

WAYNE GENCK

**SCALE UP OF
CRYSTALLIZERS**

Agitator Parameters

$$Q = N_Q N D^3 \times 7.48 \text{ (in gpm)}$$

where N is rotational speed in revolutions per minute and D is impeller diameter in feet, and

$$P = \frac{(N_P N^3 D^5 \text{sg})}{1.523 \times 10^{13}} \text{ (in hp)}$$

where D is impeller diameter in inches and SG is specific gravity

Table 1. Agitator Parameters

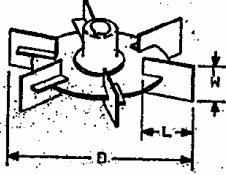
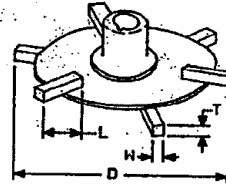
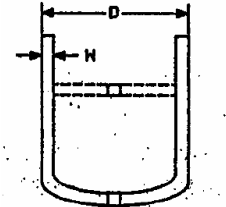

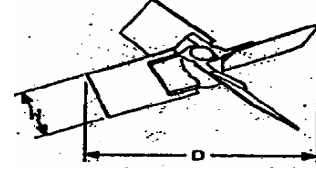

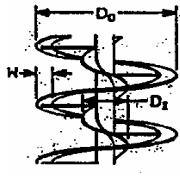
Agitator Type	N_p	N_o	$(Q/P)_R$
PBT	1.27	0.79	1.00
Hydrofoil	0.30	0.56	1.51
Rushton	5.20	0.72	0.18
GL Retreat Blade*	0.35	0.24	0.10
GL Curved Blade Turbine**	1.44	0.54	0.23

$(Q/P)_R$ = ratio of (Q/P) to that with a PBT at constant flow (Q) and diameter (D)

* 2000 gallon glass lined vessel, diameter @ 44" and $N_{Re} > 2.4 \times 10^6$

**2000 gallon glass lined vessel, diameter @ 33" and $N_{Re} > 2.4 \times 10^6$

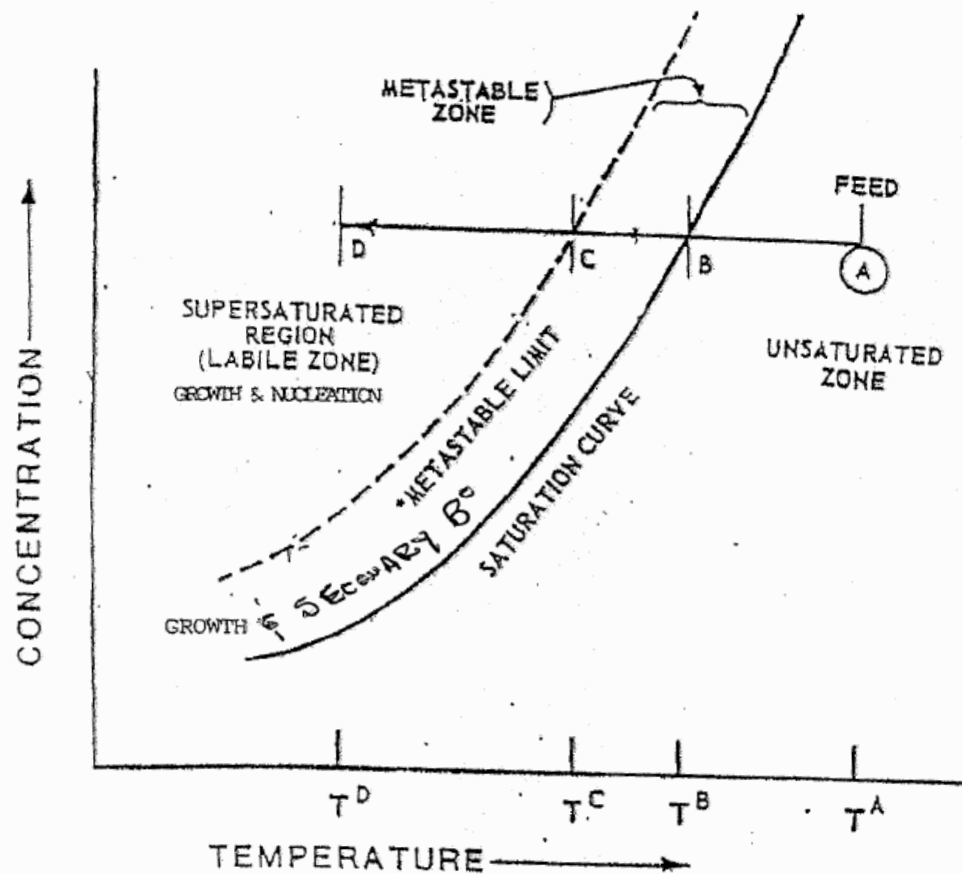
Description of Seven Basic Impellers

Number	Name	Description	Diagram	Dimensions
R-1	Flat Blade	Vertical blades bolted to support disk		$L=1/4D$ $H=1/5D$ DISC DIA. $\approx 2/3D$
R-2	Bar Turbine	6-blades bolted/welded to top and bottom of support disk		$L=1/4D$ $H=1/20D$ $T=1/20D$ DISC DIA. $\approx 2/3D$
R-3	Anchor	Two blades with or without cross arm		$H=1/10D$
A-1	Propeller 3-blades	Constant pitch/skewed back blades		$1:5$ PITCH RATIO
A-2	Axial Flow 4-blades	Constant angle at 45 degrees		$H=1/5D$ $\alpha=45^\circ$
A-3	Axial Flow 3-blades	Variable blade angle, near constant pitch		BLADE ANGLE AND WIDTH DECREASES HUB TO TIP
A-4	Double Spiral	Two helical flights; $pitch = 1/2 D_0$		$D_0 = (\text{OUTER})$ $D_1 = 1/3D_0$ $H = 1/6D_0$

Power and Flow Numbers

		N_p	N_q	Twist	$(Q/P)_R$	
Subal	A6000	0.23	0.59	16°	2.30	
axial	A310	0.30	0.56	16°	1.51	
	A200	1.27	0.79	00°	1.00	FLOW
	A210	0.53	0.55	45°	0.81	
	C100	0.29	0.46	"	0.87	R_m
Chordal	C100	0.25	0.64	13.3°	2.70	4.0
· 8	C102	0.23	0.56	13.3°	1.97	1.8
	A315	0.75	0.73	10°	1.34	2.0
	C104 ^F	0.60	0.52	18°	0.60	PRESSURE
Radial	C104	0.50	0.50		0.65	
	R100	5.20	0.72		0.18	
	R510	0.65				
	R500	0.45				SHEAR

RATIO $(Q/P) / (Q/P)_{A200}$ AT CONST. Q, D = $(\frac{N_p}{1.27})^2$



*METASTABLE LIMIT FUNCTION OF RATE OF COOLING, TEMPERATURE, IMPURITIES, DEGREE OF AGITATION, & PRESENCE OF SEEDS.

FIG. 1 - Concept of Supersaturation

$$S = T^B - T^D = \text{SUBCOOLING}$$

Supersaturation

Difference between system conditions and equilibrium;
driving force for nucleation and growth.

Methods of Generation

- Cooling
- Evaporation
- Evaporative cooling
- Chemical reaction
- Salting out
- Direct-contact cooling
- Other

Types of Mixing

- **Macro** – overall mixing in vessel/blending

RTD – residence time distribution of entering fluid element –
decaying exponential fn with wide range of possible RT's.

- **Micro** - turbulent mixing on the molecular level

$$t_{micro} = 17.3 \left(\nu / \epsilon_{loc} \right)^{1/2}$$

- Viscous – convection deformation of fluid elements
- Inverse – fn of diffusional mass transfer coefficient
- For ppts – important only at high concs. with resulting low values of time constants vs. time constants for mixing

- **Meso** - interaction of feed plumes and bulk/blending – only at rct. zone.

$$t_{meso} = A \left(\epsilon_{avg} / \epsilon_{loc} \right) \left(Q^{1/3} / N^{4/3} d_s \right)$$

which demonstrates the potentially dramatic influence of feed point location

- Baldyga et. al. Turbulent micromixing in chemical reactors – a review. Chemical Engineering Journal, 58, 183 – 195.

Engineering Models

$$\text{Nucleation} \dots B^\circ = k_1 M_T^j s^b \quad (1)$$

B° = number of nuclei formed/unit volume/unit time

k_1 = rate constant fn of temperature

M_T = slurry density

b & j are power functions

s is supersaturation

M_T allows for secondary nucleation. Other formulas include agitation speed or tip speed to a power.

Often $b = 1$ to 3 and $j = 1$

$$\text{Growth} \dots G = k_2 s^g = dL/dt \quad (2)$$

Change in characterization, length

k_2 = fn of temp, agitation, impurities and system

s = supersaturation

g = system specific

$$A_c = k_a L^2 \quad V_c = k_v L^3 \quad M_c = V \rho_c \quad (3)$$

Combining (1) and (2) yields:

$$B^\circ = k_3 G^i M_T^j \quad \text{where } i = b/g \quad (4)$$

Nucleation Mechanisms

Primary – Does not involve participation of product crystals

- Homogeneous
- Heterogeneous

Secondary – Product crystals are involved in nucleation

- Contact
- Shear
- Fracture
- Attrition
- Initial Breeding

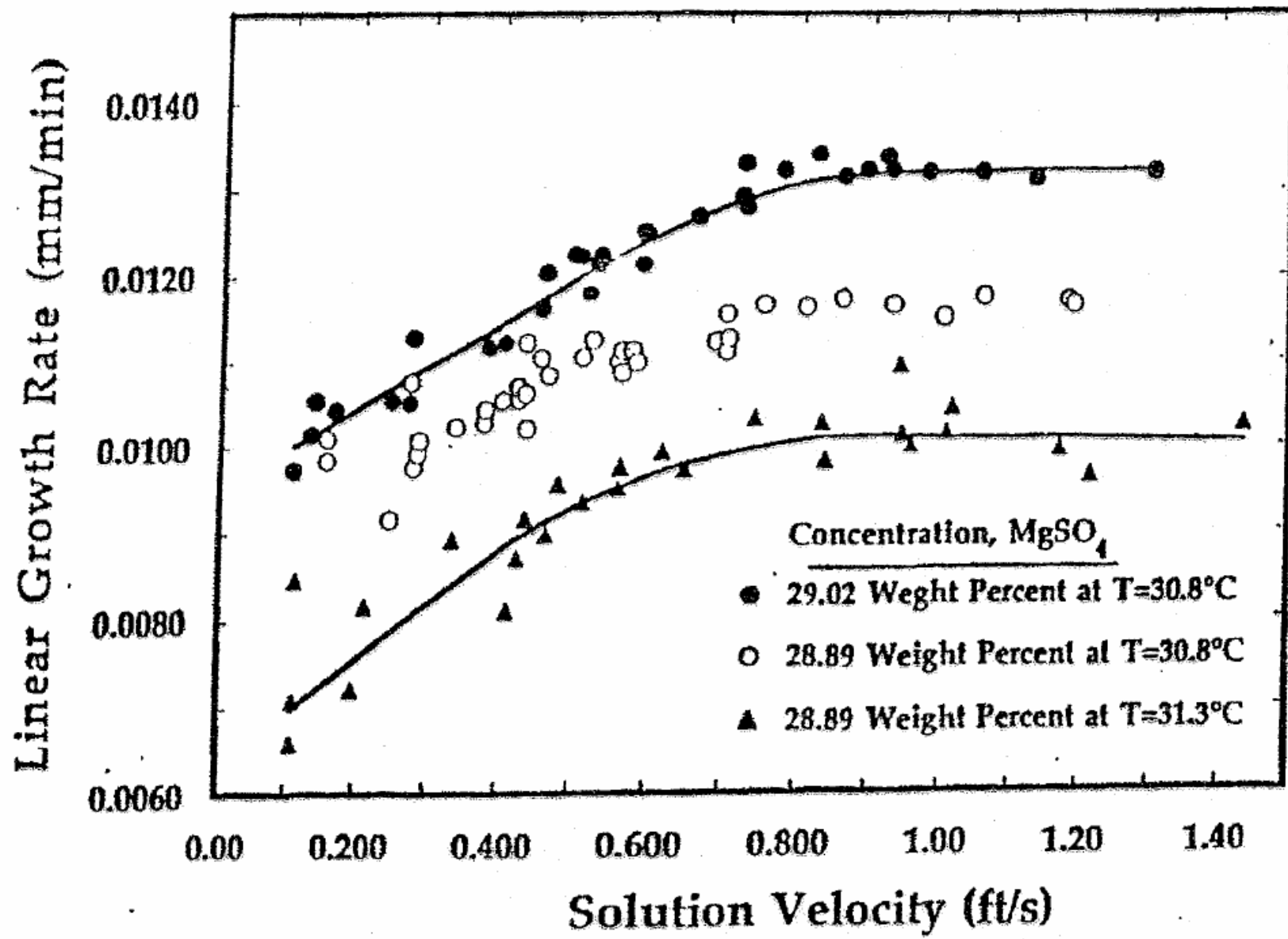
Growth Models

Steps in crystal growth

- Integration or incorporation of the crystalline unit (for example, solute molecules) into the crystal surface (lattice).
- Molecular or bulk transport of the unit from the surrounding solution to the crystal face.

Models for surface incorporation

- Growth by layers
- Growth by movement of continuous step



Crystal Growth

Methods of Expression

- Linear advance rate of an individual crystal face
- Change in characteristic dimension of a crystal
- Rate of change in mass of crystal

$$\frac{dM_c}{dt} = \frac{d(\rho_c k_v L^3)}{dt} = 3\rho_c k_v L^2 \frac{dL}{dt}$$

$$\Downarrow k_a = A_c/L^2 \quad \text{and} \quad G = \frac{dL}{dt}$$

$$\frac{dM_c}{dt} = 3\rho_c \left(\frac{k_v}{k_a}\right) A_c G$$

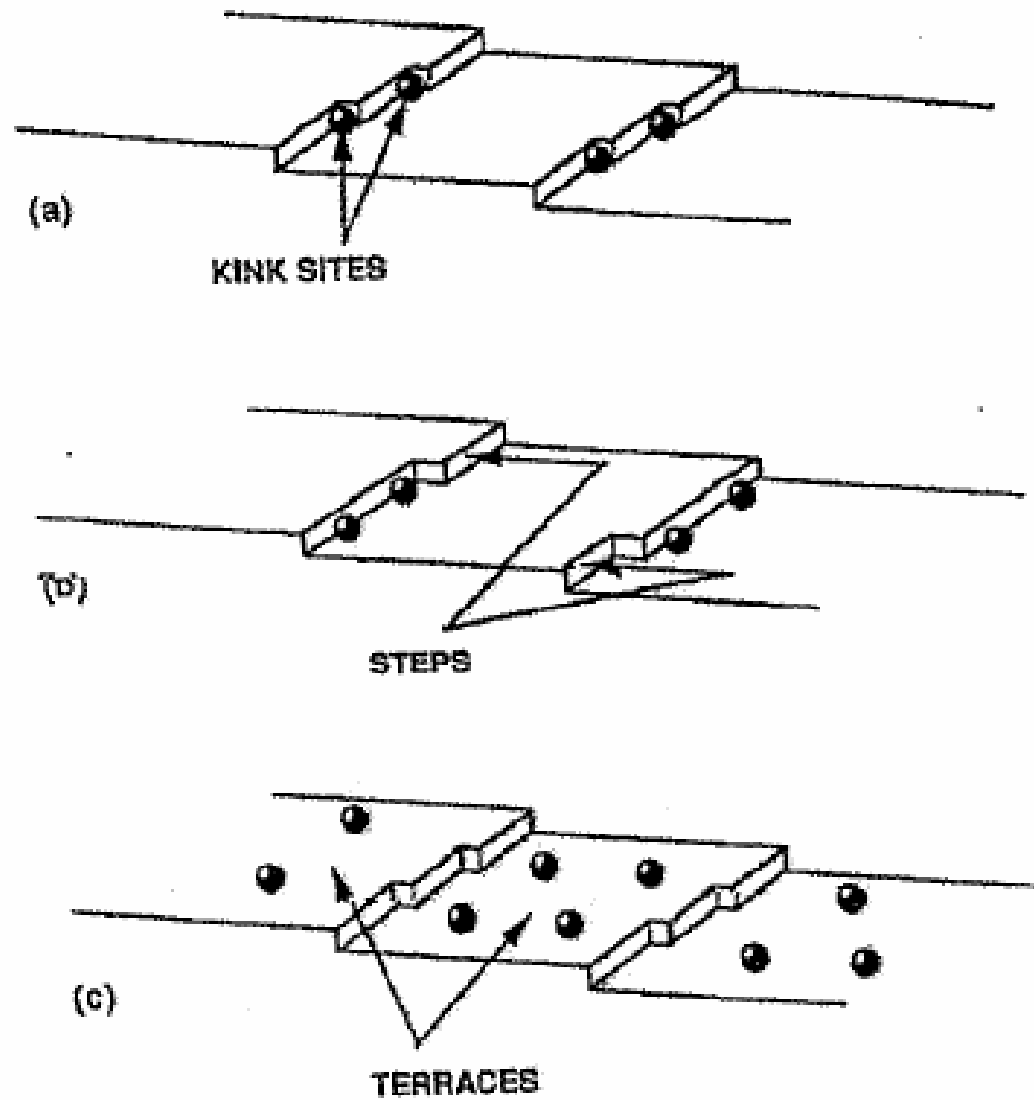


Figure 3. Key surface structures on an idealized crystal face: (a) kinks; (b) steps; and (c) terraces. Adsorbed impurities at each of these sites is illustrated. (Reproduced with permission from Mullin 1980.)

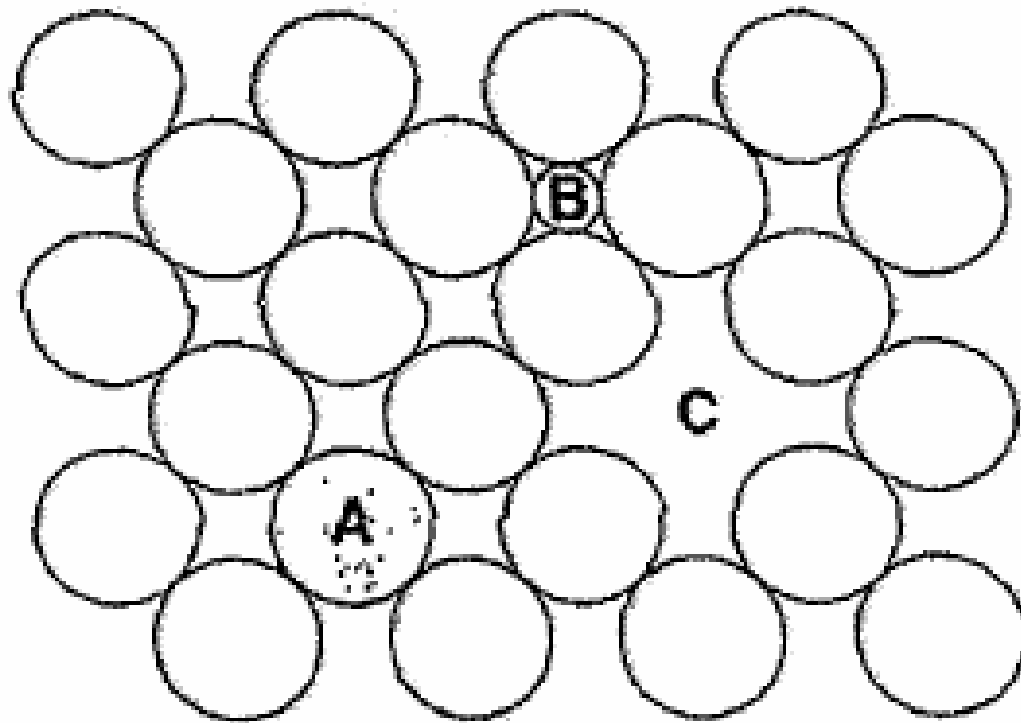
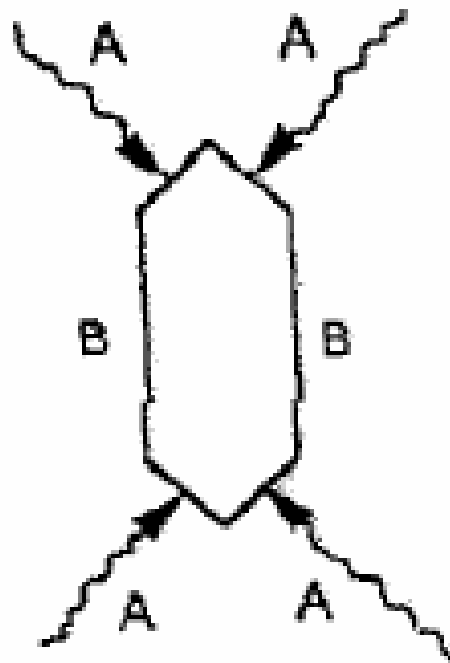


Figure 4. Point defects in crystalline lattice: (A) substitutional; (B) interstitial; and (C) vacancy.

Selective
adsorption
on 'A' faces



Change of habit

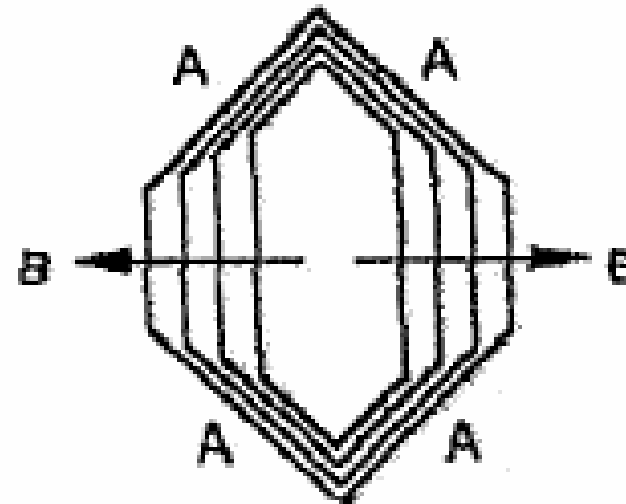


Figure . . 1 Effect of impurities on crystal growth habit.

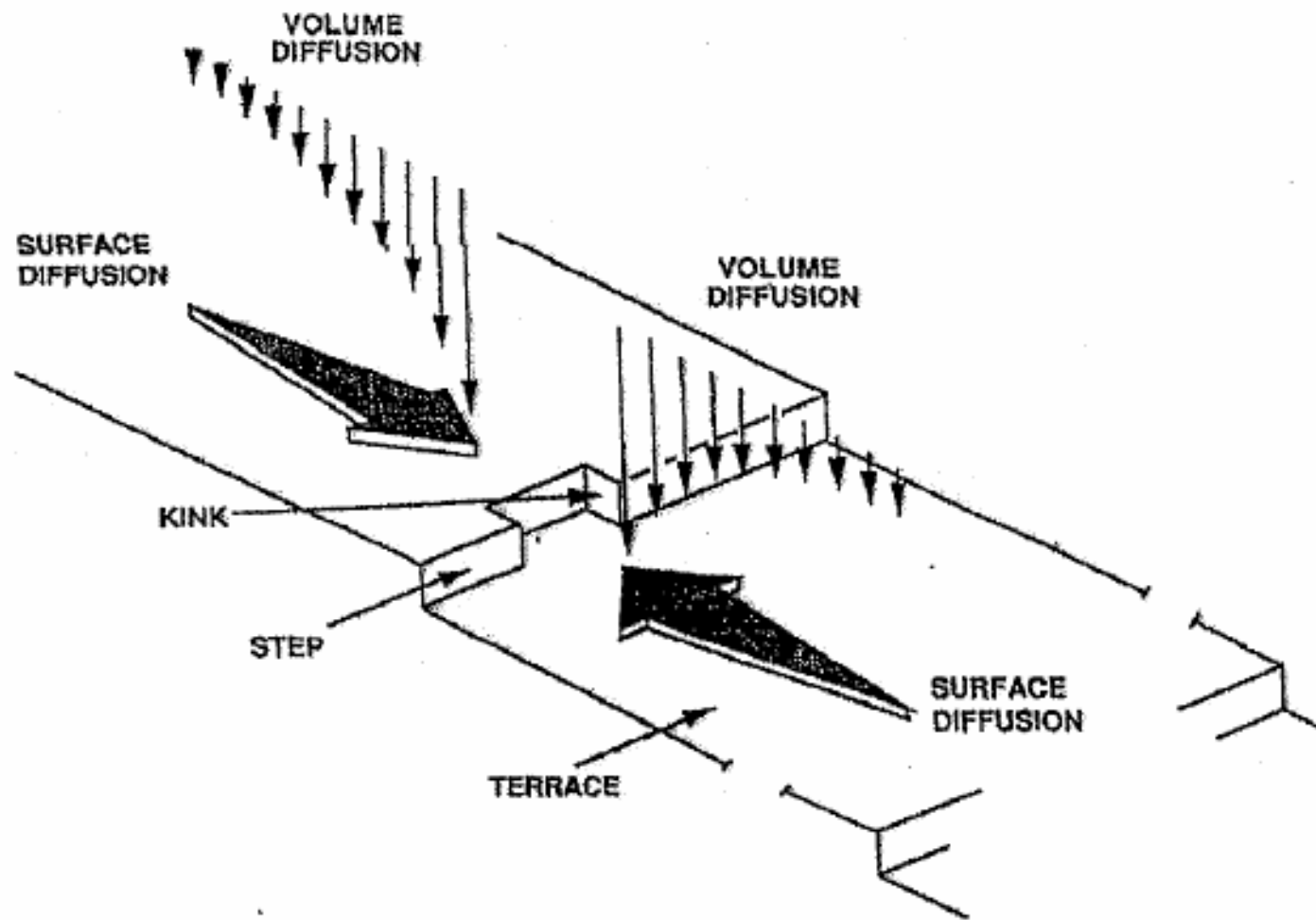


Figure 2. Important diffusional processes (volume and surface) affecting crystal growth.

Primary Heterogeneous Nucleation

Circulation must be adequate to yield a supersaturation which will suppress primary heterogeneous nucleation by keeping all areas within the metastable zone and avoiding the critical limit will result in highly undesired primary nucleation.

$$S_{\max} \propto 1/Q_c$$

Where S_{\max} is the supersaturation and the Q_c is the rate of circulation. The supersaturation must be kept below S_{\max} to avoid primary nucleation.

Secondary Nucleation

Crystal-Impeller contacts have been shown to be the dominant mechanism for low slurry densities and small vessels. It has been shown that the number of secondary nuclei produced is proportional to the energy of impact. For this case, a qualitative model is

$$B_{ci} \propto M_T N^4 D^5/V \propto M_T N(P/V)$$

For a crystallizer with constant S_{max} , Q is constant. Therefore, ND^3 is constant or $N \sim D^{-3}$. Thus, $B_{ci} \sim D^{-7}$.

The use of a large, slow speed impellers with a high N_Q relative to its N_p , such as a hydrofoil, can greatly reduce nucleation.

- P/V Constant

$$B_{ci} \propto D^{-0.67}$$

- Tip Speed Constant

$$B_{ci} \propto D^{-2}$$

N constant = S_{\max} constant

$$B_{ci} \propto D^{+2}$$

The impact of impeller contacts can be reduced by employing impellers made of softer, elastomeric materials. The problem is maintaining the integrity of the coating.

Crystal-crystal impacts become controlling at high slurry densities and large scales. In this case, it can be qualitatively show that:

$$B_{cc} \propto M_T^2 (P/V)^{1.5} d_p^6$$

Attrition/Breakage

This phenomena occurs without the need for supersaturation. Two general modes apply, being

- collisional breakup
- fluid mechanical breakup

The efficiency of the breakage process is dictated by the 2 opposing factors:

- mechanical strength of the crystals
- applied breaking forces

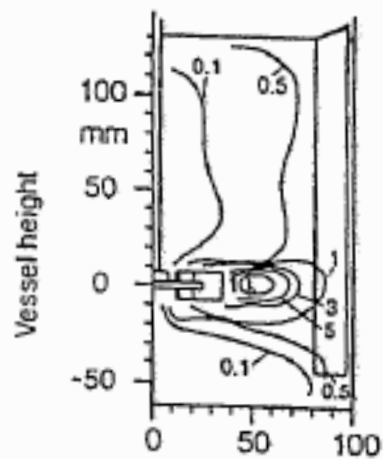
The most important stresses are:

Impact – induced

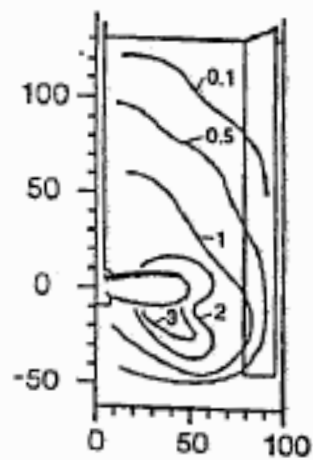
- Crystal-crystal
- Crystal-wall
- Crystal-impeller

Fluid-induced stresses

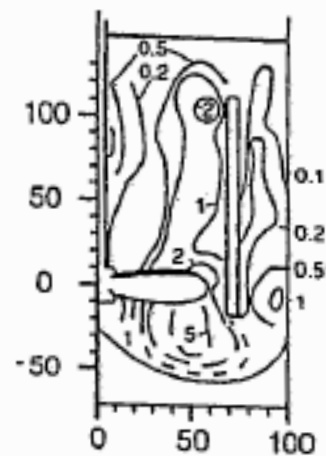
- Shear stress
- Drag stress
- Pressure/normal stress



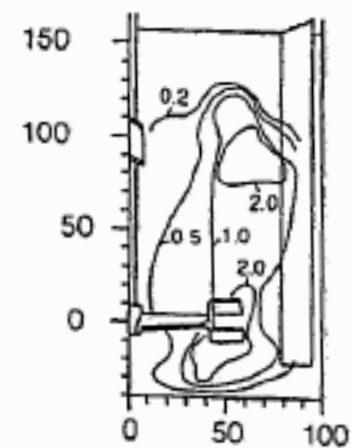
Vessel radius r
6 - blade disk turbine
 $d/D = 0.30$



Vessel radius r
3 - blade propeller
 $d/D = 0.50$



Vessel radius r
3 - blade propeller
 $d/D = 0.58$



Vessel radius r
2 - stage INTERMIG
 $d/D = 0.60$

Local specific power input based on the mean value, $\bar{\epsilon}$, for several stirrers.

POLYMORPHS

**SAME CHEMICAL COMPOUND WHICH
DIFFERS IN INTERNAL SOLID-STATE
STRUCTURE**

**DIFFERENT CRYSTAL STRUCTURES-
CRYSTALLINE POLYMORPHS**

**SOLVATES/HYDRATES
PSEUDOMORPHS**

DESOLVATED SOLVATES/HYDRATES

AMORPHOUS

Table 2. EFFECT OF VARIOUS SCALE UP STRATEGIES

Parameter	Normalized Pilot-Plant	Scale Up Strategy			
		P/V Constant	Q/V Constant	ND Constant	N_{Re} Constant
Power (P)	1.0	125	3,125	25	0.2
P/V	1.0	1.0	25	0.2	0.0016
Speed (N)	1.0	0.34	1.0	0.2	0.04
Impeller Diameter (D)	1.0	5.0	5.0	5.0	5.0
Pumping Capacity (Q)	1.0	42.5	125	25	5.0
Q/V	1.0	0.34	1.0	0.2	0.04
Tip Speed (ND)	1.0	1.7	5.0	1.0	0.2
Reynolds No. $N_{Re} (ND^2 \rho/\mu)$	1.0	8.5	25.0	5.0	1.0

Scale Up Criteria

- Constant stirrer speed

$$N_1 = N_2$$

⇒ constant circulation time and macromixing

- Constant tip speed

$$N_1 \pi d_1 = N_2 \pi d_2$$

$$N_2 = N_1 (V_2/V_1)^{-1/3}$$

⇒ constant mean impeller shear rate approximates constant mesomixing – but on scale up max shear rate ↑ and average shear rate ↓ in impeller zone – therefore distribution changes

- Constant P/V

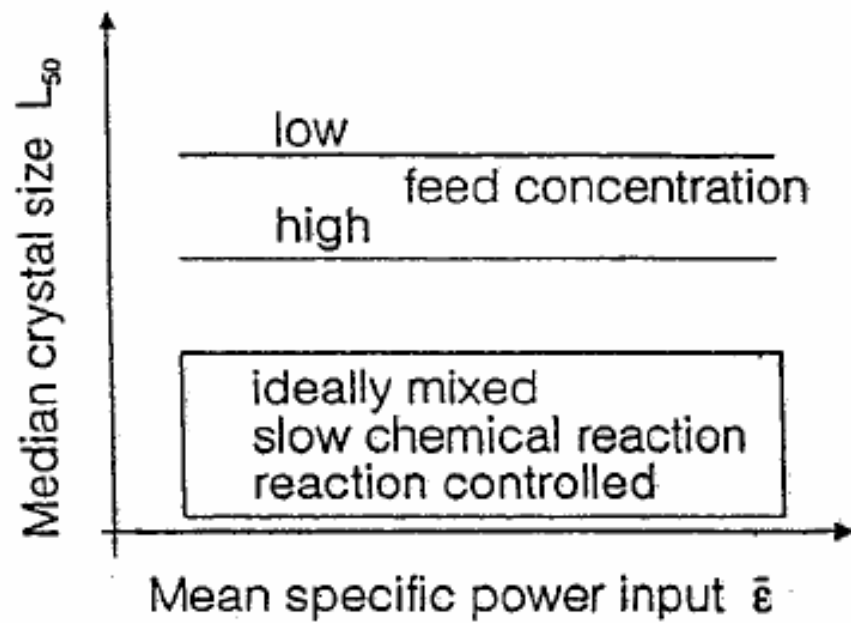
$$N_2 = N_1 (V_2/V_1)^{-2/3}$$

⇒ constant ϵ_{avg} and ϵ_{loc} energy dissipation rates

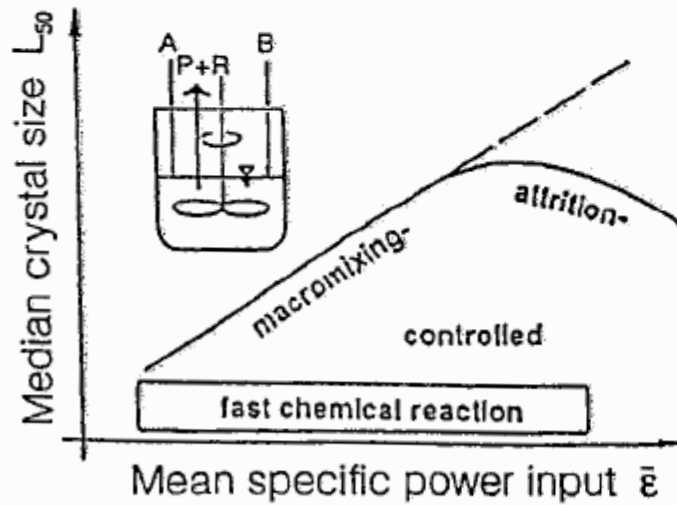
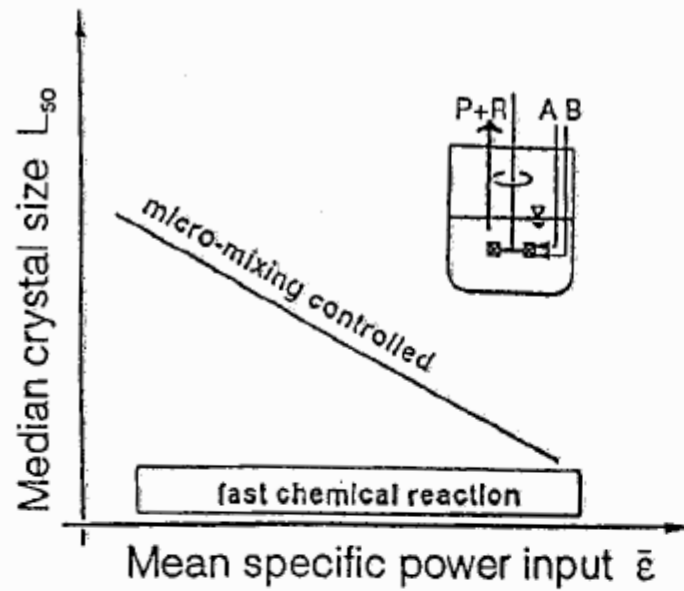
⇒ constant micromixing times related to Kolmogoroff length scale of mixing

Problems With “Rules of Thumb”

- More than 1 limiting mixing process
- Scale up @ constant micromixing times alters the mesomixing times
- Can have a dramatic influence on the B° rates which are influenced by mesomixing times for fast reactions, antisolvent addition/ppts



Median crystal size against specific power input (slow chemical reaction).



Median crystal size against specific power input (fast chemical reaction).

- A brief summary of the definitions for the predicted parameters is as follows:
 1. Maximum value of energy dissipation – microscale phenomena RE: breakage and nucleation.
 2. Local values of energy dissipation.
 3. Characteristic time of micromixing – time of microscale degradation of non-homogeneous concentrations.
 4. Shear rates – at microscale level governs process of mass transport for growing and dissolving solids.
 5. Maximum energy of collisions at zone of maximum turbulence near impeller blades – as the value increases expect an increase in breakage and secondary nucleation.
 6. Energy of collisions in bulk – although less than the maximum value, the large number of collisions in the bulk can affect breakage and secondary nucleation.
 7. Frequency of collisions of maximum energy – if higher, more breakage and secondary nucleation.
 8. Time between 2 strong collisions – average period of uninterrupted crystal growth.

Visimix Simulation

	50 gal. Pilot plant	6,250 gal. Constant P/V	6,250 gal. Plant Constant tip speed
Hydrodynamics			
Mixing power, hp	0.086	10.73	2.20
N_{Re} for flow	70300	5.75 e +05	3.39 e +05
Avg. circ. vel. m/s	0.311	0.517	0.305
Mean circ. time, s	3.79	12.7	21.6
N_{Re} impeller	1.3e + 05	1.11 e +06	6.53 e +05
Tip speed, m/s	3.20	5.44	3.21
Turbulence			
Energy dis. Avg. W/kg	0.356	0.319	0.0655
Energy dis. Max. W/kg	110	110	22.4
Vol. Zone max. dis., cub. M	0.000213	0.0268	0.0269
Characteristic micromixing time, s	4.18	4.43	9.79
Energy dis. @ baffles W/kg	0.147	0.130	0.0267
Energy dis. In bulk w/kg	0.147	0.130	0.0267
Microscale of turb. near blade, m	1.24 e-05	1.24 e-05	1.84 e-05
Microscale of turb. near baffle, m	6.46 e-05	6.66 e-05	9.89 e-05
Microscale of turb. in bulk, m	6.46 e-05	6.66 e-05	9.89 e-05
Turb. shear rate near blade, 1/s	8970	8960	4050
Turb. shear rate near baffle, 1/s	327	309	140
Turb. shear rate in bulk, 1/s	327	309	140
Liquid-solid mixing			
Max. degree axial non-uniformity, %	13.8	9.20	15.9
Max. degree radial non-uniformity, %	0.558	0.237	0.236
Max. energy of collisions, J	7.25 e-11	7.24 e-11	2.51 e – 11
Characteristic time between 2 strong collisions, sec.	38.3	42.5	72.0
Energy of collisions in bulk, J	8.77 e-13	8.11 e – 13	2.82 e – 13
Frequency of collisions of max. energy 1/s	0.0261	0.0235	0.0139

Conclusion

Visimix has proven to be an excellent aid in the design, scale up and troubleshooting of crystallization systems