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in Continuous Manufacturing and Crystallisation

On the investigation of nucleation mechanism in an oscillatory baffled crystallizer

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Structure

- Aim and motivations
- Experimental set up and calibration
- Results and discussions
- Closing remarks

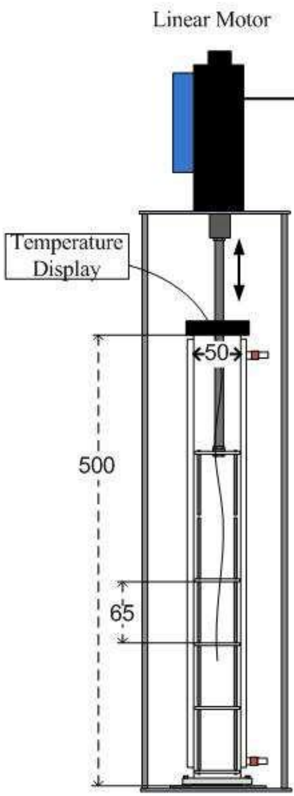
Aim and motivation for work

- Unpublished industrial data show that the oscillatory baffled crystallizer (OBC) allowed nucleation without seeds, whereas the stirred tank crystalliser (STC) must be seeded to produce crystals under comparable operating conditions

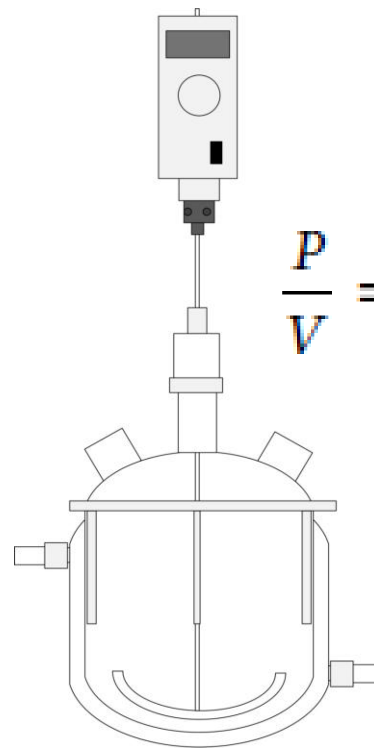
- Aim of the research is to seek scientific explanations to this phenomenon by probing into nucleation mechanisms using sodium chlorate as the model compound

Experimental set up & calibration

– An OBC (500 mL) and a STC (500 mL)



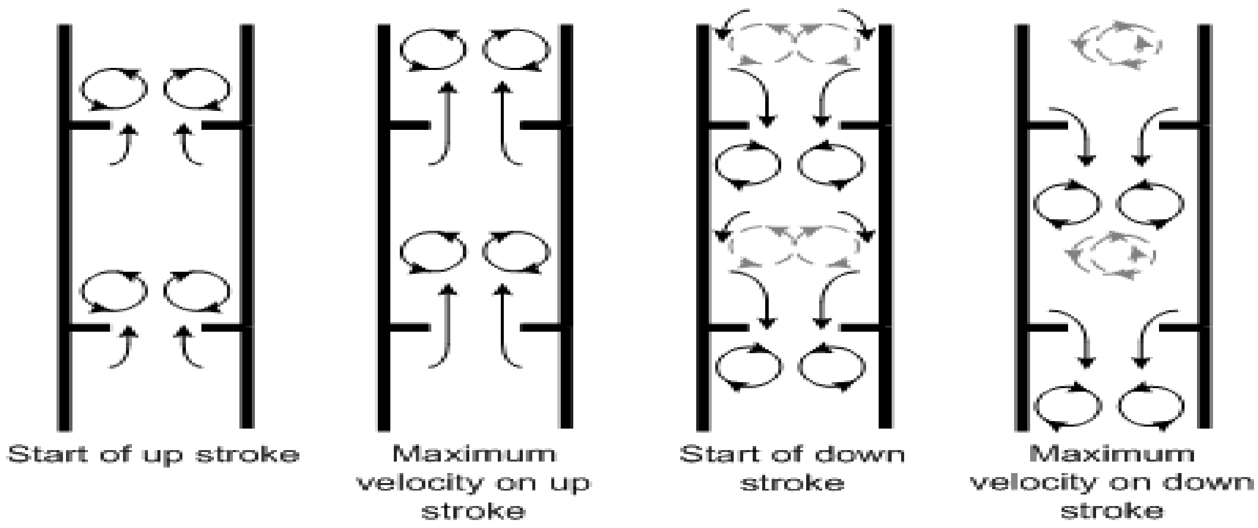
$$\frac{P}{V} = \frac{2\rho N_b}{3\pi C_D^2}\left(\frac{1-\alpha^2}{\alpha^2}\right)x_o^3(2\pi f)^3$$



$$\frac{P}{V} = \frac{P_O \rho N_s^3 D_S^5}{V_L}$$

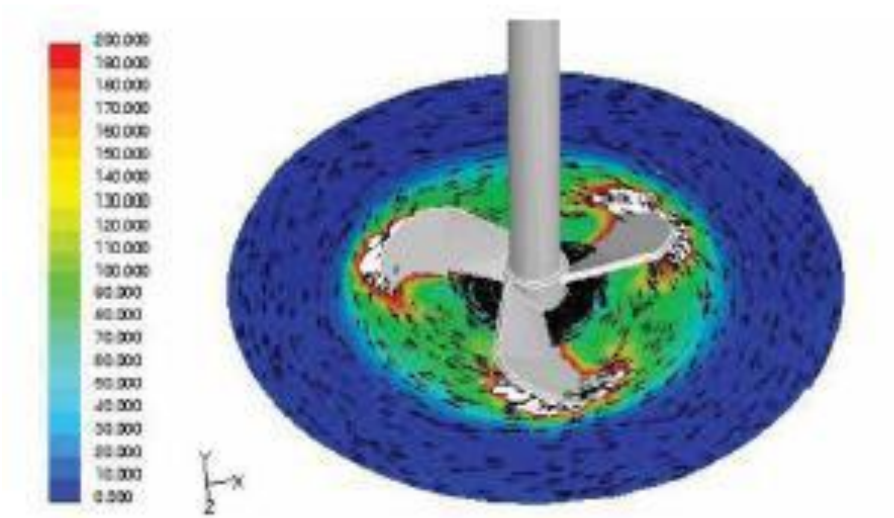
Oscillatory Baffled Crystallizer

- Uniform mixing and improved heat/mass transfer
- Increased specific surface areas, allowing easy temperature control
- Readily scaled up



Stirred tank crystallizer

- Strong mixing at impeller tips dissipated quickly
- Heat/mass transfer constraints due to ineffective mixing overall
- Complex scale up

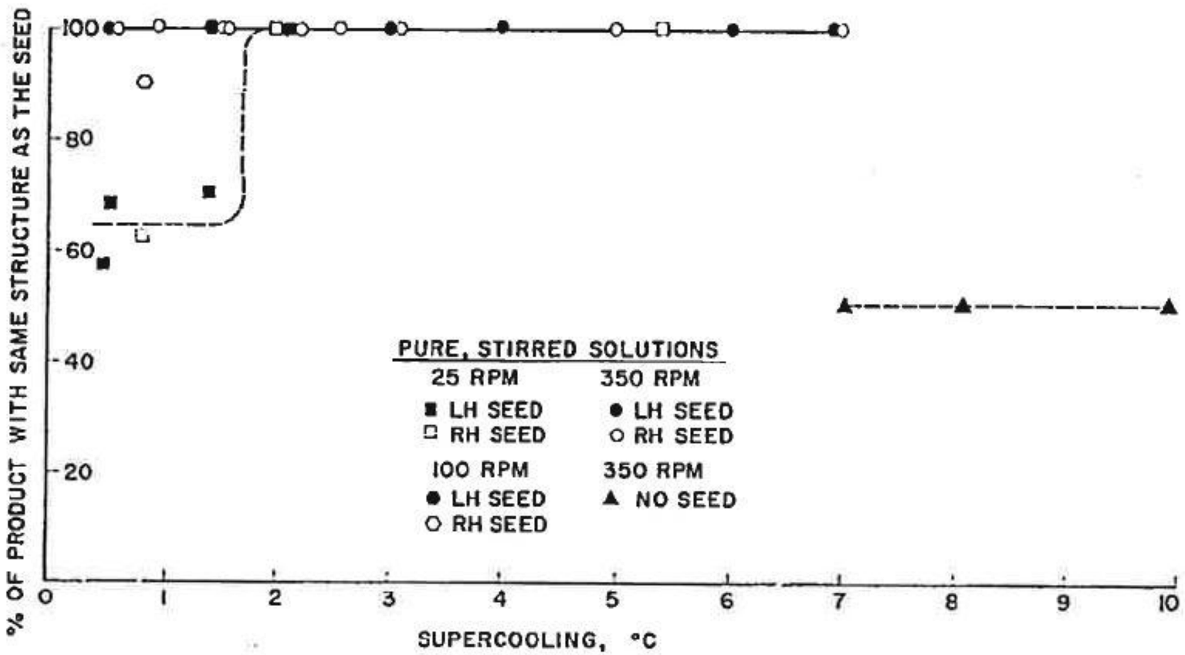


Ristic, R.I., Chem. Eng. Res. Des., 2007. **85**(7): p. 937-944

Experimental set up & calibration

– The basis and the methodology

– Previous research showed that nucleation mechanism could retrospectively be related to handedness of product crystals[1]



1. Denk, E.G. and G.D. Botsaris, J. Cryst. Growth, 1972. **13/14**: p. 493-499

Product analysis

- Polarimetry enables analysis of crystal enantiomorphism

- This is the methodology used throughout the study
- On average 3100 crystals per run were analysed and counted
- Triplet runs for each condition

Procedure

- Solution saturated at 31 °C (approximately 10 M $NaClO_3$ solution)
- Solution cooled to 30 °C
- Supersaturation at $\Delta T = 1$ is approximately 1.02
- On reaching 30 °C, solution seeded with single seed crystal for 3 minutes suspended on metal wire
- Seed withdrawn and mixing stopped
- Crystals developed overnight and analyzed

Results and discussions

Benchmark tests

Test 1 – With NO mixing as well as NO stirrer and baffles in both a STC and an OBC

100 % similarity to the seed was obtained

Test 2 – With NO mixing, but with the presence of stirrer and baffles in both a STC and an OBC (add Test 3 with the wire only)

100 % similarity to the seed was obtained

Results and discussions

Benchmark tests

Test 3 – With mixing, but only a blank metal seed wire was immersed in the solution

No crystals were obtained

Summary 1 – no primary nucleation was found to occur

With seed and with mixing in both a STC and an OBC

	P/V (Wm^{-3})					
sample	12		187		766	
	STC	OBC	STC	OBC	STC	OBC
1	100	94	100	99	100	93.2
2	100	95	100	93.4	100	93.1
3	100	96.3	100	92.9	100	98.3
Average	**100**	**95.1**	**100**	**95.1**	**100**	**94.87**
Standard Error	0	0.67	0	1.96	0	1.72

Summary 2

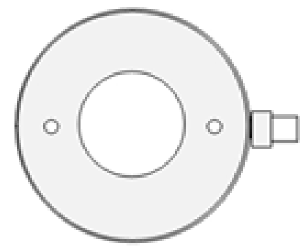
- Results found that the STC always gave crystals of the same form as the seed crystal.

- In the OBC, the product crystals were never 100 % similar to the seed, typically around 95 %.

- What has caused this production of the "*seed-dissimilar*" crystals in the OBC?

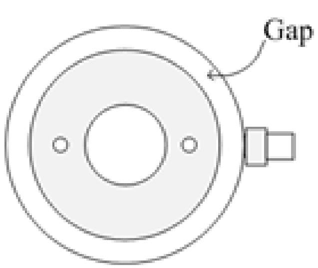
The OBC step up

- Baffles are tightly fitted to the column, the scraping action could be the main culprit



Tight fit baffle

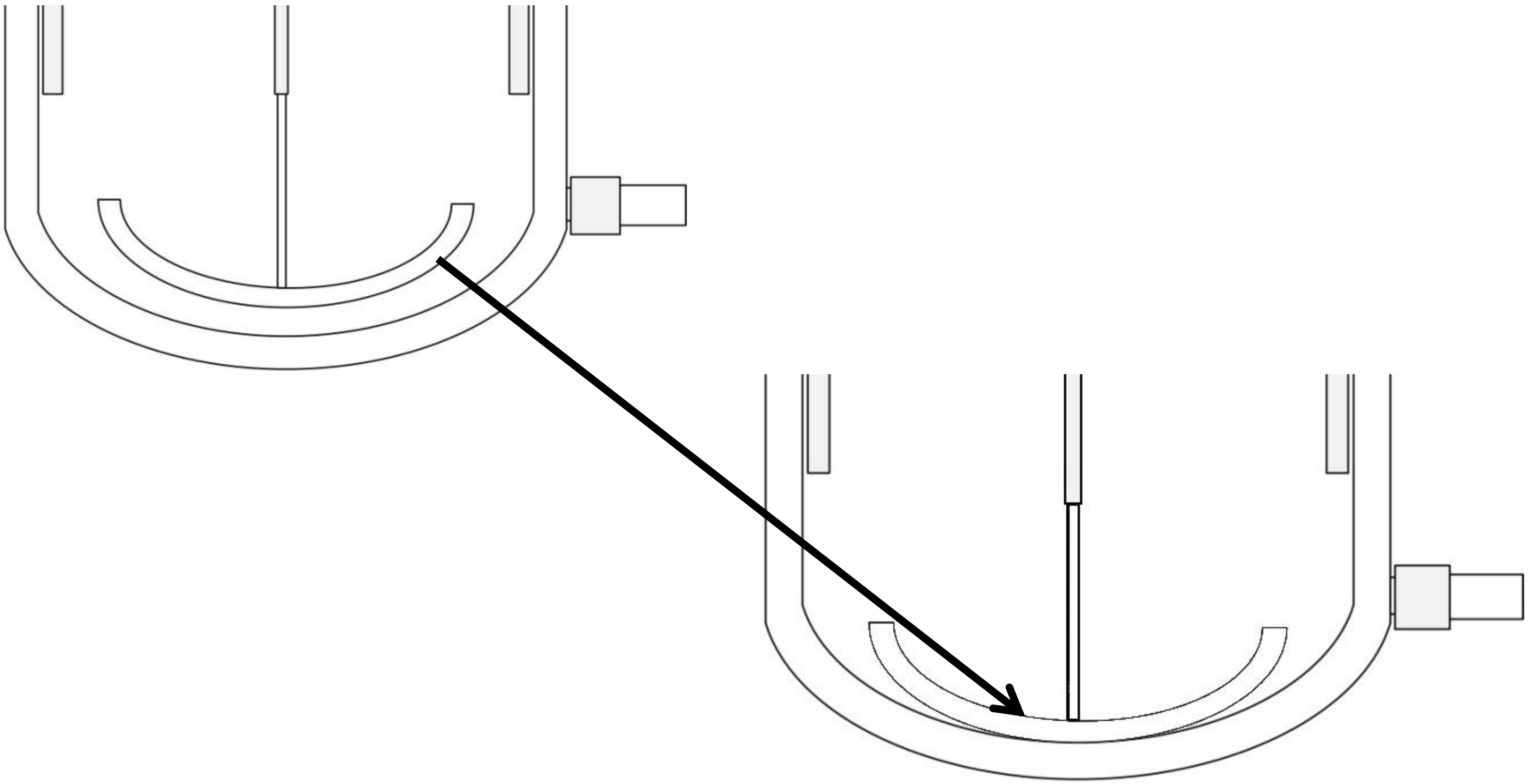
- If this was true, the removal of it from the OBC while adding it to the STC would cast some insights into this hypothesis



Loose fit baffle

The STC setup

– Scraping was introduced by simply lowering the impeller



Testing hypothesis of scraping

- When the gap was introduced in the OBC, similarities increased towards 100 %
- When the impeller was scraping the surface of the STC, *seed-dissimilar* crystals were generated.

	P/V (Wm^{-3})					
sample	12		187		766	
	STC	OBC	STC	OBC	STC	OBC
1	92.6	100	100	98.8	93.6	99.6
2	94.6	97.0	99.0	99.5	96.3	99.8
3	99.7	99.9	92.2	98.7	97.3	99.0
Average	**95.6**	**99.0**	**97.09**	**99.0**	**95.76**	**99.5**
Standard Error	2.1	1.0	2.4	0.2	1.1	0.2

Nucleation rate of seed-dissimilar crystals

- The number of crystals obtained in each experiment is known.
- Seeding was done for a fixed period of time for all tests before agitation was stopped, enabling a small number of large crystals.
- The nucleation rates could be evaluated from this information

For the Scraped OBC

Scraped	Amplitude (mm)		
Sample	7	15	30
1	97.84	98.11	93.2
2	100	95.68	90.5
3	99.92	98.43	93.1
Average	**99.25**	**97.41**	**92.27**
Standard error	0.71	0.87	0.88

Increasing amplitude generated more opposite-handed crystals

For the un-scraped OBC

Un-scraped	Amplitude (mm)		
Sample	7	15	30
1	100	99.95	98.84
2	100	99.93	99.49
3	100	99.42	98.71
Average	**100**	**99.77**	**99.01**
Standard error	0	0.17	0.24

Once again, increasing amplitude generated more opposite-handed crystals, but effect is less pronounced

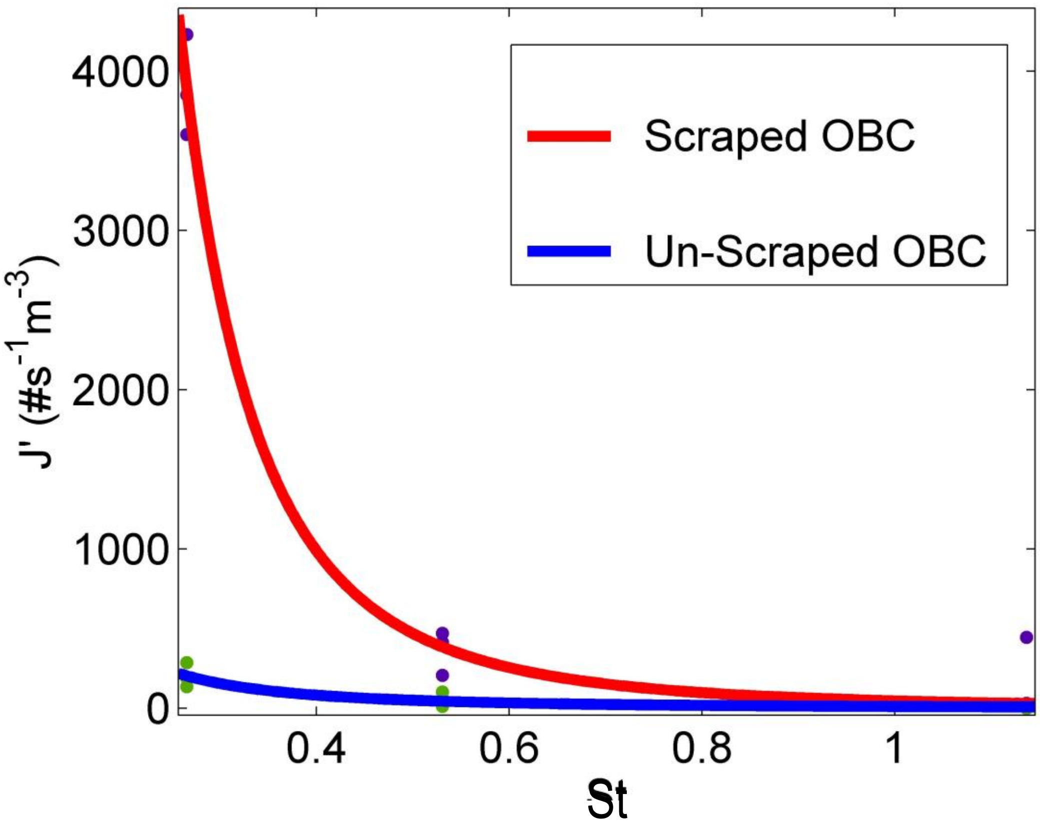
– The amplitude is related to the mixing via the Strouhal number (St)

$$St = D/(4\pi x_o)$$

– The nucleation rate of the *seed-dissimilar* crystals may be related to the Strouhal number, provided the other parameters remained unchanged and independent:

$$J' = K'(St)^m$$

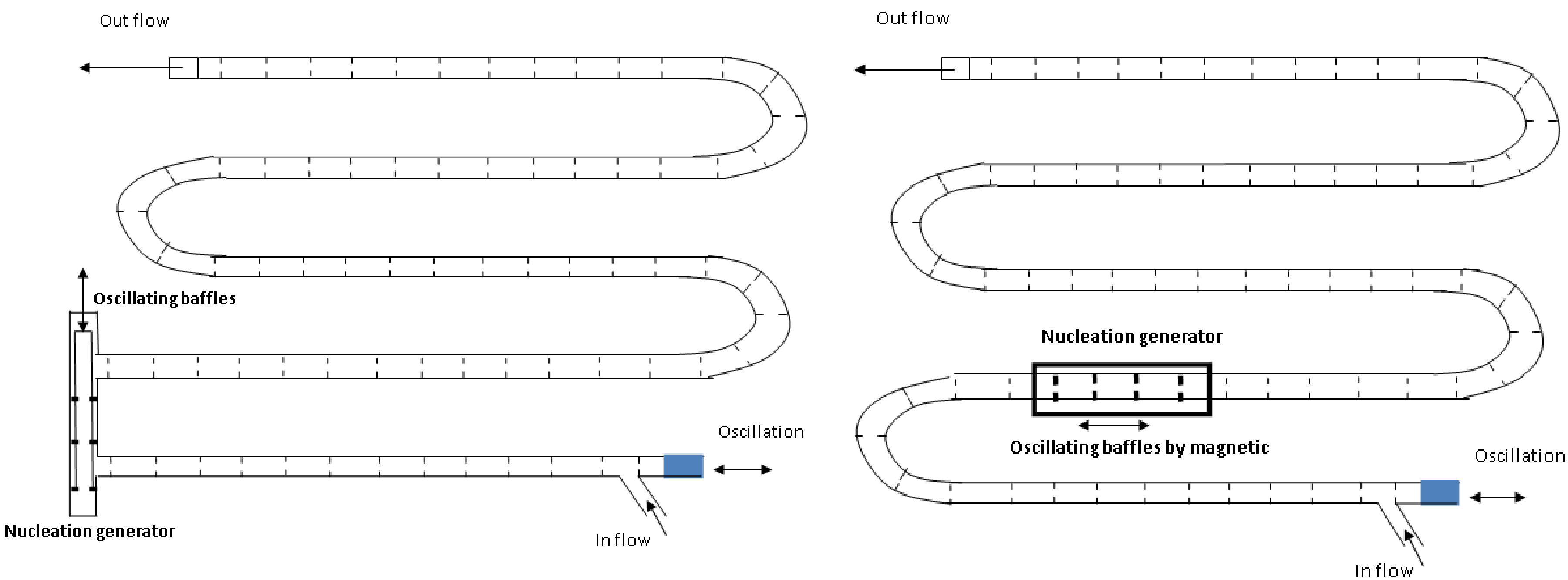
– K' is the nucleation rate constant and m is the order



	Scraped	un-scraped
m	-3.3	-2.2
K’	46	11
r^2	0.98	0.8

Scraping gave much higher nucleation rate (around 10 x) than when scraping was not present

How to utilize the finding



Could this be utilised as a nucleation generator when integrated into a COBC?

Closing remarks

- In the OBC, scraping mechanism seems to be the main driver for the *seed-dissimilar* nuclei being formed

- When scraping is removed, the similarity to seed increases, but we still see the *seed-dissimilar* nuclei. Could this be due to internal surface renewal as a function of mixing?

- Shear forces in the seed crystal boundary layer may be another explanation

- Our next target is identifying what the nucleation mechanism is

Thank you for your attention.

Are there any questions?