아라고나이트의 저온 합성시 Mg^{2+} 이온의 영향

Effect of Mg^{2+} Ion on the Synthesis of Aragonite at Low Temperature

김정환, 고상진, 박운경, 박현서, 안지환
한국지질자원연구원

Jeong-Hwan Kim, Sang-Jin Ko, Woon-Kyoung Park,
Hyun-seo Park, Ji-Whan Ahn

Korea Institute of Geoscience & Mineral Resources

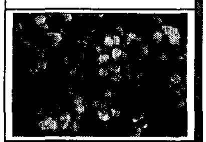
Introduction

Calcium Carbonate
↓ Calcination
Calcium Oxide
↓ Hydration
Calcium Hydroxide
↓ Carbonation
PCC (Precipitated Calcium Carbonate)

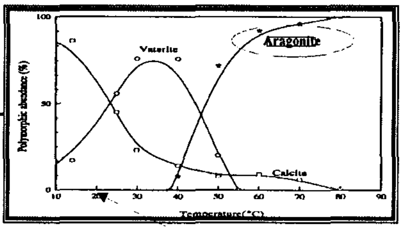
Calcite

Aragonite

Vaterite



Orthorhombic Structure,
Specific gravity 2.94~2.95
Morhs hardness 3.5~4.0,
Column, Acicular
Contain impurities such as Sr^{2+}, Pb^{2+}
Stable phase under 1atm, 75K, thermodynamically



Abundance of crystalline calcium carbonates at the metastable stage as a function of temperature

Application

Aragonite Precipitated Calcium Carbonation (PCC)
Needle-like (large aspect ratio)

- **Aragonite PCC increase aspect ratio**
  - **Great impact resistance**
  - ***Increase specific* surface area**
- ***Increase oil inhalation* amount, degree of strength and brightness**
  - **Many field used *skill of mechanical* and optical**

Function ability	Made use of sphere
Flexural strength	Strengthening plastic
High impact	Thermoplastics, Polypropylene plastics
Tensile strength	Rubber, Plastic, Paper, Paint
Light scattering	**Paper *(brightness, opacity)***

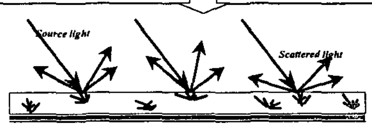
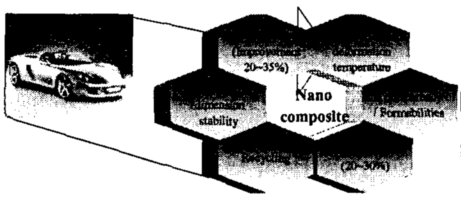


Diagram showing how the addition of acicular floc PCC Can enhance the light scattering characteristics of a formulation

Application used vehicle



Application of PCC in the plastic used vehicle
High functionality organic and inorganic composite material

Countermeasure about low fuel-efficient on Higher oil price presence

⇨ **Requirement of light weight about automobile materials**

⇨ **Reduction of 5% fuel-efficient to application for *plastic materials***

: Numerous reduction effect on the fuel consumption

Previous study

Carbonation Process

Y. Ota *J. Am. Ceram. Soc*	A suspension of $CaCl_2$-$MgCl_2$-$Mg(OH)_2$ with pH ~ 9 has been prepared by adding $Ca(OH)_2$ to $MgCl_2$ aqueous solution. $CaCO_3$ whiskers (aragonite phase) have been prepared easily by blowing CO_2-containing gas into the suspension. The whiskers have high aspect ratios ranging from 20 to 80 with diameters of 0.5-1 μm.
H.Tanaka *gypsum & Lime*	Reported that the effect of pH, temperature, flow rate of CO_2 gas and reaction time on the synthesis of acicular type aragonite. - pH 8 ~ 9 : formation range of aragonite PCC, - Reaction temp. : 80℃
Sasaki *Shigen-to-sozai*	Reported that the important factors for obtaining aragonite are the mole ratio of the staring material, $MgCl_2/CaO$, as well as the CO_2 flow rate, reaction time, pH, and temperature. With regard to the mole ratio $MgCl_2/CaO$, those researchers mentioned that the aragonite phase dominated when $MgCl_2/CaO$ was 1.6, at a temperature 35℃ and a CO_2 flow rate of 50 /min.

Synthesis of aragonite by the carbonation process

J.W.Ahn et. al. (J. Am. Ceram. Soc., Vol 87, No 2, 2004)

formation range on $Ca(OH)_2$ slurry & $MgCl_2$ aqueous solution concentration

- $MgCl_2$/ $Ca(OH)_2$ Mg^{2+}ion 0.1~0.26 mol/L, Ca^{2+}ion 0.16~0.25 mol/L concentration range optimum condition
- Confirm formation mechanism aragonite PCC in low temperature

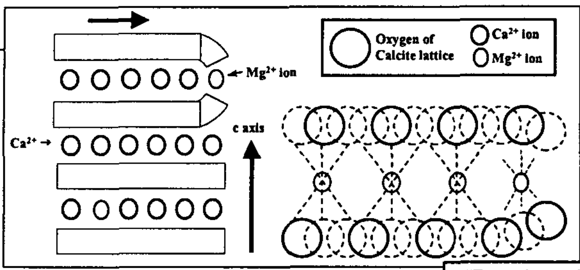
Formation mechanism of aragonite by substitute of Mg^{2+}ion

J.W.Ahn et. al. (J. of Kor. Ceramic. Society., Vol 41, No 12, 2004)

substitution Ca^{2+} ion of calcite by added Mg^{2+} ion

- distortion of lattice suppression Calcite growth Calcite solubility increasing aragonite formation yield increasing

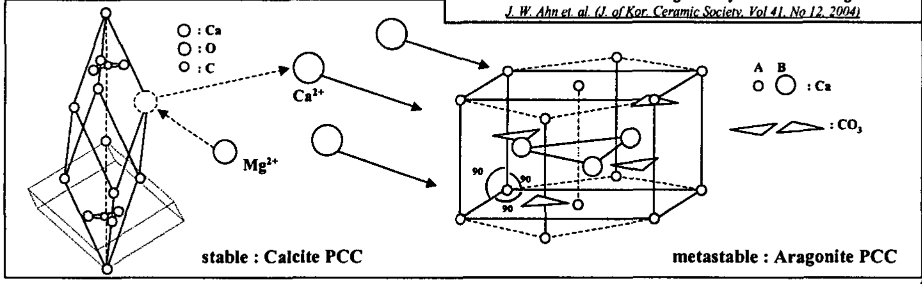
Effect of Mg^{2+} ion on calcite PCC



Substituted Mg^{2+} ion for Ca^{2+}

→ Distortion of lattice
→ Increase of Calcite solubility
→ Increase of formation yield on Aragonite

"Formation mechanism of aragonite by substitute of Mg^{2+} ion"
J. W. Ahn et. al. (J. of Kor. Ceramic Society, Vol 41, No 12, 2004)

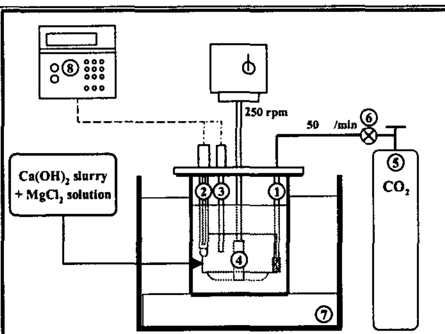


Purpose of this study

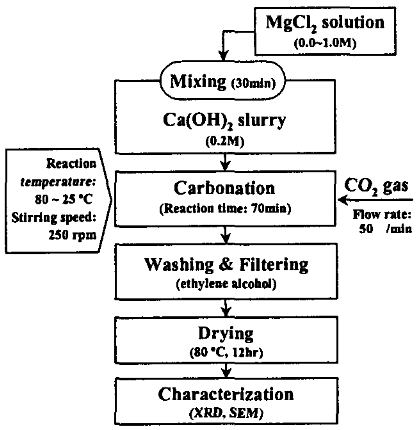
1. **Synthesis of aragonite precipitated calcium carbonate in carbonation process**
   - Concentration of reactant
   - Reaction temperature
2. **Effect of magnesium ion at high and low temperature**
   - Concentration of $MgCl_2$
   - Reaction time

Experimental

Carbonation Process
(Liquid-Gas reaction)

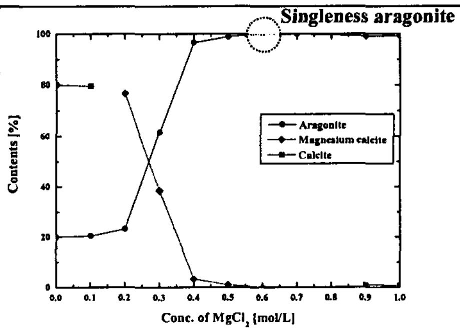


1 : Bubbler
2 : pH meter
3 : Thermometer
4 : Impeller
5 : CO$_2$ Gas cylinder
6 : Gas regulator
7 : Water bath
8 : pH meter

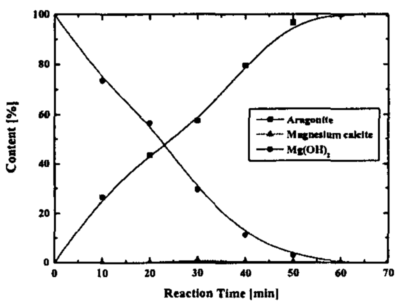


Effect of Concentration of MgCl$_2$

Reaction Temperature : 80 °C



Formation yield of precipitates with the addition of MgCl$_2$ solution

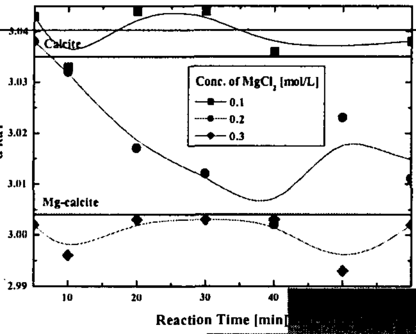


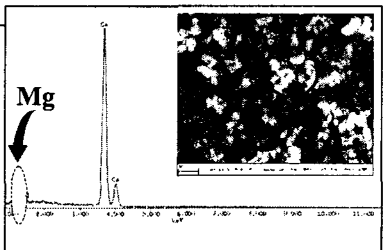
Formation yield of precipitates with the reaction time

Increase concentration of MgCl$_2$ → Aragonite increase formation yield 0.6M constant → Aragonite synthesis optimum condition 0.6M MgCl$_2$, 0.2M Ca(OH)$_2$

Mg^{2+} ion is suppression of calcite nucleation and only formation condition of aragonite in initial carbonation reaction

Analysis of calcite particle



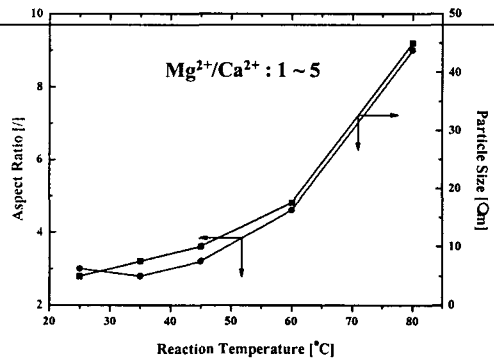


EDS (energy dispersive spectroscopy)

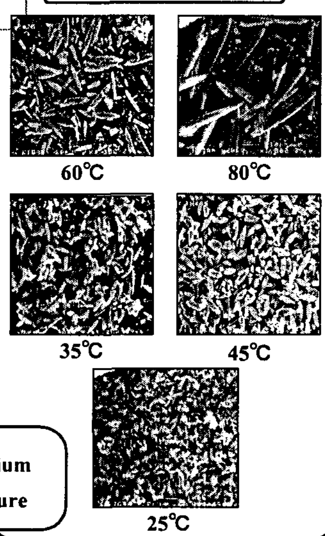
- Infiltrated Magnesium ion
- Calcite of Mg-Calcite type

Mg-calcite type infiltrated very-small-amount Magnesium in calcite

Effect of aragonite precipitated with various temperature



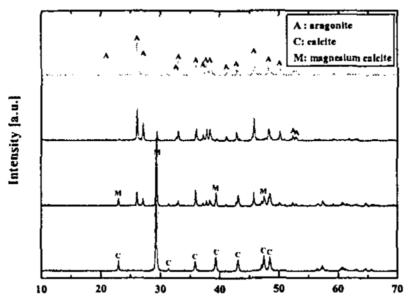
Effect of temperature on aragonite aspect ratio and particle size



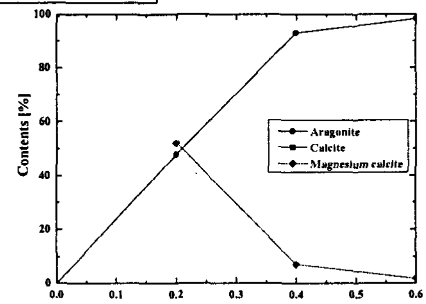
Particle size and aspect ratio of aragonite precipitated calcium carbonate increased with increasing the reaction temperature

Effect of Concentration of $MgCl_2$

Reaction Temperature : 25 °C



X-ray diffraction patterns of precipitates with the addition of $MgCl_2$ solution (M=$MgCl_2$, mol/L)



Formation yield of precipitates with the addition of $MgCl_2$ solution

Increase Concentration of $MgCl_2$ → **Aragonite increase formation yield 0.6M constant**

Synthesis of single phase aragonite PCC in the low temperature(25℃)

Conclusion

Optimum condition of aragonite formation $Ca(OH)_2$ 0.2M, $MgCl_2$ 0.6M at 80℃

Adding the $MgCl_2$ formation yield the aragonite precipitated calcium carbonate was increased whole temperature employed in this study up to 80 C. because of Mg^{2+} ion suppresses the transformation of aragonite by inhibiting nucleation and growth of the calcite.

Particle size and aspect ratio of aragonite precipitated calcium carbonate increased with increasing the reaction temperature. Temperature increased with decreasing the nucleation rate. Therefore particle size and aspect ratio increased with decreasing the nucleation rate.

Aragonite is synthesized with high formation yield at low temperature in the *$Ca(OH)_2$-$MgCl_2$-CO_2 system. However, it does not apply to the industrial,* because of the small particle size and aspect ratio of aragonite. Therefore, further studies are necessary to improve the particle size and aspect ratio at low temperature.