

# Effect of co-existing ions on lead leaching behaviour from hardened cement paste



HIROSHIMA UNIVERSITY

***Takumi Nishiwaki***

*Shaojun Zhou*

*Masaharu Yamasaki*

*Yuko Ogawa*

*Kenji Kawai*

# Background

Environmental issues happen

Industrial wastes



expectation

concrete

Recently, due to environmental problems, a recycling-oriented society is required. In the concrete field, concrete made from industrial wastes is expected.

Industrial wastes

Heavy metals



expectation

Risk of leaching  
heavy metals

**However**, some industrial wastes contain harmful **heavy metals**. Therefore utilizing the industrial wastes may be **dangerous**, due to the leaching of heavy metals which are harmful for human bodies and environment.

# Previous study

## Previous study 1

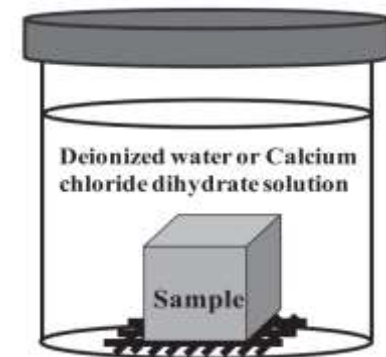
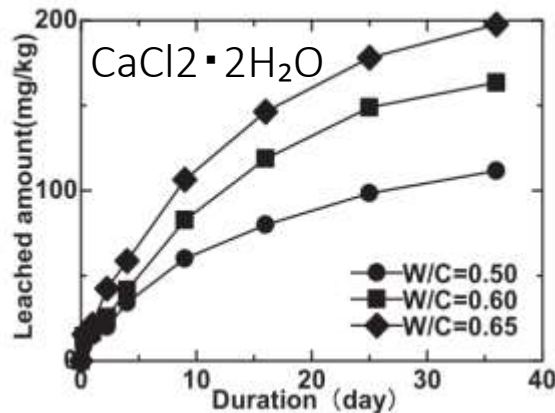
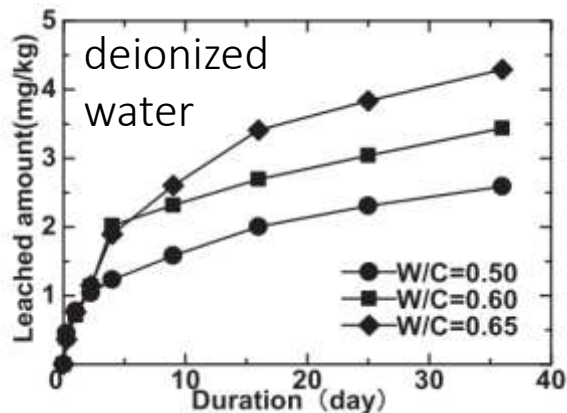
In Cement paste, Portlandite, Ettringite and CSH have an ability to adsorb and fix heavy metals.

↕ **BUT** ↕

## Previous study 2

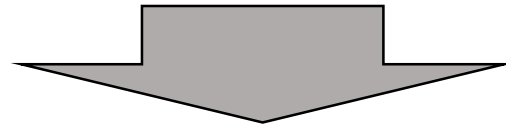
In  $\text{CaCl}_2$  solutions, the leaching amount is larger than the amount in deionized water.

The leaching amount in  $\text{CaCl}_2$  solutions is 35-40 times as much as the amount in deionized water.



# Purpose

It is necessary to investigate the leaching behaviour of lead in different circumstances.



*In this study*

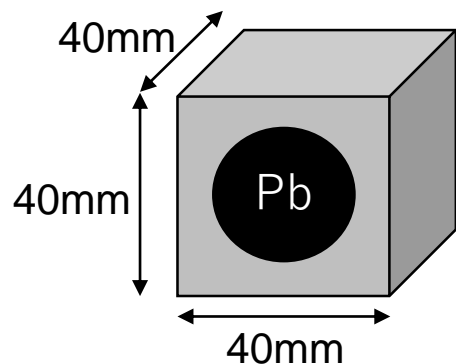
## 1. leaching behaviours

The leaching behaviours of lead from cement pastes immersed in three kinds of chloride solutions as well as those in deionized water were examined.

## 2. what affects the leaching behavior

Focusing on the difference of  $\text{Ca(OH)}_2$  content, the relationship between leaching amount and  $\text{Ca(OH)}_2$  content was investigated.

# Experimental program



*Specimens (Cement paste)*

W/C : 0.40, 0.55

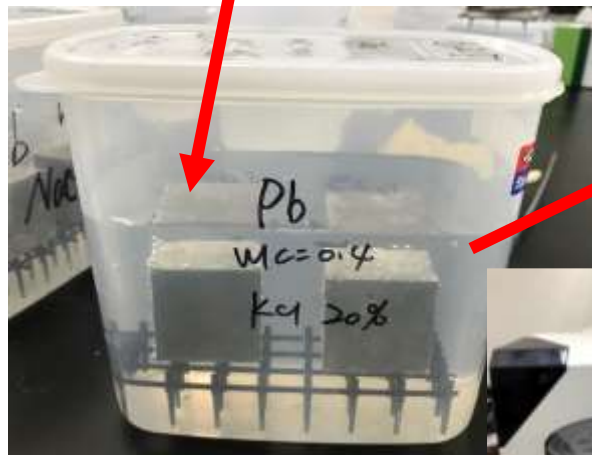
Water : Pure water

Lead : 1 mass% of cement.

mixture	W/C	Unit content [kg/m <sup>3</sup> ]		Addition [kg/m <sup>3</sup> ]
		Water	Cement	
Pb40	0.40	558	1394	13.94
Pb55	0.55	634	1153	11.53

## *Tank Leaching Test*

On 0.25, 1, 2.25, 4, 9, 16, 25, 36, 64 days from the beginning, all solutions were changed. The concentrations of lead leaching was determined by an atomic absorption spectrophotometer.

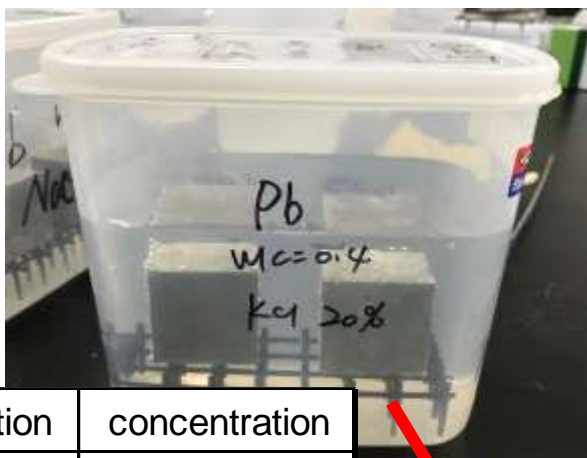


atomic absorption spectrophotometer

solution	concentration
NaCl	5, 10, 20%
KCl	5, 10, 20%
CaCl <sub>2</sub>	5, 10, 20%
deionized water	—

Solution's types of tank leaching test

# Experimental program

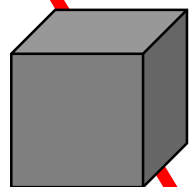


## *Tank Leaching Test*

On 0.25, 1, 2.25, 4, 9, 16, 25, 36, 64 days from start, all solutions were changed.

The concentrations of lead leaching was determined with an atomic absorption spectrophotometer.

solution	concentration
NaCl	5,10,20%
KCl	5,10,20%
CaCl <sub>2</sub>	5,10,20%
deionized water	—



0-0.1 mm  
from surface



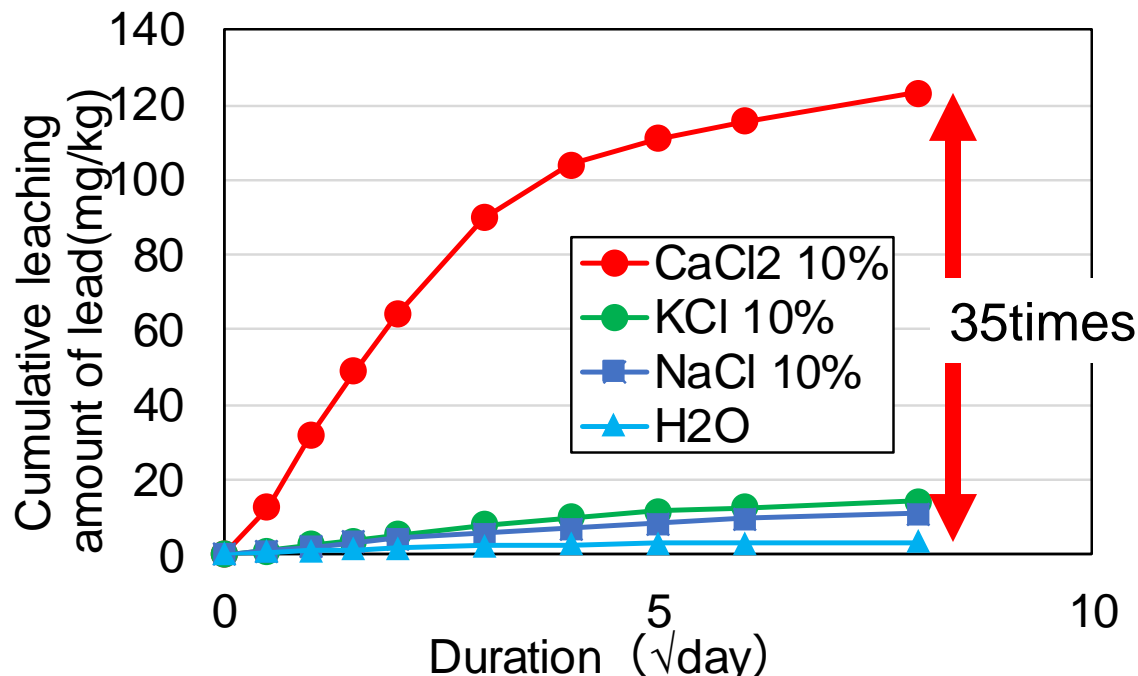
## *TG-DTA*

After 64 days of immersion, TG-DTA test was carried out to measure Ca(OH)<sub>2</sub> content.

The relation between the amount of lead leaching and Ca(OH)<sub>2</sub> content.



Focusing on 10% solutions (W/C=0.40),



$$\begin{aligned} & \text{(the amount of lead leaching [mg/kg])} \\ &= \text{(the amount of lead leaching [mg])} / \text{(the mass of specimens [kg])} \end{aligned}$$

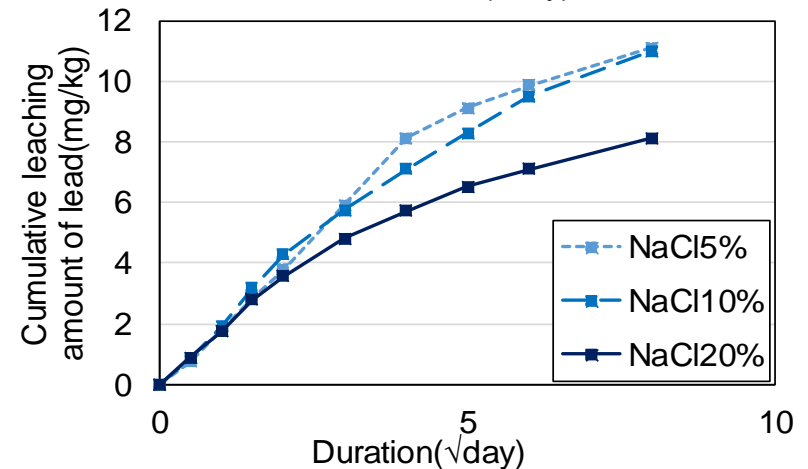
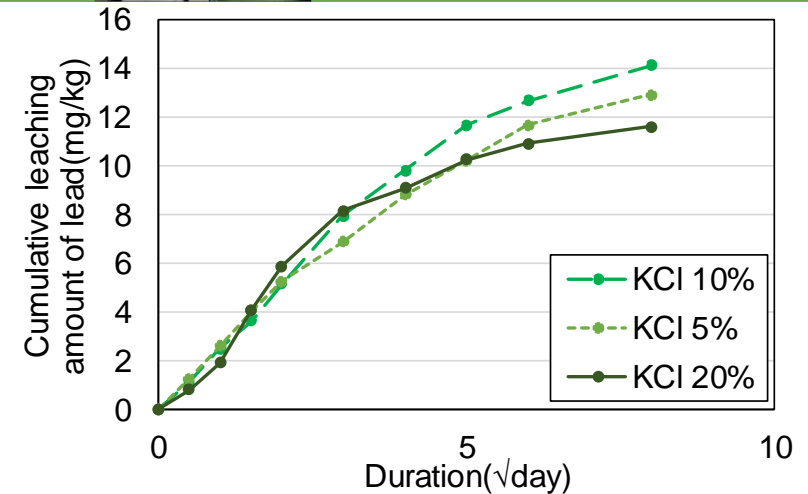
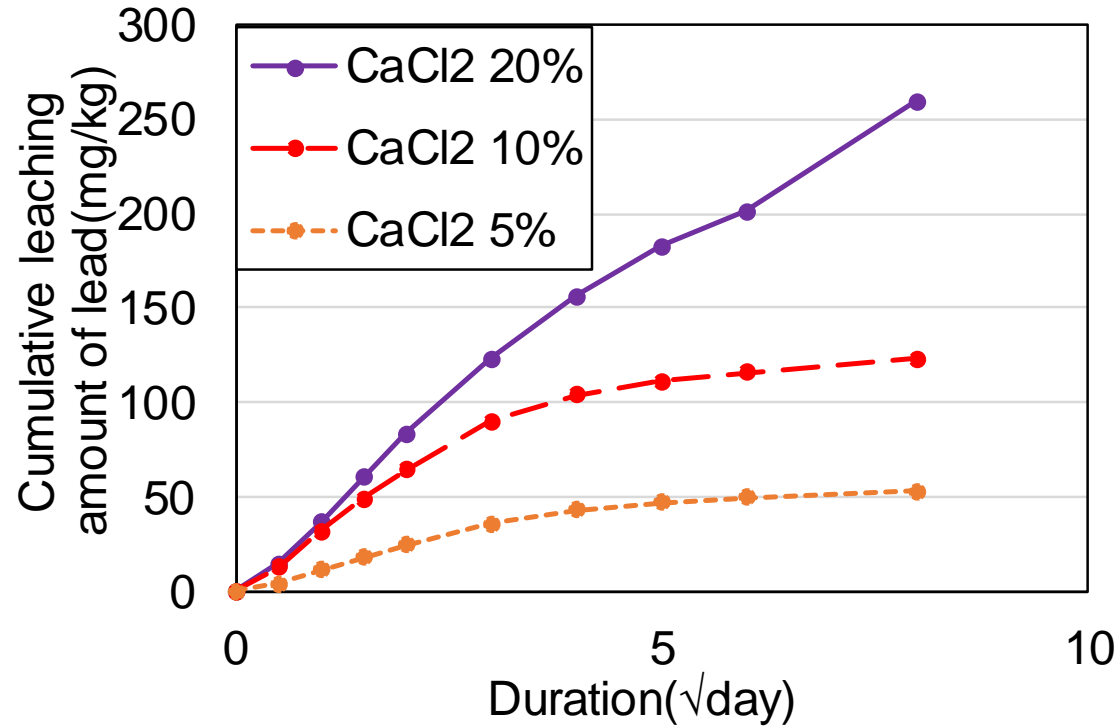
- The largest amount of lead was leached in **CaCl<sub>2</sub>** solutions, followed by KCl solutions, NaCl solutions and deionized water.
- The lead leaching amount in 10%-CaCl<sub>2</sub> solution was approximately 35 times as much as that in deionized water.

# Result



# Lead leaching

Focusing on all solutions (W/C=0.40)



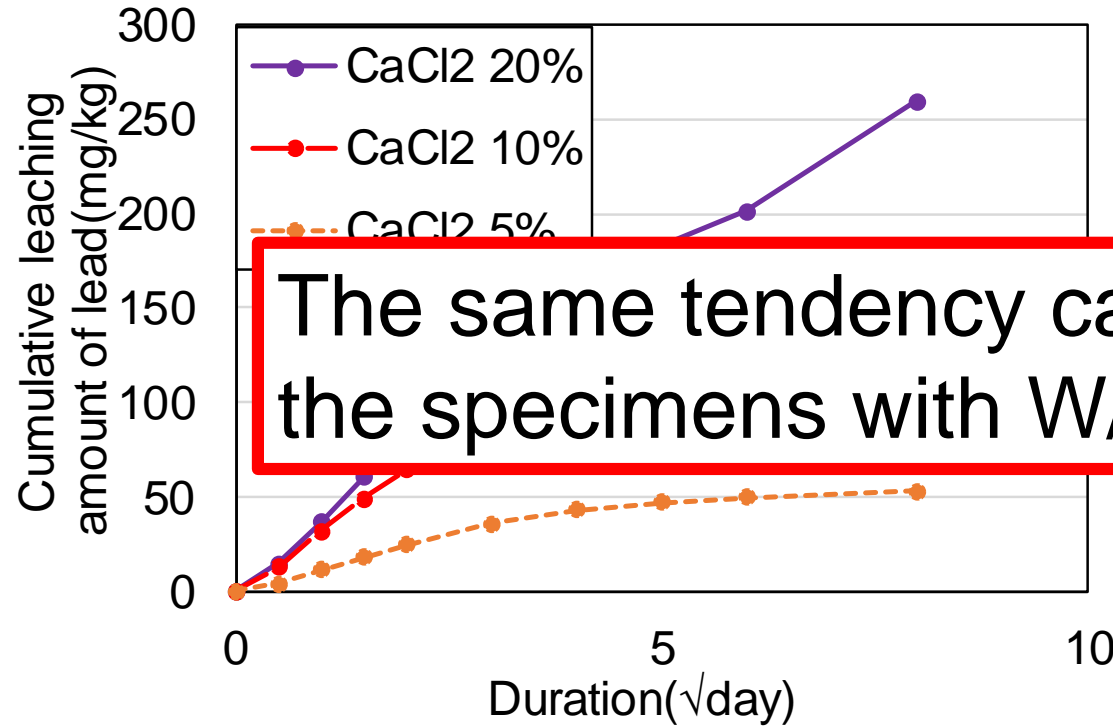
The lead leaching amount was almost proportional to the concentration of the solutions in the case of CaCl<sub>2</sub> solutions.

**On the other hand**, the lead leaching amount had no correlation with the concentration of solutions in the case of KCl solutions and NaCl solutions.

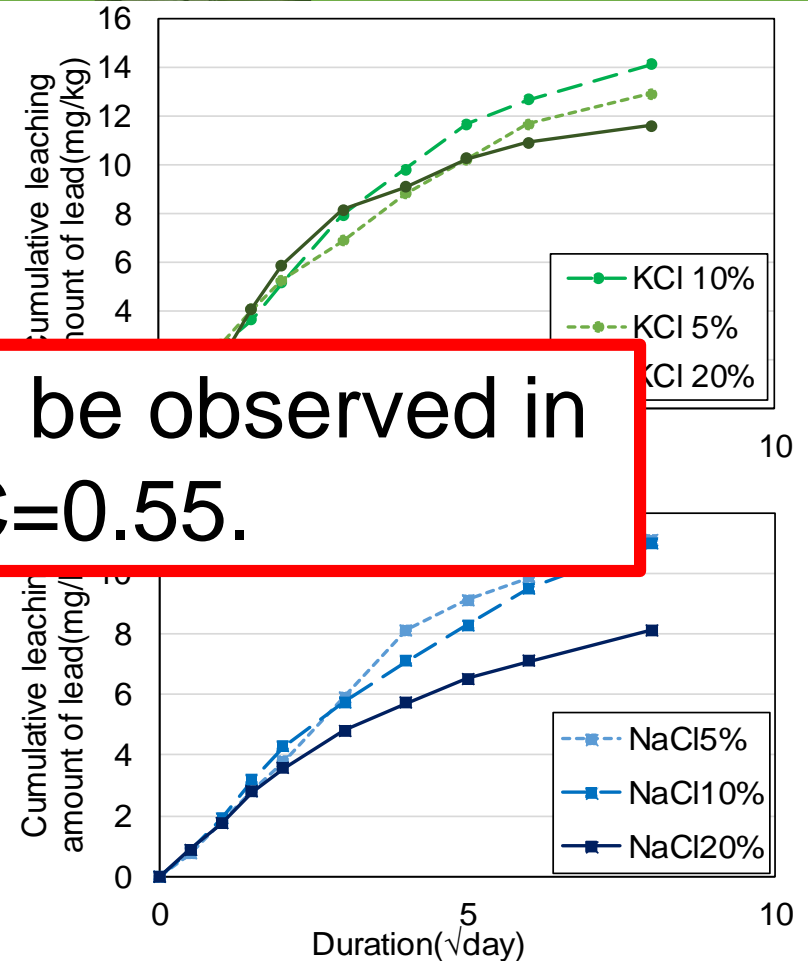




Focusing on all solutions (W/C=0.40)

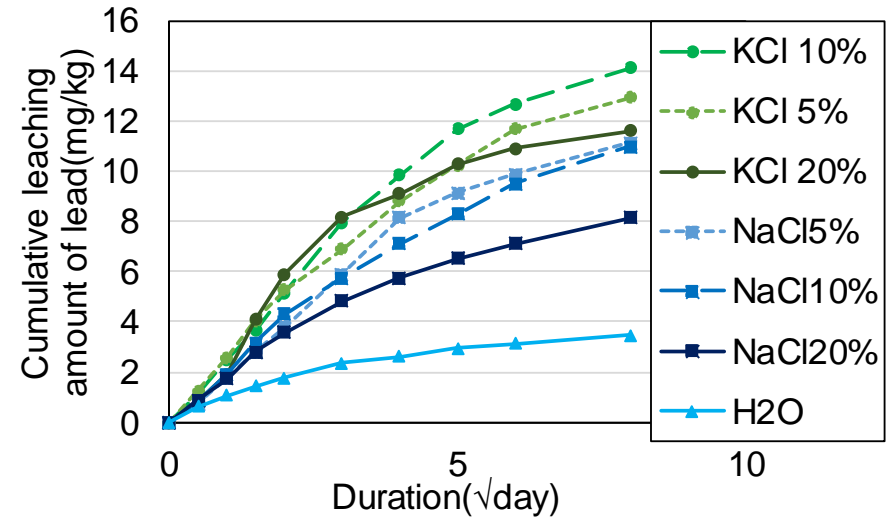
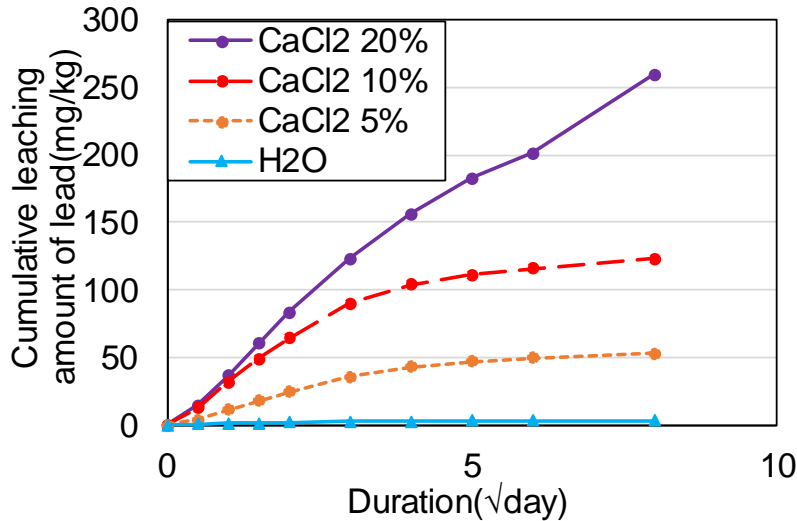


The same tendency can be observed in the specimens with W/C=0.55.



The lead leaching amount was almost proportional to the concentration of the solutions in the case of CaCl<sub>2</sub> solutions.

On the other hand, the lead leaching amount had no correlation with the concentration of solutions in the case of KCl solutions and NaCl solutions.



*Fick's second law*

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

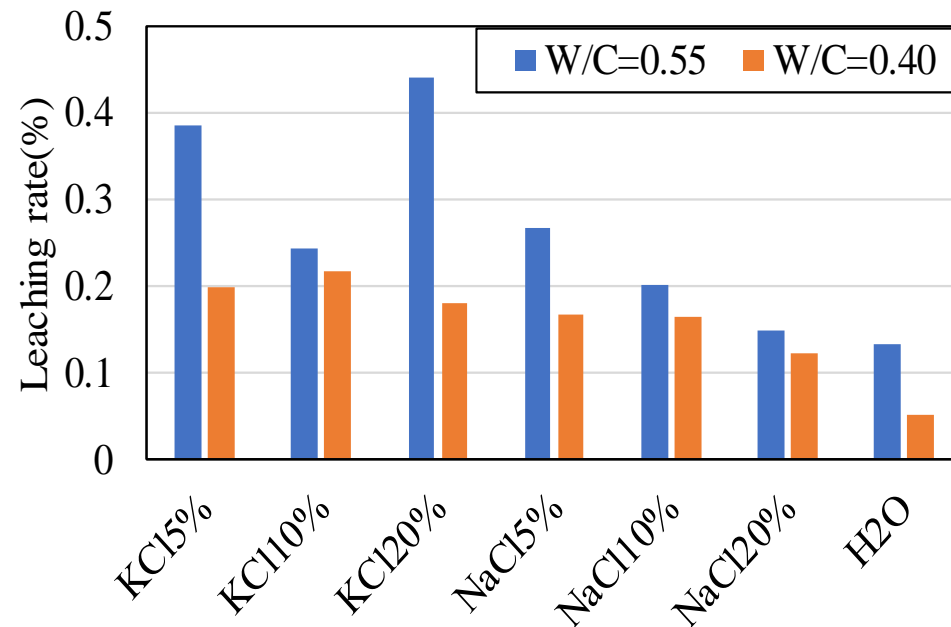
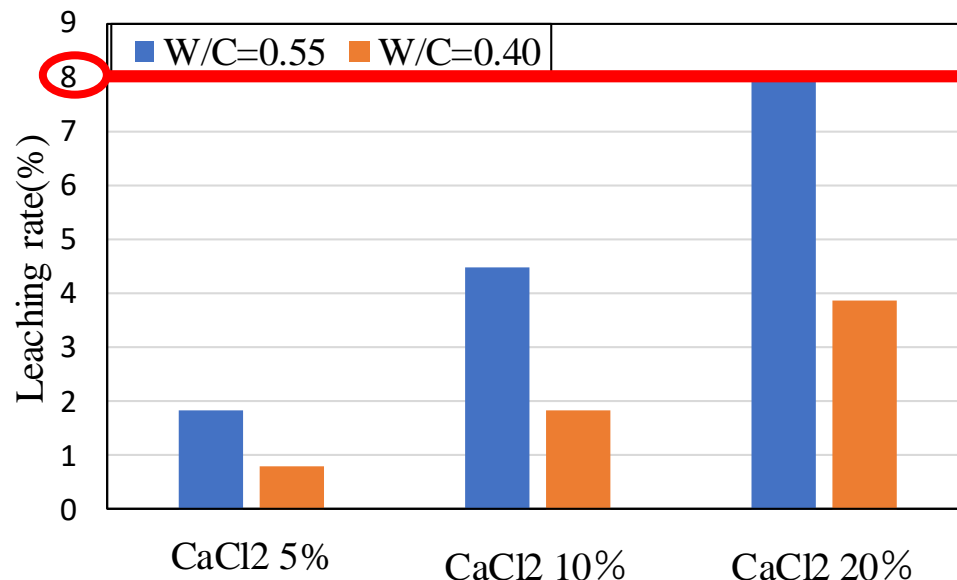
$$\rightarrow M = 2C_0S \sqrt{\frac{Dt}{\pi}}$$

C; Concentration of lead(mg/cm<sup>3</sup>)  
 C<sub>0</sub>; Initial content of lead(mg/cm<sup>3</sup>)  
 t; time(s)  
 D; Diffusion coefficient (m<sup>2</sup>s<sup>-1</sup>)  
 M; Cumulative amount (mg)  
 S; Surface area (m<sup>2</sup>)

The...  
 Be... **Further investigation will be needed to clarify the reason.** ...  
 around 4 to 9 days of immersion.



## Leaching rate

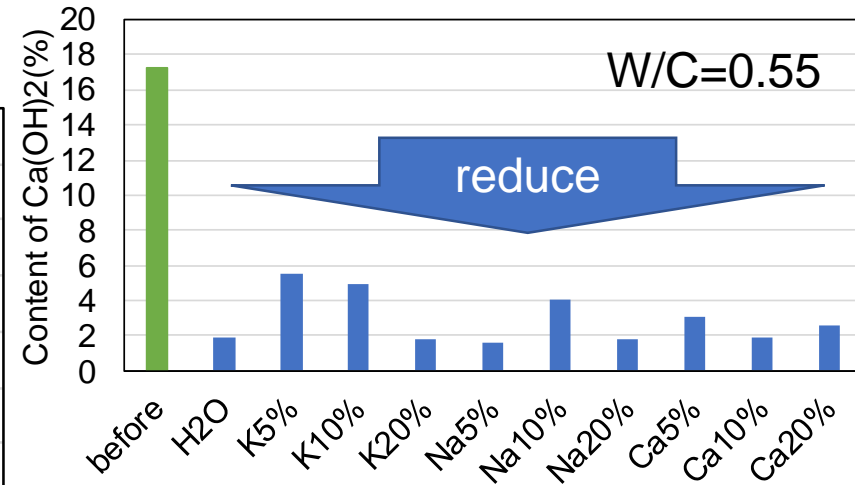
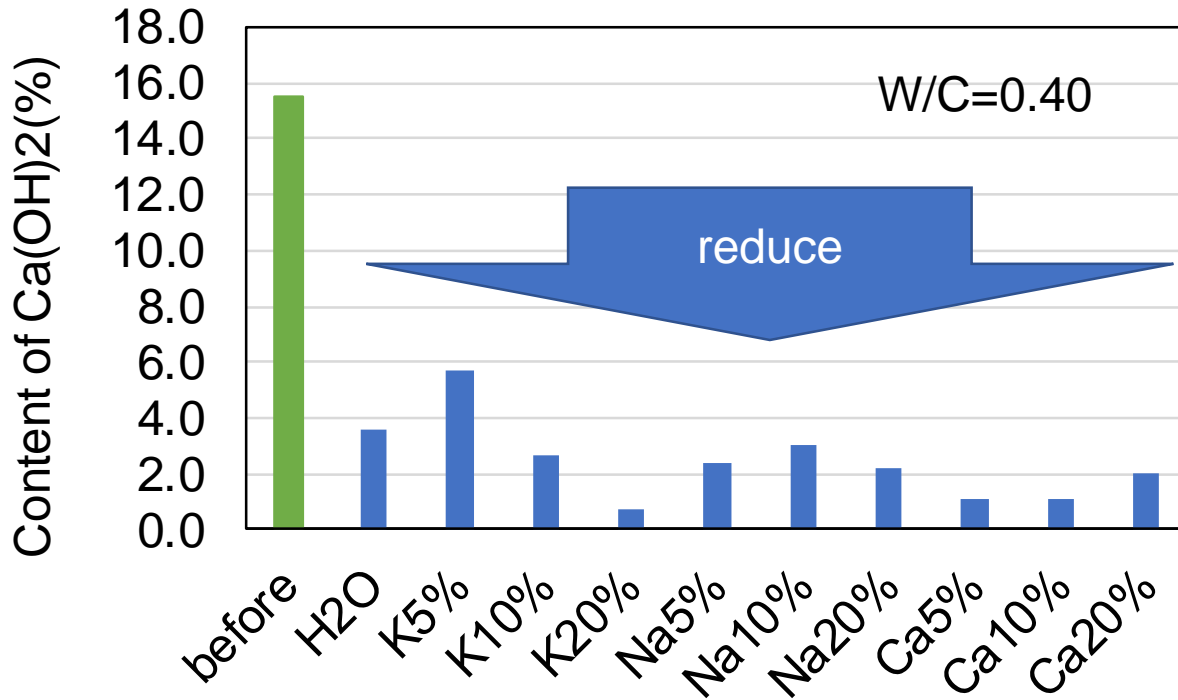


$$(\text{Leaching rate}[\%]) = \frac{(\text{Cumulative leaching amount}(\text{mg}))}{(\text{Initial content}(\text{mg}))} \times 100$$

- The leaching rate in 20% CaCl<sub>2</sub> solution was highest in all solutions.
- The rate of W/C=0.55 in CaCl<sub>2</sub> solution (highest in all specimens) was only 8%.  
→ Thus, it was shown most parts of specimens were **not** affected by chloride solutions and deionized water.



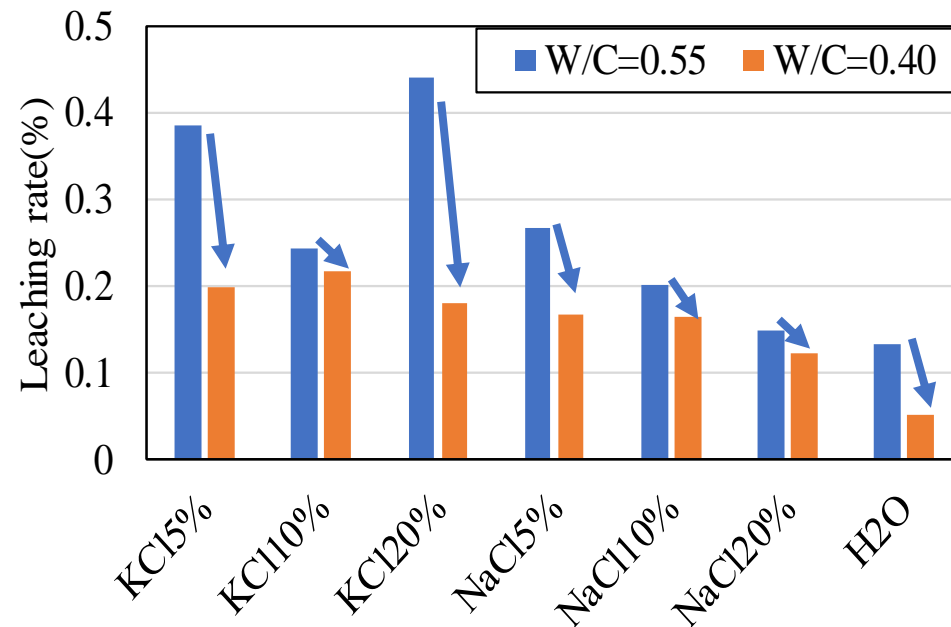
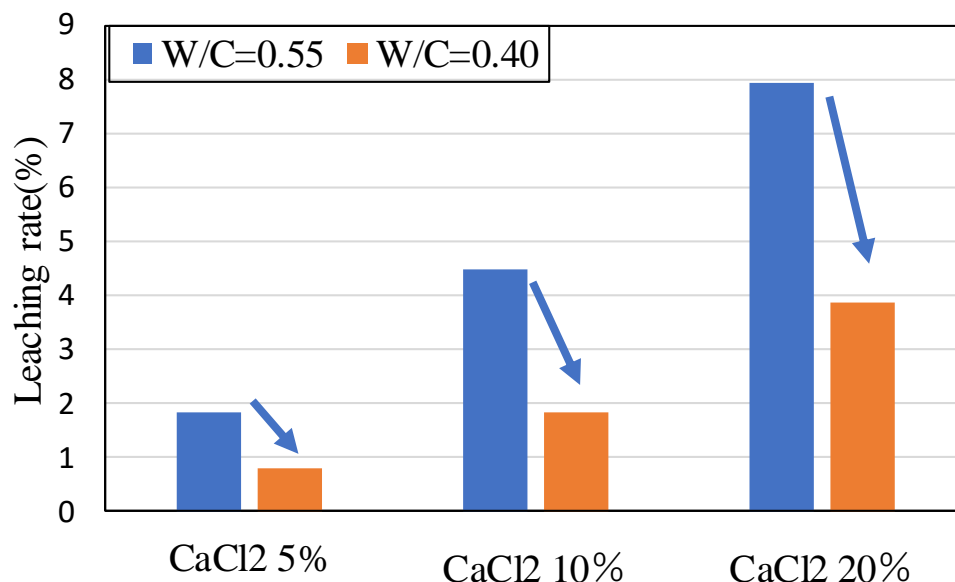
Ca(OH)<sub>2</sub> content



- The  $\text{Ca}(\text{OH})_2$  content decreased since immersion.
- Thus, all specimens could reduce an ability to fix heavy metal ions. (Previous study shows  $\text{Ca}(\text{OH})_2$  has an ability to fix heavy metal ion.)
- The difference of the  $\text{Ca}(\text{OH})_2$  content between the specimens with  $W/C=0.40$  and  $W/C=0.55$  is very small.



## Leaching rate



$$(\text{Leaching rate}[\%]) = \frac{(\text{Cumulative leaching amount}(\text{mg}))}{(\text{Initial content}(\text{mg}))} \times 100$$

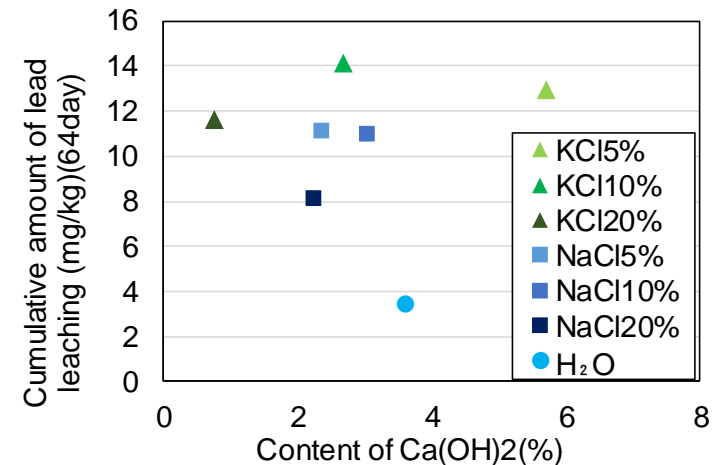
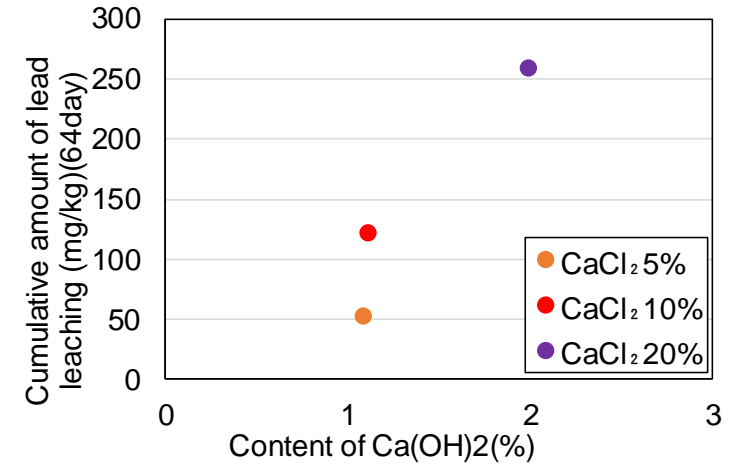
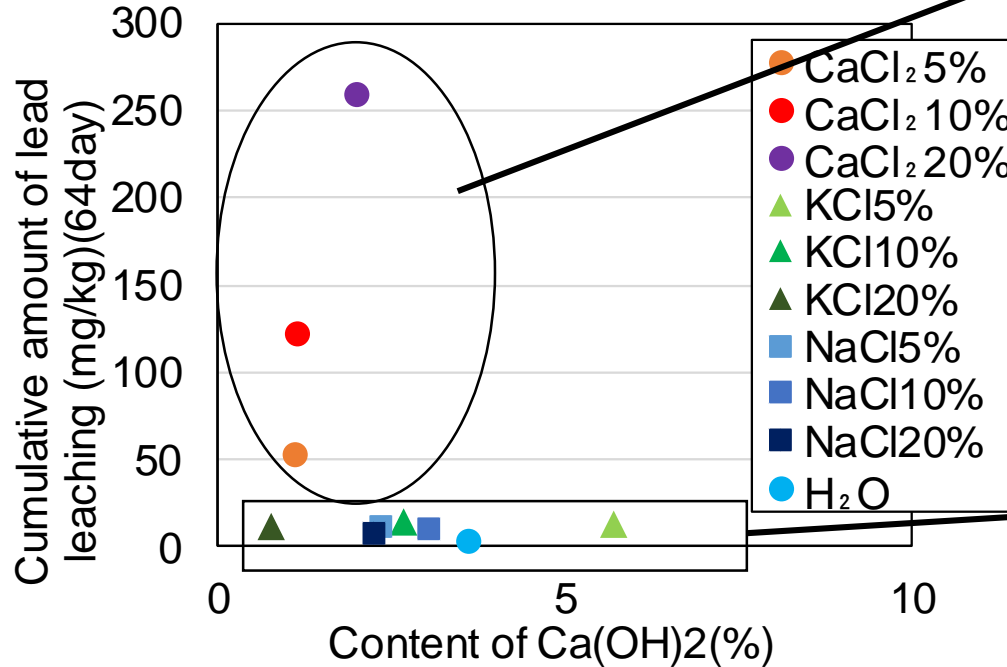
The leaching rate for the specimens with W/C=0.40 is lower than that with W/C=0.55 in each case.

The difference of the lead leaching amount in W/C is related to factors other than the difference of the Ca(OH)<sub>2</sub> content.

The difference of **pore structure** may affect this phenomenon.



Relationship between lead leaching amount (W/C=0.40) and Ca(OH)<sub>2</sub> content



There is no relationship between the cumulative leaching amounts of lead and the Ca(OH)<sub>2</sub> content in the specimens after immersion.

# Conclusion

- From the results of the tank leaching test, the largest leaching amount of lead was observed in  $\text{CaCl}_2$  solution, followed by KCl solution, NaCl solution and deionized water.
- In the case of  $\text{CaCl}_2$  solution, the lead leaching amount increased as the concentration of the solution increased. However, in the case of KCl solution and NaCl solution, the lead leaching amount was almost the same regardless of the concentration.
- Based on the results of the  $\text{Ca(OH)}_2$  content after immersion in the vicinity of the specimen surface exposed to the solution, the difference of the lead leaching amount in the type of solution is not directly related to the  $\text{Ca(OH)}_2$  content in the specimen after immersion.

# References

## References

- 1.Kawai, K., Kikuchi, H., Takaya, H., and Hayashi, A. Adsorption and Desorption Properties and Leaching Behavior of Lead in Cement Hydrates, *Cement Science and Concrete Technology*, 65, pp. 126-131(2011)
- 2.Uchikawa, H, Fixation of hazardous substance in waste and sludge by cement Ceramics, 12, pp.103-117 (1977)

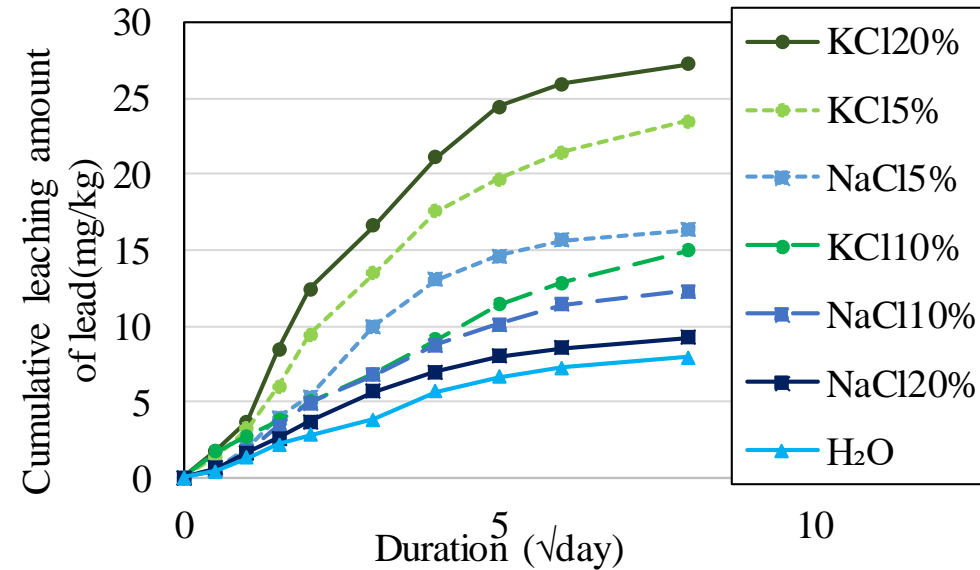
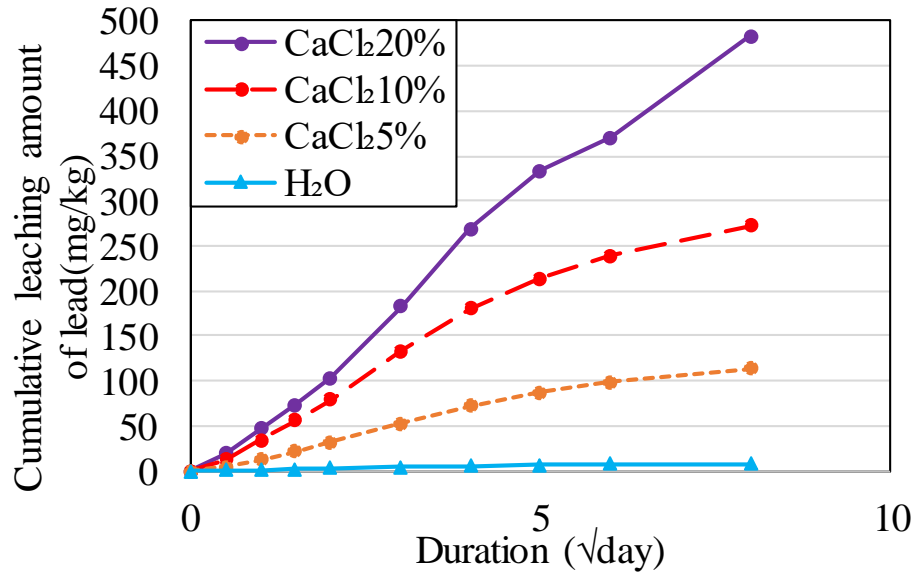
Thank you for your kind attention.



# Appendix



Focusing on W/C=0.55,

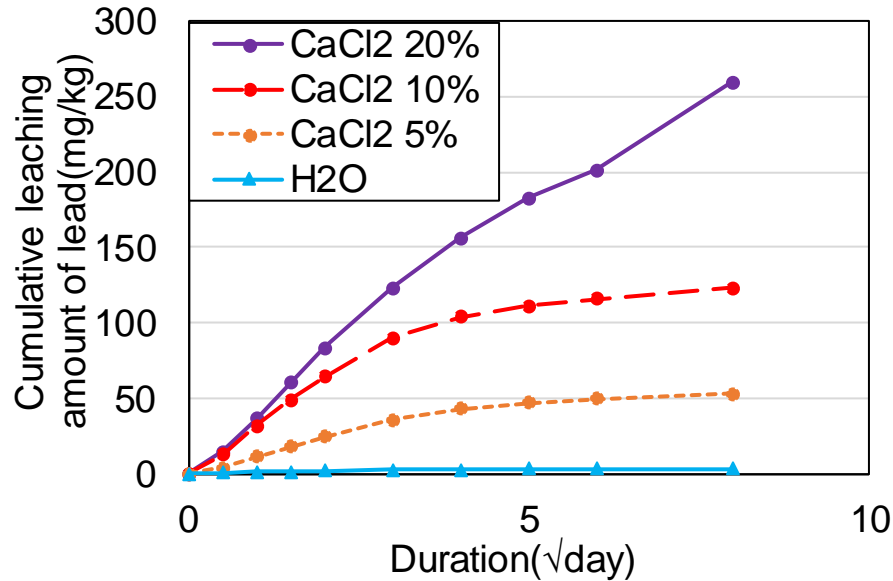


(the amount of lead leaching[mg/kg])  
 = (the amount of lead leaching[mg])/(the mass of specimens[kg])

The same tendency can be observed in the specimens with W/C=0.40.



Focusing on CaCl<sub>2</sub> solutions,



Previous study show

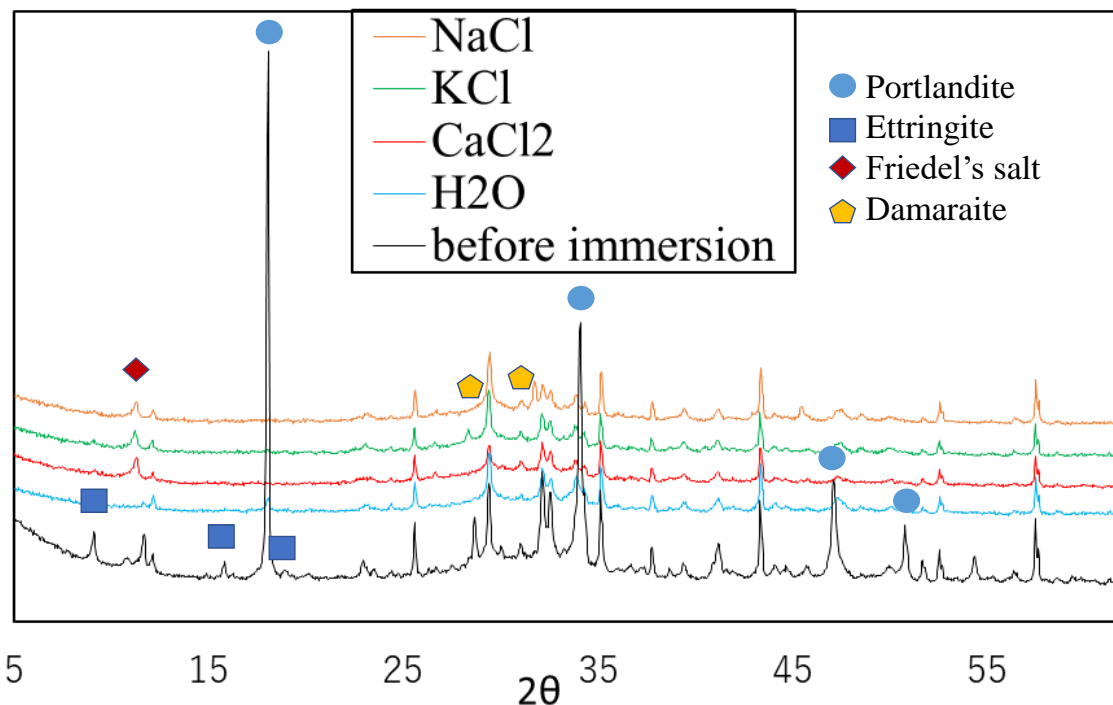
Concrete is deteriorate in high concentration CaCl<sub>2</sub> solution.

One of the causes of this phenomenon is generation of 3CaO · CaCl<sub>2</sub> · 15H<sub>2</sub>O.



In this study,

the cause which leaching amount was highest in CaCl<sub>2</sub> solutions can be deterioration to generate 3CaO · CaCl<sub>2</sub> · 15H<sub>2</sub>O in the specimens.



Focusing on  $W/C=0.40$ ,

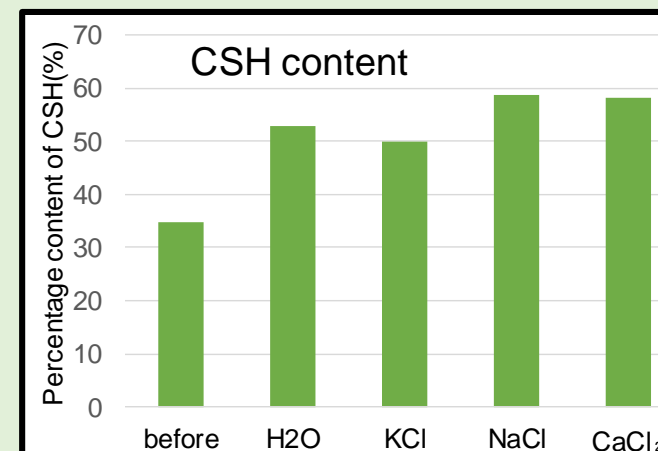
## Qualitative analysis

Damaraitite was confirmed in the specimens immersing chloride solutions.

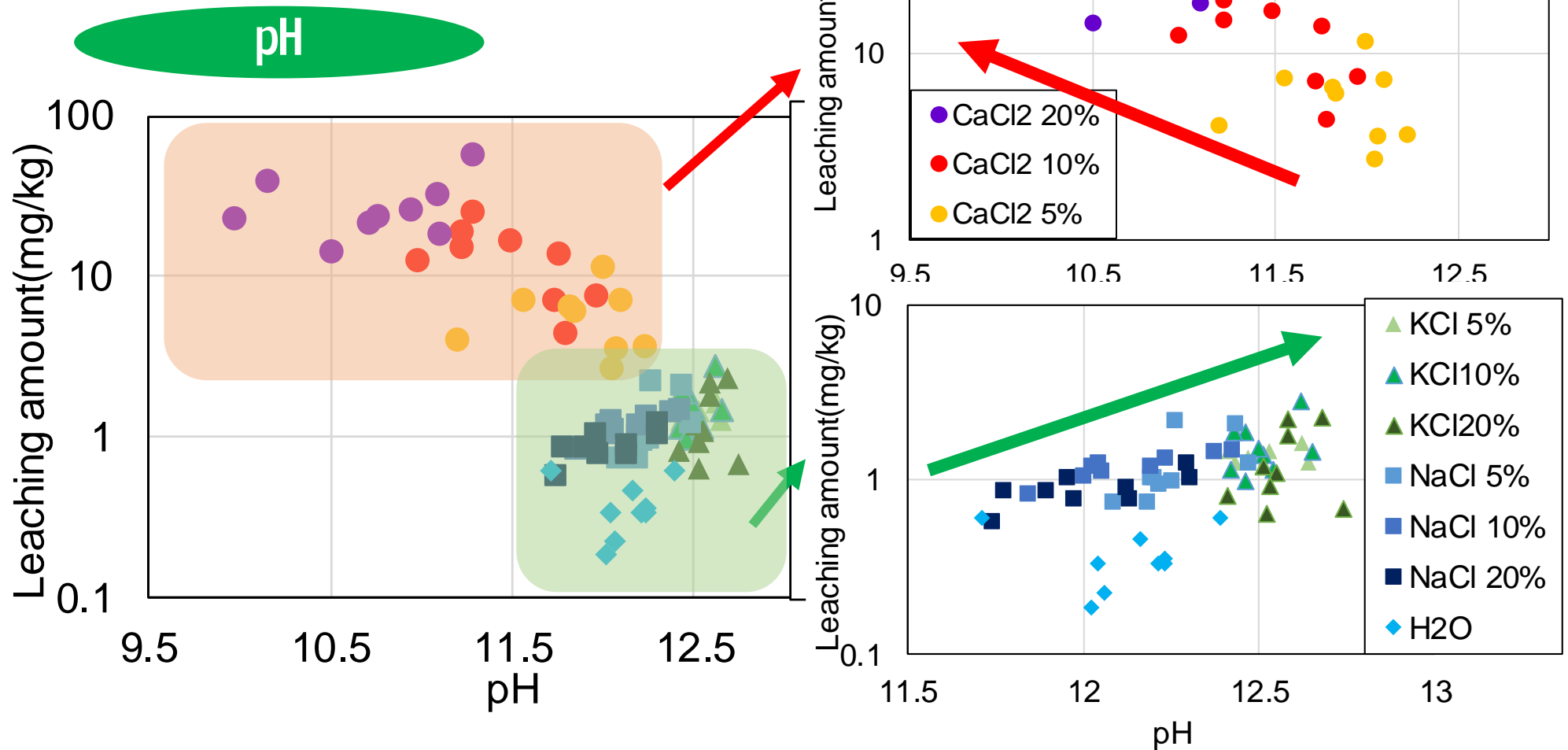
## Quantitative analysis

Decreasing Portlandite and Ettringite was confirmed.

Increasing CSH was also confirmed. However, it was not clear the relation between their changing amount and immersed solution.



# Result



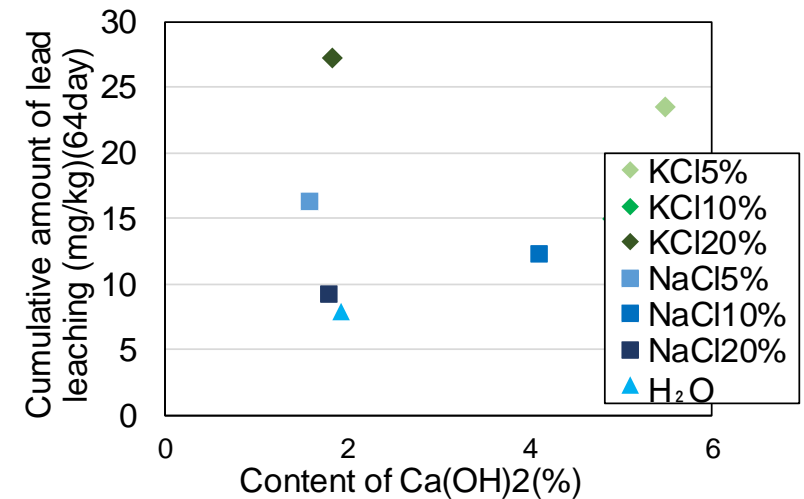
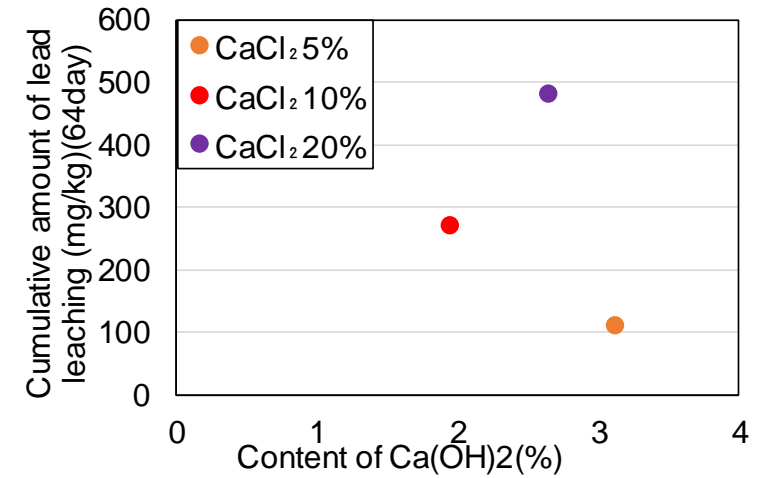
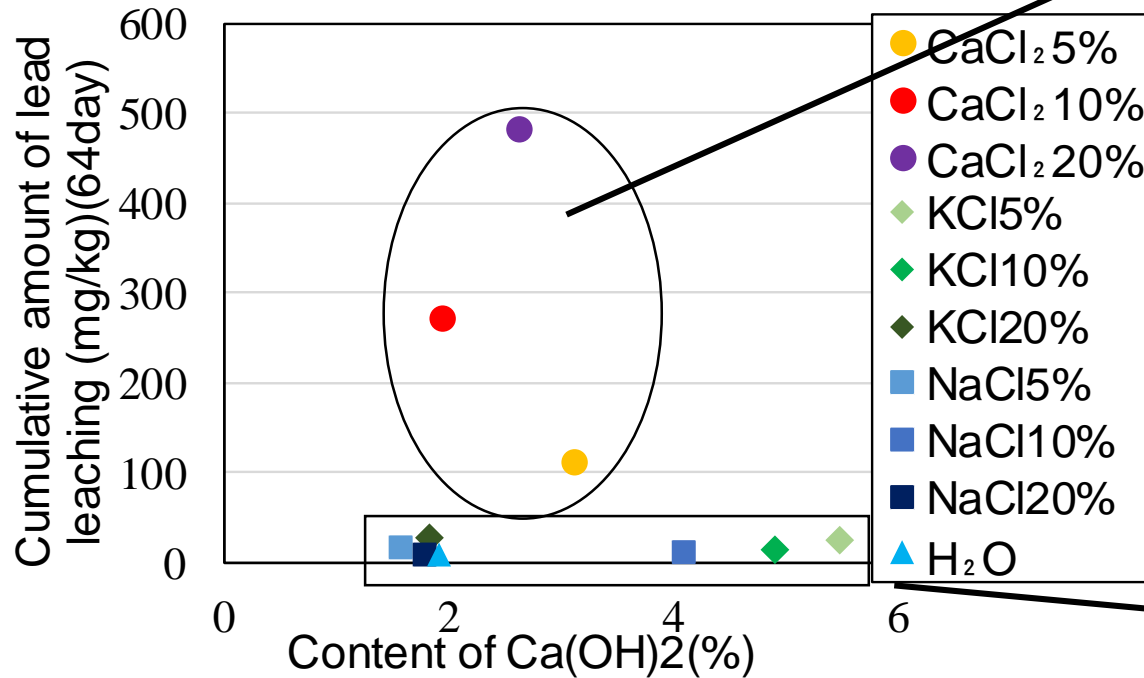
These figures show there were a relation between leaching amount and pH . However, it wasn't clear that pH affected the leaching amount dominantly.

# Result



# Amount of Ca(OH)<sub>2</sub>

Relation between lead leaching rate (W/C=0.55) and amount of Ca(OH)<sub>2</sub>



There is no relationship between the cumulative leaching amounts of lead and the Ca(OH)<sub>2</sub> content in the specimens after immersion.