DEVELOPMENT OF SPENT SALT TREATMENT PROCESS USING ZEOLITE

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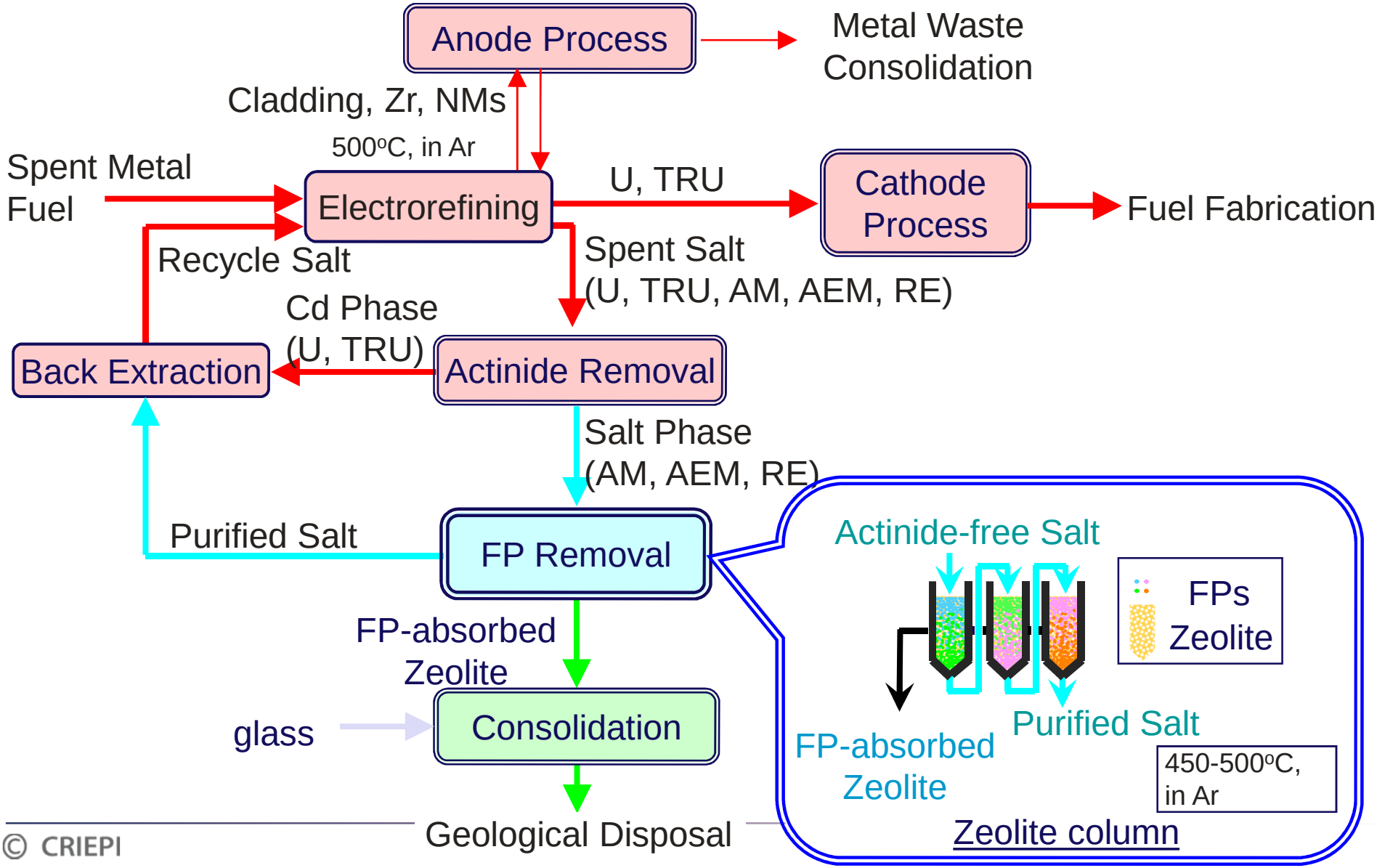
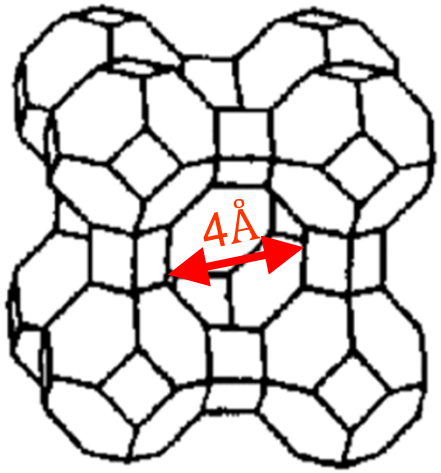
CRIEPI
Central Research Institute of Electric Power Industry

CRIEPI's Salt Waste Treatment Process



Development of Salt Waste Treatment



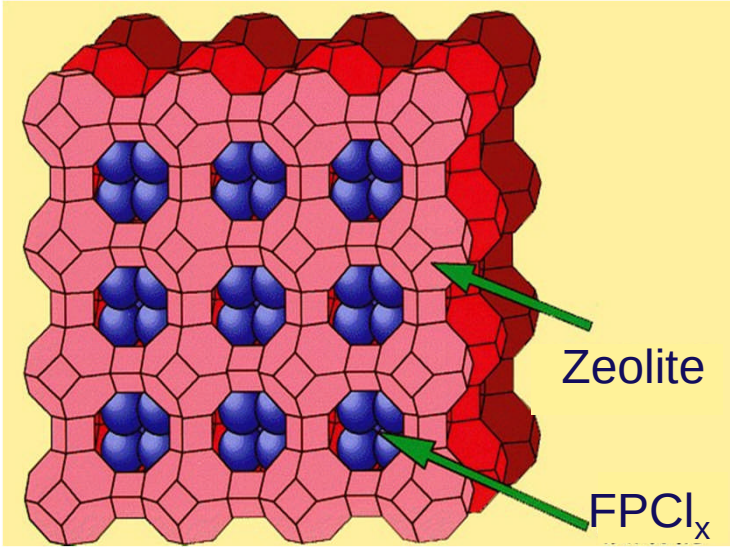
Zeolite 4A (anhydrous)

$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$

Structure of Zeolite

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

- Na^+ in zeolite exchanges with FP^{x+} in salt
- $FPCl_x$ is captured in cage structure



$FP_y[(AlO_2)_{12}(SiO_2)_{12}]Cl_z$

FP is absorbed on zeolite

Situation of Spent Salt Treatment Process Development

- Absorption behaviors of cation FPs at equilibrium state have been studied*.

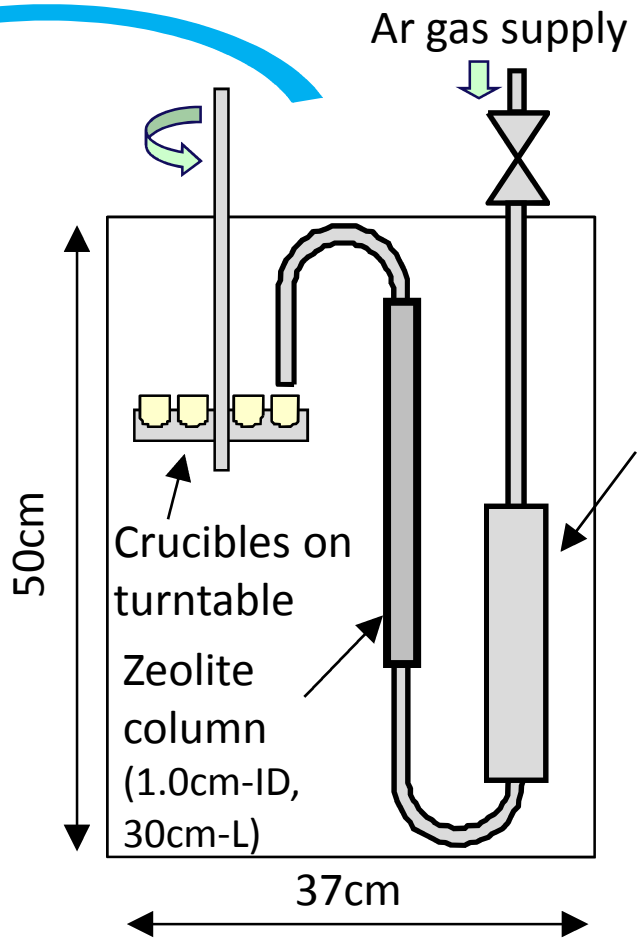
  ** Tsukada et al., Nucl. Technol., 162, 229 (2008).*

- For obtaining both high DF and high throughput, “zeolite column system” is under development. This system needs kinetic study of the absorption behavior.
- On the other hand, absorption behaviors of anion FPs have not been studied well.

- Therefore, tests using column apparatus and anion absorption study are under way.

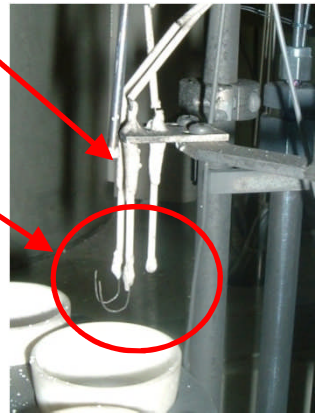
Small Scale Column Test

450-500°C, in Ar



Salt exit

Salt detector



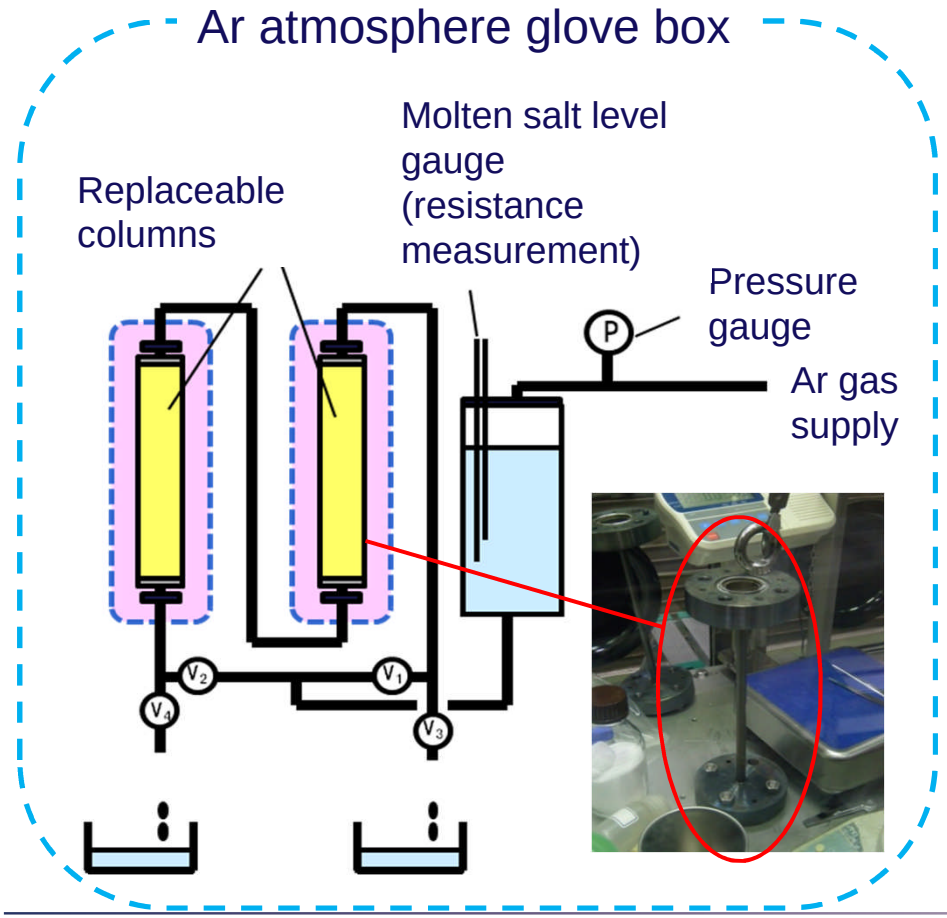
Recovered salt in crucibles

⇒ Feasibility of "column method" was confirmed*.

** Uozumi et al., FR09, Kyoto, Japan, 2009-12.*

Engineering-scale Column Apparatus

- Engineering-scale zeolite column apparatus was installed in Ar glove box for technological feasibility study.

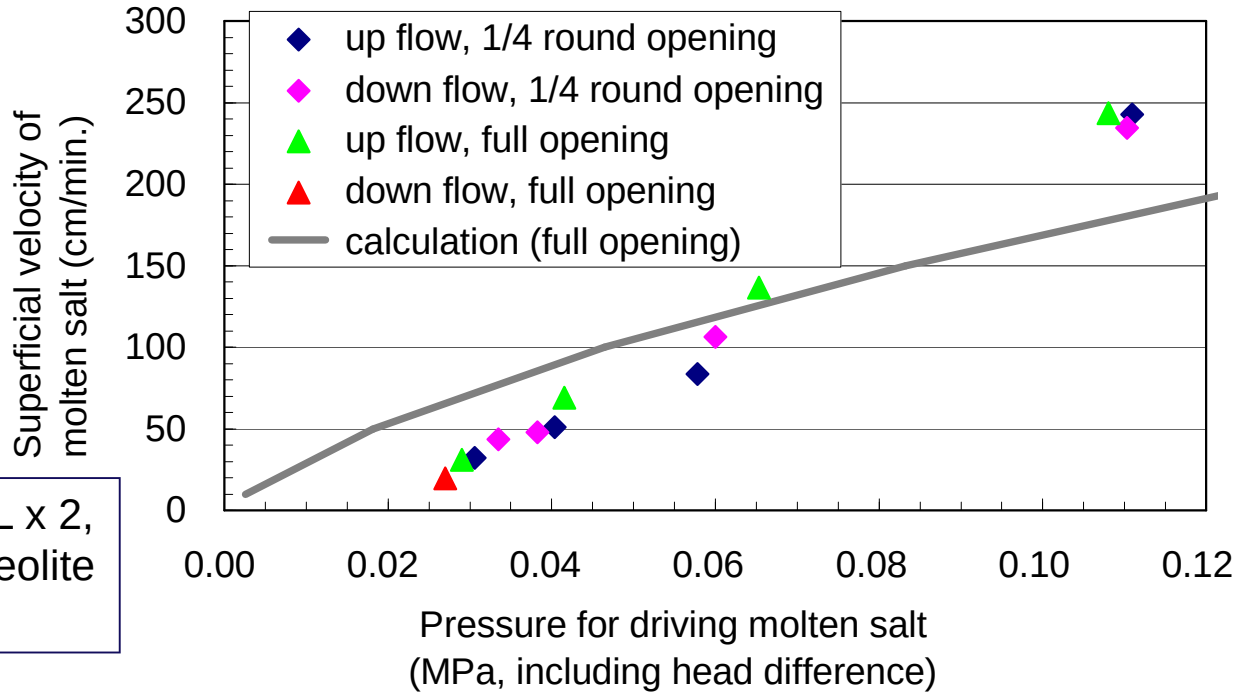


Apparatus before and after installation in glove box

- Column length：30cm
- Column ID：1.0 ～ 3.5cm
- Zeolite：up to 450g
- Salt：up to 11kg
- 2 columns in series

Molten Salt Flow Passing through Columns

- Flow rate increased almost in proportional to driving pressure.
- Experimental results roughly agreed with calculation.
- Driving pressure was much lower than columns filled with powder form zeolite (less than 1/100).

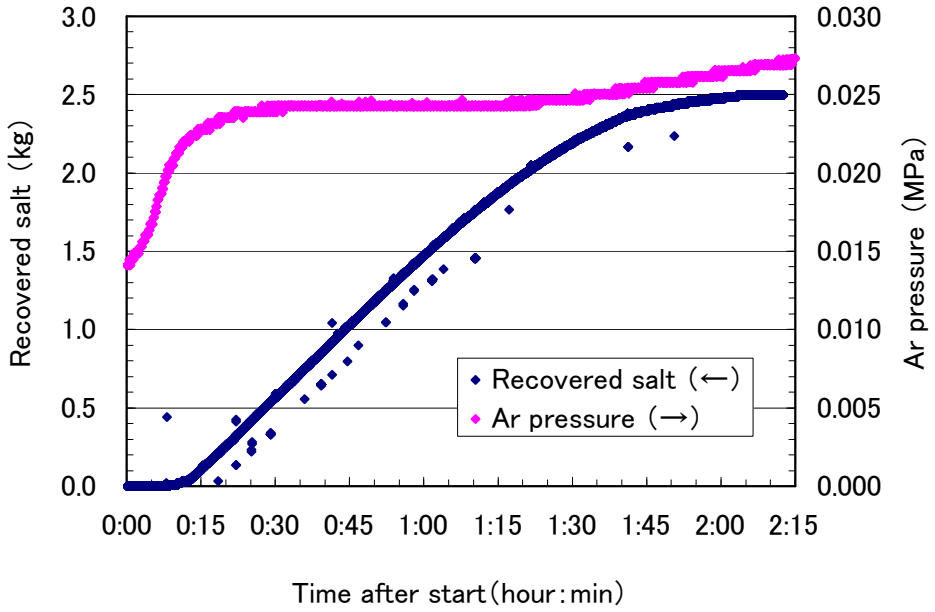


Column: 1cm-ID x 30cm-L x 2, filled with granular form zeolite (2.2mm-OD)

Salt flow rate passing though columns vs. driving pressure including calculation based on empirical equations

Demonstration Test to Decontaminate Simulating FP

- 2.8 kg of molten CsCl-LiCl-KCl salt (Cs: 2 wt.%) salt was pushed to pass through columns filled with 36.5g of zeolite (granular form, pretreated by aqueous solutions).
- Though Ar gas pressure increased at the beginning, molten salt flowed at almost stable rate (at 19.5cm/min.).

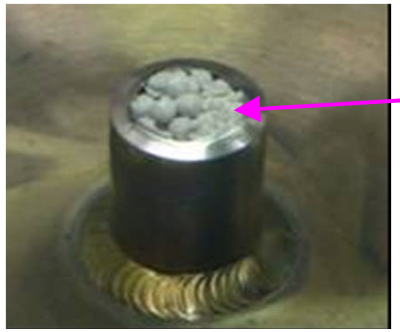


Accumulated amount of recovered salt and change of Ar gas pressure

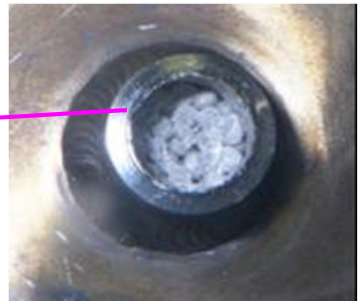
Zeolite Remained in Columns and Adhering Salt

- Columns were sectioned for analyzing zeolite and adhering salt.
- Zeolite granules in the upper positions were easily detached themselves. On the contrary, those in the bottom positions were hard to be removed and contained small fractions (collapsed zeolite?).
- Though columns were purged by Ar gas, "adhering salt ratios" ranged 26～38%, which were much higher than the target (≦ 7%) for minimizing salt waste.
- Probably, another innovative method will be necessary for further salt removal.

Section of upper part



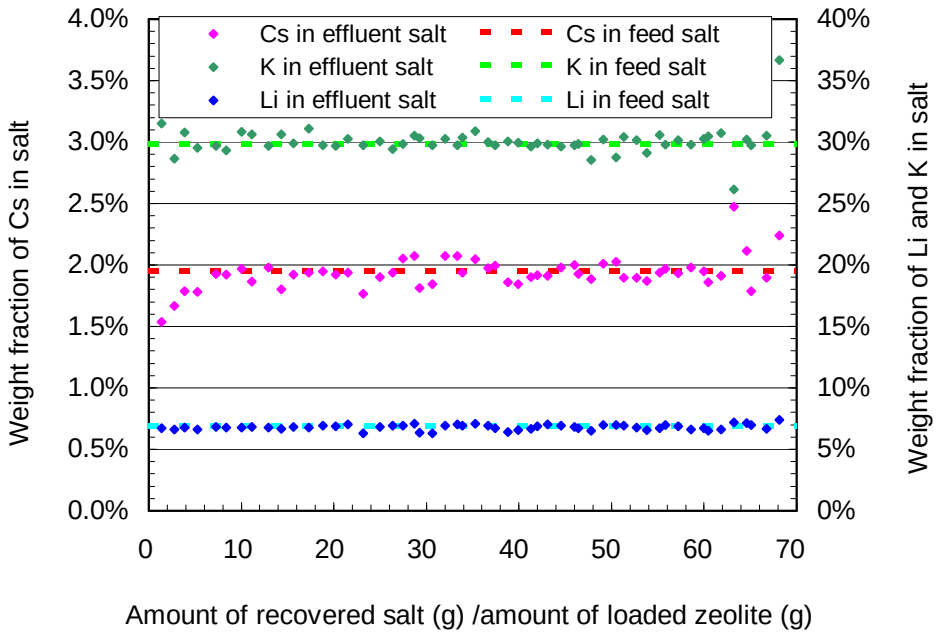
Section of lower part



Inside of lower part
(after zeolite removal by tweezers)

Change of Salt Composition after Passing through Columns

- A break-thorough curve for Cs concentration in effluent salt was obtained.
- Since the zeolite was pre-treated for Na removal, no significant concentration change was observed for Li and K.



Change of salt composition during column test

FP absorption property in zeolite columns, Comparison with literature data

- The break-through curve showed similar tendency to the literature data, which was taken by ANL.

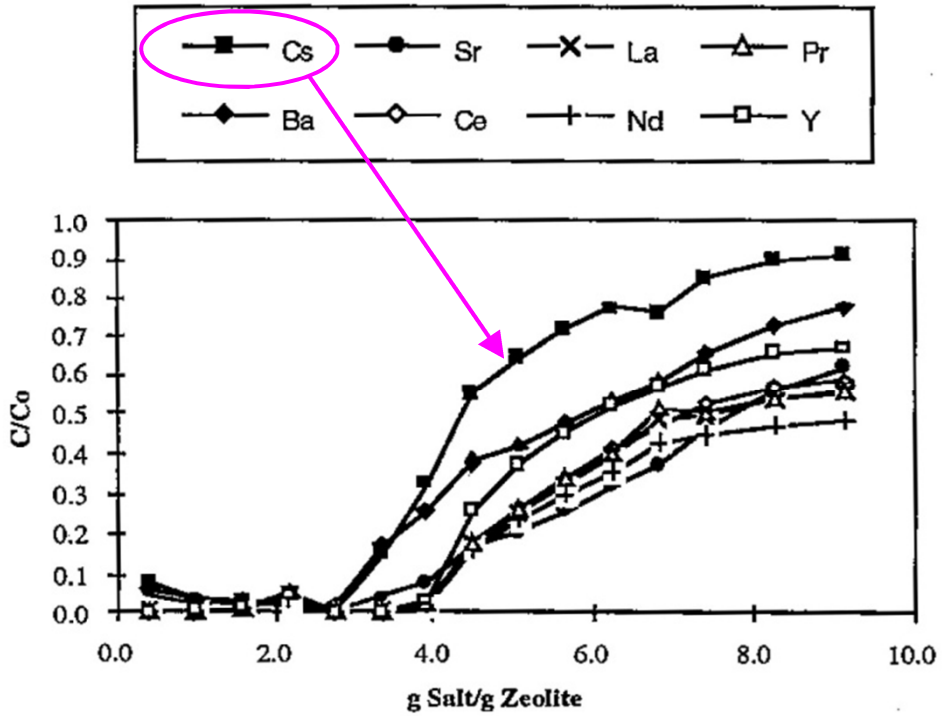


Figure 5. Breakthrough Curves for Fission Products in Test 1031 at 725 K and 0.5 cm/min

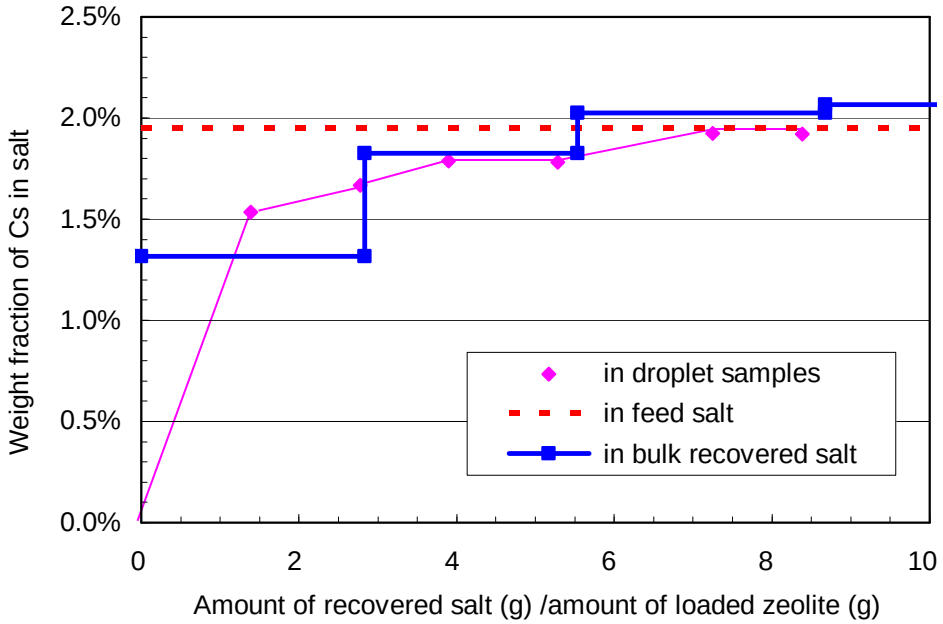
from Pereira *et al.*, 2nd *Int. Symp. on extraction and processing for the treatment and minimization of wastes*, 1996

Estimation of Absorbed Amount of Cs

- Absorbed amount of Cs was estimated from 3 different ways;
  - Dissolution of zeolite remained in column after washing in water,
  - Composition change of salt droplet samples collected periodically, and
  - Composition change of bulk recovered salt.

- The estimated values almost agreed in the range of 6.8×10^{-3}〜7.9×10^{-3} mol-Cs
  (= 0.32〜0.37 Cs / zeolite cage).
- However, these values were quite smaller than estimation by Langmuir equation of Tsukada et al.* (= 3.2 Cs / zeolite cage).

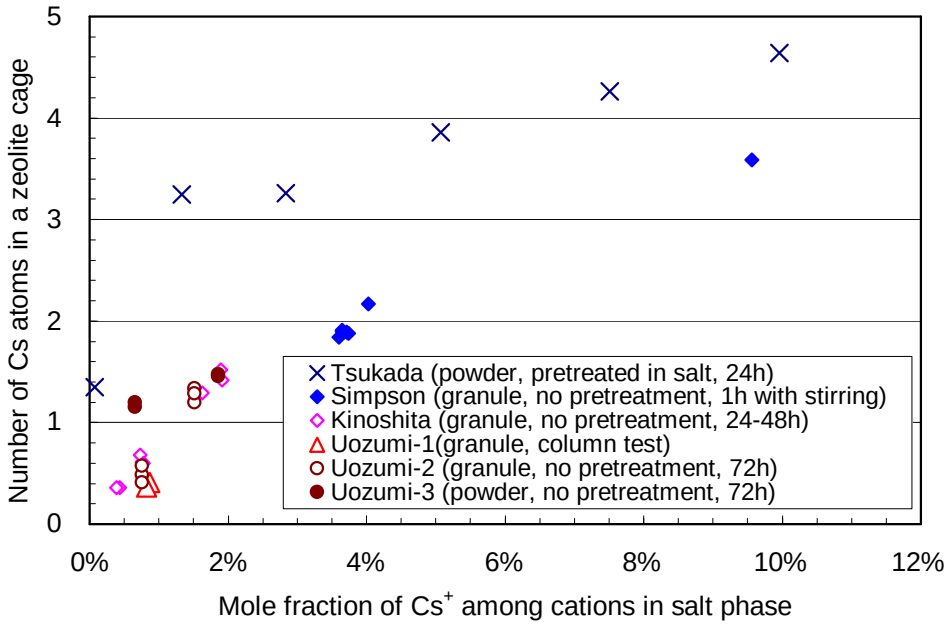
** Tsukada et al., Nucl. Technol., 162, 229 (2008).*



Change of salt composition during column test

Cs Absorption Capacity on Type-A Zeolite

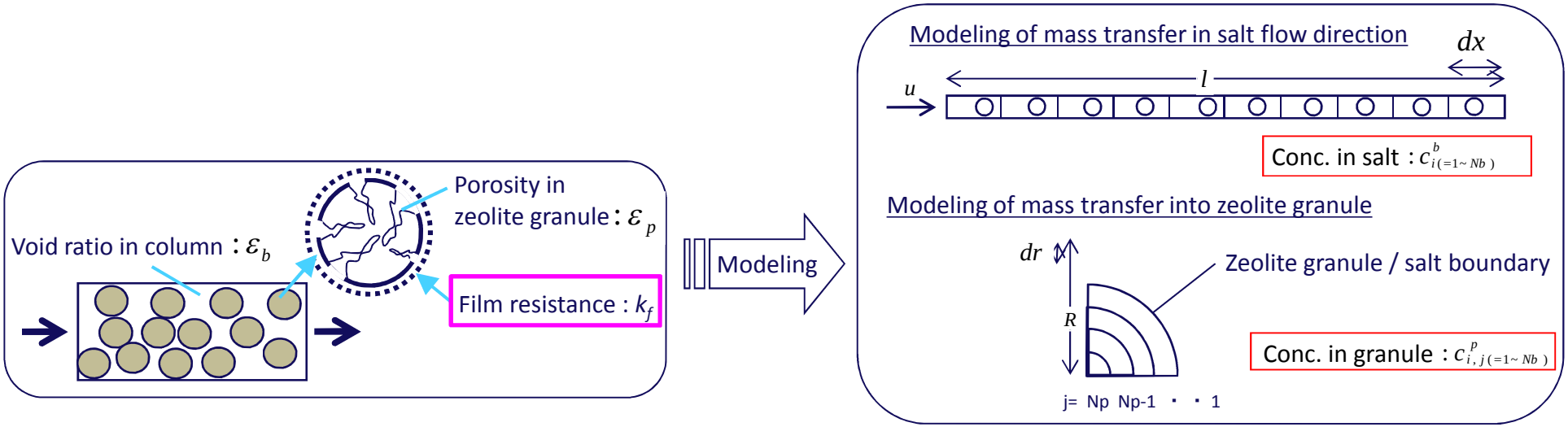
- There is some difference on Cs absorption isotherm among tests depending on type of zeolite and pretreatment.
- Adjustment of Langmuir constants will be necessary.



Cs absorption isotherm on type-A zeolite

Absorption Kinetic Study by Calculation Code

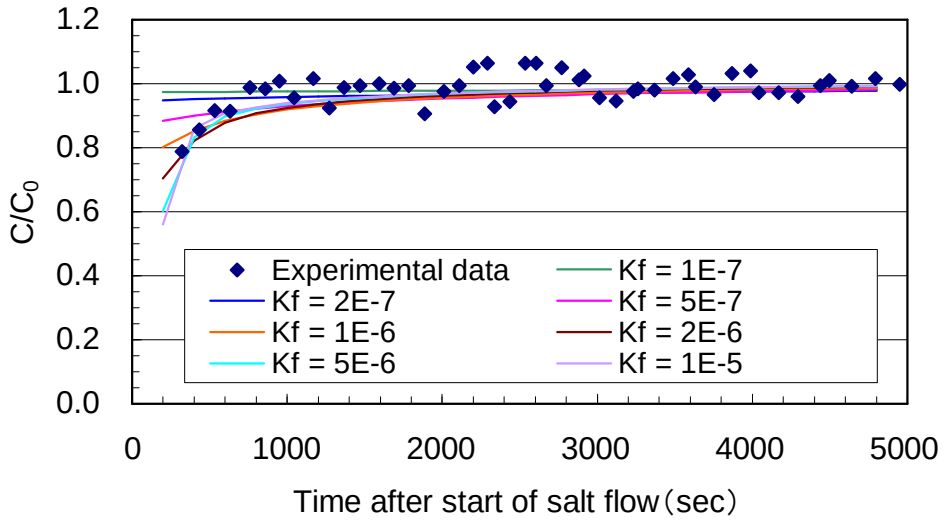
- A calculation code was developed for estimating the column system performance at Fukushima-Daiichi NPP, which was introduced to decontaminate radioactive Cs from accumulated water.
- By adapting corresponding parameters for the salt treatment process, this code will be applied to present the column test results.



Modeling of FP absorption on zeolite

Absorption Kinetic Study by Calculation Code, Tentative Results and Future Plan

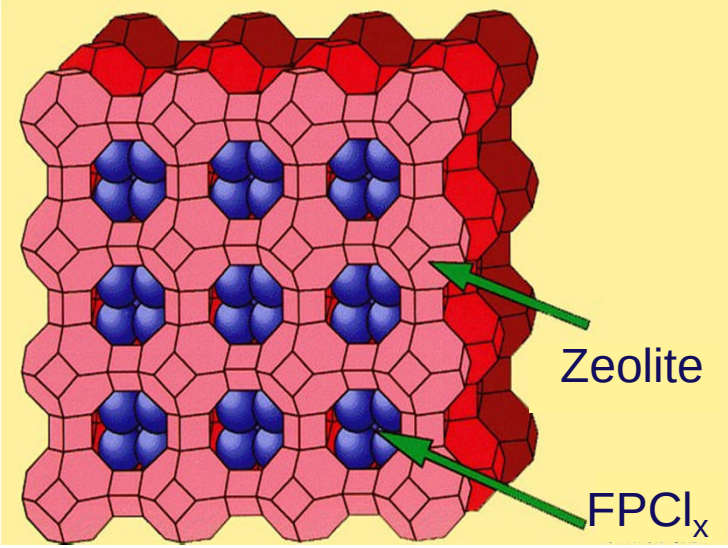
- By changing kinetic parameters such as "Film resistance: k_f", Cs concentration in the recovered salt changes.
- Through parameter fitting, appropriate kinetic parameters will be assessed and these values will be checked by additional column experiments.



Example of code calculation: K_f value dependence of Cs concentration in salt after zeolite column treatment

Study on Anion Absorption, Back Ground

- Previous study showed that Cl, which exist as anion in salt, is also absorbed on zeolite. Therefore, FPs exist as anion in salt may also be absorbed.

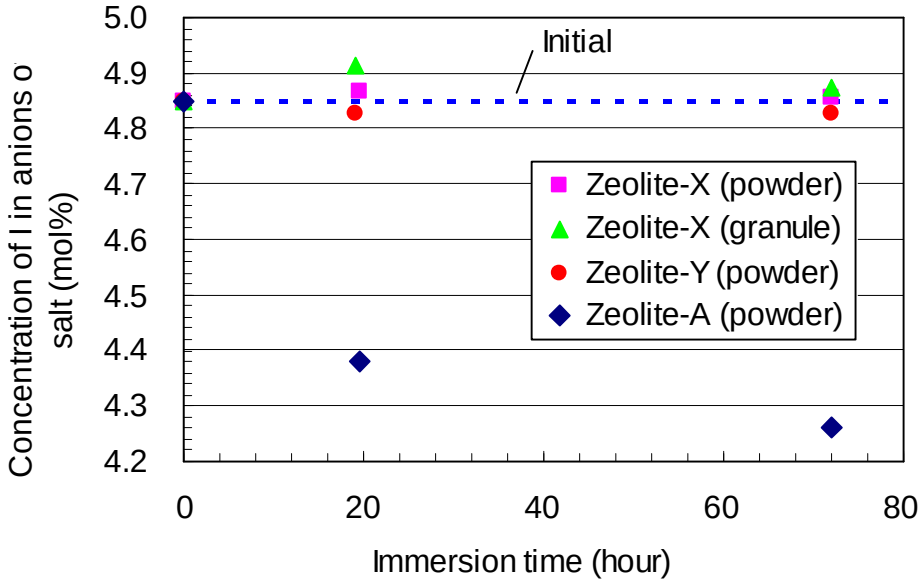


$FP_y [(AlO_2)_{12}(SiO_2)_{12}] Cl_z$

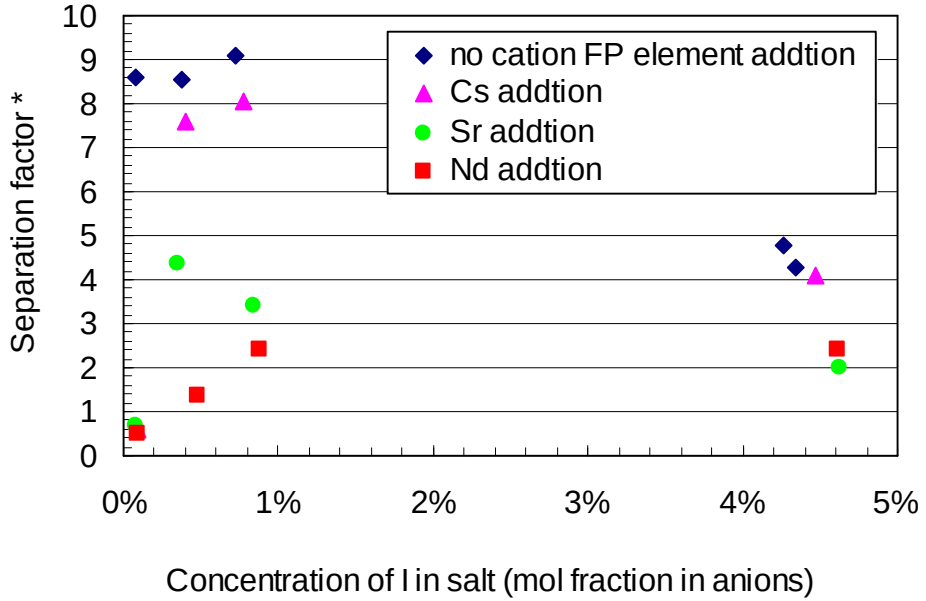
Some portion of Cl^- can be replaced by other anions in salt ?

Study on Anion Absorption, Iodine

- Some experiments were performed using I (iodine) as representative of anion FPs and selective absorption of I by type-A zeolite was observed.
- Absorption of I was affected by co-existing cation FP elements.



Change of concentration of I in salt after immersion of zeolite

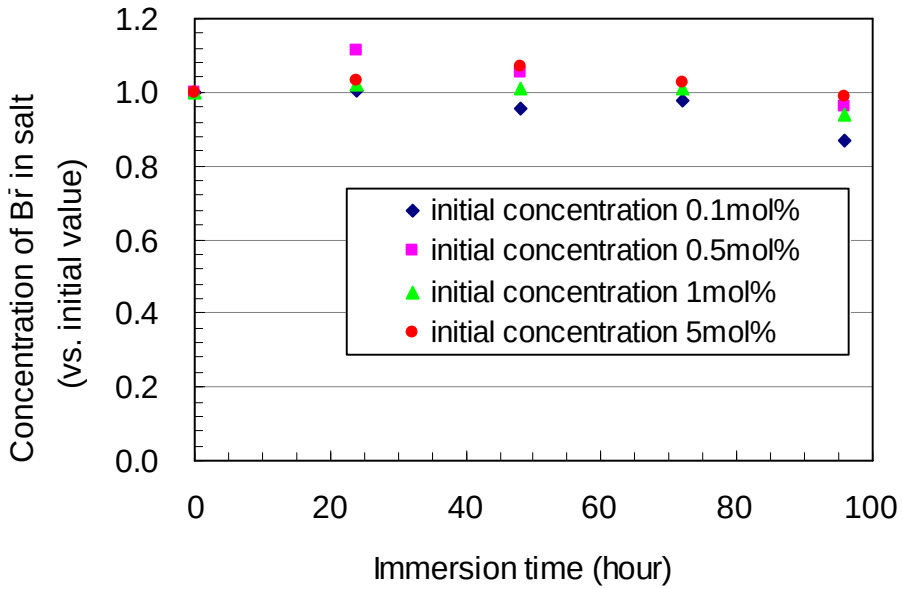


Change of separation factor of I vs. Cl at different I concentration and co-existing cations

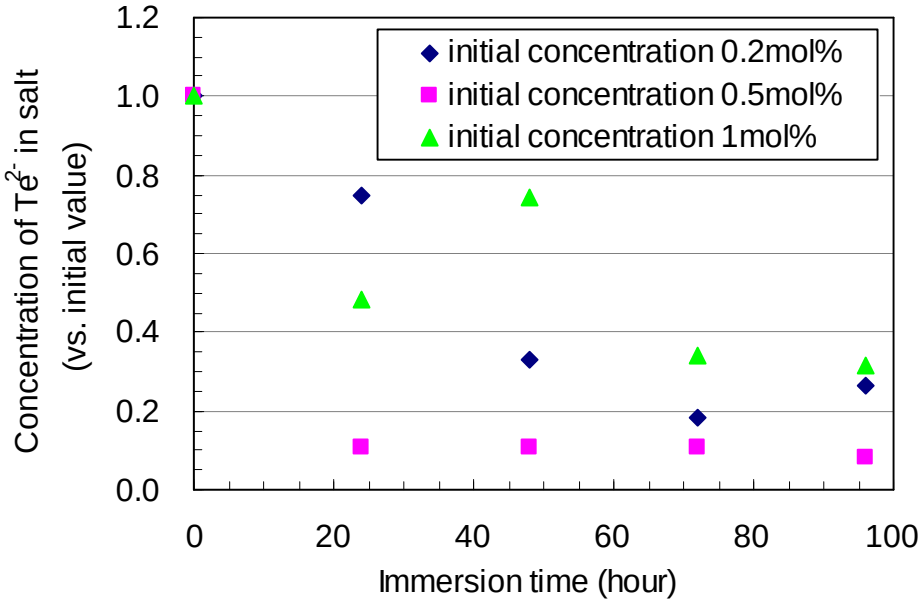
** :Separation factor = [I/Cl in zeolite]/[I/Cl in salt]*

Study on Anion Absorption, Bromine and Tellurium

- For studying anion absorption mechanism, absorption of Br^- and Te^{2-} were measured.
- Tentative results indicated strong absorption of Te^{2-}.



Change of concentration of Br^- in salt after immersion of zeolite



Change of concentration of Te^{2-} in salt after immersion of zeolite

Study on Anion Absorption Mechanism

- Anion absorption behavior seems to have strong relationship with its ionic radius and charge density.

	Radius of anion or zeolite pore
Type-X, -Y zeolite	0.37 nm
Te^{2-}	0.221 nm
I^-	0.216 nm
Type-A zeolite (4A)	0.21 nm
Br^-	0.195 nm
Cl^-	0.181 nm

- Computational science study will be performed in order to clarify the anion absorption mechanism, so that the difference among anions can be explained.

Conclusion

- Current situation of CRIEPI's spent salt treatment process development was summarized.
- By "engineering scale column tests" and "code calculation", kinetic study on column behavior will be performed.
- Anion FP absorption behavior will be also examined.

- Design basis for the column apparatus will be obtained.