A novel approach describing struvite crystal aggregation and granulation in the fluidized bed for phosphorus recovery from swine wastewater

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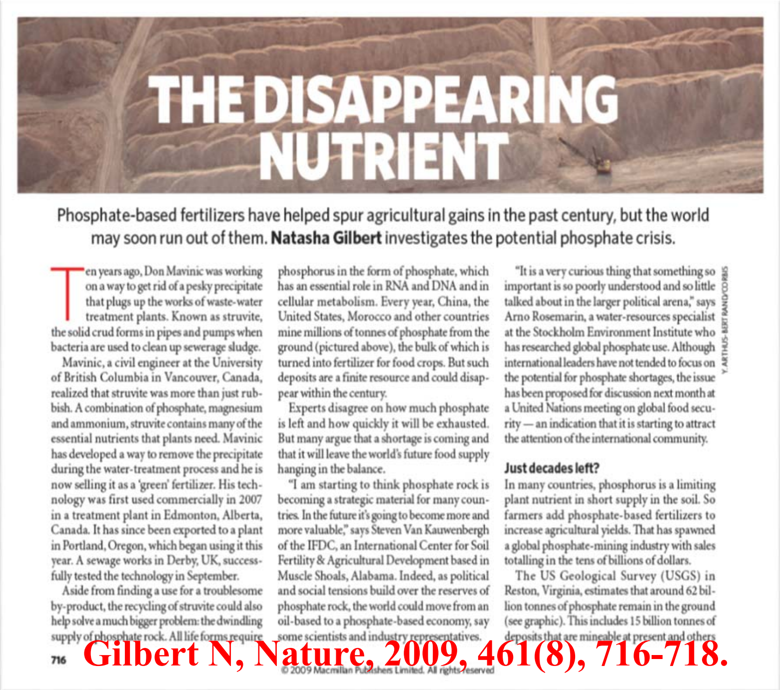
Struvite recovery from wastewater

$$Mg^{2+} + NH_4^{+} + H_nPO_4^{\,3-n} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + nH^{+}$$



THE DISAPPEARING NUTRIENT

Phosphate-based fertilizers have helped spur agricultural gains in the past century, but the world may soon run out of them. **Natasha Gilbert** investigates the potential phosphate crisis.

Ten years ago, Don Mavinic was working on a way to get rid of a pesky precipitate that plugs up the works of waste-water treatment plants. Known as struvite, the solid crud forms in pipes and pumps when bacteria are used to clean up sewerage sludge.

Mavinic, a civil engineer at the University of British Columbia in Vancouver, Canada, realized that struvite was more than just rubbish. A combination of phosphate, magnesium and ammonium, struvite contains many of the essential nutrients that plants need. Mavinic has developed a way to remove the precipitate during the water-treatment process and he is now selling it as a 'green' fertilizer. His technology was first used commercially in 2007 in a treatment plant in Edmonton, Alberta, Canada. It has since been exported to a plant in Portland, Oregon, which began using it this year. A sewage works in Derby, UK, successfully tested the technology in September.

Aside from finding a use for a troublesome by-product, the recycling of struvite could also help solve a much bigger problem: the dwindling supply of phosphate rock. All life forms require phosphorus in the form of phosphate, which has an essential role in RNA and DNA and in cellular metabolism. Every year, China, the United States, Morocco and other countries mine millions of tonnes of phosphate from the ground (pictured above), the bulk of which is turned into fertilizer for food crops. But such deposits are a finite resource and could disappear within the century.

Experts disagree on how much phosphate is left and how quickly it will be exhausted. But many argue that a shortage is coming and that it will leave the world's future food supply hanging in the balance.

"I am starting to think phosphate rock is becoming a strategic material for many countries. In the future it's going to become more and more valuable," says Steven Van Kauwenbergh of the IFDC, an International Center for Soil Fertility & Agricultural Development based in Muscle Shoals, Alabama. Indeed, as political and social tensions build over the reserves of phosphate rock, the world could move from an oil-based to a phosphate-based economy, say some scientists and industry representatives.

"It is a very curious thing that something so important is so poorly understood and so little talked about in the larger political arena," says Arno Rosemarin, a water-resources specialist at the Stockholm Environment Institute who has researched global phosphate use. Although international leaders have not tended to focus on the potential for phosphate shortages, the issue has been proposed for discussion next month at a United Nations meeting on global food security — an indication that it is starting to attract the attention of the international community.

Just decades left?

In many countries, phosphorus is a limiting plant nutrient in short supply in the soil. So farmers add phosphate-based fertilizers to increase agricultural yields. That has spawned a global phosphate-mining industry with sales totalling in the tens of billions of dollars.

The US Geological Survey (USGS) in Reston, Virginia, estimates that around 62 billion tonnes of phosphate remain in the ground (see graphic). This includes 15 billion tonnes of deposits that are mineable at present and others

Y. ARTHUS-BERTRAND/CORBIS

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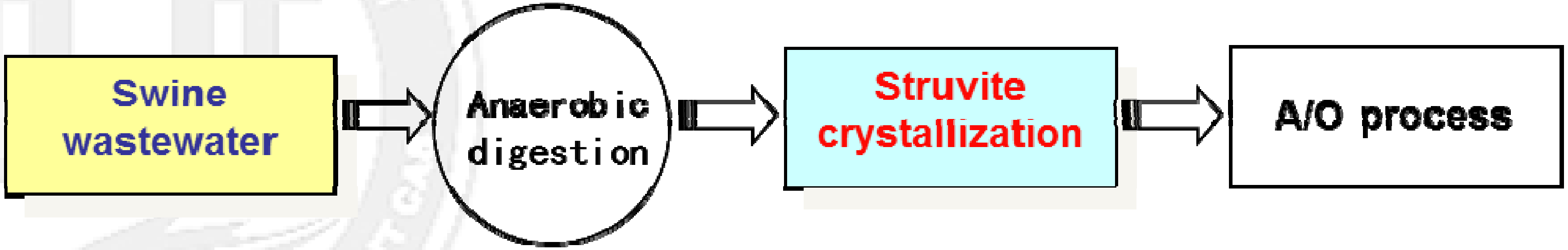
Gilbert N, Nature, 2009, 461(8), 716-718.

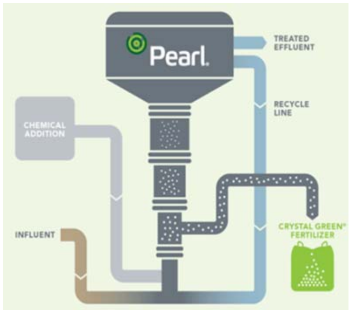
- To relieve **the scarcity of phosphorus rock** resources worldwide

- The recovered struvite can be used as **a good fertilizer** in agriculture for its slow release rate.

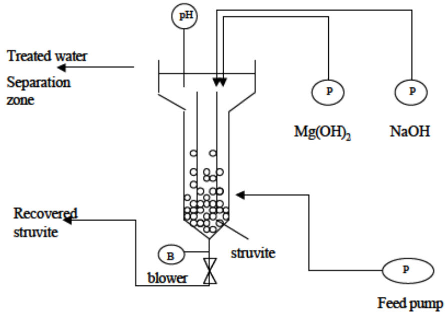


Struvite recovery using the fluidize bed

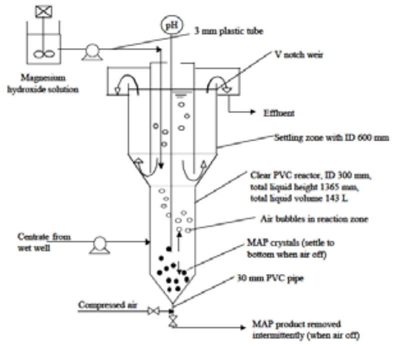
Continuous Stirred-Tank Reactor



Fluidized bed



Fluidized bed



Fluidized bed

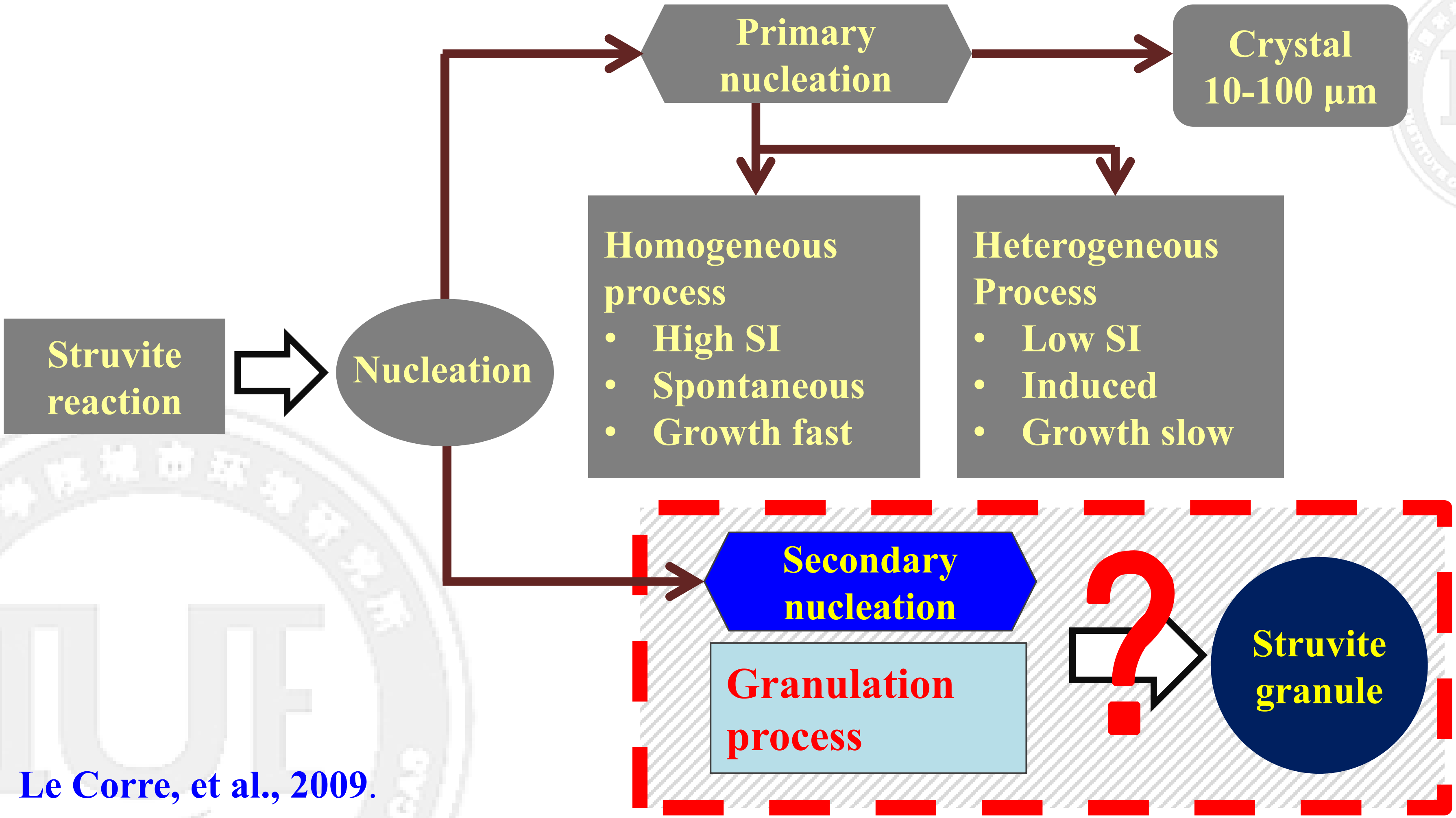
Regy et al., CEEP, 2010

Fluidizef bed Preferable

- Solid and liquid retention times are not systematically similar, and the products can be continuously harvested
- **Millimeter-scale granules** with high purity

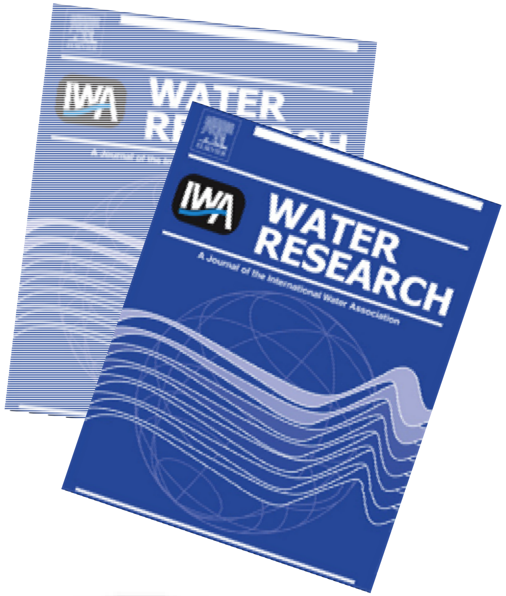
Knowledge on granulation process is lacking

Particle evolution process



Le Corre, et al., 2009.

Knowledge on granulation mechanism is lacking



Modeling phosphorus removal and recovery from anaerobic digester supernatant through struvite crystallization in a fluidized bed reactor

Md. Saifur Rahaman, Donald S. Mavinic, Alexandra Meikleham, Naoko Ellis, Water Research, **2014**, 51, 1-10

Model-driven experimental evaluation of struvite nucleation, growth and aggregation kinetics

S.C. Galbraith, P.A. Schneider, A.E. Flood, Water Research, **2014**, 56, 122-132

Multi-pronged models of struvite growth have been developed from data obtained in a continuous-discrete reactor system (Ali and Schneider, 2008; Hanhoun et al., 2012). However, a very limited number of articles can be traced to the modeling of a fluidized bed crystallizer. In a

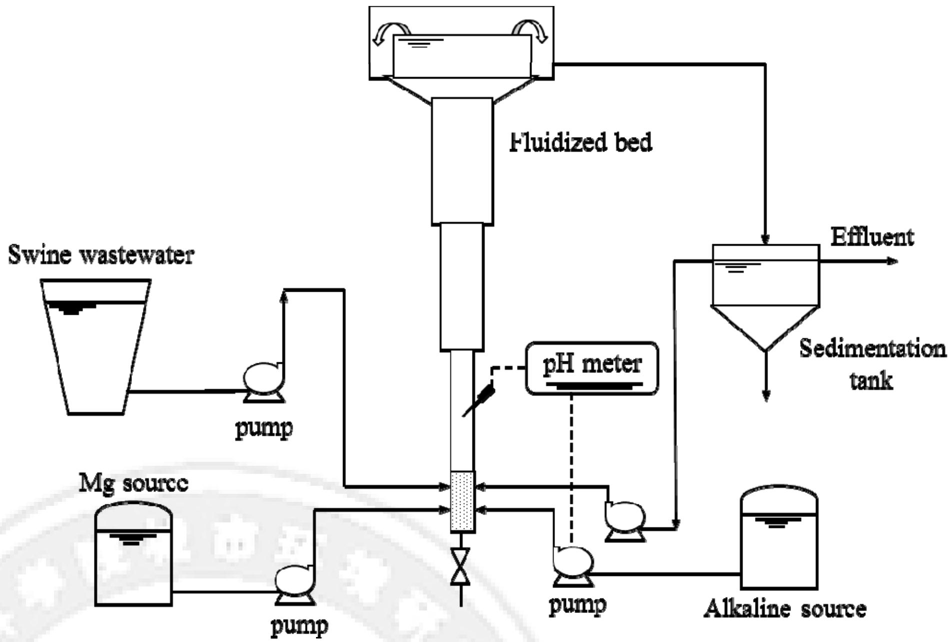
the product crystals over the original model, which was based on perfect size classification of crystals. However, the growth rate expression in this model did not include the effect of crystal size and solid content on crystal growth. Furthermore,

Problems:

- Particle growth rate, operational parameters are hard to determined
- Reactors scale-up still requires knowledge from lab-scale experiments ,which pose problems at process control and optimization

Experimental setup

- **The operational system and the property of swine wastewater**



Fattah et al. (2012)

Parameter	Value
pH	7.22-8.24
COD (mg/L)	198.0-612.4
SS (mg/L)	73.3-613.3
VSS (mg/L)	73.3-326.7
PO_4-P (mg/L)	92.1-128.9
TP (mg/L)	116.2-139.3
NH_4-N (mg/L)	264.7-638.9
TN (mg/L)	287.2-785.1

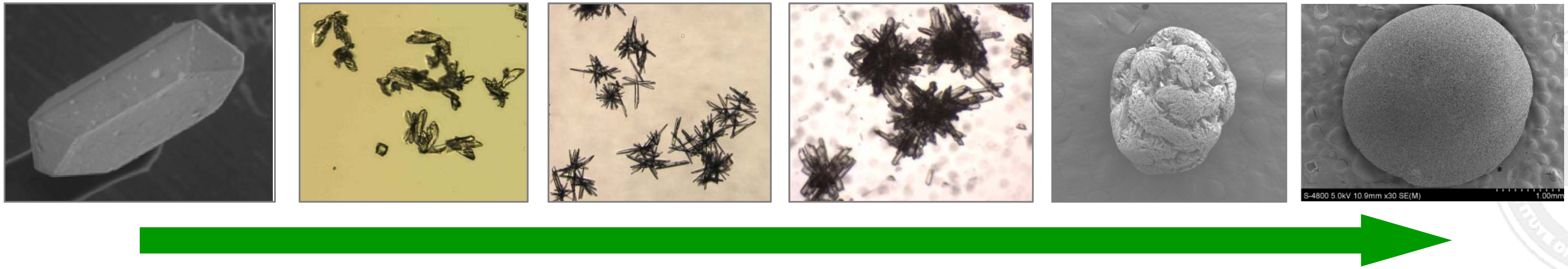
Hydraulic loading was stepwise set at 203.3, 271.1, 338.8, 406.6, 474.4 and 542.1 L/(d·L) corresponding to **the up-flow velocity at 30, 40, 50, 60, 70 and 80 mm/s**, respectively

Analytical methods

- **Morphology**: SEM, stereomicroscope, **image processing**
- **Solid content**: mass & number concentrations
- **Crushing strength:** strength tester machine
- **Granule composition**: XRD + FTIR + elemental analyses + mass balance

Particle measurement method

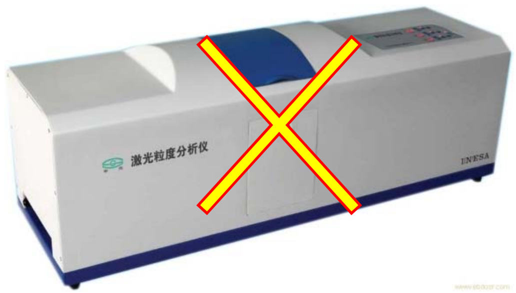
Struvite particles in the fluidized bed



Crystal 10-100 µm   Aggregate 200-1500 µm   Granule 1-5 mm

To determine the particles varying from micron- to milimeter-scale

Stereomicroscope



Laser particle analyzer

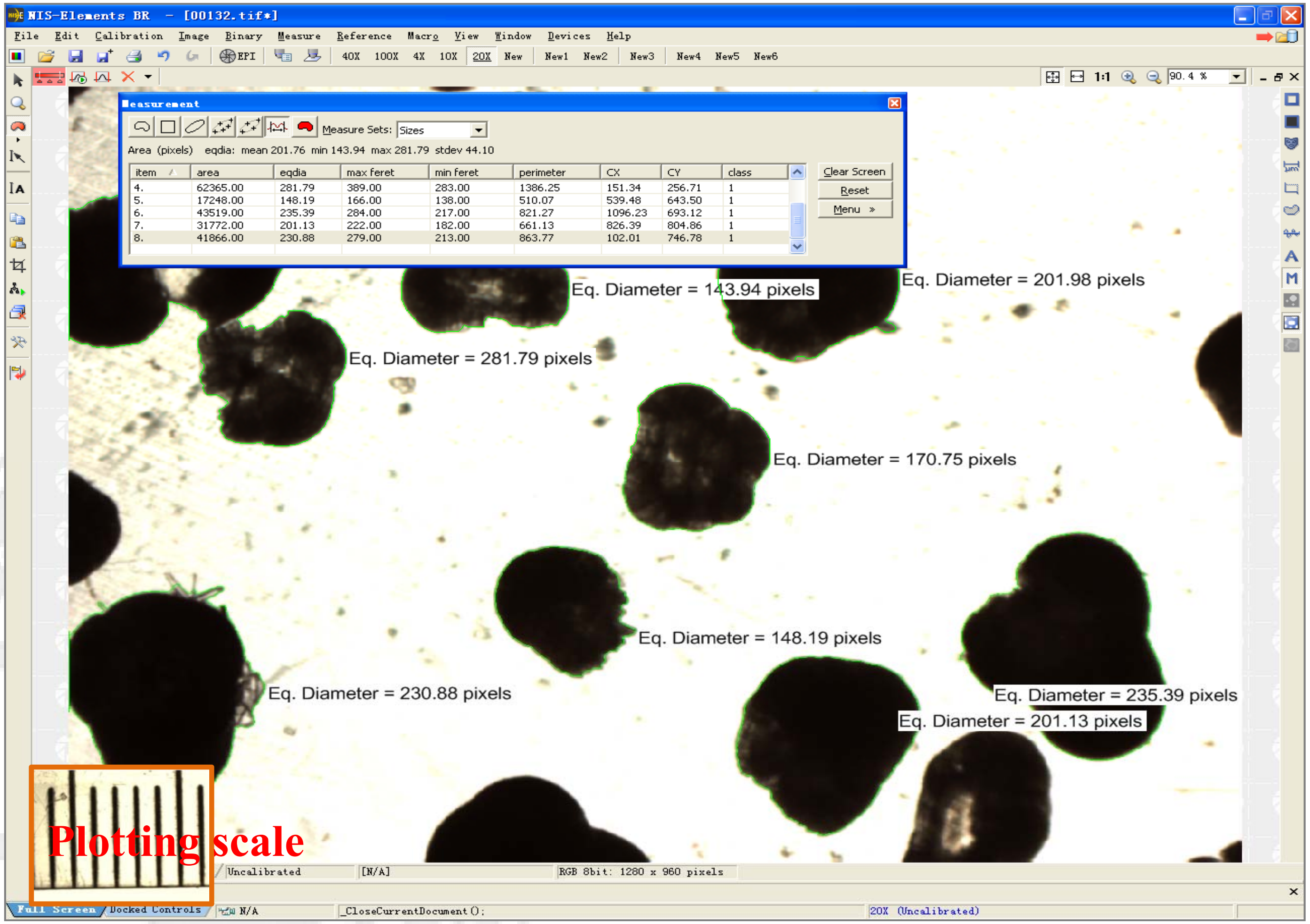
Sieving

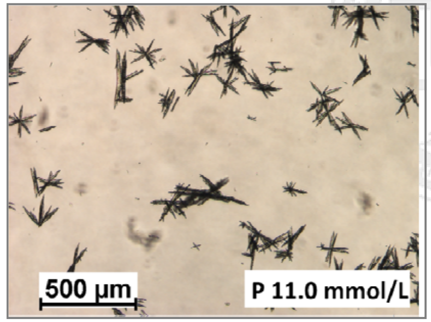
- Laser diffraction is proper to nano- and micron-scale particles
- Sieving is discontinuous, not suitable for distribution analysis

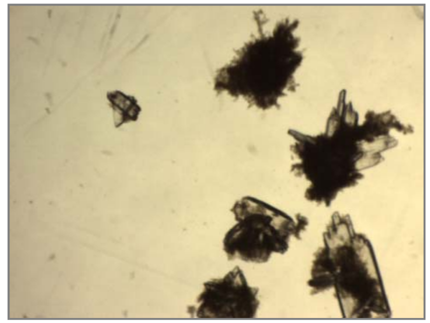
Image processing software

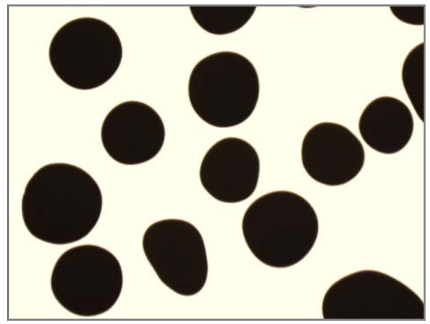
Nikon NIS-Elements BR 2.30:

- Recording the area, equivalent diameter, perimeter, macro axis and minor axis
- The size distribution of particles is determined through statistical analysis

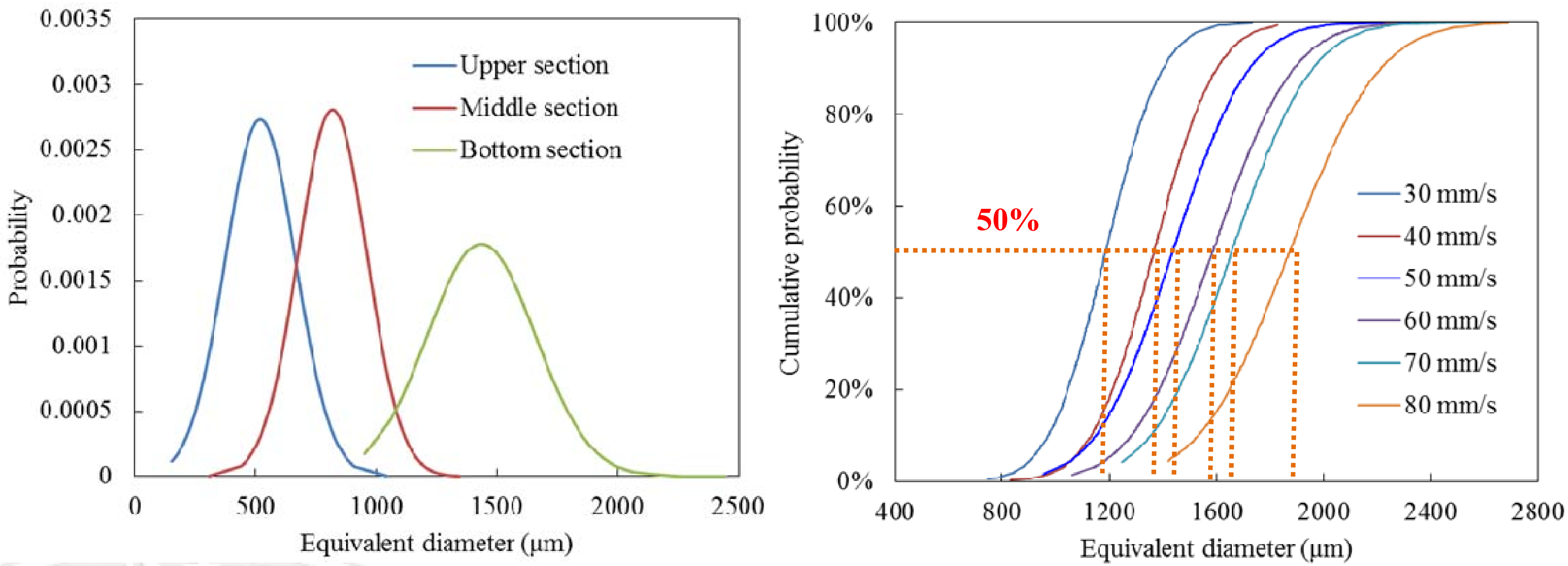








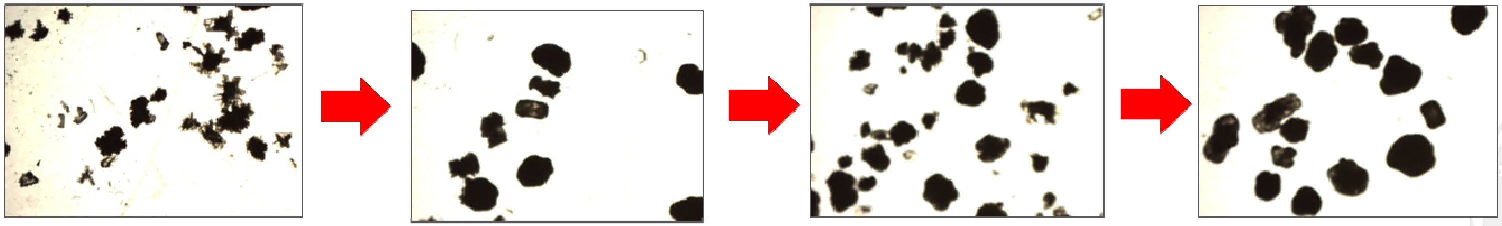
Particle size distribution



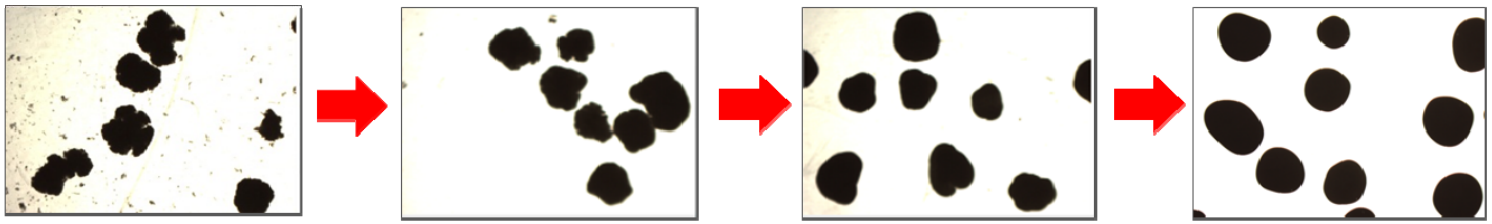
- **After collecting the information of particle sizes, the particle size distribution can be drawn, and the equivalent diameter can be calculated**
- Compared to top and middle sections, higher diameter values and wider size distribution were observed for the pellets generated at the bottom section.
- Higher up-flow rates could harvest more big granules.

Particle evolution

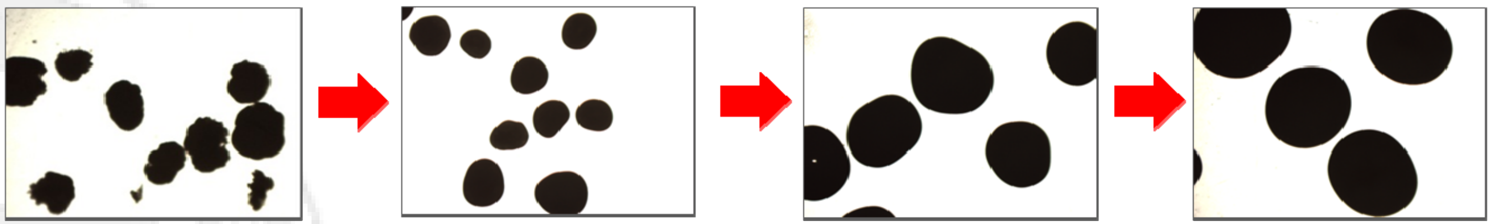
- Top section



- Middle section

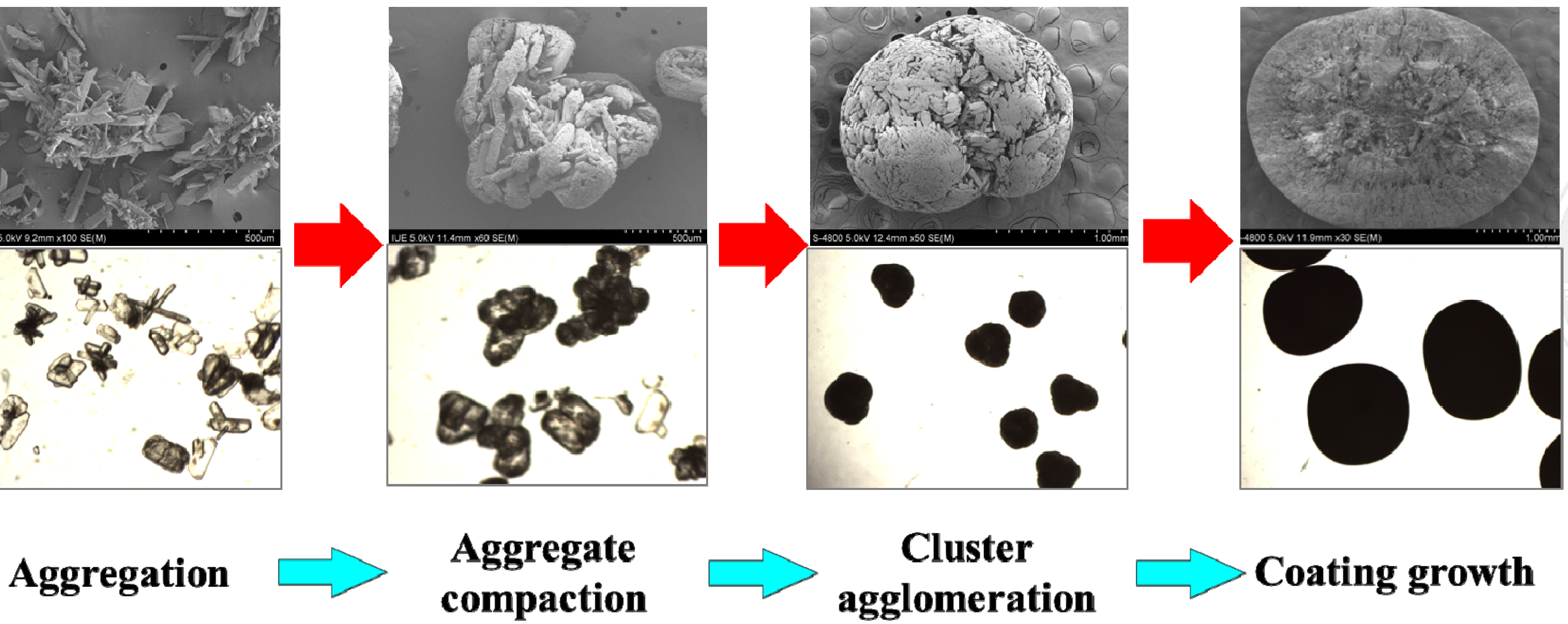


- Bottom section



- Top section: loose aggregates → compact aggregates
- Middle section: compact aggregates → rough granules
- Bottom section: rough granules → smooth granules

inition to the types of particles



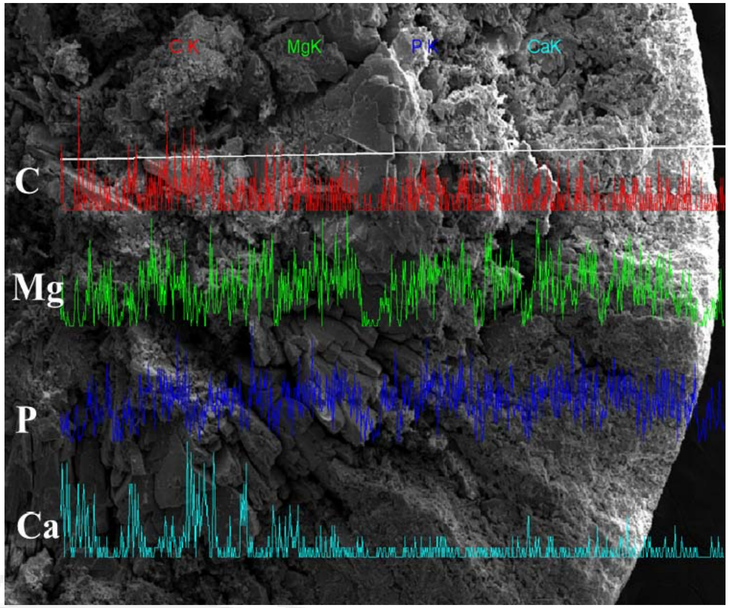
ggregates (AG): formed with needle-shaped or rod-shaped crystals

ompact aggregates (CA): aggregates with compact structure

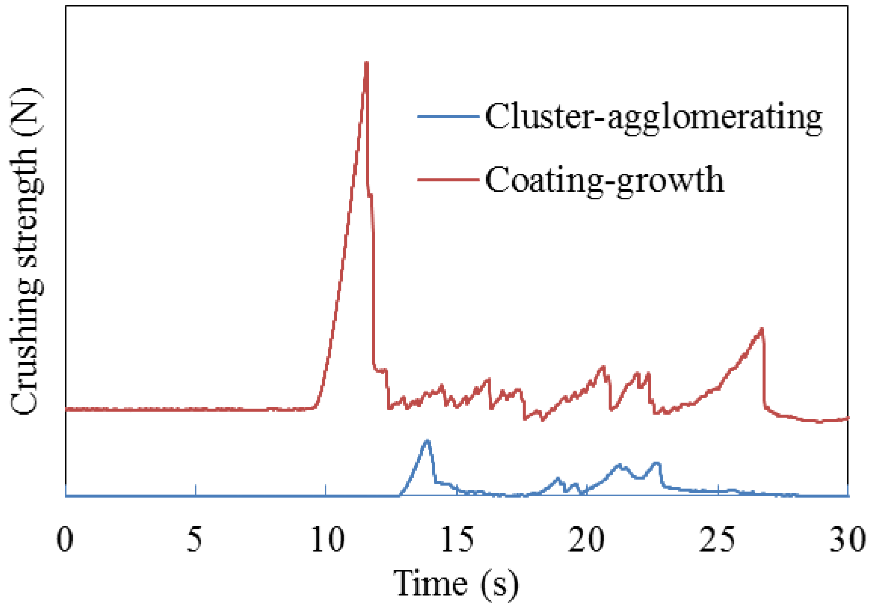
uster-agglomerating granule (CL): granules containing several clusters

oating-growth granule (CT): smooth granules with the construction of

Growth of coating-growth granules



Elemental distribution

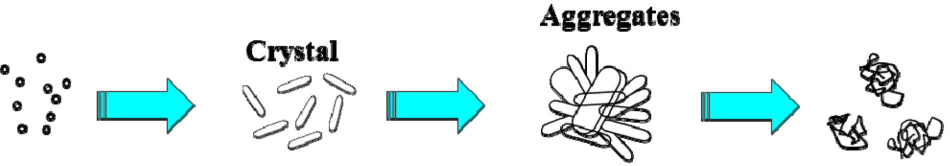


Crushing strength

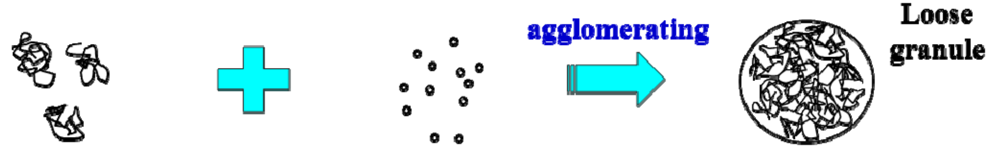
- **Through analysing the morphology, elemental distribution (C/Mg/P/Ca) and crushing strength of coating-growth granules, it can conclude that coating-growth granules were formed with cluster-agglomerating granules as the nuclei.**

anulation process

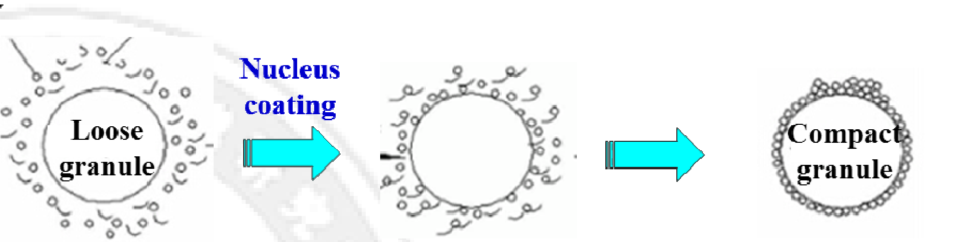
section: aggregates →compact aggregates



dle section: compact aggregates→cluster-agglomerating



tom section: cluster-agglomerating→ coating-growth



- Nucleation
- Crystal growth
- Aggregation
- Aggregate compaction
- Cluster-agglomeration
- Coating-growth

hematic illustration for granulation in the fluidized bed

erational parameter

	Unit	1	2	3	4	5	6
Up-flow rate	(mm/s)	30.0	40.0	50.0	60.0	70.0	80.0
$d_{0.5}$[a]	(μm)	1185.7	1496.5	1435.8	1746.6	1656.7	1871.8
Mass concentration	(g/L)	693.74	600.63	777.13	876.20	863.77	820.13
Number density	(n/L)[c]	100418	57529	55924	42319	39334	20605
v_m[f]	g/(L·d)	-	-6.65	12.61	7.08	-0.89	-3.12
v_n[f]	n/(L·d)	-	3064	115	972	213	1338
v_r[f]	μm/(L·d)	-	22.2	-4.3	22.2	-6.4	15.4
Particle shape[d]		CA+CL(<50%)	CL	CL+CT(<25%)	CL+CT(<50%)	CL+CT(~50%)	CL(<50%)+CT
Up-flow rate	(mm/s)	15.3	20.4	25.5	30.6	35.7	40.8
$d_{0.5}$	(μm)	563.9	674.1	820.3	962.9	1051.5	1174.0
Mass concentration	(g/L)	521.86	577.31	583.12	609.13	656.29	1010.95
Number density	(n/L)	-[e]	-	308082	189763	163945	95607
v_m	g/(L·d)	-	3.96	0.42	1.86	3.37	25.33
v_n	n/(L·d)	-	-	-	8451	1844	4881
v_r	μm/(L·d)	-	7.9	10.4	10.2	6.3	8.8
Particle shape		AG	CA	CA+CL(<25%)	CA+CL(<50%)	CL	CL+CT(~50%)
Up-flow rate	(mm/s)	7.5	10.0	12.5	15.0	17.5	20.0
$d_{0.5}$	(μm)	347.9	609.1	520.9	703.5	982.9	1341.6
Mass concentration	(g/L)	203.54	267.27	329.25	377.90	349.84	372.13
Number density	(n/L)	-	-	-	-	-	-
v_m	g/(L·d)	-	4.55	4.43	3.48	-2.00	1.59
v_n	n/(L·d)	-	-	-	-	-	-
v_r	μm/(L·d)	-	18.7	-6.3	13.0	20.0	25.6
Particle shape		AG	AG	AG	CA	CA	CA

portant parameters: mass (v_m) and radius (v_r) growth rates, number (v_n)

wth mode

her analyses on growth mode

Dominant by cluster-agglomeration

	Unit	1	2	3	4	[illegible]	[illegible]
Up-flow rate	(mm/s)	30.0	40.0	50.0	60.0	70.0	[illegible]
$d_{0.5}$[a]	(μm)	1185.7	1496.5	1435.8	1746.6	1656.7	[illegible]
Mass conc.	(g/L)	693.74	600.63	777.13	876.20	863.77	820.1[illegible]
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Number density	(n/L)	-[e]	-	308082	189763	163945	[illegible]
Particle shape		AG	CA	CA+CL	CA+CL	CL	CL+C[illegible]

Dominant by coating growth

ster-agglomeration: particle number reduction is significant

nclusion

Image processing method can **effectively describe** struvite aggregation and granulation process in the fluidized bed;

Operational parameters, such as equivalent diameter ($d_{0.5}$), radius (v_r) growth rate and number (v_n) reduction rate, can be easily calculated;

Different **particle growth modes** and their corresponding properties can be recorded, which will be good to **process control and optimization**.

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Thank you for your attention

knowledgements

work is supported by the Chinese Hi-Tech Research and

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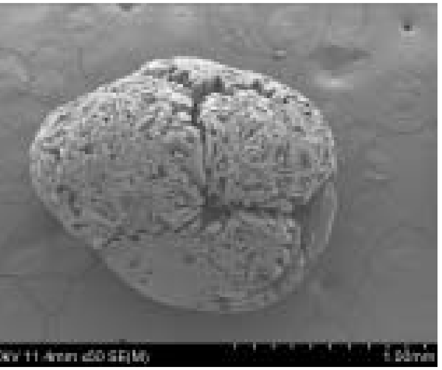
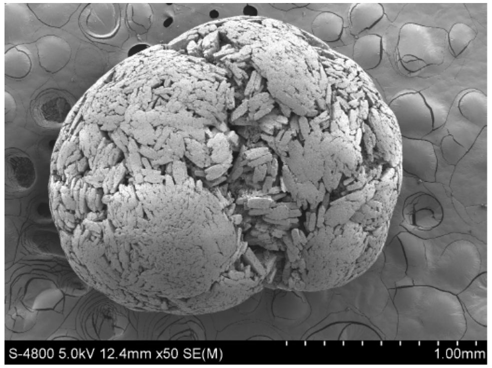
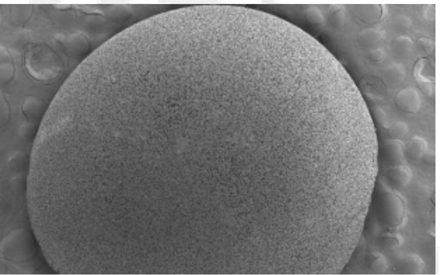
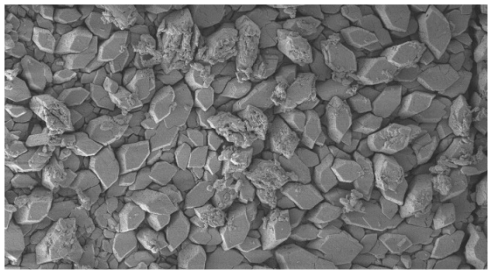
ulation by cluster agglomeration

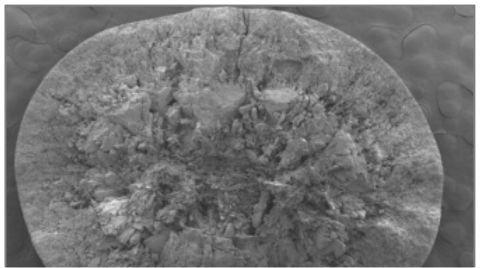




ulation by coating

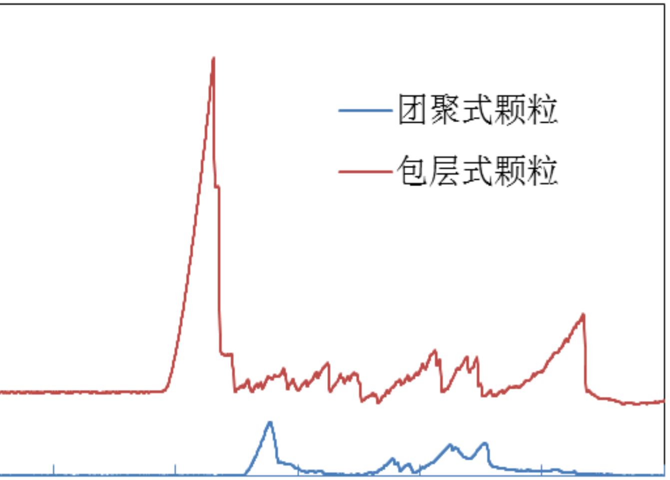






粒破碎强度

		1	2	3	4	5	6
上升流速	(mm/s)	30.0	40.0	50.0	60.0	70.0	80.0
$d_{0.5}$[a]	(μm)	1185.7	1496.5	1435.8	1746.6	1656.7	1871.8
破碎强度	(N)	1.79	4.33	4.64	7.59	9.54	12.61
颗粒形貌		CA+CL	CL	CL+CT	CL+CT	CL+CT	CL+CT



- 颗粒粒度大小与破碎强度有正相关关系
- 团聚式颗粒破碎强度与每个絮团相差不大
- 包层式颗粒破碎强度主要由致密