 = 341.25 & \dot{m}_K &= 0.25 \times 455 = 113.75 \\ \dot{M}_N &= 0.77 \times (0.7 \times 4095) = 2207.2 & \dot{M}_K &= 0.23 \times (0.7 \times 4095) = 659.3 \\ \dot{M}_c &= 0.3 \times 4095 = 1228.5 \end{aligned}$$

The appropriate heat capacities and other quantities are

$$\begin{aligned} c_N &= 1581 & c_K &= 1581 \\ c_c &= 705.8 \\ T_f &= 369.15 & T_e &= 357.15 \\ L_c &= 2.32 \times 10^5 \end{aligned}$$

The unknowns are \dot{M}'_K , \dot{M}'_c , T_i . Equation (??) introduces a further unknown \dot{M}'_N and requires two further values

$$\dot{M}_e = 4.4 \quad L_e = 2.3 \times 10^6 .$$

The product of the surface area of the vessel and the heat transfer coefficient $A_T H$ and the air temperature T_{amb} will be discussed later.

4.2 Results

The mass flow rate of water and NaCl in the outer vessel area may be calculated immediately from (??) as follows:

$$\dot{M}'_N = \dot{m}_N + \dot{M}_N - \dot{M}'_e = 2544.05 \quad (20)$$

This leaves a system of 3 equations (??) – (??) to solve for 3 unknowns. The solution of the system is given by the following equations:

$$T_i = \frac{1.4818 \times 10^{13} T_e - 5.9065 \times 10^{10} T_e^2 + 2.9348 \times 10^{13} + 2.9 \times 10^6 A_T H (T_e - T_a)}{1.4949 \times 10^{13} - 5.914 \times 10^{10} T_e + 1.094 \times 10^4 A_T H (T_e - T_a)} \quad (21)$$

$$\dot{M}'_c = \frac{-3.3778 \times 10^8 + 1.1172 \times 10^6 T_e + 0.625 A_T H (T_e - T_a)}{-1.45 \times 10^5 + 547.0 T_e} \quad (22)$$

$$\dot{M}'_k = \frac{4.7551 \times 10^7 - 2.2391 \times 10^4 T_e - 0.625 A_T H (T_e - T_a)}{-1.45 \times 10^5 + 547.0 T_e} . \quad (23)$$

A selection of solutions is provided in Table 1. The surface area of the vessel, A_T , is set to 75 m² for all calculations. In the first two lines the heat transfer coefficient between the vessel and the air, H , is set to zero, so there is no need to set an air temperature. The next two examples are for an air temperature 30K above freezing. The final two are for 10K below freezing. In the problem description the slurry temperature is 357.15 K. Three of the examples use this value. However, it seems likely that this temperature may vary throughout the year (unless the evaporation rate is reduced accordingly). The other three examples take $T_e = 353.15$ K.

H	T_a	T_e	T_i	\dot{M}'_k	\dot{M}'_c
0		357.15	358.4	785.42	1216.1
0		353.15	354.4	822.95	1178.6
50	293.15	357.15	358.44	782.44	1219.11
50	293.15	353.15	354.43	820.03	1181.52
50	263.15	357.15	358.45	781.05	1220.5
50	263.15	353.15	354.45	818.57	1182.98

Table 1: Values of T_i , \dot{M}'_k and \dot{M}'_c for various conditions

When $T_e = 357.15$ K the temperature in the central pipe varies only slightly, between 358.4 and 358.45, for the three cases considered. The mass flow rate of crystals with no heat transfer from the vessel is 1216.1 kg/s. Allowing heat transfer through the vessel walls increases this by 3 kg/s when the ambient temperature is relatively high. When it is cold the rate increases by 4.4 kg/s. Although the heat transfer coefficient has been chosen arbitrarily, this clearly demonstrates that the production rate is increased if the vessel cooling is increased. Similar statements may be made for the cases where $T_e = 353.15$ K. However, in this case it is clear that the crystal production decreases from the previous case.

5 Conclusions and recommendations

In summary, based on the mathematical analysis and assumptions in §?? and §??., we come to the following conclusions.

Temperature

There are two regions where large temperature changes occur: across the impeller and at the free surface. The temperature throughout the inner pipe is approximately constant, except for in the vicinity of the free surface boundary layer. Physically this means that convection dominates the temperature and density distribution. Turbulent diffusion is negligible. Temperature and density changes in the central pipe only occur at the impeller and at the free surface. A similar argument holds in the outer regions of the vessel.

Moreover, any heat variation is all in boundary layers. *Cooling the sides of the vessel should change this and as a result give bigger crystals.* In the absence of information, the heat transfer coefficient H between the vessel and the air was chosen empirically in §??. Nevertheless, the ensuing analysis clearly demonstrated that the production rate of crystals is increased if the vessel cooling is increased.

Supersaturation

There is no significant supersaturation occurring anywhere in the crystallizer vessel. This is due to nucleation caused by the turbulent flow, which is present everywhere but is particularly intense at the impeller and within the inner pipe.

Crystal growth and size

The size distribution diagram provided (Figure 2) shows that very few crystals above $1000\ \mu\text{m}$ are produced. This is confirmed by the analysis of §??. In fact, our calculations show that crystals of size $1000\ \mu\text{m}$ take $t \approx 30\text{s}$ to form in the crystallizer. This means that the largest harvested crystals travel three times round the system before falling out.

Furthermore, the vertical velocity near the re-entrainment region allows small crystals to drop out.

Based on crystal growth basics, it appears that the operating conditions of the crystallizer result in too many nucleation sites, mainly due to the turbulence and the recycling of the brine. This of course inhibits pure crystal growth.

Clearly, there is some trade off to be considered between pure crystal growth and the formation of aggregates (multi-crystals) promoted by turbulence.

More importantly, *reducing the recycling of the brine should reduce the tail on the size distribution diagram, but not affect the peak.* It should also significantly reduce the number of nucleation sites, which in turn should lead to more rapid crystal growth. Turbulent aggregation will still provide a tail.

References

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