European Geosciences Union general assembly April 14-19, 2024 - Vienna, Austria

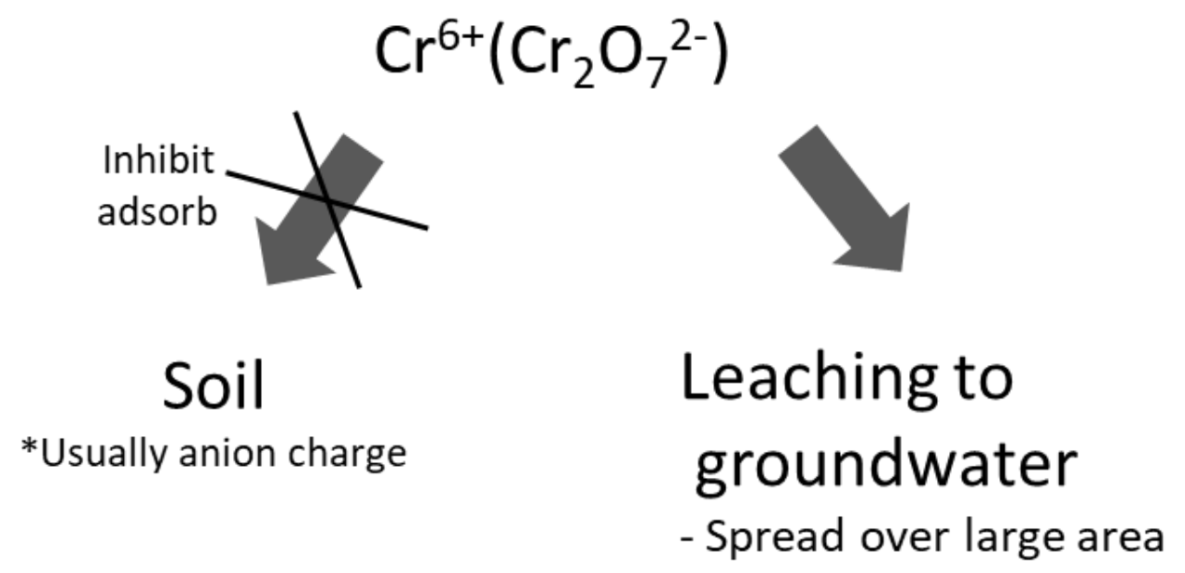
April 18, 2024 -Vienna, Austria

Immobilization Mechanisms of Hexavalent Chromium When Reduced by Fe^{2+}-Bearing Clay Minerals Depending on Solution pH

Changyu Moon[1], Hee-sun Moon[2], Kyoungphile Nam[1*]
[1]Department of Civil & Environmental Engineering, Seoul National University, Seoul, South Korea
[2]Korea Institute of Geoscience and Mineral Resources, South Korea
Author e-mail: chan1570@snu.ac.kr

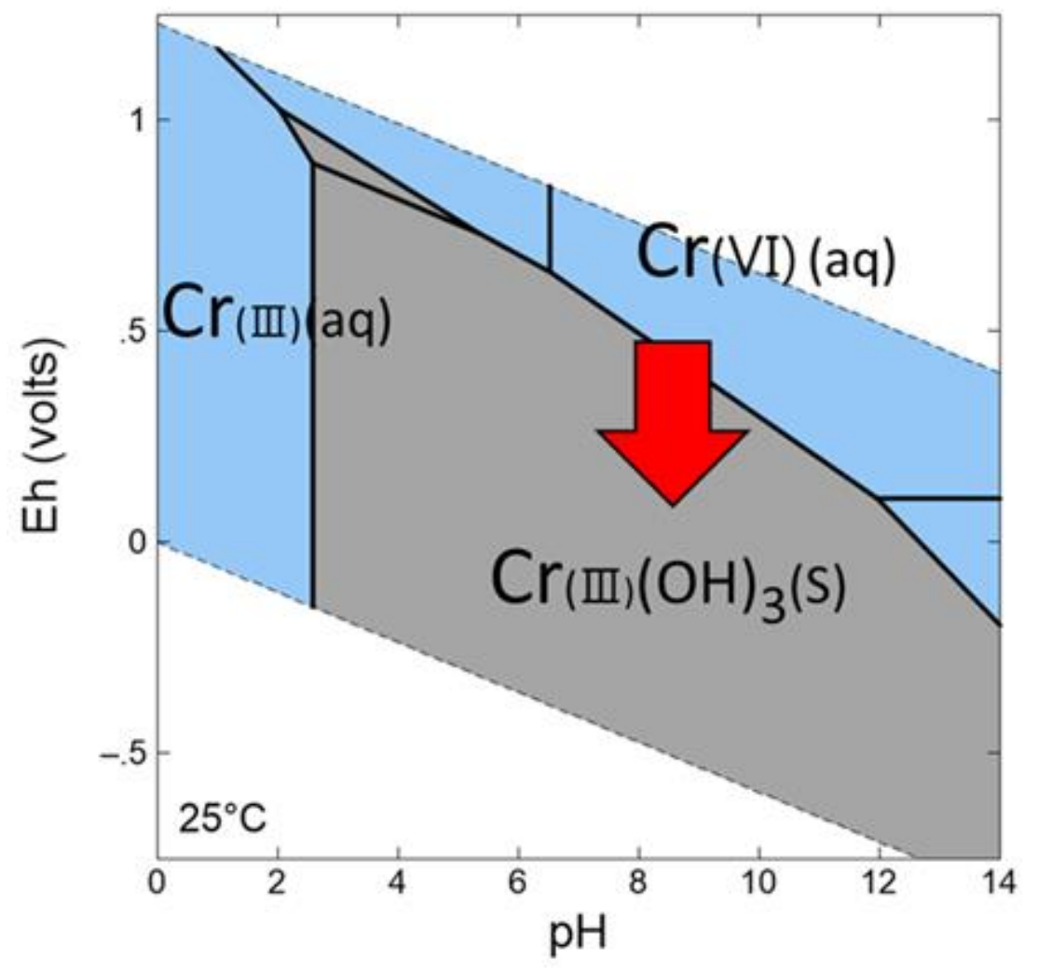
Introduction

Chromium contamination in groundwater



- ➢Chromium, originating from industrial activities, is commonly released in its hazardous hexavalent form (Cr^{6+}).
- ➢Cr^{6+} is typically exist as an oxyanions, exhibiting limited sorption on soil, and thus easily leaching into groundwater.
- ➢The elevated risk of widespread chromium contamination urgently necessitates the development of effective remediation technologies.

Redox sensitive inorganics

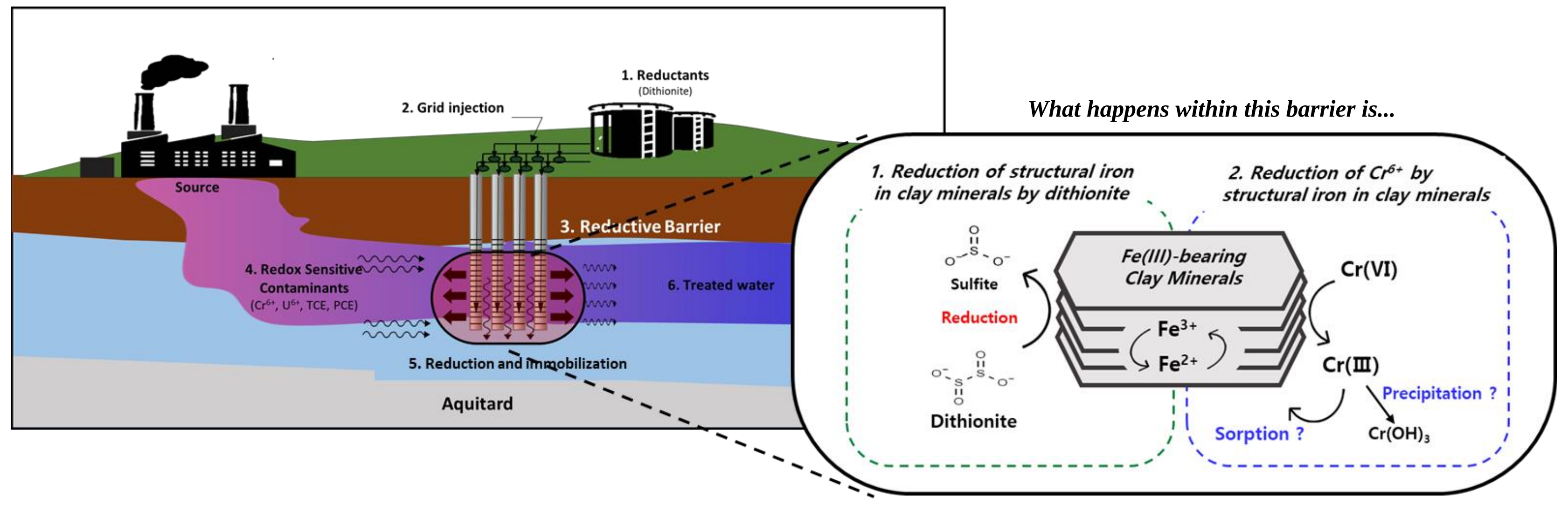


- ➢Chromium species can undergo changes in their oxidation state based on the prevailing environmental redox conditions.
- ➢Under reducing conditions, the hexavalent chromium (Cr^{6+}) is transformed into the less harmful trivalent chromium (Cr^{3+}).
- ➢"The reduced Cr^{3+} can exist as a cation or precipitate as chromium hydroxide ($Cr(OH)_{3(s)}$) depending on the pH, which exhibits significantly lower mobility in the aquifer compared to Cr^{6+}, allowing for chromium immobilization

*In Situ R*edox Manipulation (ISRM) for remediation chromium in groundwater

- ➢ The injection of a liquid reductant, such as dithionite, into an aquifer promotes the formation of a reducing environment, establishing an in-situ reductive barrier.
- ➢ When contaminated groundwater containing dissolved Cr^{6+} flows through this engineered reductive barrier, the Cr^{6+} is effectively reduced to its less toxic and less mobile form, Cr^{3+}.
- ➢This in situ reductive barrier technology has been successfully applied at the Hanford site, demonstrating high effectiveness in immobilizing chromium contamination while minimizing adverse impacts on the subsurface environment.

Schematic design of ISRM



Potential of structurla iron in clay mineral as a electron shuttle

- ➢ Clay minerals can incorporate varying amounts of structural Fe^{3+} (0.01-26 wt%) through isomorphous substitution of Al^{3+}, resulting in Fe^{3+}-bearing clay minerals.
- ➢ In the presence of a reductant like dithionite, the structural Fe^{3+} in clay minerals is reduced to Fe^{2+}, which can continuously reduce contaminants, allowing Fe^{3+}-bearing clay minerals to act as an electron shuttle. (Joe-Wong., 2017, Bishop et al., 2014, Vinuth et al., 2015)
- ➢A key advantage of this technique is the ability to utilize natural subsurface media for contaminant remediation by merely introducing a reducing agent.

Question. So, how much is chromium reduced? What happens when it is reduced?

✓ To apply this technology, the understanding of the behavior/mechanism of chromium reduction and immobilization is necessary.

Objectives

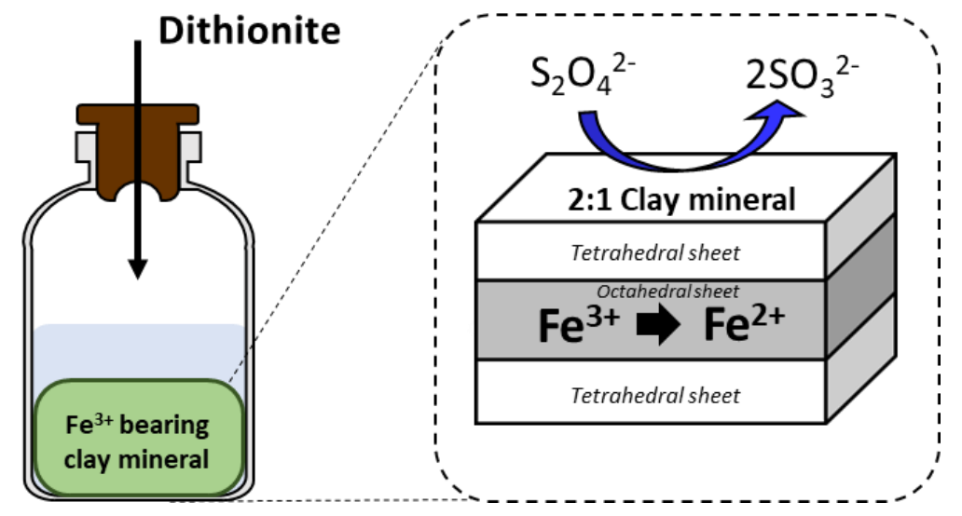
Investigate the immobilization behavior of hexavalent chromium utilizing Fe^{3+}-bearing clay mineral as an electron shuttle at different pH

① Effect of pH on reduction hexavalent chromium by Fe^{2+} bearing clay minerals

② Investigate of immobilization mechanism of reduced chromium at different pH

Experimental schematics

(1) Reduction structural Fe^{3+} in clay minerals by dithionite

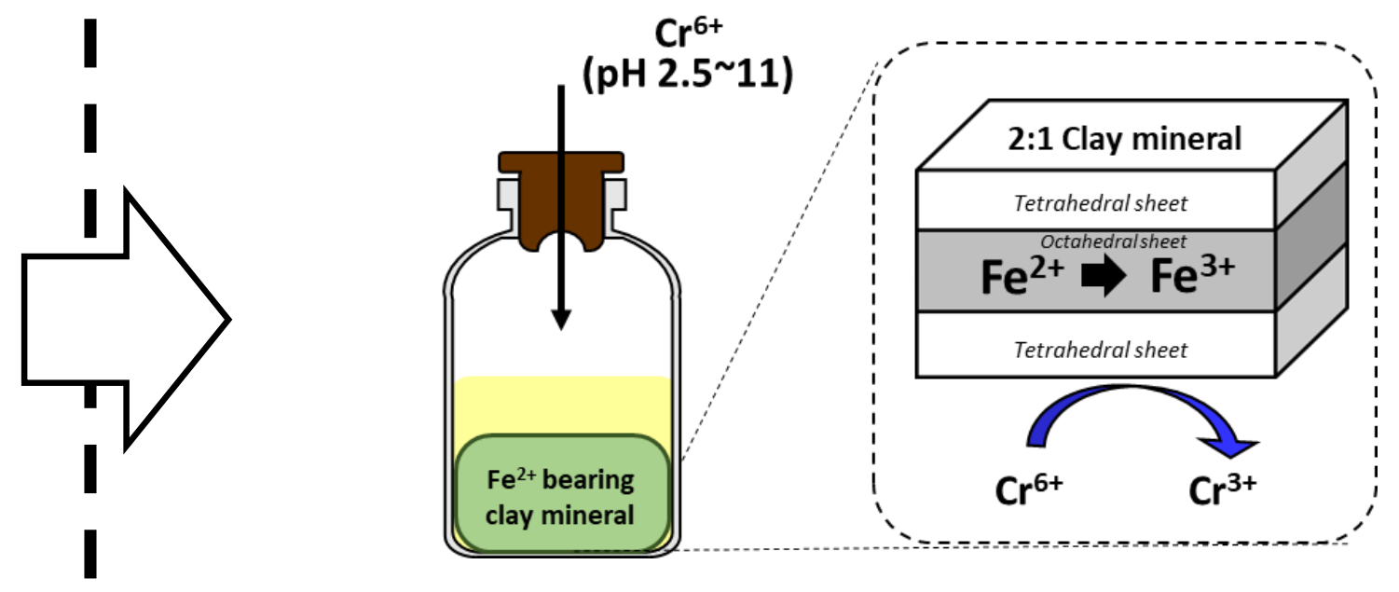


Types of Fe^{3+}-bearing clay minerals

A. Montmorillonite (SWy-3)
Structure $(Na,Ca)_{0.33}(Al,Mg,(Fe)_n)_2(Si_4O_{10})OH)_2 \cdot nH_2O$
Total structural iron (Fe^{3+}) contents: 2.3 wt%
After treatment: Fe^{2+}/Total Fe: 0.67

B. Nontronite (NAu-1)
Structure:$(CaO_{0.5},Na)_{0.3}Fe^{3+}{}_2(Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$
Total structural iron (Fe^{3+}) contents: 22.3 wt%
After treatment: Fe^{2+}/Total Fe: 0.50

(2) Reduction Cr^{6+} by structural Fe^{2+} in clay minerals



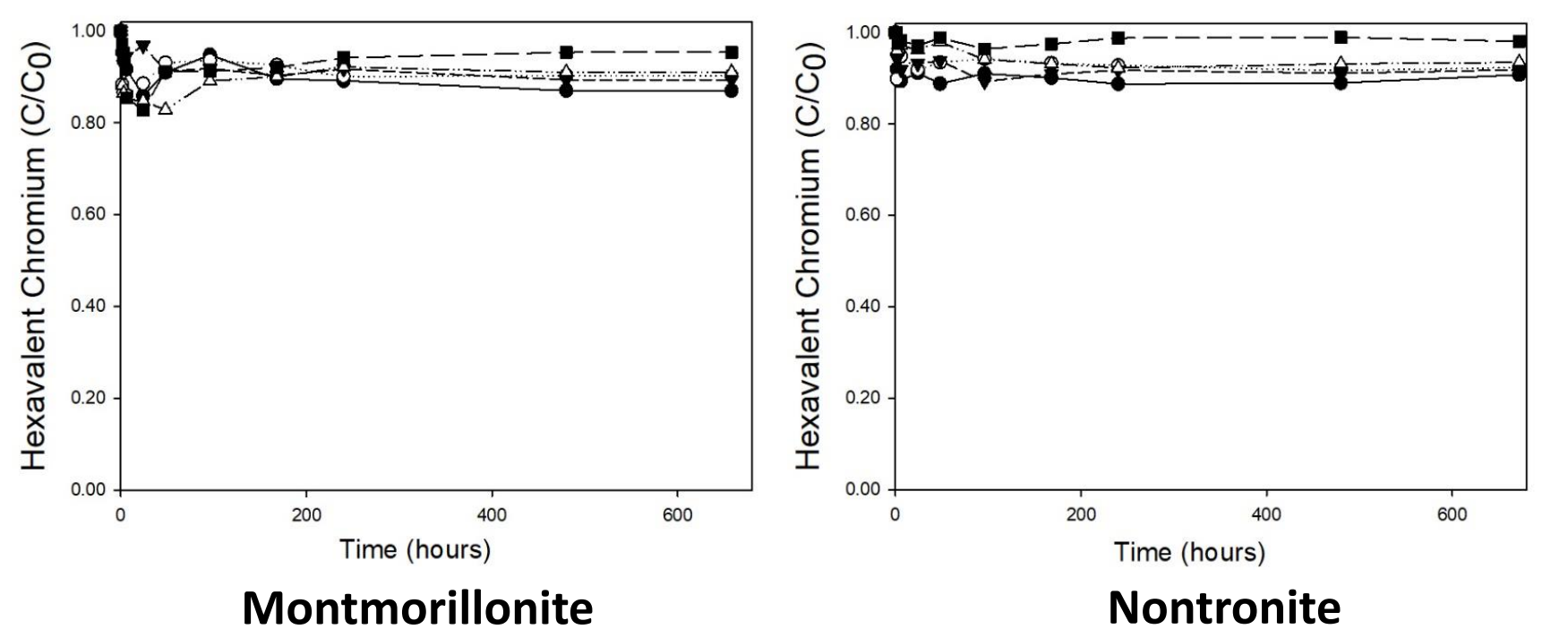
Reduction exp.

- The Cr^{6+} solution was injected into a batch containing treated/untreated clay minerals.
- Tested at pH 2.5 - 11

Results

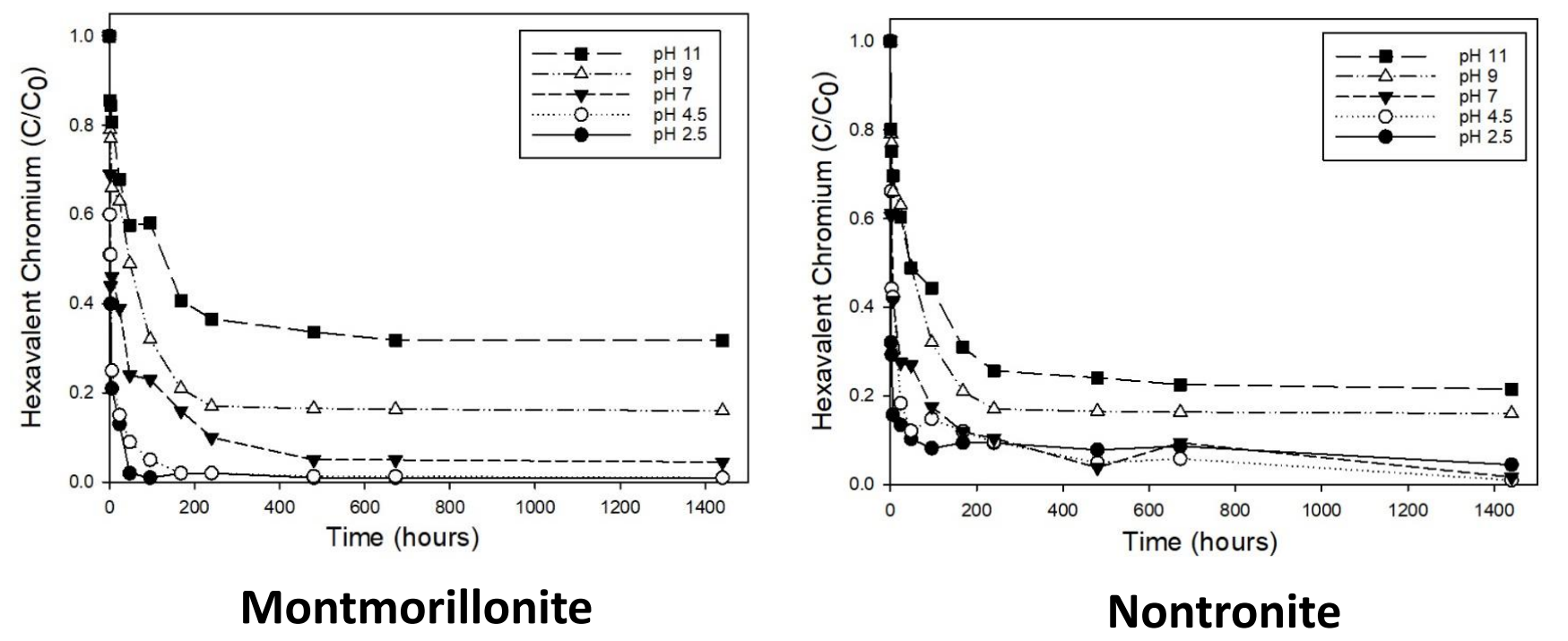
Removal of Cr^{6+} in the presence of clay mineral at different pH

With untreated clay minerals (Fe^{3+}-bearing)



Montmorillonite **Nontronite**

With treated clay minerals (Fe^{2+}-bearing)



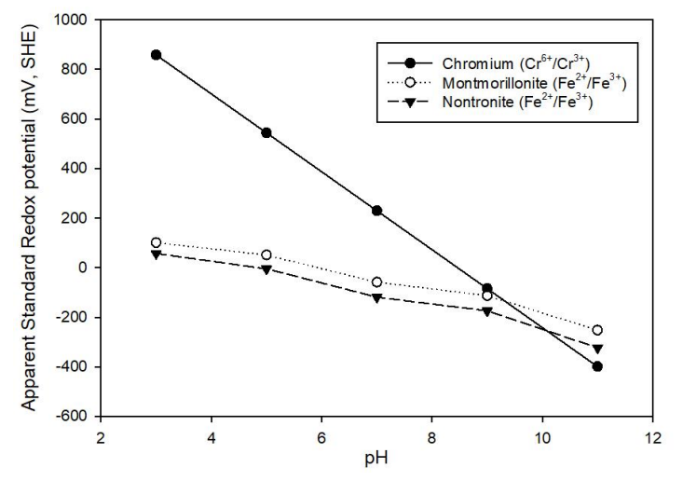
Montmorillonite **Nontronite**

- Removal of Cr^{6+} was negligible in the solution with *Fe^{3+}-bearing* untreated clay mineral.
- In the solution with treated clay mineral, Cr^6 was removed by being reduced by structural Fe^{2+}.
- As pH decreased, higher rates and extent of Cr^{6+} reduction were observed.

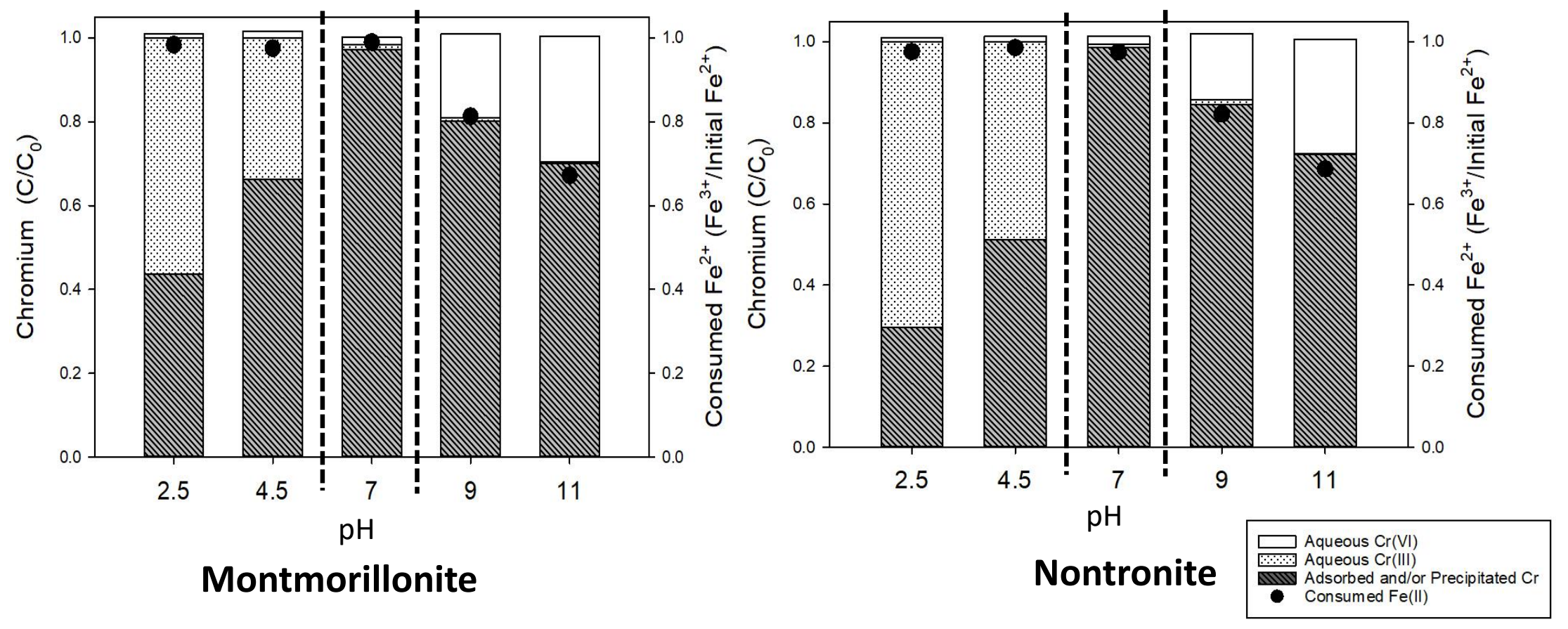
✓Reasons of higher rates and extent at acidic pH

Reduction rate
The observed reaction constant increased at lower pH conditions, attributed to the involvement of hydrogen ions in the reduction reaction
$3Fe^{2+} + Cr^{6+} + 8H^{+} \rightarrow 3Fe^{3+} + Cr^{3+} + 4H_2O$

Reduction extent
As the pH increased, the difference in redox potential diminished, indicating that the reaction was thermodynamically less favorable



Distribution of Cr in clay mineral solution

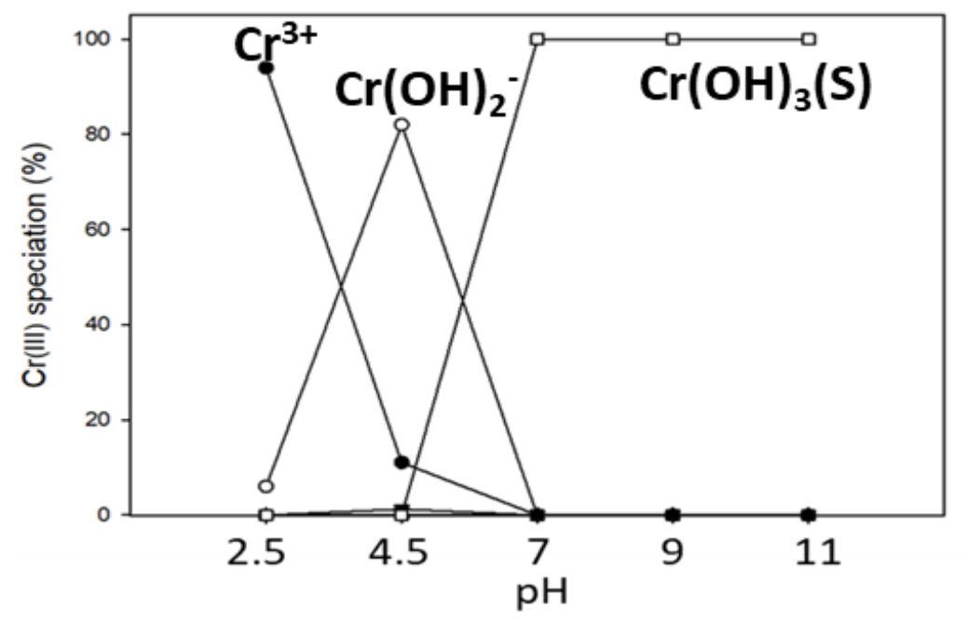


Montmorillonite **Nontronite**

- *At pH 2.5 and 4.5*
  - Structural Fe^{2+} was fully consumed
  - 30~66 % aof Cr^{3+} were found to be associated with clay mieneral.
- *At pH 7*
  - Structural Fe^{2+} was fully consumed
  - Cr^{3+} was not present in solution, but rather all was found to be associated in clay minerals.
- *At pH 9 and 11*
  - Not all of structural Fe^{2+} was consumed
  - Cr^{3+} was not present in solution

Immobilization mechanism of Cr^{3+} by Fe^{2+}-bearing clay minerals

(1) Visual Minteq model (ver.3.1) prediction



- According to the Visual Minteq model (version 3.1) prediction, Cr^{3+} can be present in the aqueous solution at pH 2.5 and 4.5, while it can be precipitated at pH 7 and above.

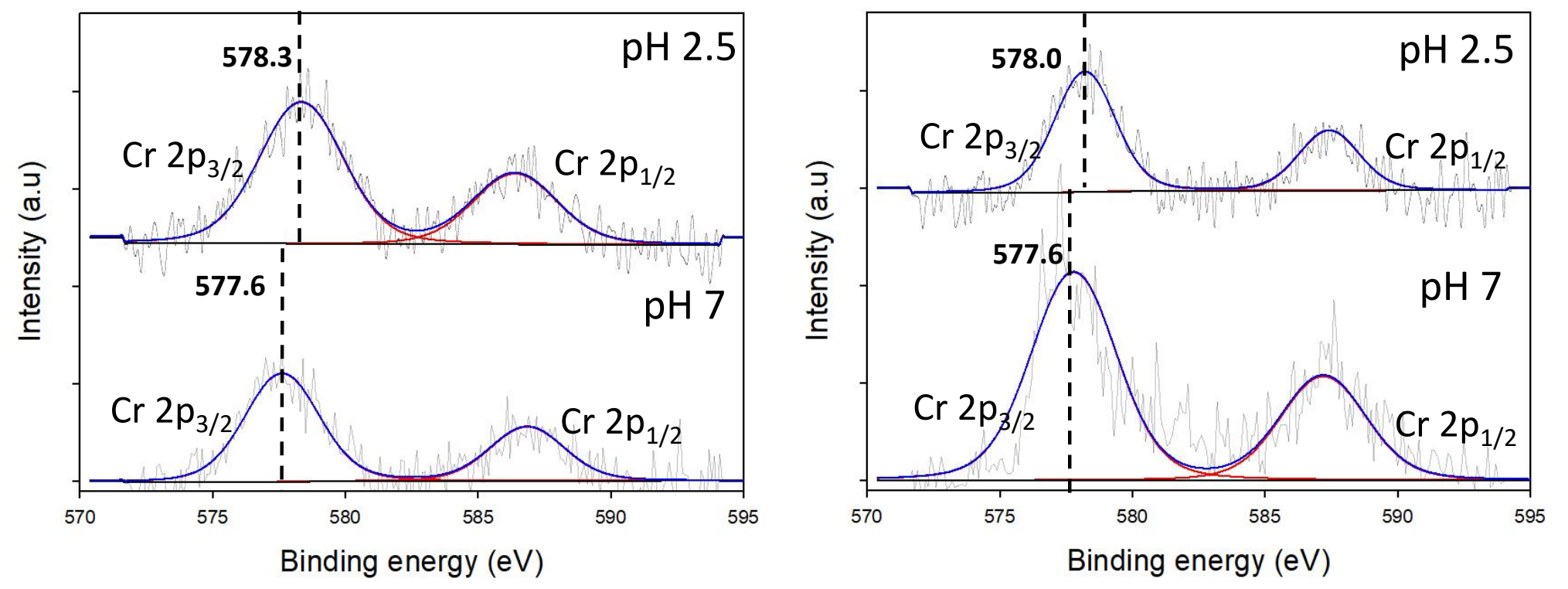
(2) Surface adsorbed Cr^{3+} determined by DTPA extraction

Types of clay minerals	pH	Cr^{3+} associated with clay minerals (%) (A)	DTPA extractable Cr^{3+} (%) (B)	Adsorbed Cr^{3+}(%) (B/A)	
Montmorillonite	2.5	0.437	0.447	102	*Adsorption occurs*
	4.5	0.663	0.663	100	
	7	0.973	0.025	3	*Precipitation occurs*
	9	0.801	0.026	3	
	11	0.701	0.004	1	
Nontronite	2.5	0.296	0.281	95	
	4.5	0.512	0.487	95	
	7	0.986	0.052	5	
	9	0.845	0.006	1	
	11	0.721	0.003	0	

✓ *Diethylenetriamine pentaacetate (DTPA) is chelating agent that can remove adsorbed Cr^{3+}*

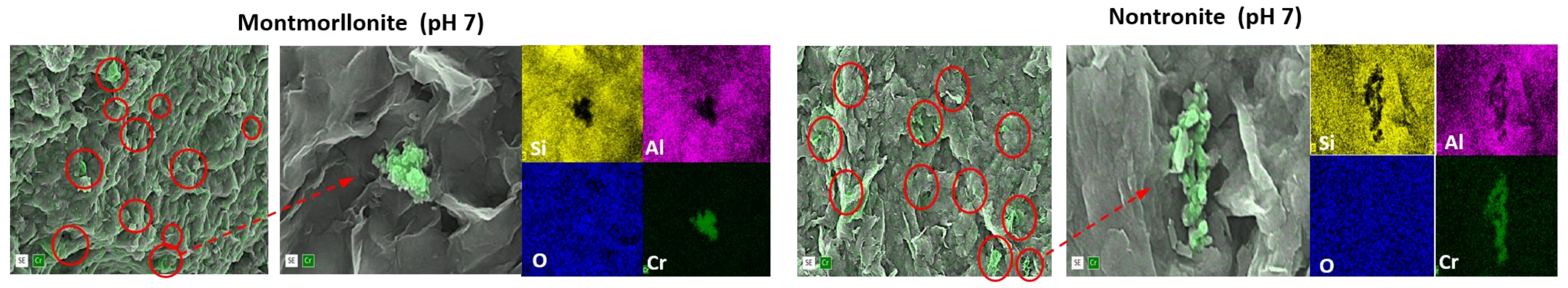
- The DTPA extraction experiment results confirmed that at pH 2.5 and 4.5, all Cr^{3+} was desorbed by DTPA, while desorption hardly occurred at pH 7 and above, which can be attributed to precipitation occurring

(3) XPS Analysis



- The peak for $Cr2p_{3/2}$ observed between the binding energies of 577-579 eV indicates Cr^{3+} (Wu et al., 2012).
- Significant differences in peak binding energy were observed between pH 2.5 and 7. Specifically, presence of a peak at 577.6 eV at pH 7 suggests the presence of $Cr(OH)_3$ (Biesinger et al., 2004)

(4) SEM-EDS analysis



- The SEM-EDS analysis confirmed the existence of chromium on the clay mineral surface at all pH conditions.
- The chromium precipitates were clearly observed at pH above 7.

Conclusions

Fe^{2+}-bearing clay mineral can reduce and immobilize hexavalent chromium (Cr^{6+}) efficiently.
① As pH decreased, the reduction extent and rate is increased
② The reduced chromium (Cr^{3+}) was immobilized by sorption onto clay mineral surface at pH 2.5 and 4.5, and was precipitated in the form of $Cr(OH)_3$ at pH 7 and above.
→ We suggest the pH 7 is the optimal condition for the remediation of hexavalent chromium utilizing clay minerals

Acknowldegement

This work was financially supported by Mid-Career Researcher Program through National Research Foundation (NRF) grant funded by the Ministry of Science and ICT (MSIT) (No. 2022R1A2C109273213)