Application of Molecular Dynamics Calculation on Absorption Behavior of Anions in Type-A Zeolite in Molten LiCl-KCl Salt

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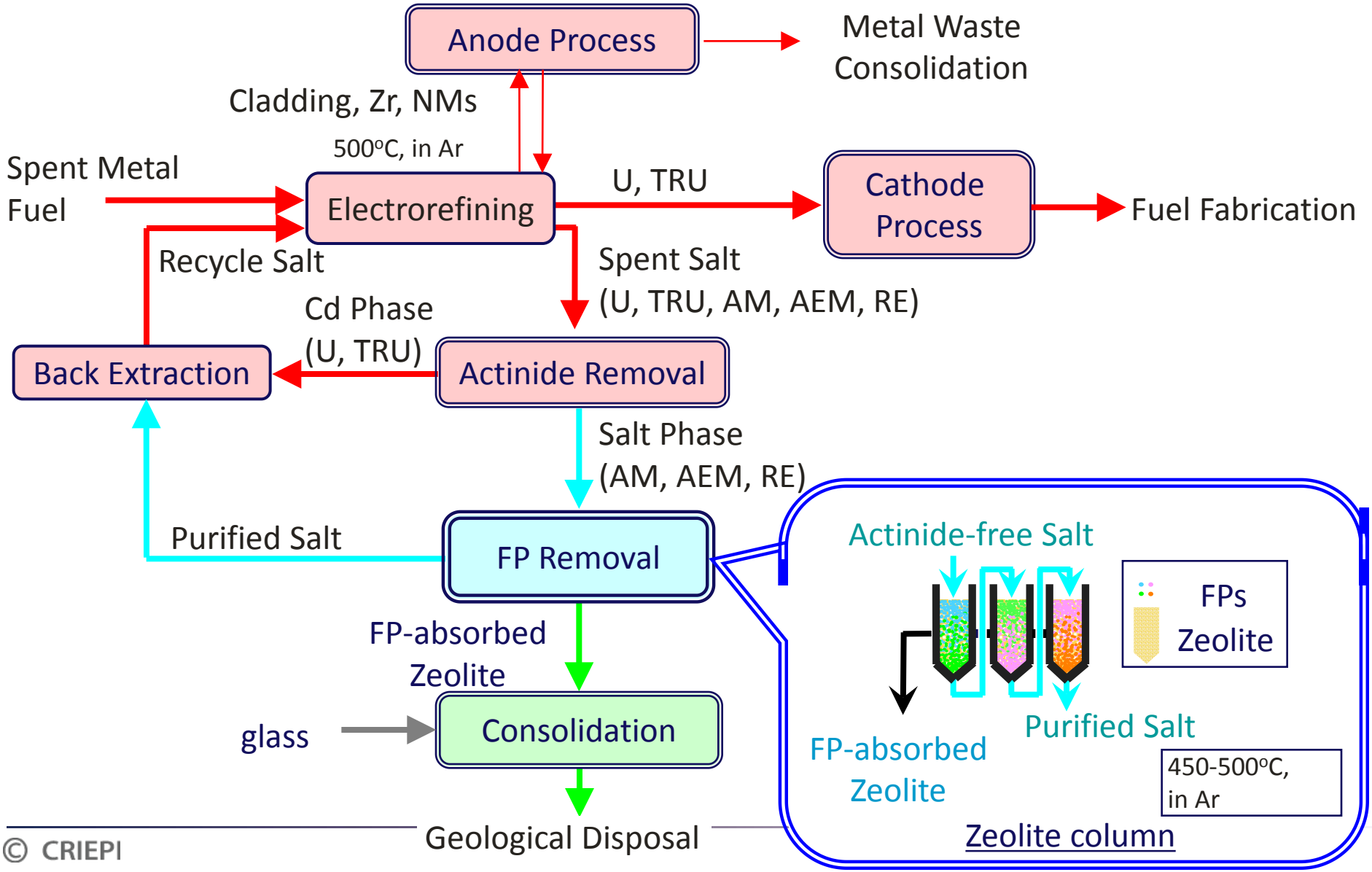
CRIEPI's Salt Waste Treatment Process



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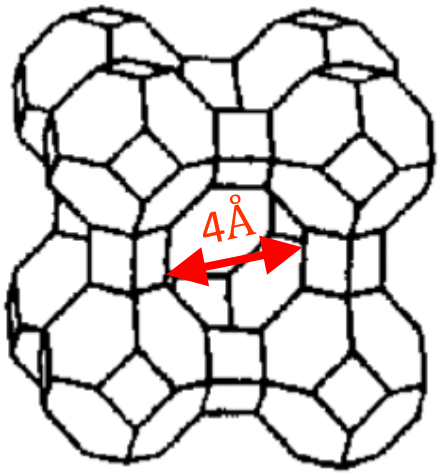
Absorption of Anion FPs in Zeolite

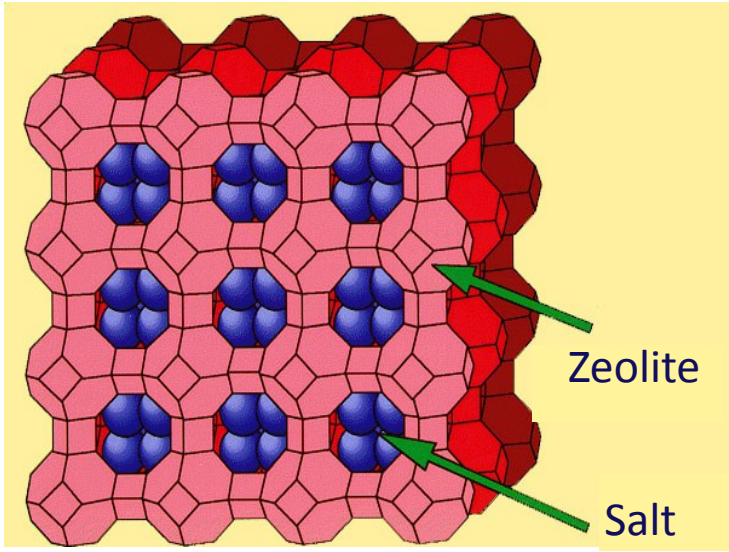


Zeolite 4A (anhydrous)
$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$

Structure of Zeolite

Contact with LiCl-KCl salt containing anion FPs (450-500°C, in Ar)

- Na^+ in zeolite exchanges with cations in salt.
- Anion FP is captured in cage structure as a part of salt component.

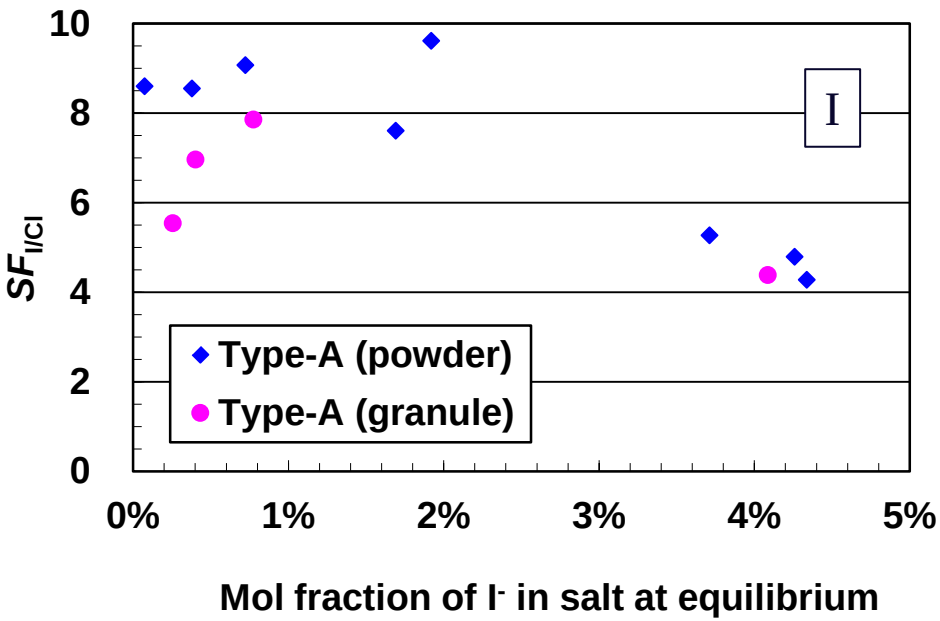


$Li_xNa_yK_z[(AlO_2)_{12}(SiO_2)_{12}]Cl_vFP_w$

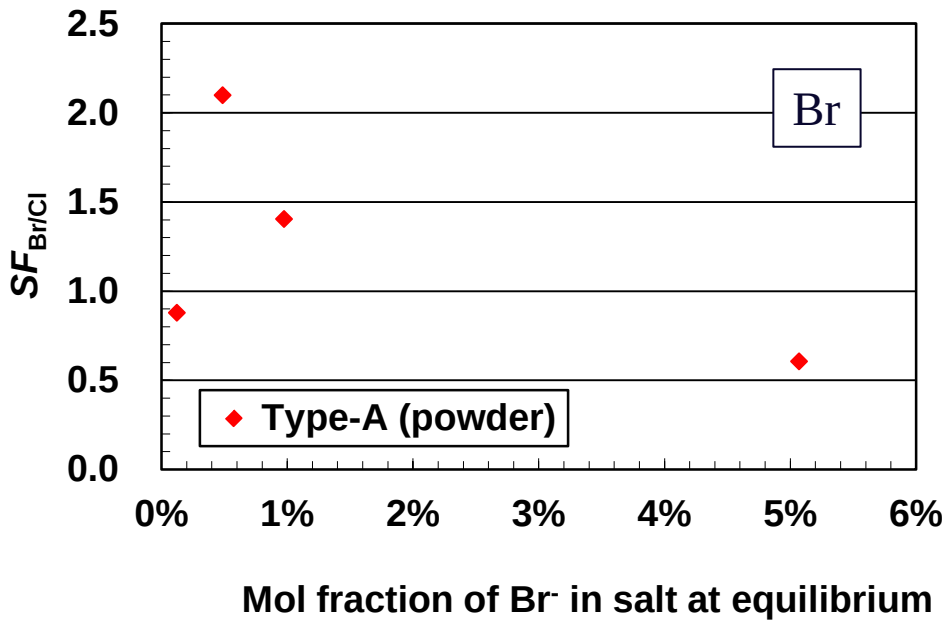
Anion FP is absorbed in zeolite.

Absorption behaviors of Iodine and Bromine*

- Zeolite immersion experiments in LiCl-KCl-KI melt exhibited greater absorption of I^- vs. Cl^- in type-A zeolite. Number of halogen atoms in a zeolite cage varied between 9 and 12 depending on I concentration in melt.
- Br^- in LiCl-KCl-KBr melt did not exhibit such absorption behavior.



Change of $SF_{I/Cl}$ at different I concentration in LiCl-KCl-KI melt



Change of $SF_{Br/Cl}$ at different Br concentration in LiCl-KCl-KBr melt

$SF_{A/Cl}$ = [A/Cl in zeolite]/[A/Cl in salt]

*: K. Uozumi, *J. Nucl. Mater.*, **447**, 233 (2014).

Sizes of Anion and Zeolite Cage Entrance

- Difference in ion radii between I^- and Br^- seems main reason for the difference in absorption behavior. (Especially, radius of I^- is close to zeolite cage entrance radius.)
- However, inner space of zeolite cage is limited.

Another method is required to study such absorption behaviors.

Zeolite or anion	Radius of anion or zeolite cage entrance (nm)
Cl^-	0.181
Br^-	0.196
I^-	0.220
Type-A zeolite with Na (4A)	0.21
Type-A zeolite with Ca (5A)	0.25

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Purpose of Present Study

Molecular dynamics (MD) calculation method was applied to understand the difference in absorption behavior.

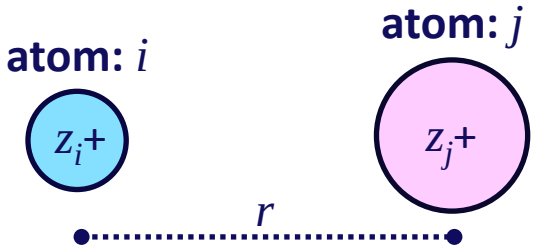
<u>What MD is?</u>

- Each atom is regarded as a rigid sphere.
- Potential between each atom pair is given.
- Each atom moves according to Newtonian mechanics.
- Calculate position and velocity of each atom for more than several kilo steps with small time intervals, such as in the order of femto (10^{-15}) second.
- After relaxation of the system is attained, properties of the system, such as density, lattice constant, enthalpy, and distribution of atoms, are estimated.

Potential Model* and Calculation Program

$$u_{ij} = \underbrace{\frac{z_i \cdot z_j \cdot e^2}{4 \cdot \pi \cdot \varepsilon_0 \cdot r_{ij}}}_{\text{Coulomb term}} - \underbrace{\frac{\boxed{c_i \cdot c_j}}{r_{ij}^{\,6}}}_{\text{van der Waals term}} + \underbrace{f_0 \cdot \left(\boxed{b_i + b_j}\right) \cdot \exp\left(\frac{\boxed{a_i + a_j} - r_{ij}}{\boxed{b_i + b_j}}\right)}_{\text{Short-range repulsion term}}$$

$$+ \underbrace{D_{1ij} \cdot \exp\left(-\beta_{1ij} \cdot r_{ij}\right) + D_{2ij} \cdot \exp\left(-\beta_{2ij} \cdot r_{ij}\right)}_{\text{Covalent bonding term**}}$$



**: The covalent bonding terms were adopted for only Si-O and Al-O bonding of zeolite structure in the present study.

MXDORTO*** was used for MD calculation in the present study.

* : M. Nakano, *Appl. Clay Sci.*, **23**, 15 (2003).
*** : K. Kawamura, *Japan Chemistry Program Exchange*, #029 (1996).

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Procedure -1: Elemental Parameter Optimization

- Densities of LiCl, NaCl, KCl, LiBr, NaBr, KBr, LiI, NaI, and KI, at approximately 300K were estimated by MD calculations and compared with literature values.
- If density values under high pressure were available, corresponding MD calculations were also conducted.

- Elemental parameters (a, b, c) of Li, Na, K, Cl, Br, and I were optimized.
- For confirmation, lattice constants at 300 - 500K and formation enthalpies at 300 - 800K vs. those at 298.15K calculated using the optimized parameters were compared with literature values.

- Elemental parameters of Al, Si, and O were obtained by modifying the parameters used to simulate the behavior of beidelite*.

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*: M. Nakano, *Appl. Clay Sci.*, **23**, 15 (2003).

Procedure -2: Enthalpy Calculation of Zeolite (1)

- Formation enthalpy of the system is calculated by integrating interatomic potential for all atom pairs.

- Formation enthalpies of zeolite containing 9 - 12 alkali halides per zeolite cage were calculated.
- Alkali element was first fixed to Li or K. Then, mixture of Li, K, and Na in accordance with experimental results was adopted.
- Compositions of halogens in Cl-Br or Cl-I systems were varied.

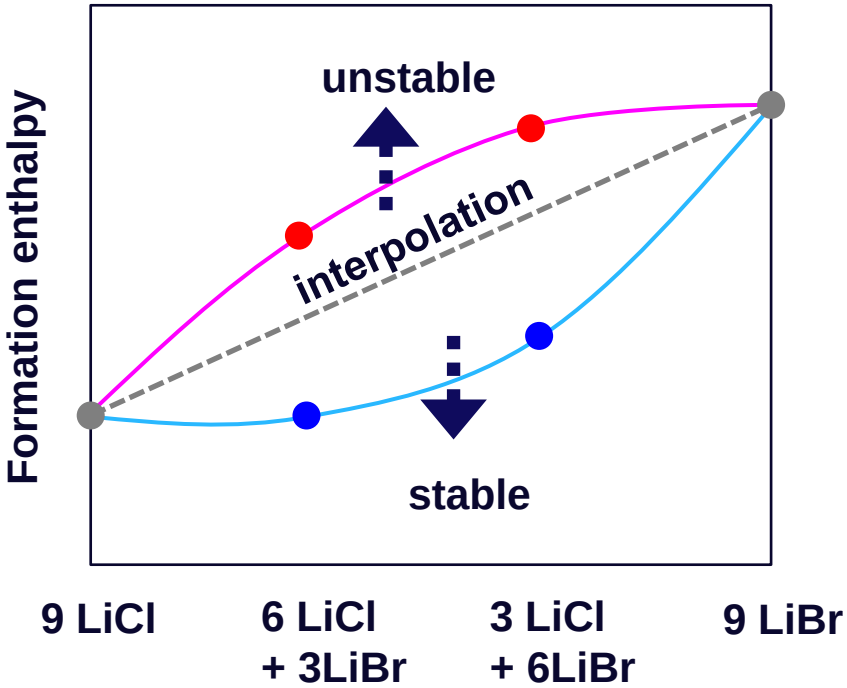
Ex) <u>Cl-Br system with Li containing 9 alkali halides</u>

- 10 calculations were conducted for 9 LiCl, 8 LiCl + 1 LiBr, 7 LiCl + 2 LiBr, -----, 1 LiCl + 8 LiBr, and 9 LiBr.

Procedure -2: Enthalpy Calculation of Zeolite (2)

- Formation enthalpy values at various anion compositions were compared with interpolation values between both compositions containing only one kind of halogen element, such as 9 LiCl and 9 LiBr.

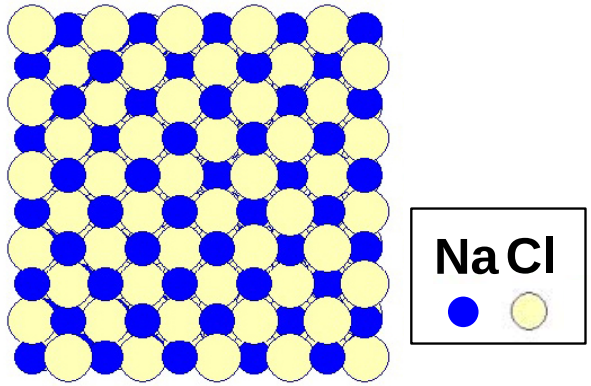
- If calculated enthalpy value is more negative than interpolation value, the mixed system is thermodynamically more stable due to mixing two kinds of halogen atoms in zeolite.
- In addition to enthalpy, density, lattice constant, and position of each atom in zeolite were also estimated.



Calculation conditions

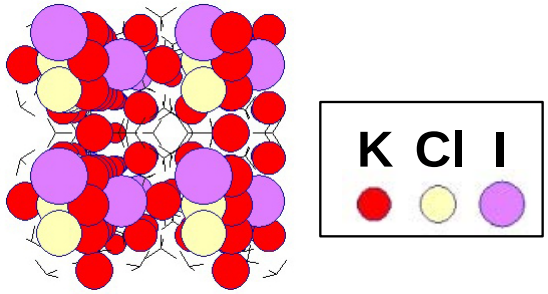
Elemental Parameter Optimization

- Cell system: 5 x 5 x 5 or 10 x 10 x 10 (totally 1000 or 8000 atoms)
- Calculated steps: > 5 x 10^4
- Pressure: 0.1MPa – 25GPa
- Temperature: approx. 300K – 800K



Enthalpy Calculation of Zeolite

- Cell system: 2 x 2 x 2 (Al:96, Si:96, O:384, aklali:168 – 192, halogen:72 – 96 atoms)
- Calculated steps: > 3 x 10^6
- Pressure: 0.1MPa
- Temperature: 773K
- 3 different initial positions of alkali and halogen atoms



- Time interval: 2 fs for both calculations

Results -1: Optimized Elemental Parameters

Atom	Atomic weight (10^{-3} kg mol^{-1})	z (e)	a (nm)	b (nm)	c (kJ^2 mol^{-2} nm^3)
Li	6.941	1.000	0.1070	0.0047	0.01227
Na	22.990	1.000	0.1493	0.0120	0.01841
K	39.098	1.000	0.1781	0.0120	0.03273
Cl	35.453	-1.000	0.2061	0.0190	0.05727
Br	79.904	-1.000	0.2175	0.0189	0.05932
I	126.905	-1.000	0.2386	0.0215	0.06136
O	15.999	-1.4125	0.1908	0.0150	0.05973
Al	26.982	2.250	0.1022	0.0080	0.0
Si	28.086	2.400	0.0942	0.0150	0.0

Atom-atom	D_1 (kJ mol^{-1})	β_1 (nm^{-1})	D_2 (kJ mol^{-1})	β_2 (nm^{-1})
Al-O	26778.0	40.0	-1936.0	20.0
Si-O	34300.0	40.0	-3121.0	20.0

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Results -2: Verification of Optimized Parameters (1)

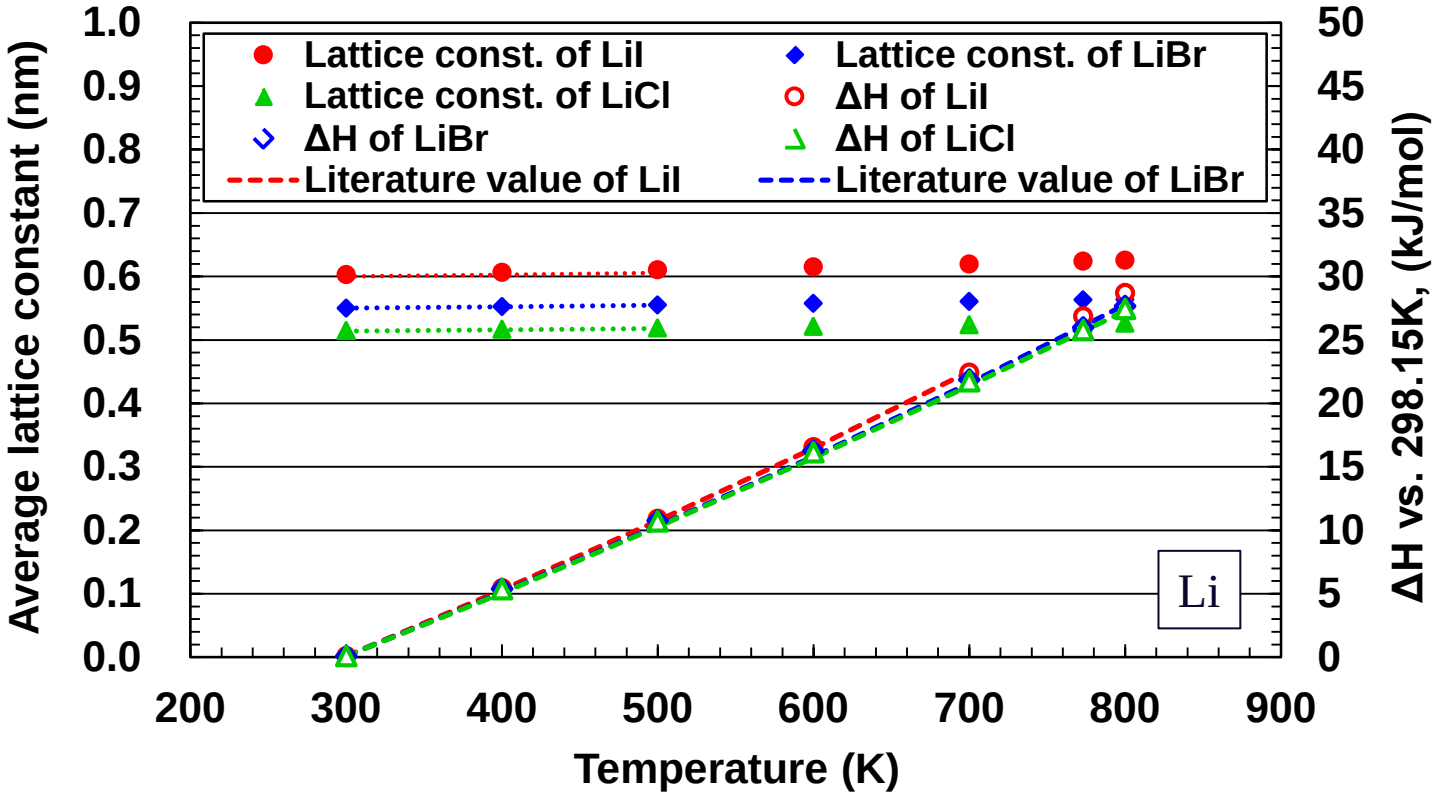
- Densities of the alkali halides agreed with literature values within 0.6%.
- Lattice constants and formation enthalpies also agreed with literature values within 0.9% and 0.5 kJ/mol, respectively.
- Difference in lattice constants among *a*, *b*, and *c* axes at approximately 300K was less than 0.05% for each compound.
- Lattice constant of zeolite-4A agreed with literature value (Calculation: 1.244nm, literature: 1.232nm*).

↓

- Optimized values were appropriate to be used in the following enthalpy calculation.

* : H. Tominaga, *Zeoraito no Kagaku to Ouyou*, Kodansha Scientific, Tokyo, (1998) [in Japanese].

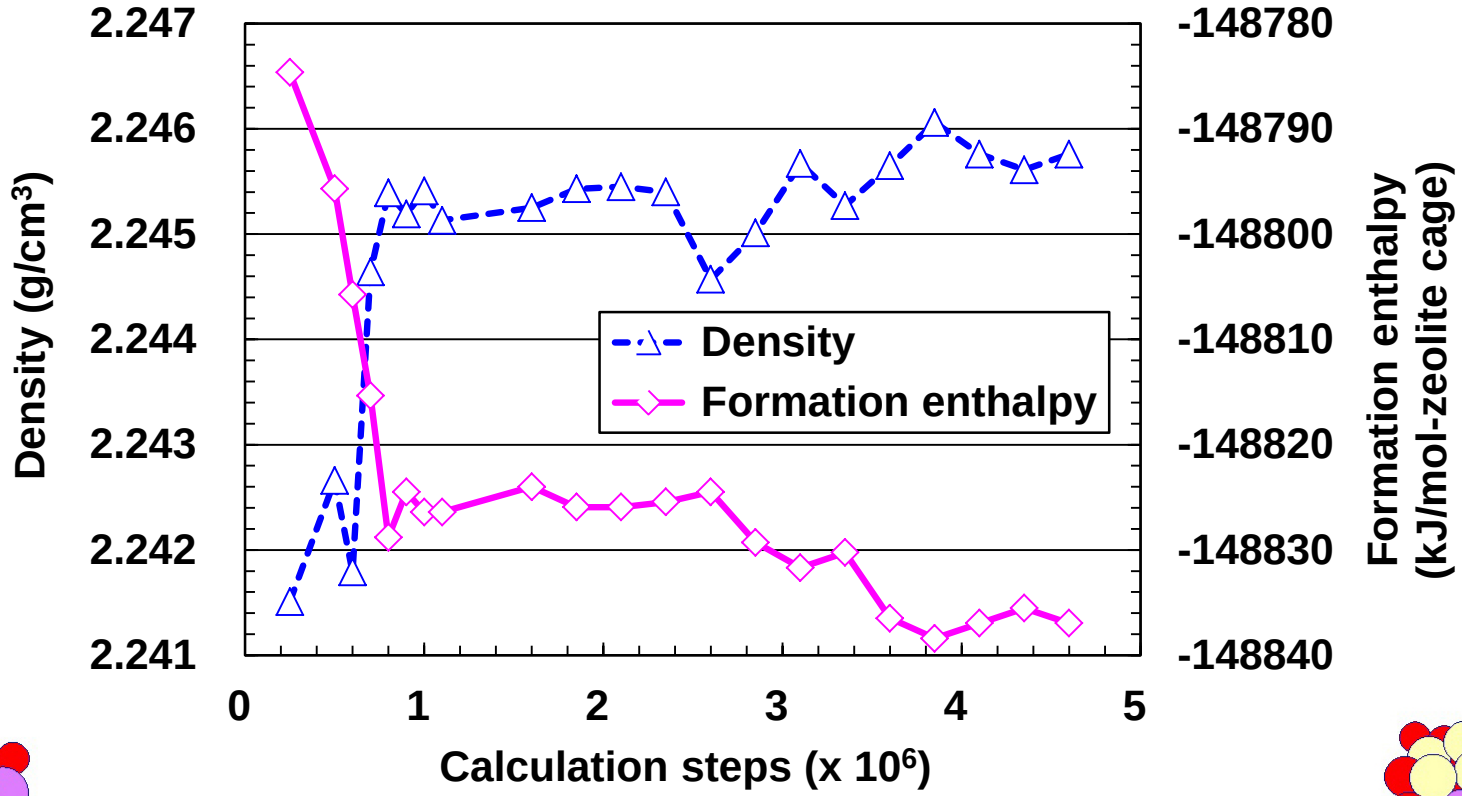
Results -3: Verification of Optimized Parameters (2)

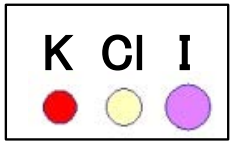


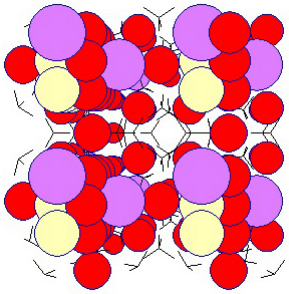
Comparison of lattice constants and formation enthalpies (ΔH) of lithium halides between calculated values (symbols) and literature data (dashed lines)

Results -4: Changes during Enthalpy Calculation

- More than 3 x 10^6 steps were calculated for relaxation of the system and average of last 1 x 10^6 steps were used.

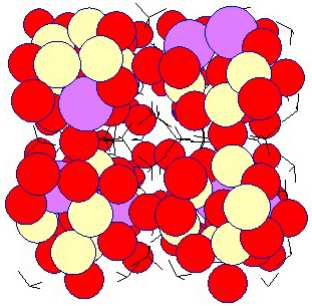






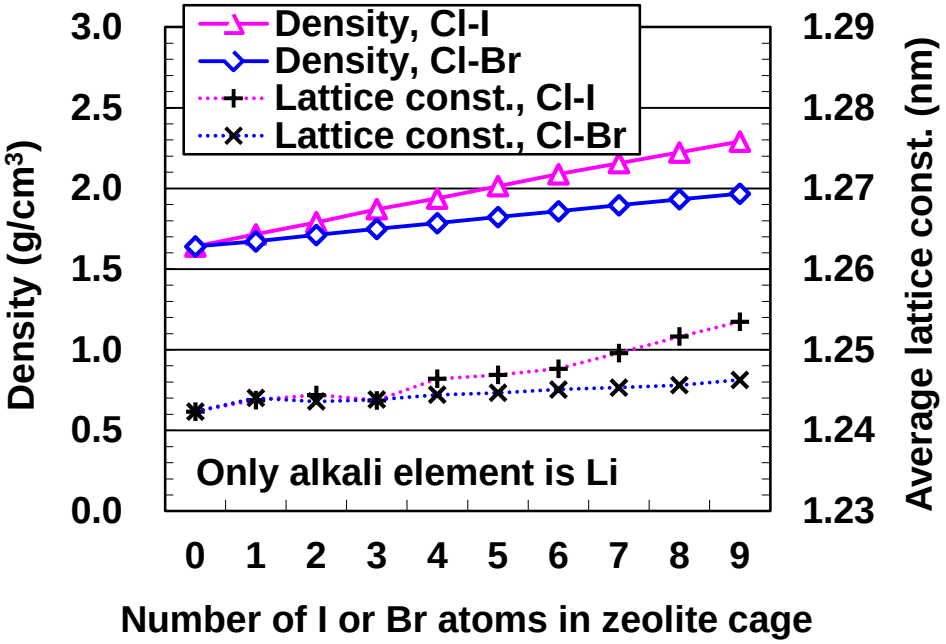
Changes in density and formation enthalpy during calculation of zeolite containing 21K + 7Cl + 2I

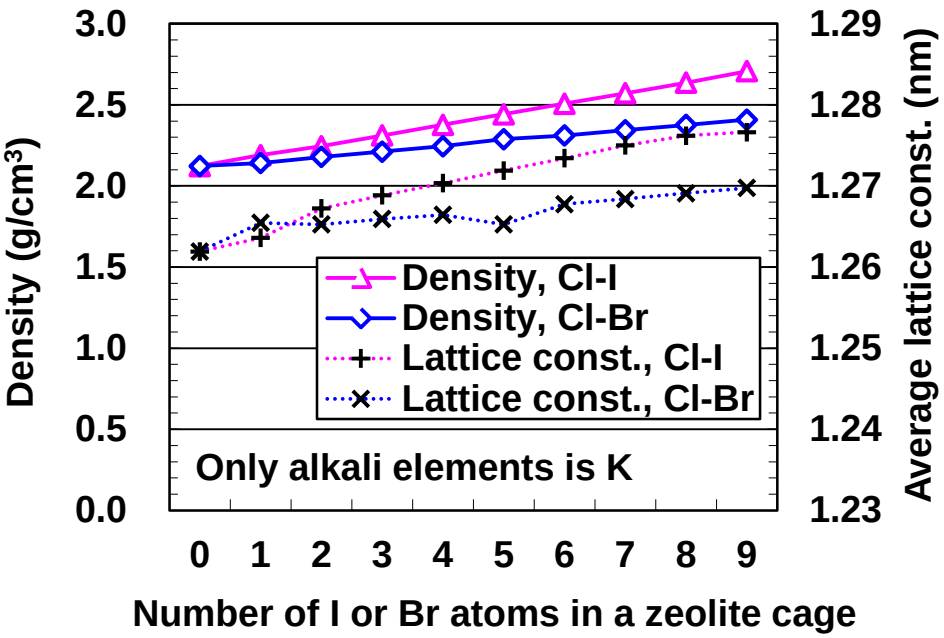
4.6 x 10^6 steps



Results -5: Density and Lattice Constant

- Density and lattice constant increase as Cl is replaced with Br or I owing to difference in atomic weights and ion radii.
- In particular, the increase is larger in the case of replacement with I than in the case of Br.





Changes in density and lattice constant of zeolite containing 9 halogen atoms in zeolite upon replacement of Cl with I or Br

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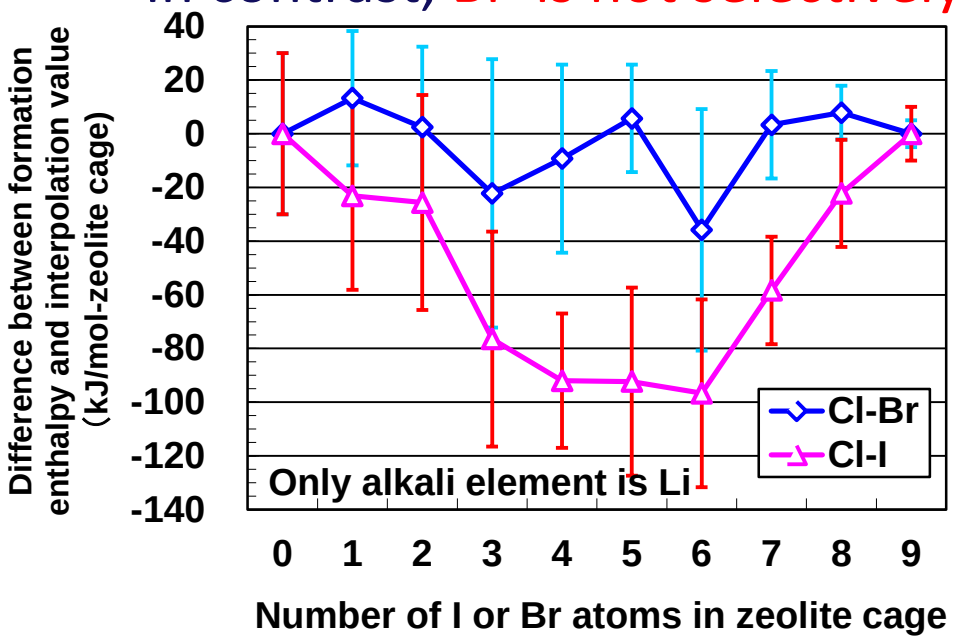
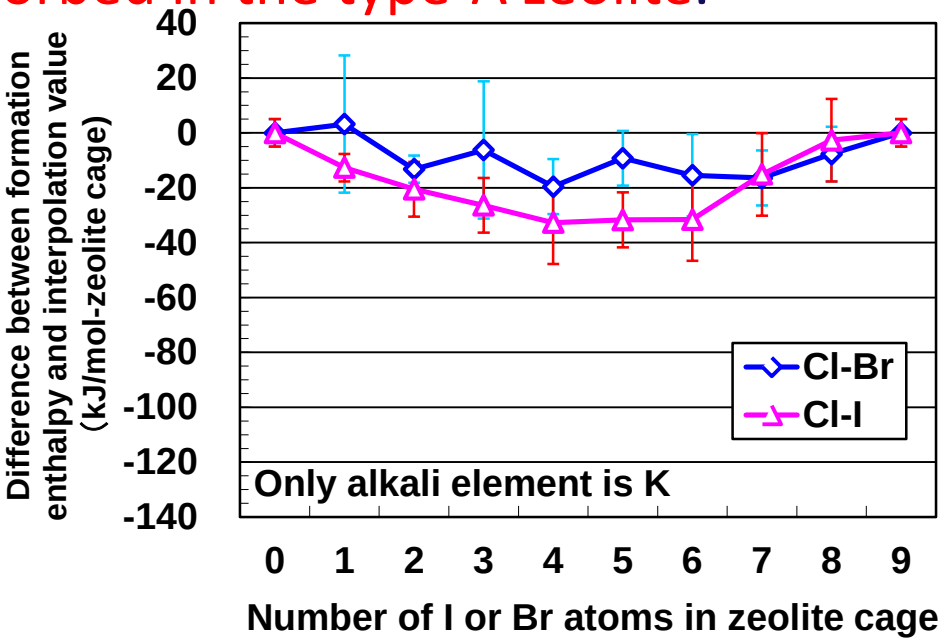
Results -6: Enthalpy vs. Interpolation Value (1)

- Differences in enthalpies are apparently negative in Cl-I mixture system.

- When a few I^- ions are absorbed in zeolite, it is preferable for more I^- to be absorbed than $I^-/(I^- + Cl^-)$ ratio in the salt.
- In contrast, Br^- is not selectively absorbed in the type-A zeolite.

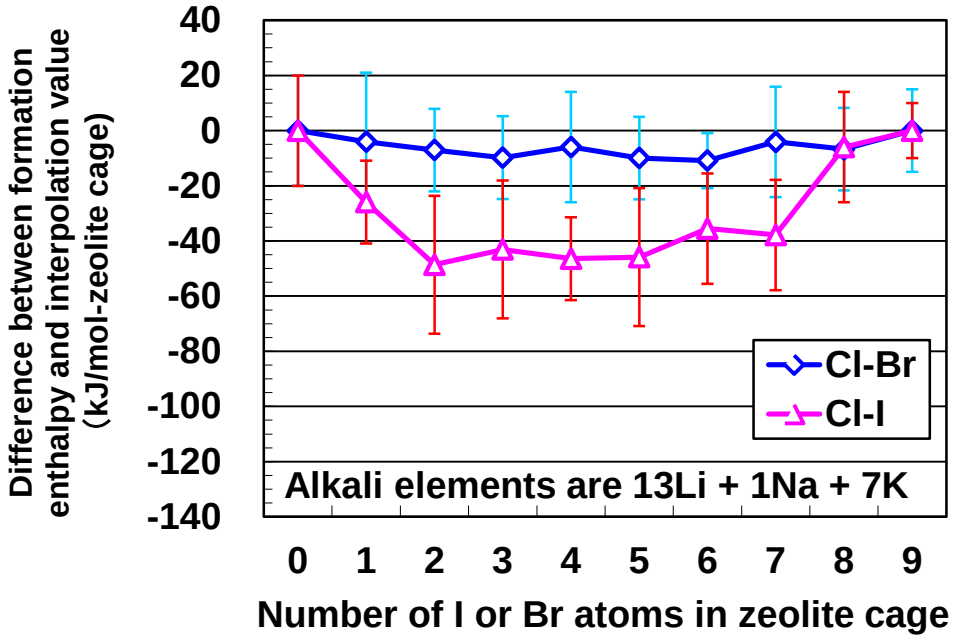




Difference between formation enthalpy and interpolation value
(Total number of halogen atoms in zeolite cage is 9)

Results -7: Enthalpy vs. Interpolation Value (2)

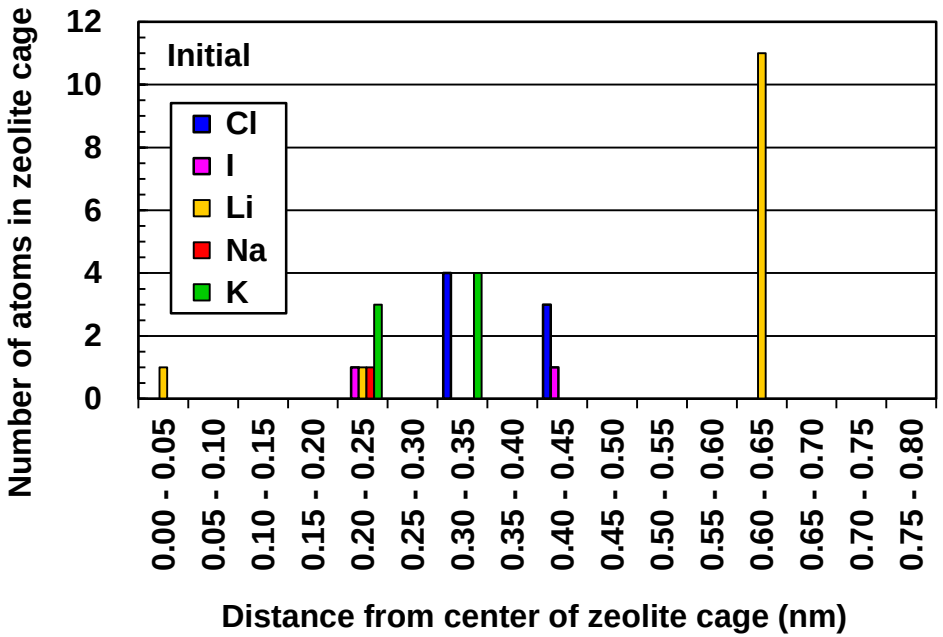
- In the case of zeolite consists of 13Li + 1Na + 7K alkali composition, the tendency of negative enthalpy in Cl-I mixture system and small difference in Cl-Br mixture system are similar.
- Similar tendencies are exhibited for the zeolite containing 10, 11, and 12 halogen atoms in zeolite cage.

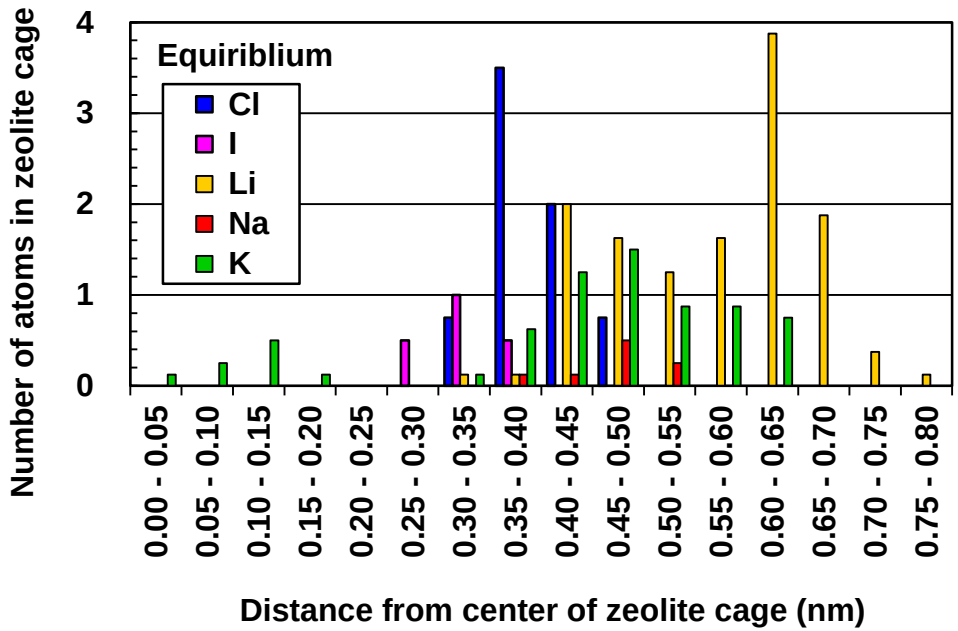


Difference between formation enthalpy and interpolation value (Total number of halogen atoms in zeolite cage is 9)

Results -8: Distribution of Atoms in Zeolite

- Most of alkali atoms are located in outer part of zeolite cage because such cations are attracted by negative electric charge of zeolite structure.
- Thus, halogen atoms are located in inner part.
- However, one K atom is located near the center of each zeolite cage.





Distances of alkali and halogen atoms from center of each zeolite cage in initial and equilibrium (after 7.35 x 10^6 calculation steps) states in zeolite containing 13Li + 1Na + 7K + 7Cl + 2I.

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Conclusion

- Molecular dynamics calculations were conducted to study the difference in absorption behavior in type-A zeolite between I^- and Br^-.
- Difference in calculated formation enthalpies of zeolite containing alkali halides indicated that I^- is preferentially absorbed in type-A zeolite to above the $I^-/(I^-+Cl^-)$ ratio in the salt phase. Meanwhile, such intensive absorption was not observed for Br^-.

- Therefore, the experimental results were qualitatively reproduced.

- As the next step, estimation of absorbent composition in zeolite from the salt phase composition by thermodynamically relating the zeolite and salt phases should be tried.

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