Clarification for removal mechanism of Boron using co-precipitation with magnesium hydroxide

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Background

Boron

- An essential atom for various industries such as electronics, semiconductor, medicine and glass industries
- Effects against humans

  →problems with cardiovascular, coronary, nervous and reproductive systems
- Effect against plants

  →excessive boron uptake results in dwarfing or death of plants
- The maximum concentration limits;

  Industrial drainage→10 mg/L*

  Drinking water→1 mg/L* (**WHO guideline, 2011*)

Semiconductor

Glass fiber

Eye lotion

Background

Previous study

①Ion-exchange resin

→○ High sorption density

× High operation cost

②Boron adsorption with MgO

→× Low sorption density

× Production of lots of sludge

Co-precipitation

The phenomenon that ions precipitate beyond thermodynamic range of the precipitation, accompanied by the precipitation of slightly soluble substance.

The objective of this study

To clarify the sorption mechanism in B co-precipitation with magnesium hydroxide by comparing adsorption experiments and co-precipitation experiments.

Experimental method

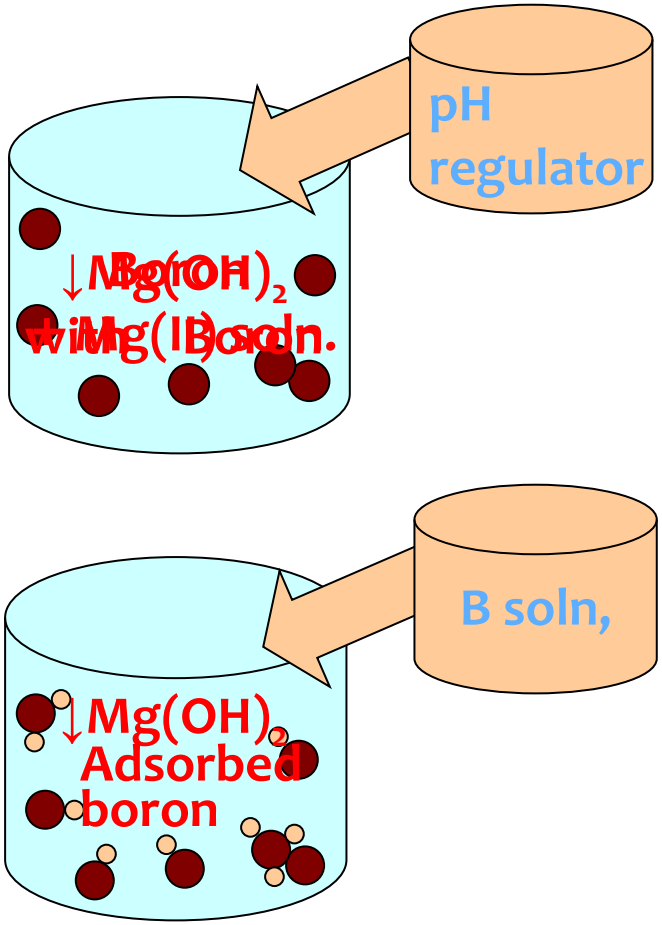
Co-precipitation* experiments and simple *Adsorption* ones are *distinguished closely.

- ***Co-precipitation experiment***

  formation of magnesium hydroxide particles occurred in the presence of boron.

- ***Adsorption experiment***

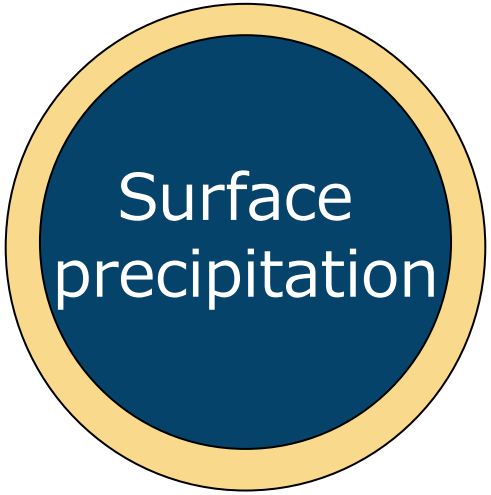
  magnesium hydroxide particles was prepared at first, followed by boron adsorption.



Mechanism of Co-precipitation

Production of surface precipitation

Three dimensional sorption phenomena into the solid.

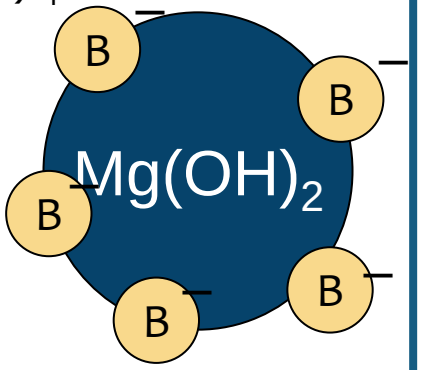


Formation of surface complexation

Ions directly adsorb onto the surface of precipitates by coordinate bond.

$2[\equiv MgOH] + B(OH)_4^- \Leftrightarrow \equiv Mg2B(OH)_4^+ + 2OH^-$

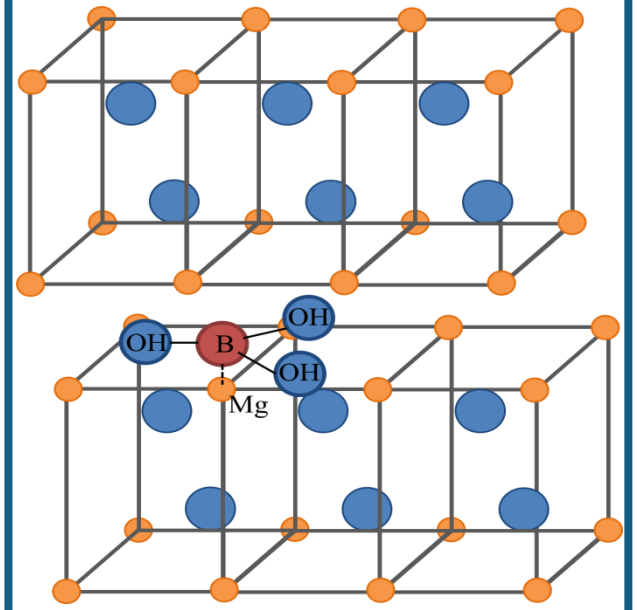
$[\equiv MgOH] + B(OH)_4^- \Leftrightarrow \equiv MgB(OH)_4^+ + OH^-$



Ref.) M.Funte, Desalination, 2009

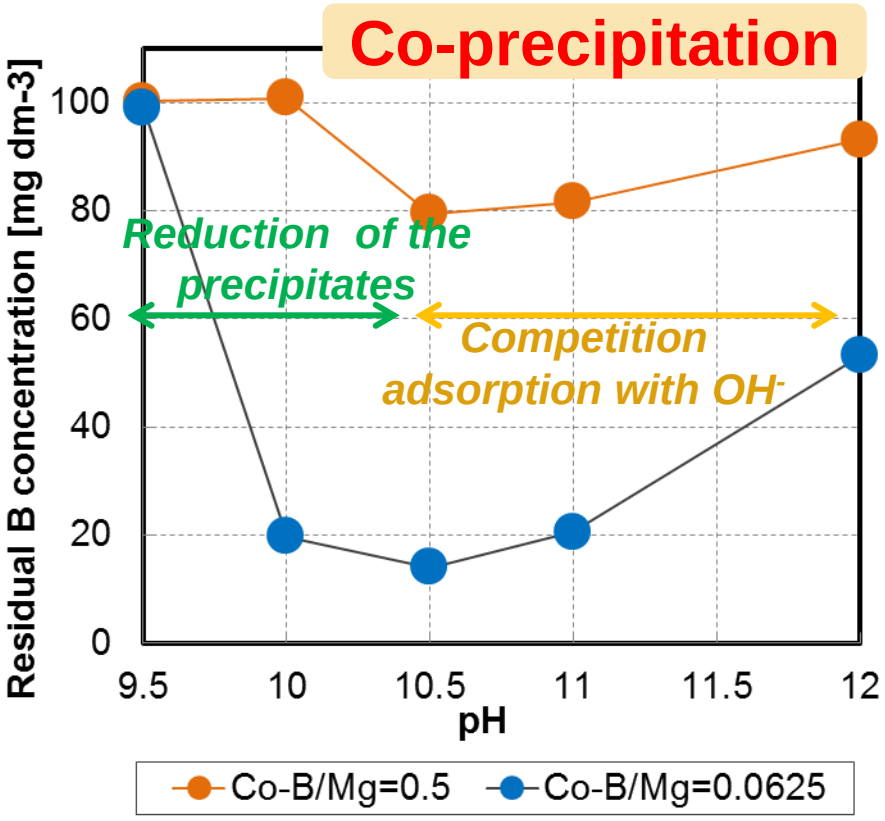
Ions uptake between precipitates

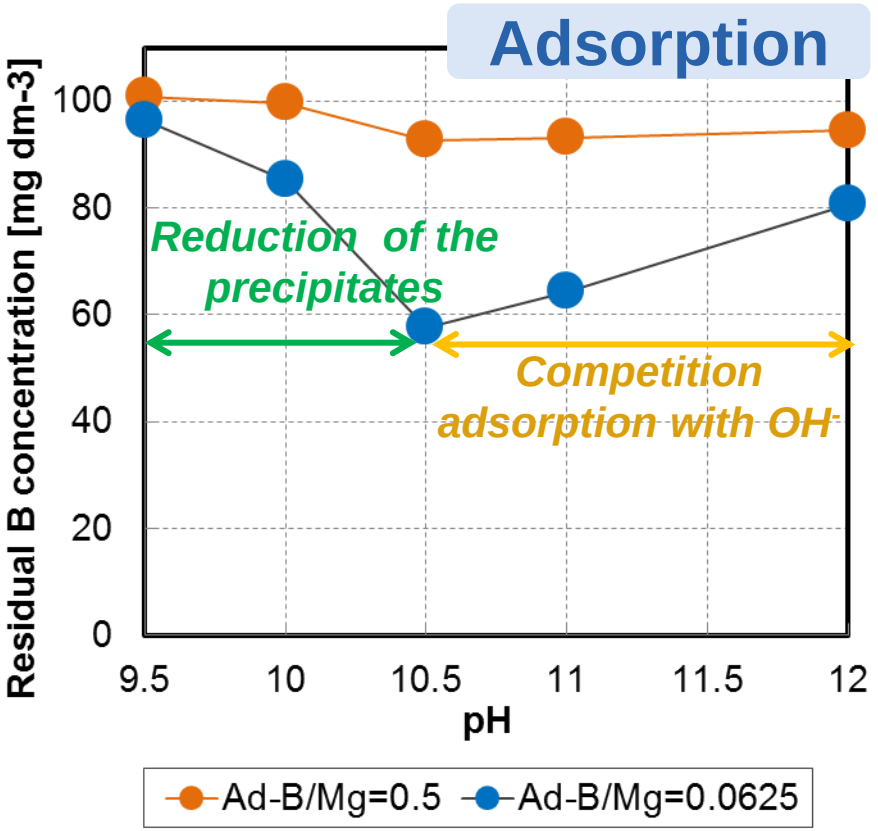
H_3BO_3 was absorbed into the precipitates layers.



Ref.) K.SASAKI, MMIJ, 2013

Evaluation of the effect of pH





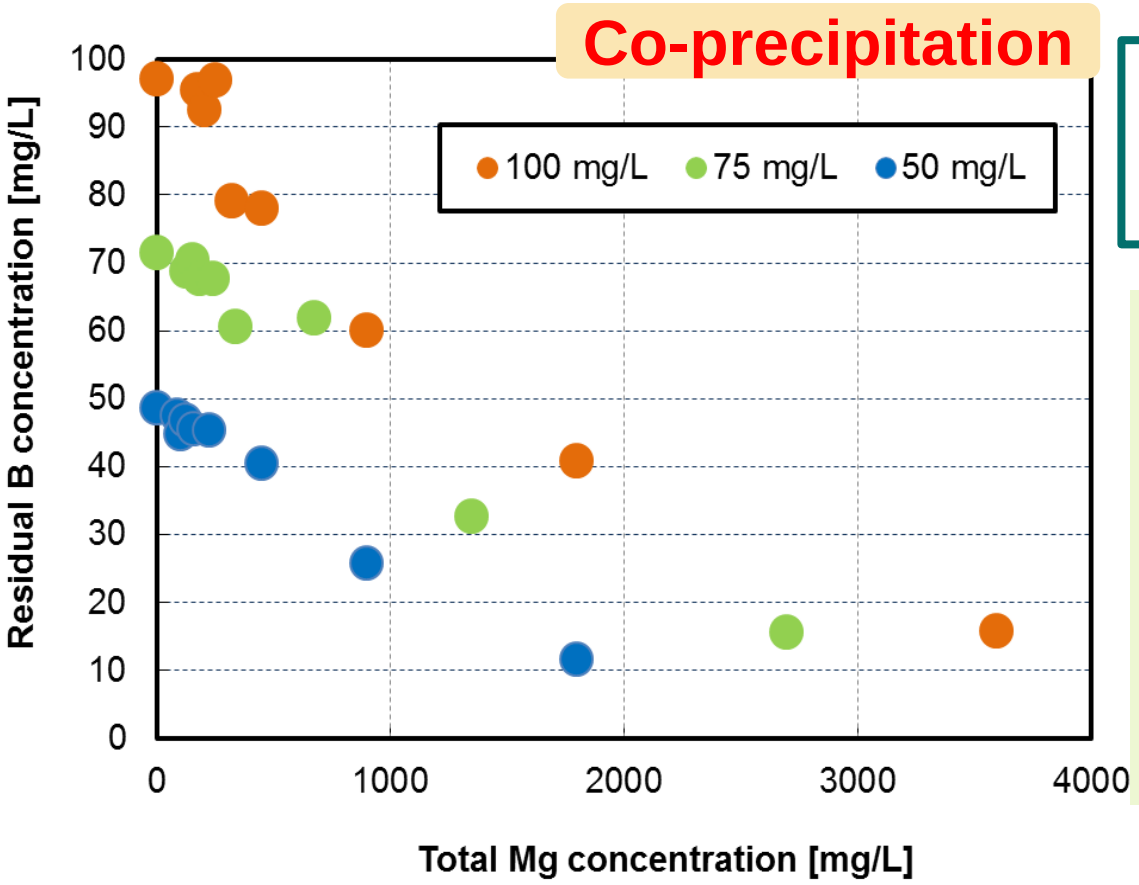
Experimental condition

- Initial B conc. → 100 mg/L
- Initial B/Mg molar ratio → 0.0625, 0.5

➢ Both in the co-precipitation and the adsorption experiments, the maximum B removal was achieved at pH 10.5.

⇒*All other experiments were carried out at pH 10.5.*

Boron removal experiment



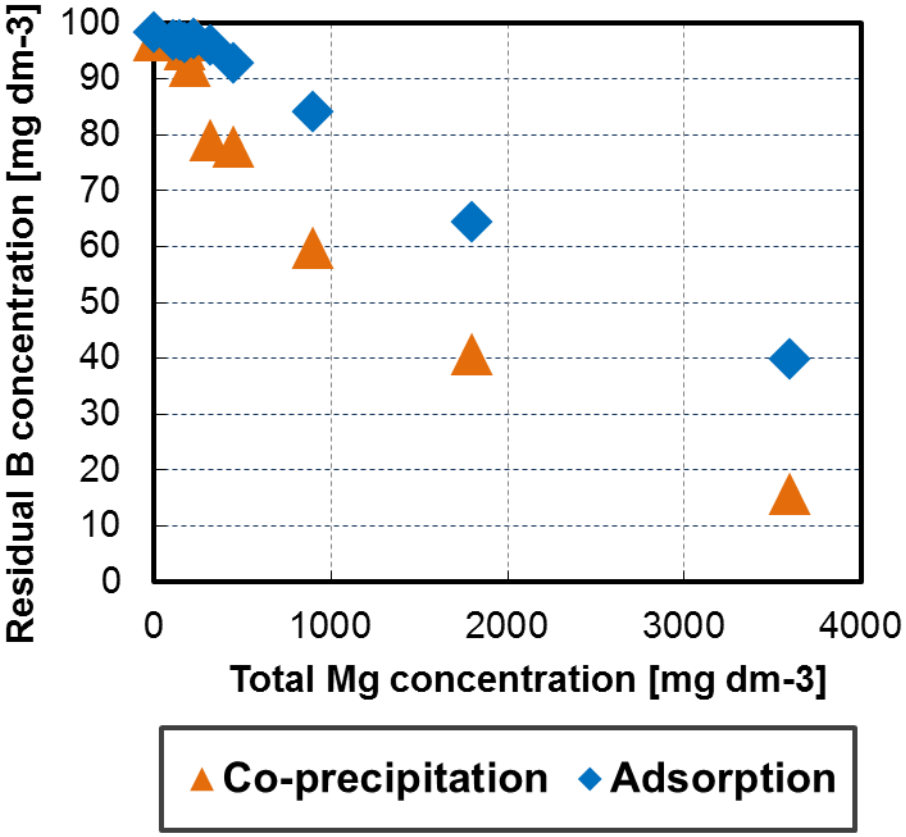
Experimental condition

- Initial B conc.→50, 75,100 mg/L
- Initial B/Mg molar ratio→ 0.0625-0.9

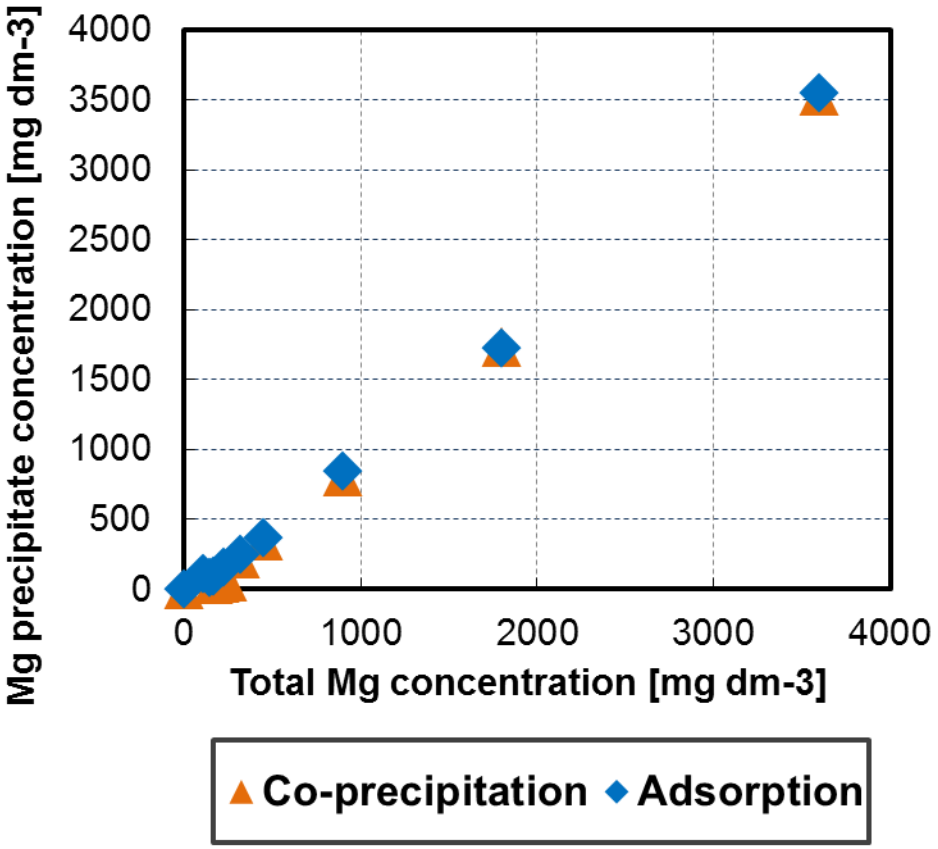
- More B removal was achieved when more dosage of Mg was given.
- When the initial B/Mg molar ratio was 0.0625, residual B concentration almost dropped to 10 mg/L.

Boron removal experiment

Residual B conc. VS. Total Mg conc.



Mg precipitate conc. VS. Total Mg conc.

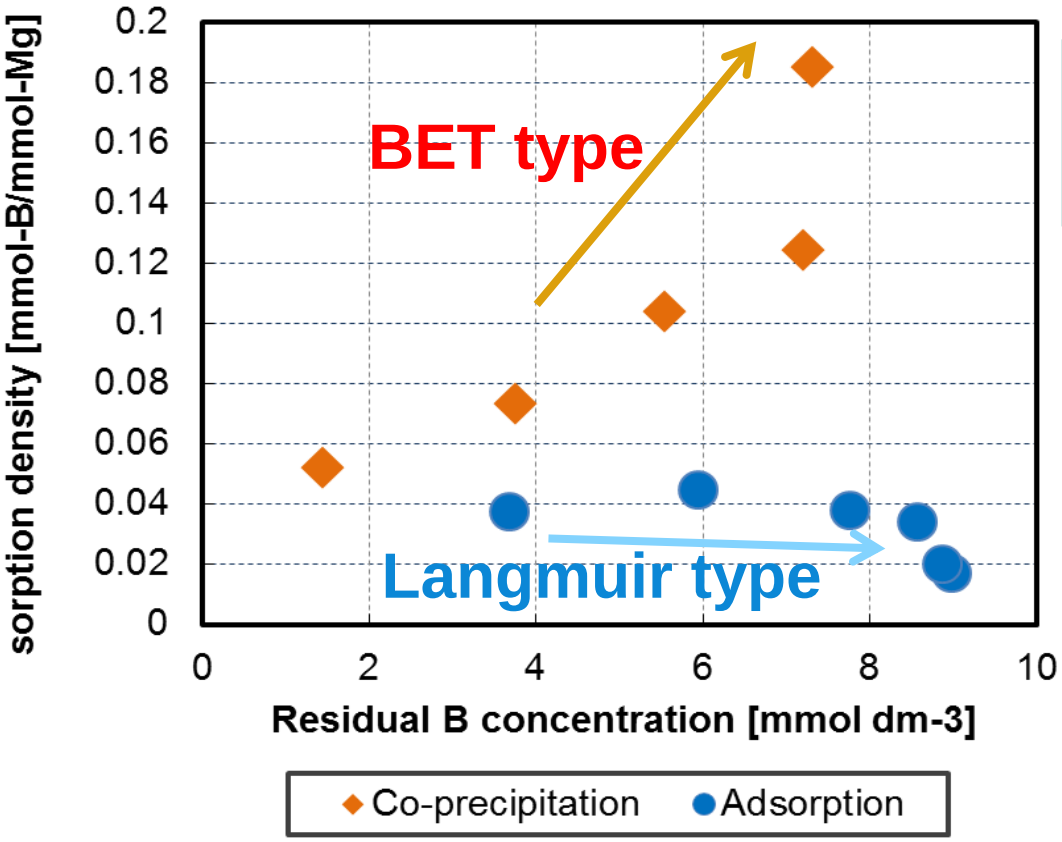


Experimental condition

- Initial B conc. →100 mg/L
- Initial B/Mg molar ratio → 0.0625-0.9

- More B was removed during co-precipitation than adsorption.
- More precipitates were obtained during adsorption than co-precipitation.

Sorption isotherm



Experimental condition

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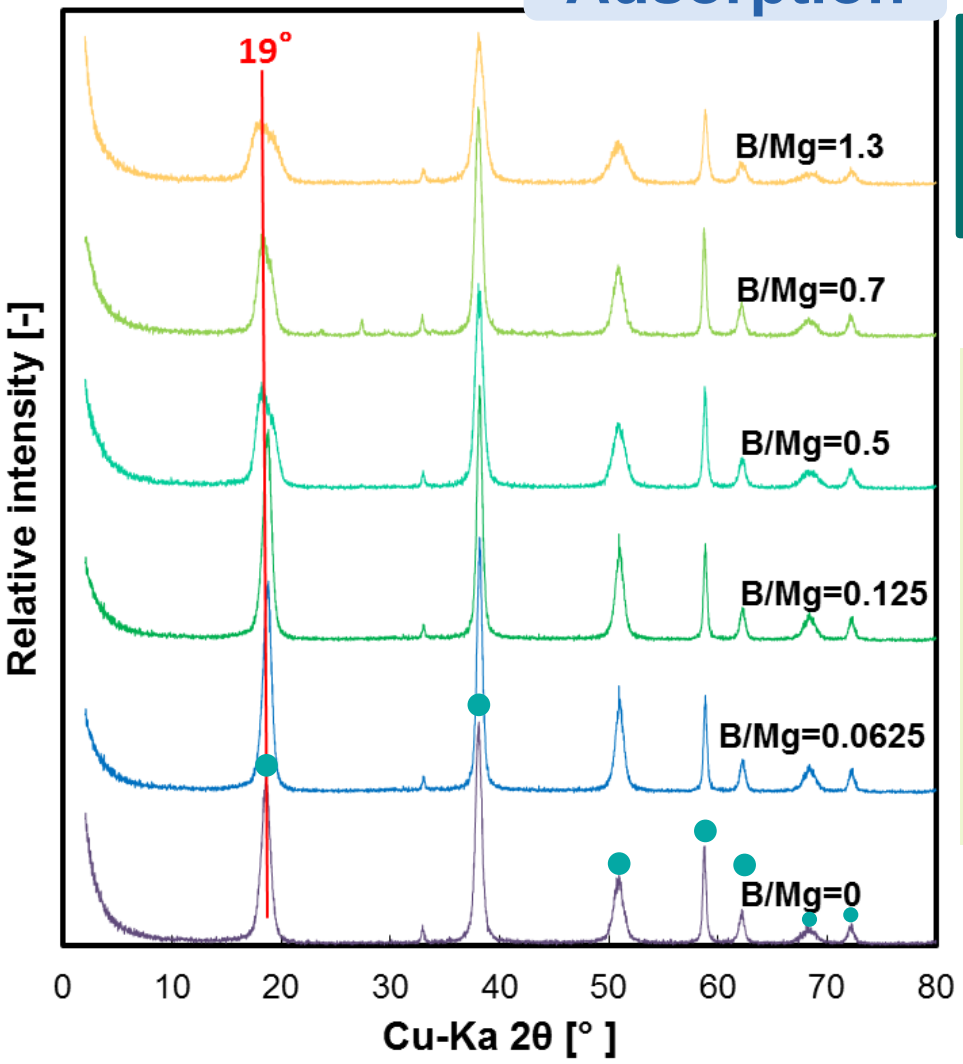
- Initial B/Mg molar ratio → 0.0625-0.9

Sorption isotherm

- Co-precipitation: BET type,
  → three dimensional B uptake
- Adsorption: Langmuir type,
  →two dimensional B uptake

XRD analysis

Adsorption



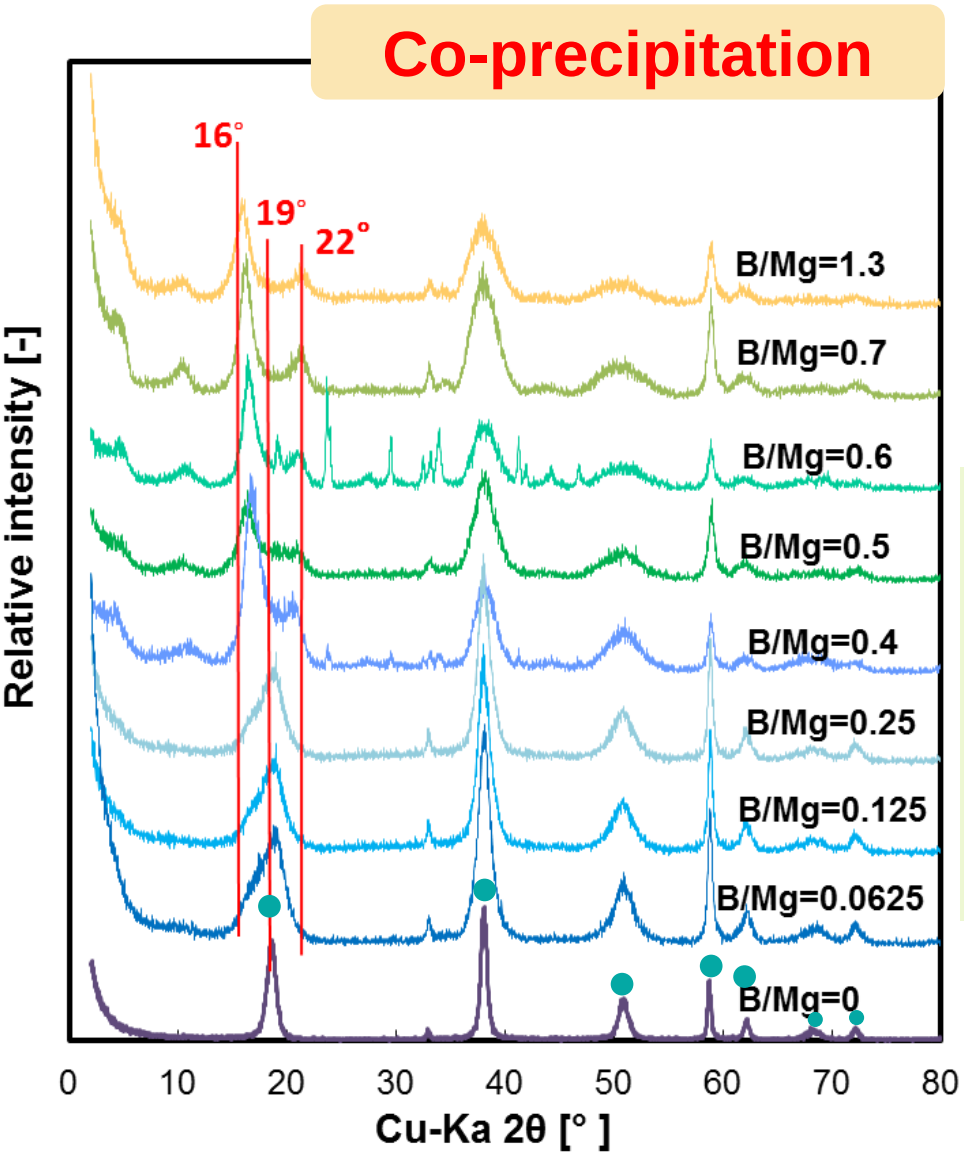
Experimental condition

- Initial Mg conc.→200 m/L
- Initial B/Mg molar ratio → 0.0625-0.9

- The structure of the precipitates did not changed.
- The cristallinity became worse at high B/Mg molar ratio.
  →Two dimensional Boron adsorption was occurred.
  →Boron was inserted between the surface of Mg(OH)2 layers.

● $Mg(OH)_2$: Brucite

XRD analysis



Experimental condition

- Initial Mg conc.→200 m/L
- Initial B/Mg molar ratio → 0.0625-0.9

➢ The structure of the precipitates changed and Hydromagnesite was produced when the initial B/Mg was over 0.4.

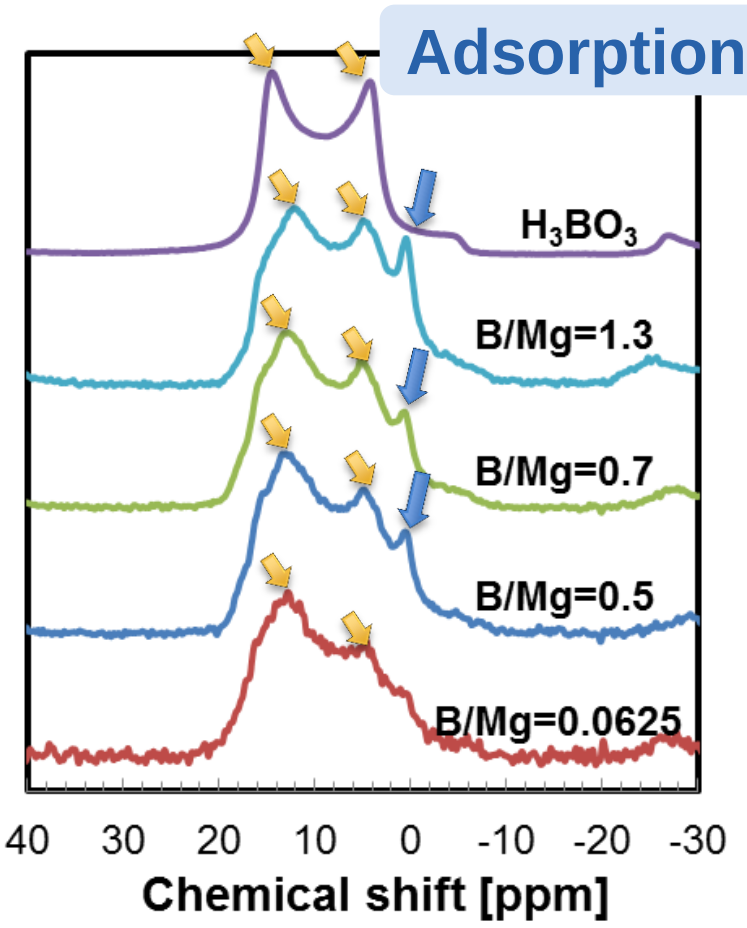
→ Hydromagnesite, which has a sheet-like structure, caused three dimensional B uptake during co-precipitation.

● $Mg(OH)_2$: Brucite

NMR analysis

3-coordinated boron : Broad chemical shift due to the quadrupolar interaction

4-coordinated boron : One sharp chemical shift at 0ppm



Experimental condition

- Initial Mg conc.→200 m/L
- Initial B/Mg molar ratio → 0.0625-0.9

- H_3BO_3 was inserted between $Mg(OH)_2$ layers during adsorption.
- The formation of surface complexation was promoted at high B/Mg molar ratio.

$2[\equiv MgOH] + B(OH)_4^- \Leftrightarrow \equiv Mg2B(OH)_4^+ + 2OH^-$

$[\equiv MgOH] + B(OH)_4^- \Leftrightarrow \equiv MgB(OH)_4^+ + OH^-$

Ref.) M. Funte, Desalination, 2009

NMR analysis

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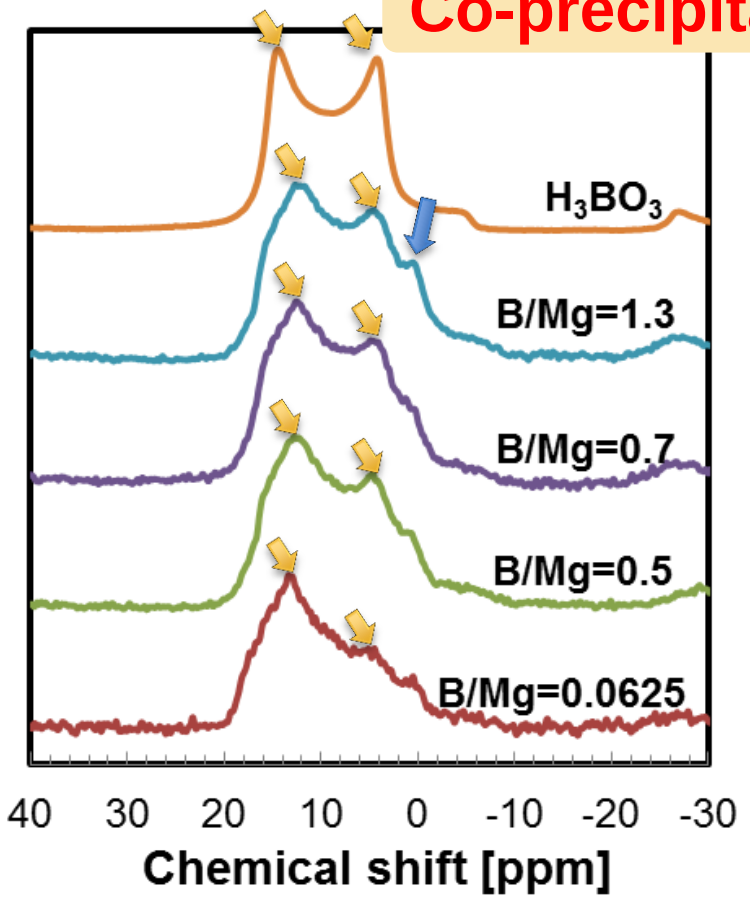
Co-precipitation



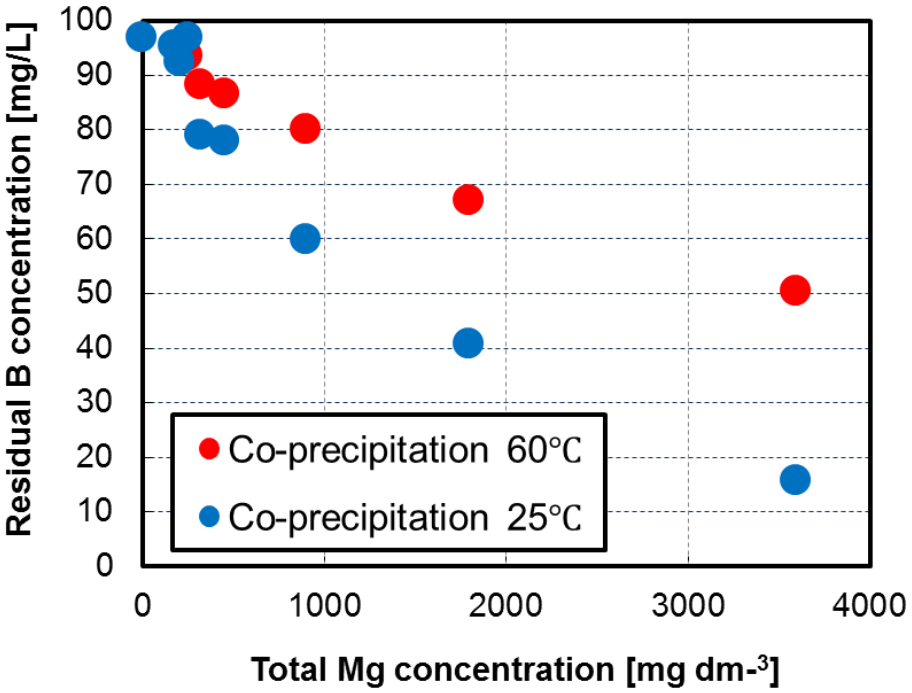
Experimental condition

- Initial Mg conc.→200 m/L
- Initial B/Mg molar ratio → 0.0625-0.9

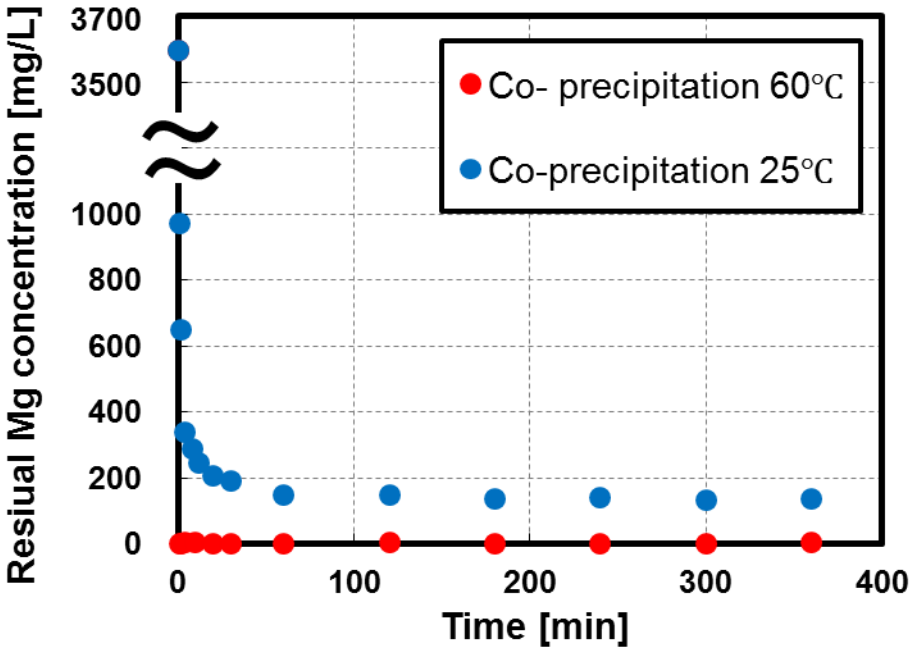
- At any initial B/Mg molar ratio, the predominant B specie was 3-coordinated boron.
- H_3BO_3 was inserted between hydromagnesite layers during adsorption.

Evaluation of the effect of temperature

1 hour experiment



Long reaction time experiment



Experimental condition

- Initial B conc. →100 mg/L
- Initial B/Mg molar ratio → 0.0625
- Temperature → 25, 60℃

- More B was removed at 25℃ than 60℃.
- Rate of precipitation was fast at 60℃.
  →$Mg(OH)_2$ was precipitated prior to the production of surface precipitation

Conclusion (1)

	Co-precipitation	Adsorption
Sorption isotherm	BET type	Langmuir type
Crystal structure	hydromagnesite $[Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O]$	Brucite $[Mg(OH)_2]$
Boron specie	3-coordinated boron	3-coordinated boron & 4-coordinated boron
Boron sorption mechanism	H_3BO_3 absorption between hydromagnesite layers	I) H_3BO_3 absorption between Brucite layers
		II) Formation of the surface complexation at high initial B/Mg molar ratio

Conclusion (2)

- More boron was removed during co-precipitation than adsorption.
- Adsorption;
  - B was absorbed between the $Mg(OH)_2$ layers while surface complexation was formed when the initial B/Mg molar ratio was high.
- Co-precipitation;
  - Hydromagnesite was produced when the initial B/Mg molar ratio was over 0.4, which suggests that B was absorbed between the hydromagensite layers.
  - Magnesium hydroxide was produced when the initial B/Mg molar ratio was under 0.4, which suggests that B was absorbed between the magnesium hydroxid layers.

Hydromagnesite

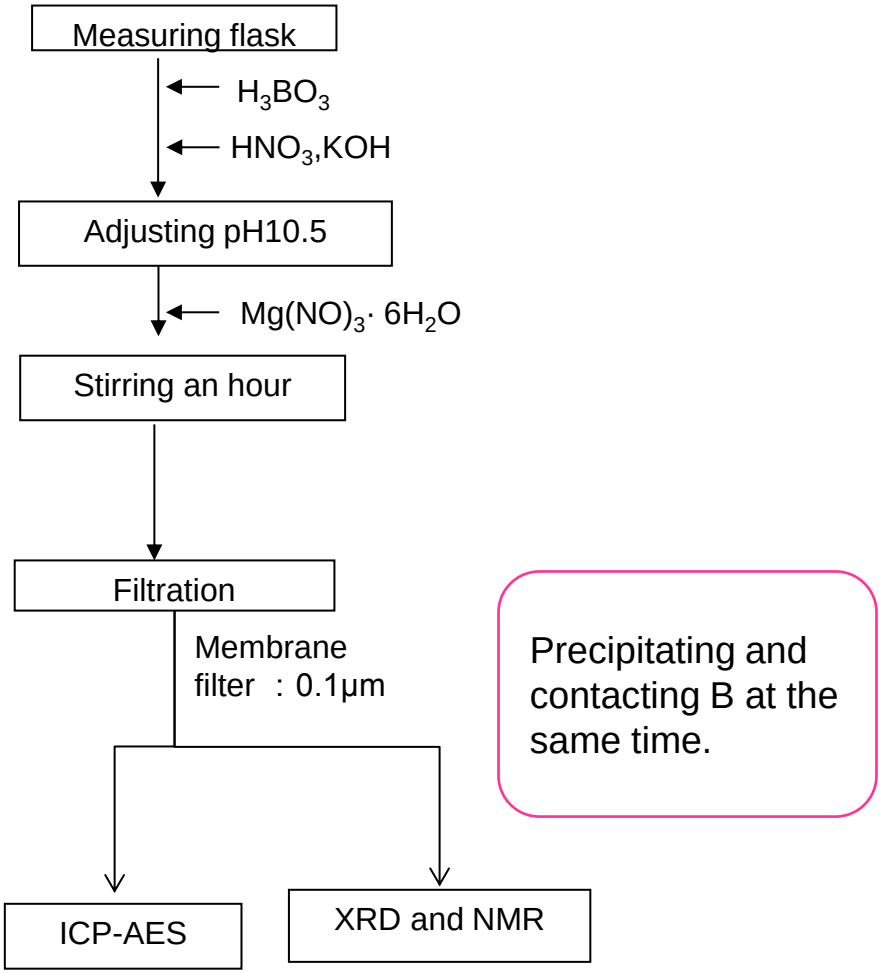
* $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ (JCPDS 25-513)

NMR

* NMR(Nuclear Magnetic Resonance)

Experimental method

Co-precipitation



Adsorption