A Study of H-Y Zeolite and LiCl - KCl Salt Interactions

Prashant Bagri and Michael Simpson

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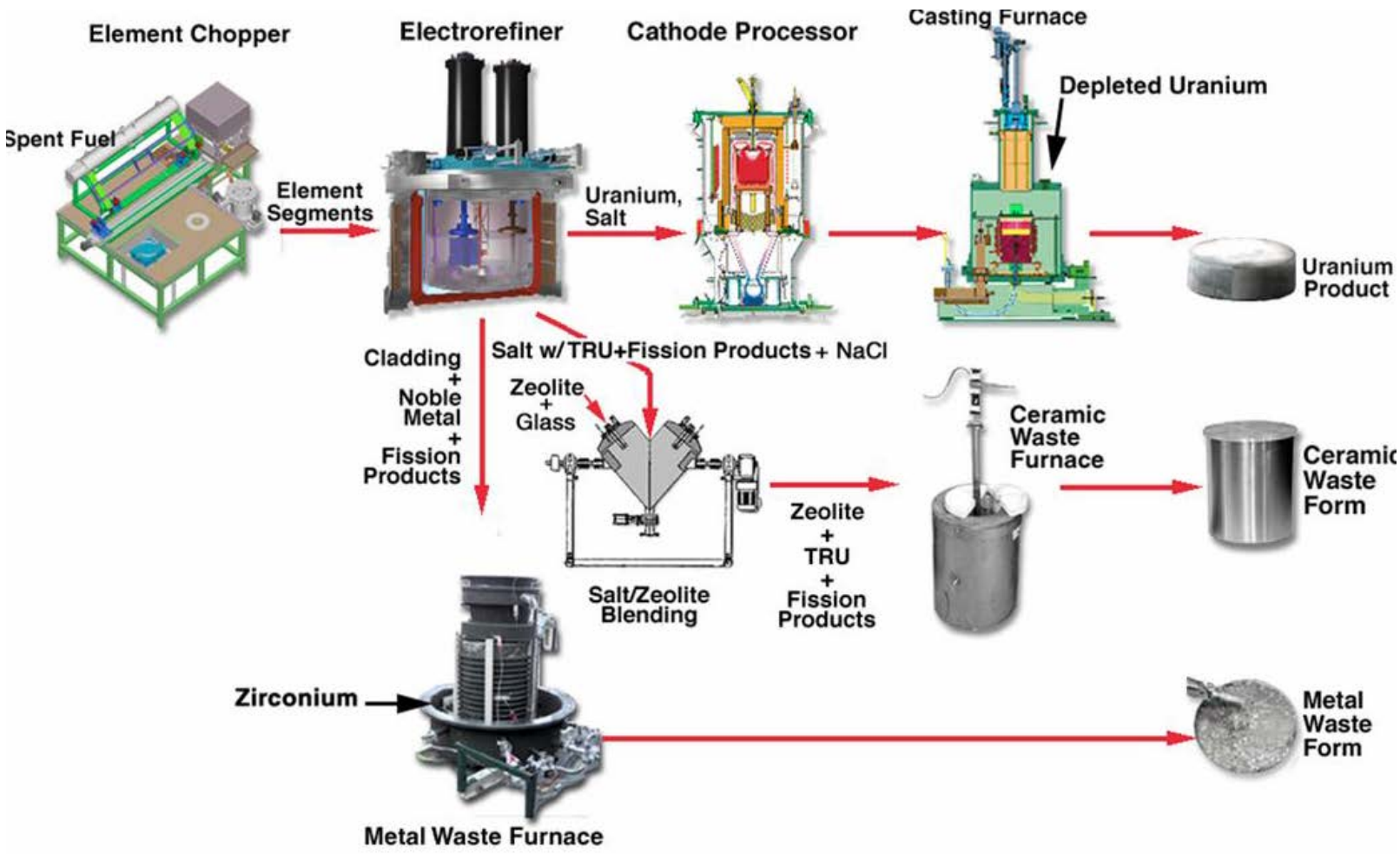
Introduction/Background

Pyroprocessing of EBR-II Fuel



Ceramic Waste Process

ELECTROREFINER

Electrorefiner Salt

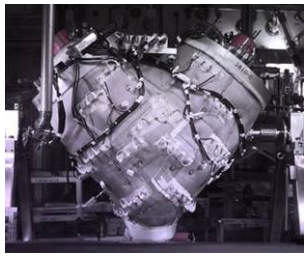
SALT CRUSHER

Crushed Salt

MILL/CLASSIFIER

Ground Salt

HEATED V-MIXER



Glass added after producing salt-loaded zeolite

Glass and Salt-Loaded Zeolite

FURNACE

CERAMIC WASTE

ZEOLITE MILL

Milled Zeolite

ZEOLITE DRYER

Dried Zeolite

Salt Occlusion in Zeolites (Baseline Process)

- This is one of the first steps in the baseline ceramic waste process:

$$Na_{12}\left(AlO_2\right)_{12}\left(SiO_2\right)_{12} + nMCl_x \rightarrow Na_{12}\left(AlO_2\right)_{12}\left(SiO_2\right)_{12} \bullet \left(nMCl_x\right)$$

- Maximum loading: n ~ 12
  - 28 wt% salt in salt-loaded zeolite
- Ideal loading for ceramic waste process: n~ 3.8
  - 11 wt% salt in salt-loaded zeolite

New Idea: React Salt with H-Exchanged Zeolite

This is the conventional approach to loading salt into zeolite:

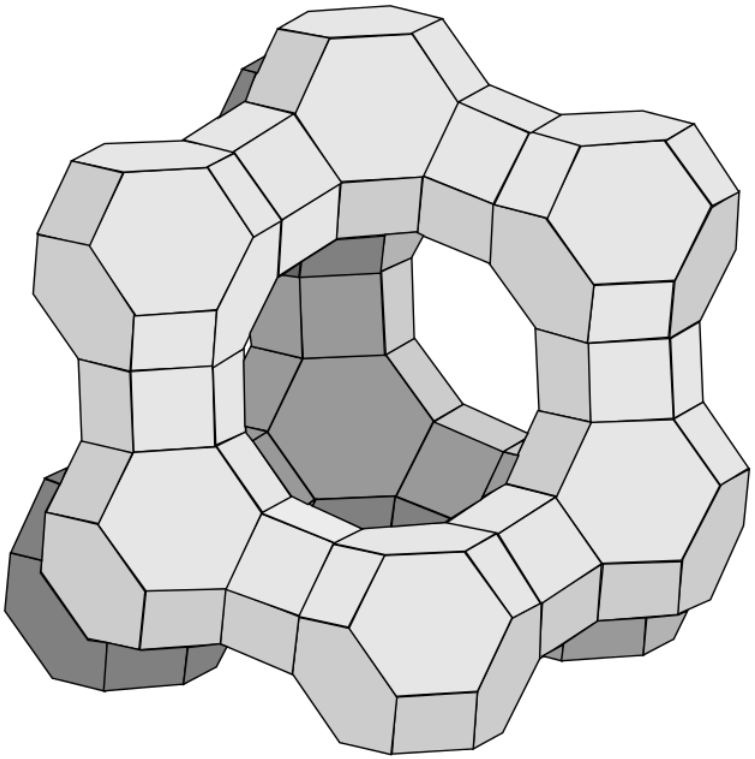
$$LaCl_{3(s)} + 3Na\text{-}zeolite_{(z)} = La\text{-}zeolite_{(z)} - 3NaCl_{(z)}$$

If the zeolite is H-exchanged, it has been shown that the following occurs:

$$LaCl_{3(s)} + 3H\text{-}zeolite_{(s)} = La\text{-}zeolite_{(s)} + 3HCl_{(g)}$$

Loss of the Cl^- would reduce the mass of the waste and result In the fission products being less mobile in an aqueous environment.

Faujasites (Y-type zeolites)

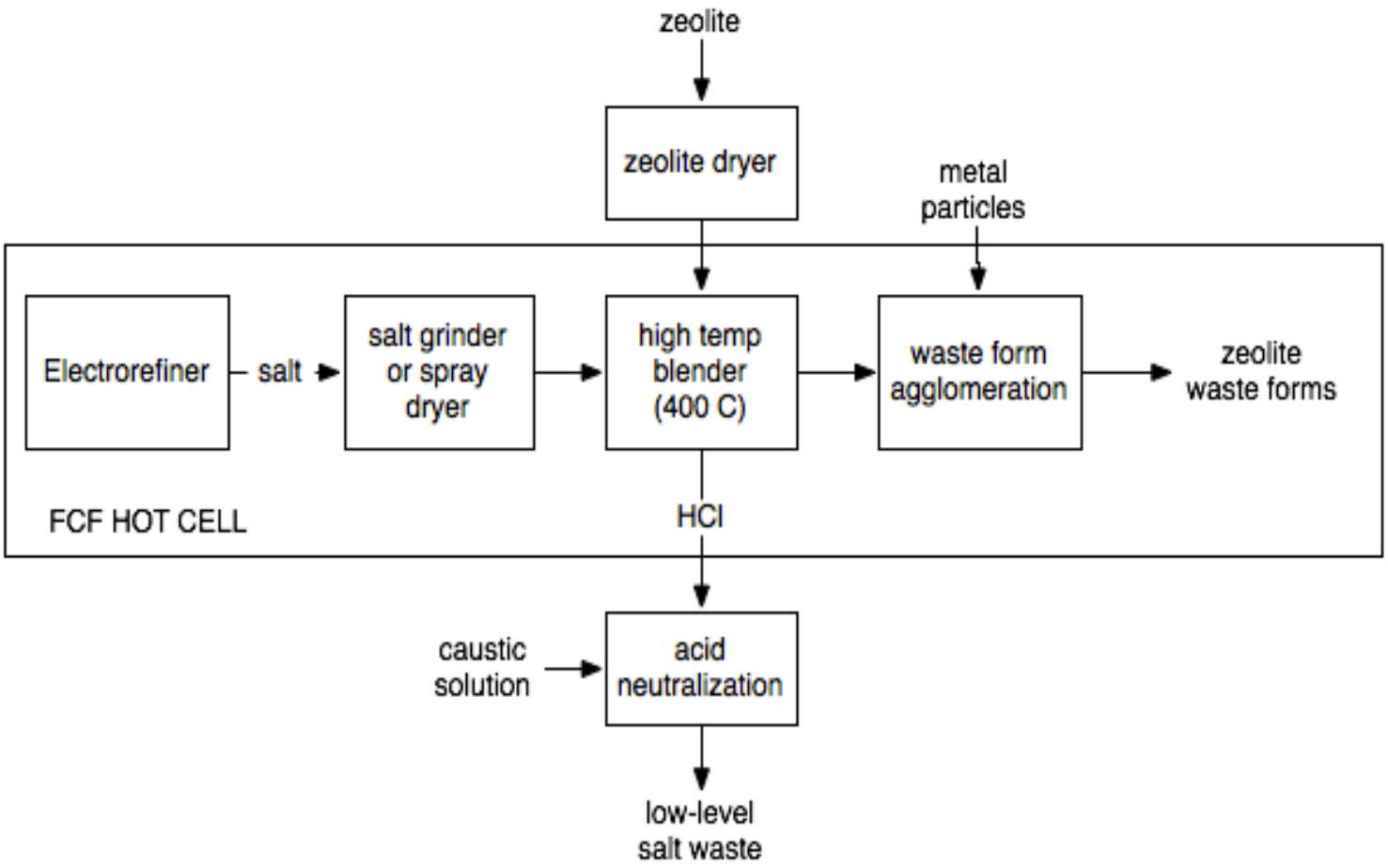


Faujasite (7-8 A pores)

Zeolite-A (3-5 A pores)

Problem is that zeolite-A is not stable in the H^+ exchanged state.

Proposed New Process



Research Objectives

- Demonstrate ion exchange between H-Y zeolite and eutectic LiCl - KCl
- Determine optimal process parameters (temperature cycle)
- Assess feasibility of the proposed process for reducing both waste generation and cost

Experimental Section

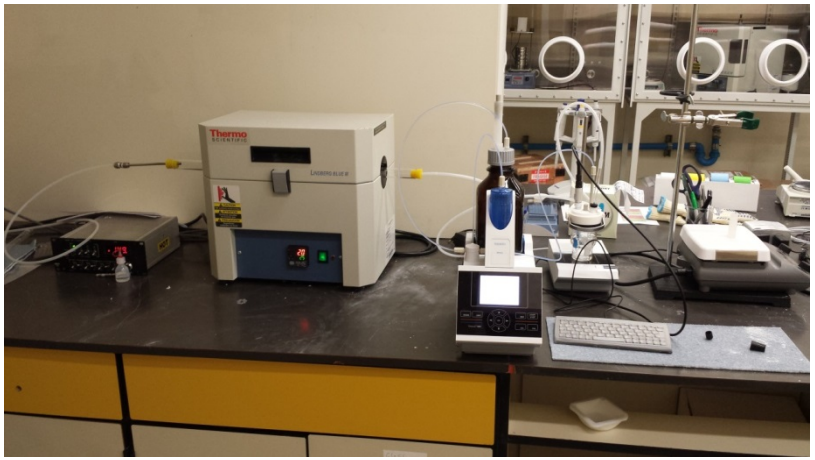
Commercially Available H-Y

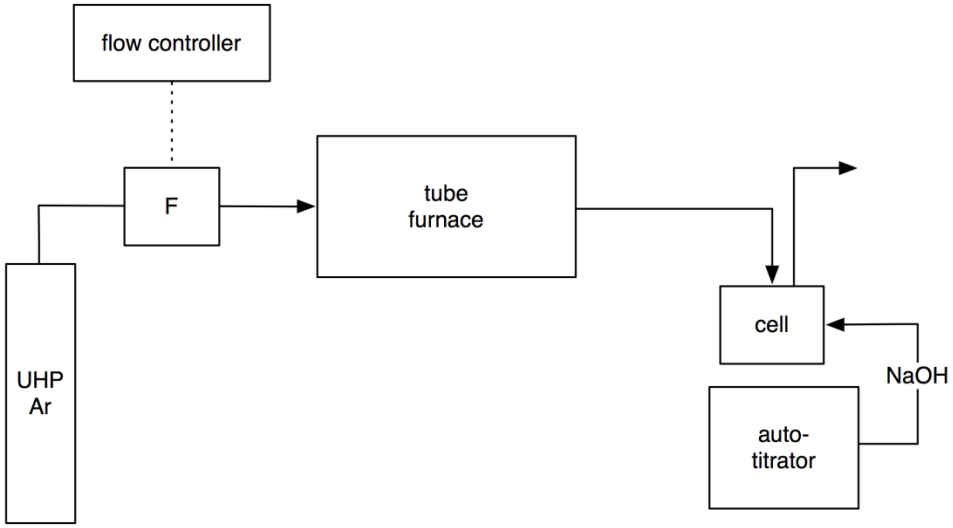
Zeolyst Product	Si/Al Ratio	Surface Area (m^2/g)
CBV-400	2.55	730
CBV-600	2.6	660
CBV-720	15	780
CBV-760	30	720
CBV-780	40	780
CBV-901	40	700

Lower Si/Al ratio favors higher loading of waste.
Higher Si/Al ratio favors superior thermal stability.
Initial tests run with CBV-400 and CBV-720.

Experimental Apparatus

- Salt + zeolite pre-mixed in glove box.
- Statically heated in tube furnace with flowing dry argon gas.
- Off-gas directed into titration cell connected to autotitrator operating in pH-stat mode.
- Allows continuous monitoring of rate of HCl gas evolution.





Titration of HCl off-gas

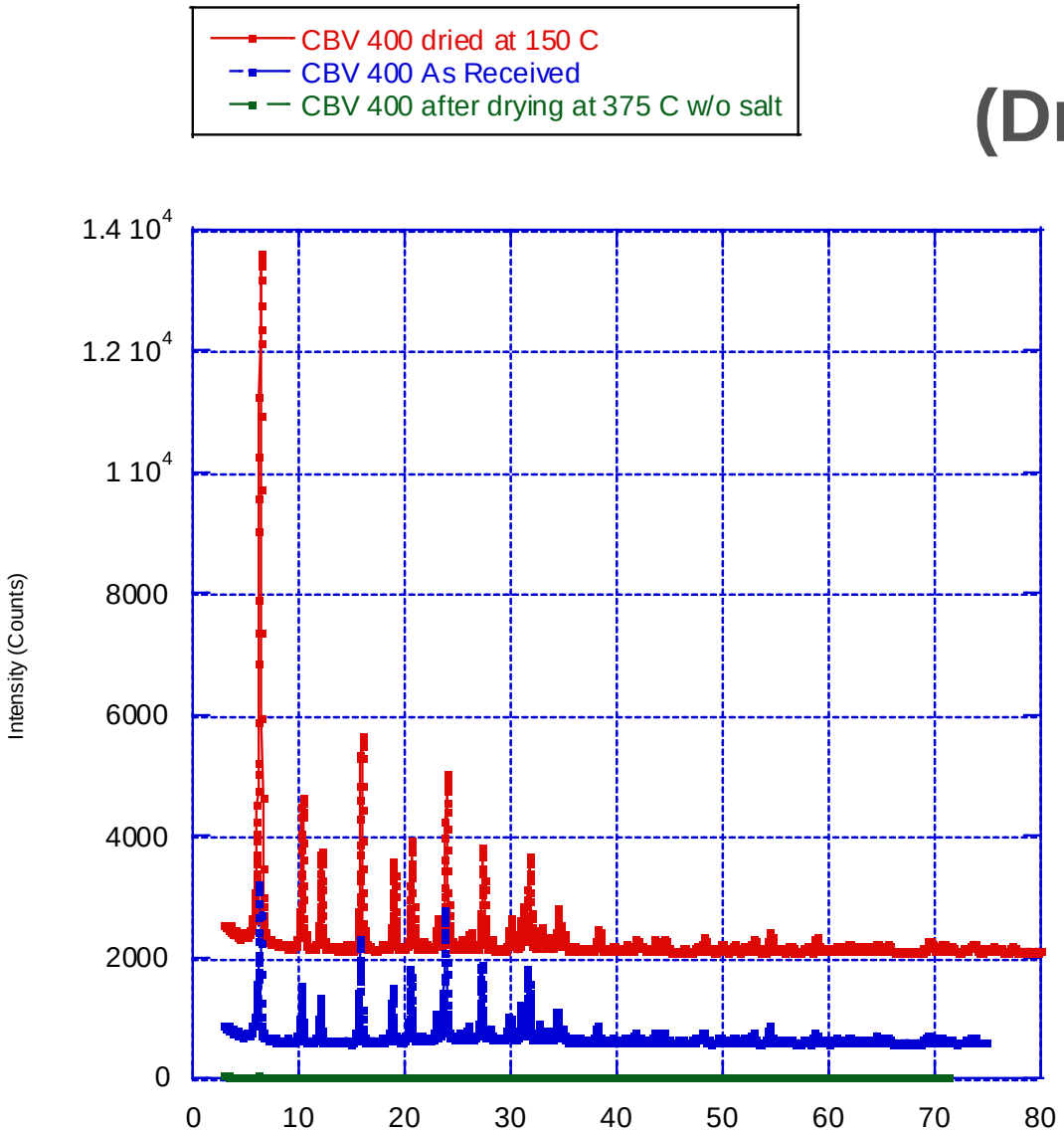
- The argon from the end of the quartz tube was diverted into a aqueous trap at pH 10. The pH was maintained constant using an autotitrator. Any HCl evolved during the experiment will undergo following reaction.

$$HCl_{(g)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O$$

- To maintain a constant, the system titrates NaOH. Hence a time dependent rate of HCl can be obtained from the volume of NaOH titrated.

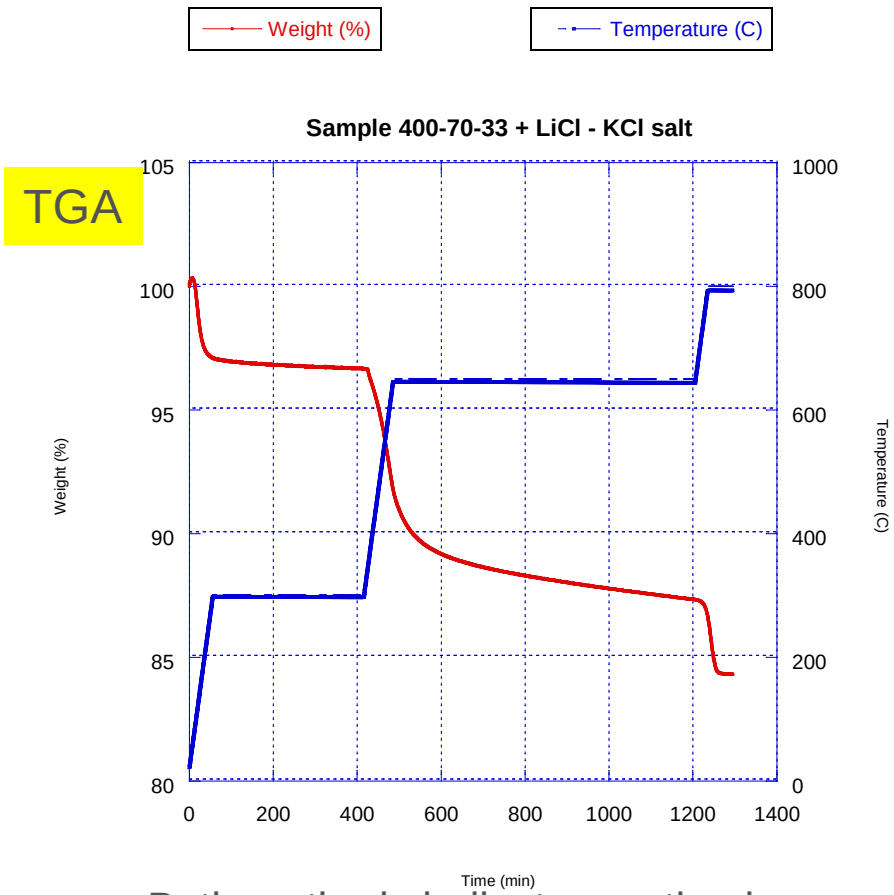
Results

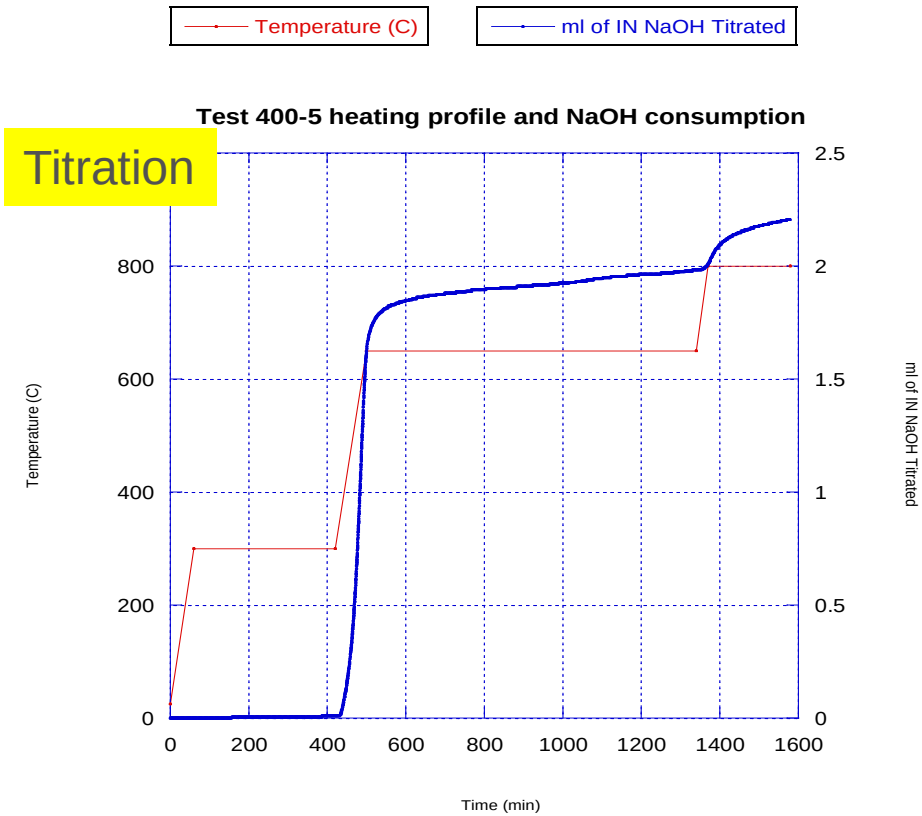
XRD of H-Y Zeolite (Dried at 150 C & 375 C)



- Initially, zeolite was dried at 375 C, but this resulted in total loss of crystallinity.
- Drying at 150 C preserved the crystal integrity of the zeolite.
- This zeolite was then tested for reaction with HCl.

Titration vs TGA





- Both methods indicate reaction is occurring at about 350-400 C.
- Advantage of TGA is faster experiments
- Advantage of HCl titration is evidence of the specific ion exchange reaction.

Titration Test Results with H-Y Dried at 375C+

Test No.	Maximum Drying Temperature (C)	Maximum Reaction Temperature (C)	% Ion Exchange	% Free Chloride
400-1	400	550	8.19%	42.6
400-2	400	550	0%	61.9
400-3	550	300	0%	115.6
400-4	375	650	5.63	14.0
400-5	375	800	6.54	46.2
400-6	375	800	5.75	45.6
720-1	375	650	11.70	24.1

Very low ion exchange results, presumably due to loss of crystallinity

Titration Test Results with H-Y Dried at 150 C

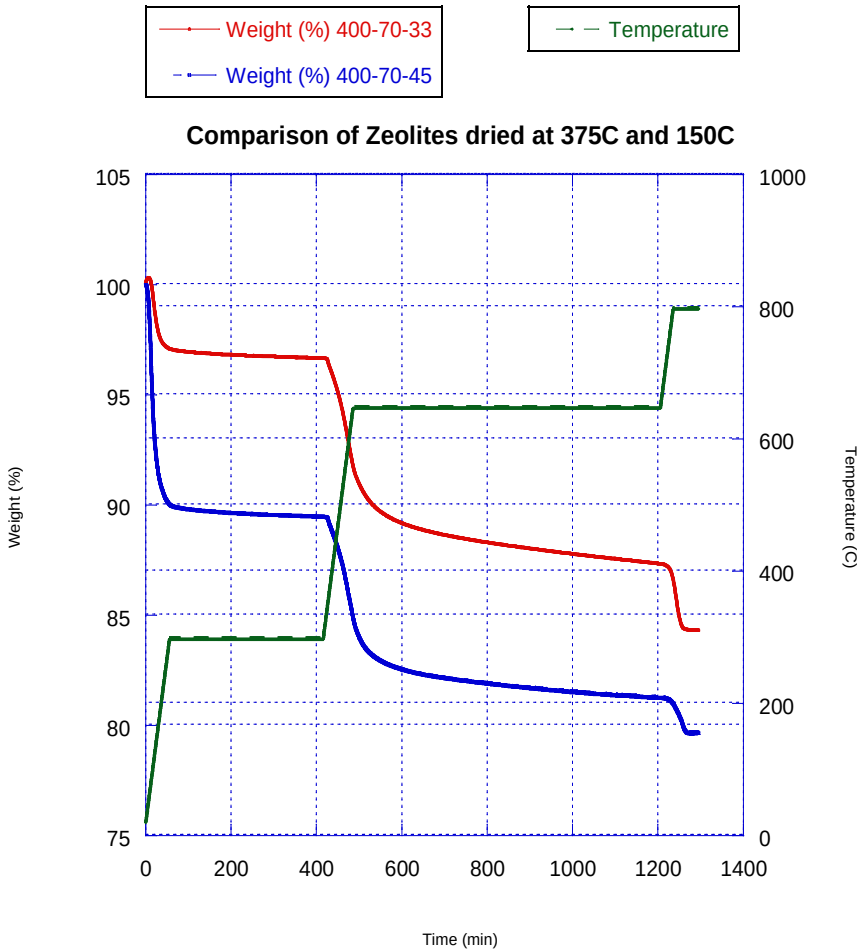
Test No.	Maximum Drying Temperature (C)	Maximum Reaction Temperature (C)	% Ion Exchanged	% Free Chloride
400-7	150	650	32.05	25.0
400-8	150	300	0	121.2
400-9	150	650	34.70	14.5
720-2	150	650	49.58	26.3
720-3	150	650	45.73	14.0
720-4	150	300	0	99.6

Significantly better results with zeolite dried at 150 C.
But improvements still needed.

Drying Temperature Effect

- TGA indicates about 10% wt loss of zeolite dried at 150 C
- Future testing planned to find optimal drying temperature.
  - Low residual H_2O
  - High crystallinity

Dried at 150 Dried at 375



Conclusions

- Preliminary investigation of the salt-zeolite solid state reaction was successfully performed. Li^+ and K^+ can be exchanged into H-Y zeolite in agreement with literature.
- Up to about 50% of the theoretical maximum amount of HCl was observed to have evolved. This was achieved with very limited salt/zeolite pre-mixing. Zeolite with higher Si/Al ratio seem to undergo more ion exchange.
- Sorption and reaction occur in two different temperature regimes.
- Initial drying temperature must be kept low to prevent collapse of H-Y zeolite structure.

Acknowledgement

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Questions ??