$Ca(OH)_2$-Na_2CO_3-NaOH 시스템에서 발생하는 NaOH의 재활용 특성

박현서, 김정환, 정선희, 김정아, 안지환
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Recycling Properties of NaOH Produced in $Ca(OH)_2$-Na_2CO_3-NaOH System

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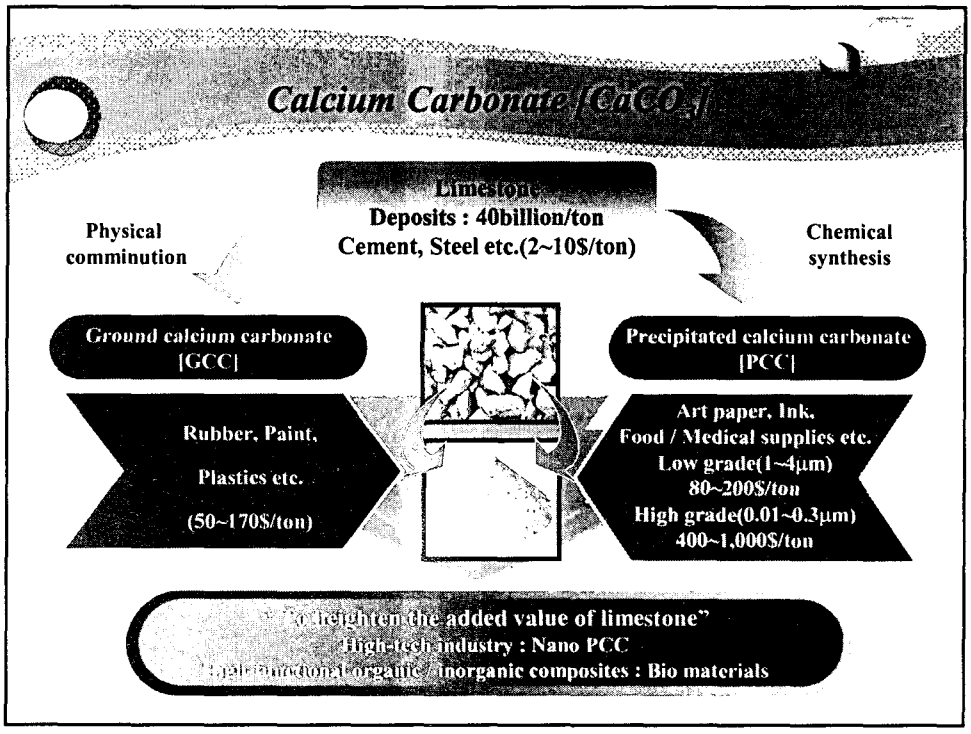
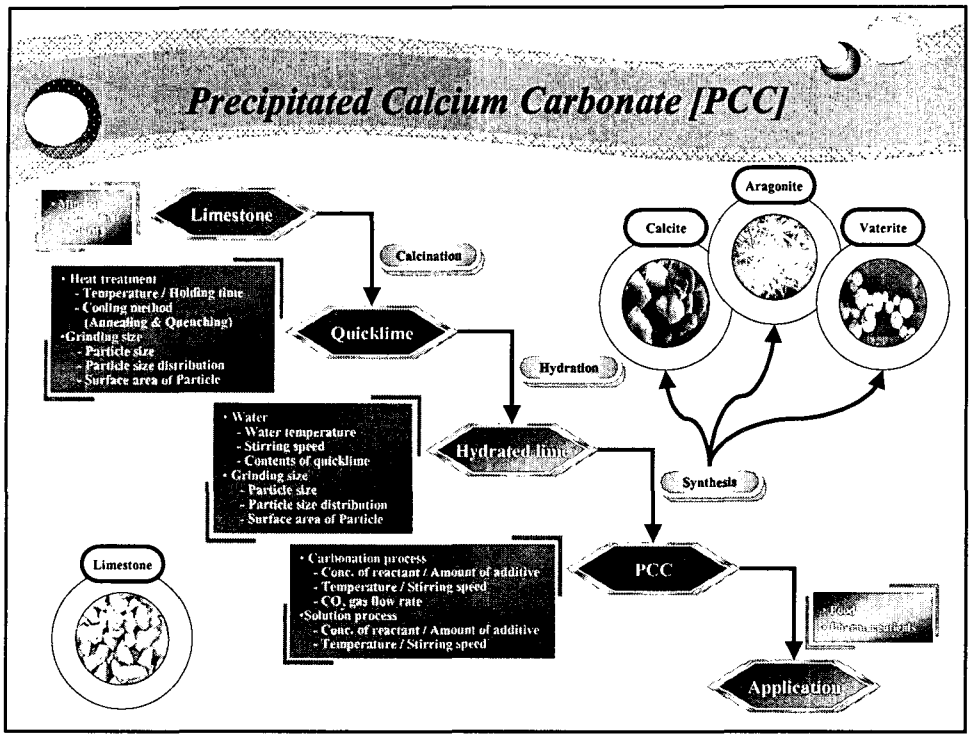
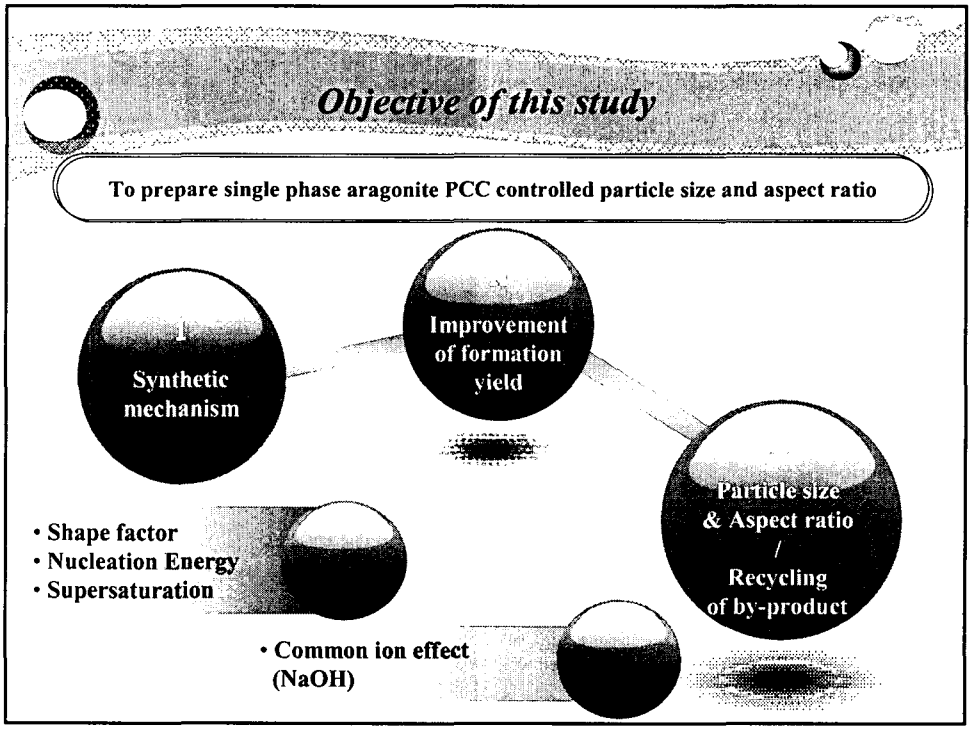
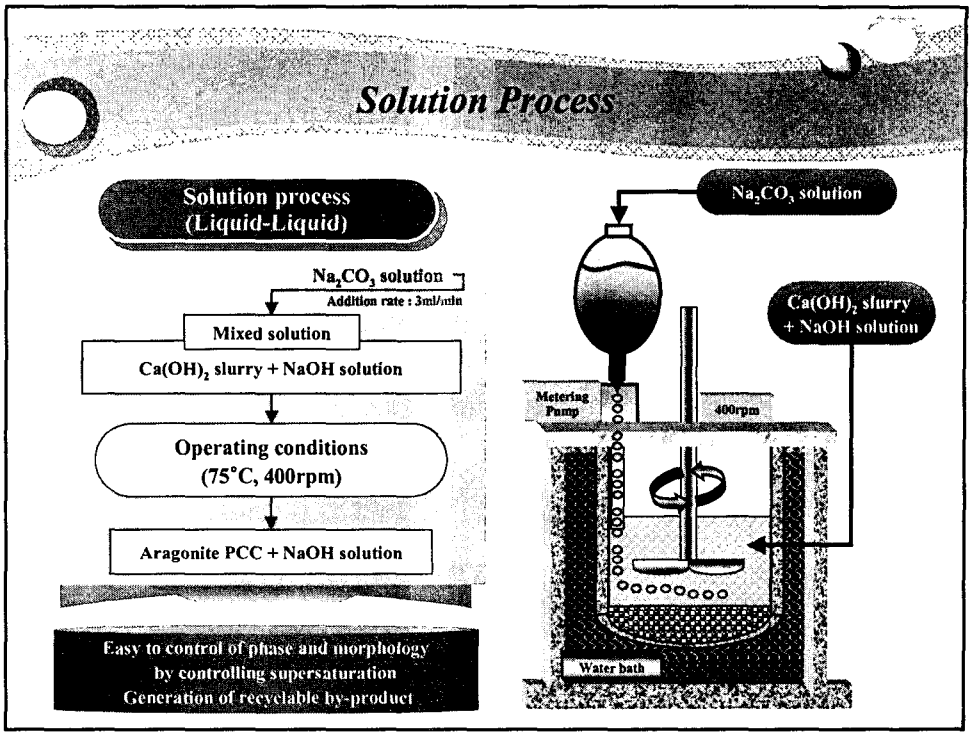
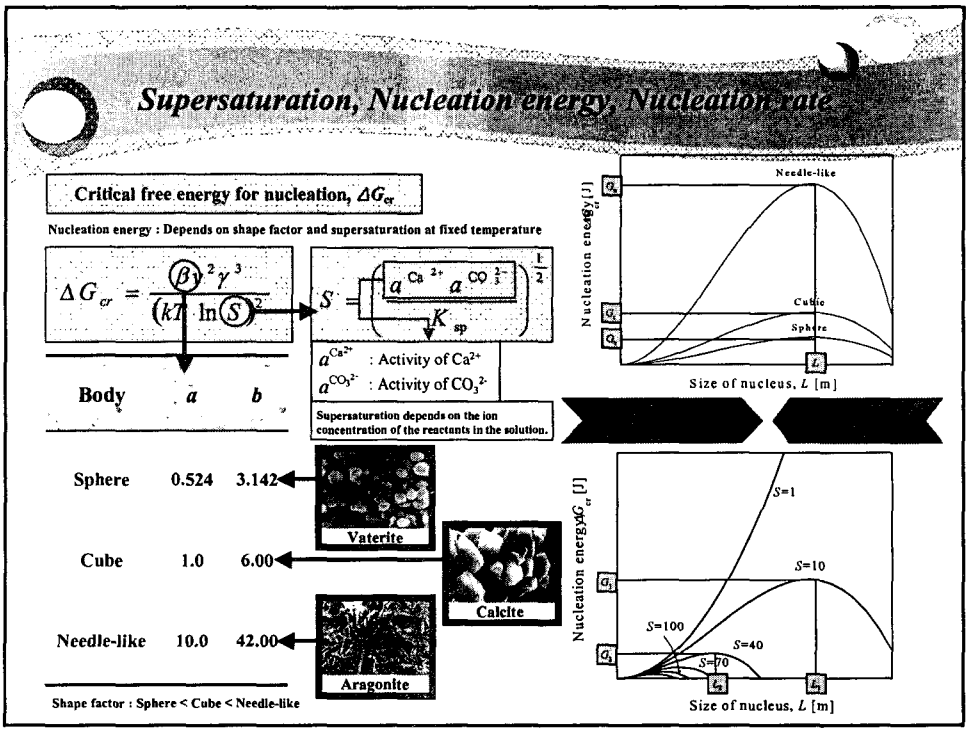
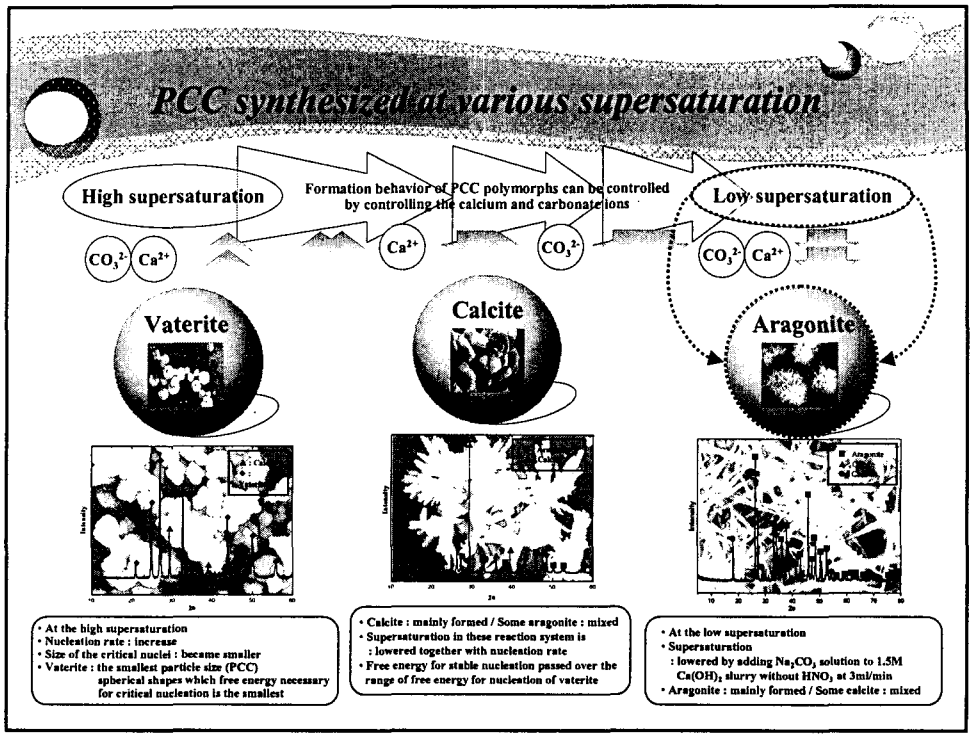


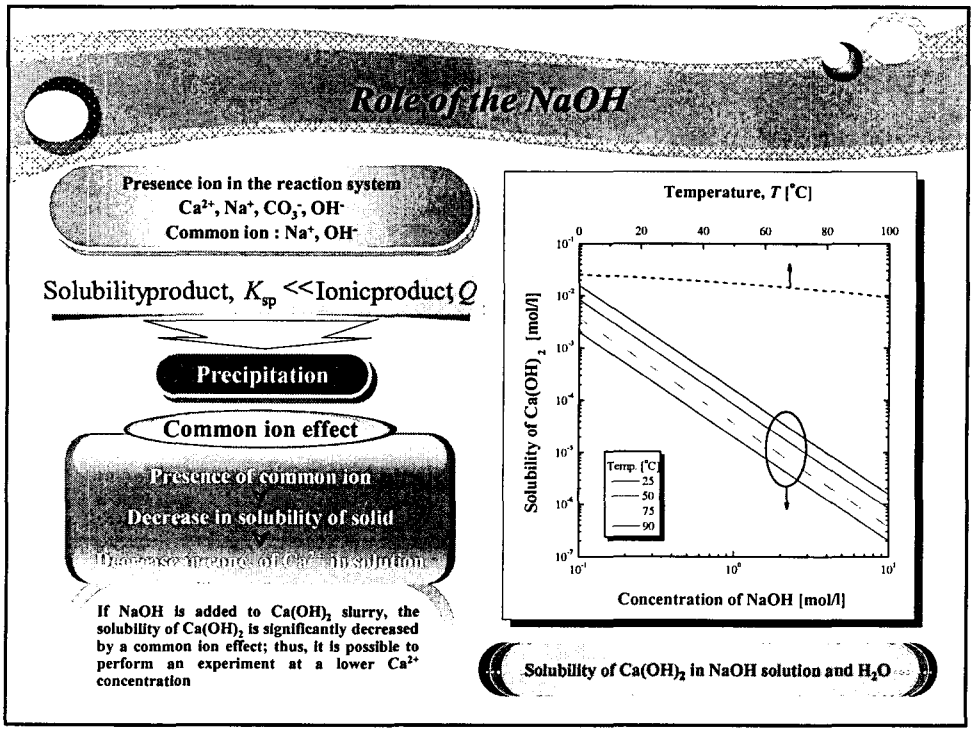

Precipitated Calcium Carbonate [PCC]
Limestone
Calcination
Quicklime
Hydration
Hydrated lime
Synthesis
PCC
Application
Aragonite
Calcite
Vaterite
• Heat treatment
- Temperature / Holding time
- Cooling method
(Annealing & Quenching)
•Grinding size
- Particle size
- Particle size distribution
- Surface area of Particle
• Water
- Water temperature
- Stirring speed
- Contents of quicklime
• Grinding size
- Particle size
- Particle size distribution
- Surface area of Particle
Limestone
• Carbonation process
- Conc. of reactant / Amount of additive
- Temperature / Stirring speed
- CO2 gas flow rate
•Solution process
- Conc. of reactant / Amount of additive
- Temperature / Stirring speed


Objective of this study
To prepare single phase aragonite PCC controlled particle size and aspect ratio
Synthetic mechanism
Improvement of formation yield
Particle size & Aspect ratio / Recycling of by-product
• Shape factor
• Nucleation Energy
• Supersaturation
• Common ion effect (NaOH)

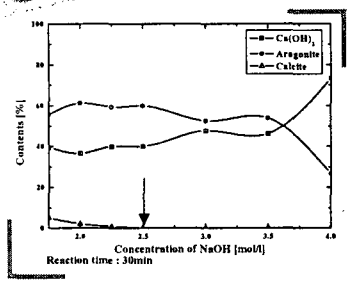

Solution Process
Solution process
(Liquid-Liquid)
Na_2CO_3 solution
Addition rate : 3ml/min
Mixed solution
$Ca(OH)_2$ slurry + NaOH solution
Operating conditions
(75°C, 400rpm)
Aragonite PCC + NaOH solution
Easy to control of phase and morphology
by controlling supersaturation
Generation of recyclable by-product
Na_2CO_3 solution
$Ca(OH)_2$ slurry
+ NaOH solution
Metering Pump
400rpm
Water bath


Supersaturation, Nucleation energy, Nucleation rate
Critical free energy for nucleation, ΔG_{cr}
Nucleation energy : Depends on shape factor and supersaturation at fixed temperature
$\Delta G_{cr} = \frac{(\beta)^2 \gamma^3}{(kT \ln S)^2}$
$S = \frac{a^{Ca^{2+}} a^{CO_3^{2-}}}{K_{sp}}$
$a^{Ca^{2+}}$: Activity of Ca^{2+}
$a^{CO_3^{2-}}$: Activity of CO_3^{2-}
Supersaturation depends on the ion concentration of the reactants in the solution.
Body a b
Sphere 0.524 3.142
Cube 1.0 6.00
Needle-like 10.0 42.00
Shape factor : Sphere < Cube < Needle-like
Vaterite
Calcite
Aragonite
Needle-like
Cubic
Sphere
Nucleation energy [J]
Size of nucleus, L [m]
S=1
S=10
S=100
S=40
S=70
Nucleation energy ΔG_{cr} [J]
Size of nucleus, L [m]


PCC synthesized at various supersaturation
High supersaturation
Formation behavior of PCC polymorphs can be controlled by controlling the calcium and carbonate ions
Low supersaturation
CO_3^{2-} Ca^{2+}
Ca^{2+}
CO_3^{2-}
CO_3^{2-} Ca^{2+}
Vaterite
Calcite
Aragonite
• At the high supersaturation
• Nucleation rate : increase
• Size of the critical nuclei : became smaller
• Vaterite : the smallest particle size (PCC) spherical shapes which free energy necessary for critical nucleation is the smallest
• Calcite : mainly formed / Some aragonite : mixed
• Supersaturation in these reaction system is : lowered together with nucleation rate
• Free energy for stable nucleation passed over the range of free energy for nucleation of vaterite
• At the low supersaturation
• Supersaturation : lowered by adding Na_2CO_3 solution to 1.5M $Ca(OH)_2$ slurry without HNO_3 at 3ml/min
• Aragonite : mainly formed / Some calcite : mixed

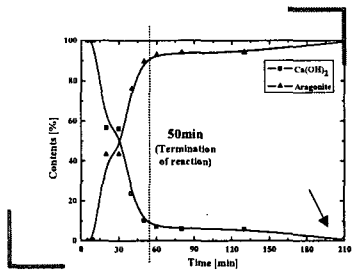

Role of the NaOH
Presence ion in the reaction system
Ca^{2+}, Na^+, CO_3^-, OH^-
Common ion : Na^+, OH^-
Solubilityproduct, K_{sp} <<Ionicproduct Q
Precipitation
Common ion effect
Presence of common ion
Decrease in solubility of solid
If NaOH is added to $Ca(OH)_2$ slurry, the solubility of $Ca(OH)_2$ is significantly decreased by a common ion effect; thus, it is possible to perform an experiment at a lower Ca^{2+} concentration
Temperature, T [°C]
Solubility of $Ca(OH)_2$ [mol/l]
Concentration of NaOH [mol/l]
Temp. [°C]
25
50
75
90
Solubility of $Ca(OH)_2$ in NaOH solution and H_2O

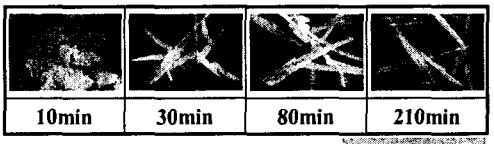
Synthesis of single-phase aragonite PCC



2.0M	2.5M	3.0M	4.0M

- Unreacted $Ca(OH)_2$ was increased with the increasing of NaOH.
- Formation yield of calcite was decreased continually and disappeared at 2.5M.
- With the increase of NaOH, the aspect ratio of aragonite decreased with the increase in thickness

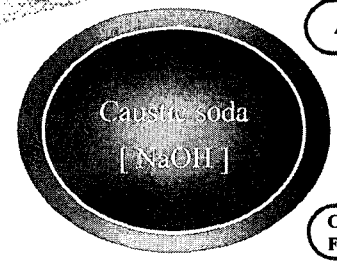




10min	30min	80min	210min

- Calcite was not appeared and aragonite nuclei were formed around ten minutes after the start of the reaction.
- Single phase aragonite with aspect ratio of 20 was obtained. (NaOH : 2.5M / Addition rate of Na_2CO_3 : 5ml/min / Reaction time : 210 min)
- Particle size & aspect ratio : Increase
- Dissolution reaction of $Ca(OH)_2$: Rate limiting step of the overall reaction
  → Dissolution rate of $Ca(OH)_2$ << Formation rate of calcium carbonate

Recycling of NaOH

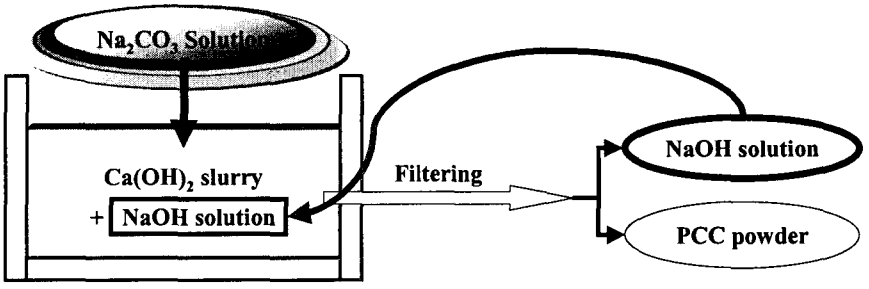


About 200~270$/ ton

Alkali sources

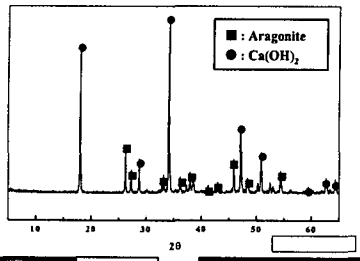
Cleaning of water & wastewater, Removal of dust & gas

Chemistry : 33%, Paper & steel industry : 25%,
Fiber/Soap Industry : 12%, Food, electronics industry etc.

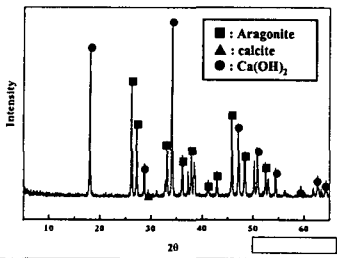


Recycling of NaOH

Reagent (5.0 M)



By-product (NaOH) + Reagent



× 4000 × 8000 × 4000 × 8000

By-product : Existence of some calcite
The purity of by-product is lower than the reagent. However, particle size was not changed.

Summary

Formation mechanism of PCC polymorphs

Supersaturation (nucleation rate)	Conc. of Ca^{2+}	Conc. of CO_3^{2-}	Polymorphs
High	High	High	Vaterite
⇕	High, Low	High, Low	Calcite, Aragonite
Low	Low	Low	Aragonite

Synthesis of single-phase aragonite

- ♦ At the lowest supersaturation, the formation yield of aragonite was highest.
- ♦ The concentration of calcium ion in the solution was reduced by common ion effect at 2.5M NaOH, resulting in the formation of single-phase aragonite.
- ♦ The optimum synthetic conditions of single phase aragonite PCC
  - Concentration of NaOH : 2.5M / 400rpm / 75°C
  - Reaction time : 210min (Ripening time : 160min)
- ♦ Recycling of by-product (NaOH) : confirmation of possibility

In the synthetic reaction of precipitated calcium carbonate
⇨ Control of concentration of Ca^{2+} and CO_3^{2-} ions
☛ PCC polymorphs and formation yield were controlled ☚