Ion Recognition Approach to Waste Volume Minimization

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Waste Minimization via Ion Recognition Separations

- Simply stated, the approach is the selective removal of cations and/or anionic groups that significantly impact waste classification or pose specific processing problems
  - Radionuclides that are major contributors to decay rate (Cs, Sr)
  - Non-radioactive components that affect waste form stability or volume (Na^+, NaOH)
- Selective removal of Cs, Sr is well-documented
- Focus of this presentation is selective extraction of NaOH from caustic waste

Background-Pseudohydroxide Extraction

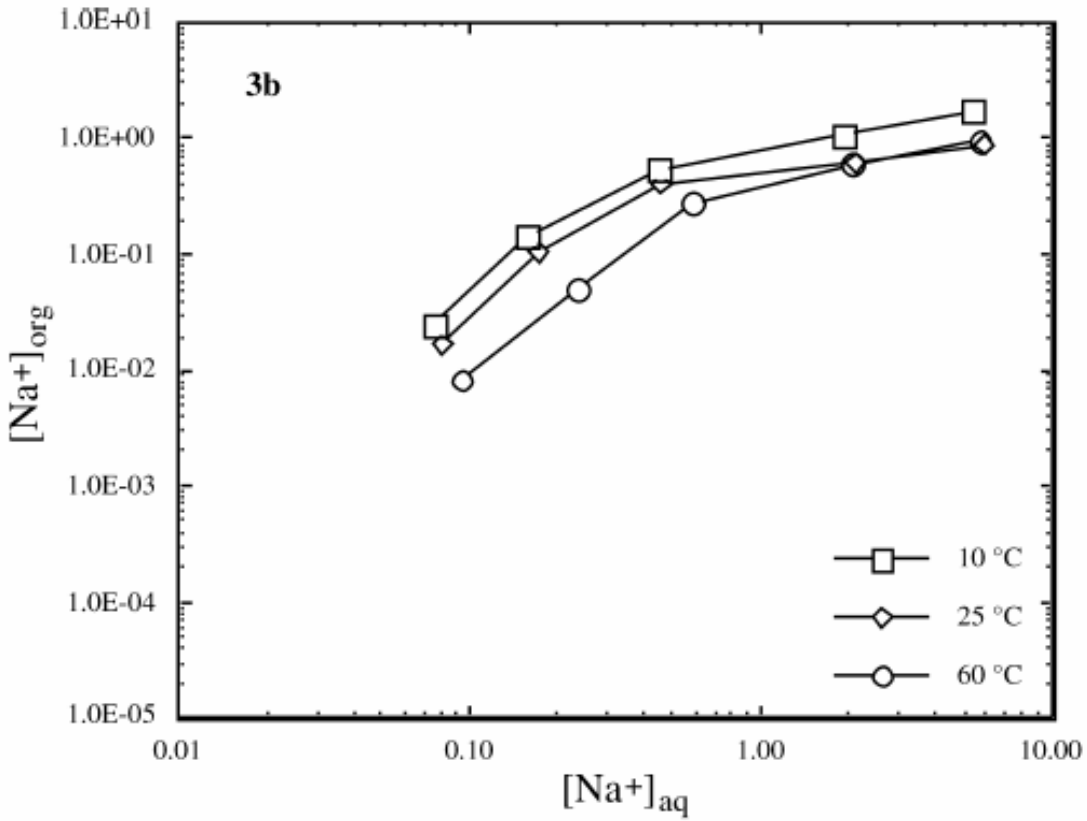
- **Extraction of sodium hydroxide from caustic aqueous solutions using weak hydroxy acids in hydrophobic diluents has been demonstrated (Lummetta, Moyer)**
  - **Cation exchange mechanism has been proposed (acid-base reaction0**

    $ROH(org) + Na^{+}(aq) \leftrightarrow Na^{+}RO^{-}(org) + H^{+}(aq)$, or

    $ROH(org) + Na^{+}(aq) + OH^{-}(aq) \leftrightarrow Na^{+}RO^{-}(org) + H2O(aq)$
  - **Extractants evaluated include:**
    - **Alkyl phenols and fluorinated alcohols in 1-octanol**
    - **3,5-di-*tert*-butylphenol in Isopar L® with 1-octanol as a modifier**
    - **3.5-di-*tert*-butylphenol in Isopar L® with Exxal 8® as a modifier**

Extraction performance

- **Reasonable extraction coefficients have been obtained using the more-acidic alkyl phenols and fluorinated alcohols**



Isotherms for extraction by 3,5-di-*tert*-butyl phenol at 10, 25, and 60°C.

Selectivity performance

- Testing has been performed using aqueous NaOH and Al-containing waste simulants
  - Simple simulant containing NaOH, $NaNO_3$, and $NaAl(OH)_4$
  - Waste leachate simulant containing $NaAlO_2$, $NaNO_3$, Na_2CO_3, NaOH and Cs tracer
- Results indicate no extraction of Al
- Net effect is removal of Na as NaOH (other anions associated with Na are not extracted)
- Distribution coefficients for Cs are similar to those for Na at low NaOH concentrations
- Cs removal is a prerequisite to PHE

Unresolved Technical Issues

- Kinetics of extraction processes (Na, Cs)
- Physical (hydraulic) behavior pertinent to ion exchange and solvent extraction
- Kinetics of $Al(OH)_3$ precipitation
- Physical behavior of precipitate
  - Density
  - Surface active tendencies
- Mass transfer performance under process conditions
  - High O:A ratio to obtain needed extraction factors
  - Variations due to equipment selection

Precipitate formation

- Primary complication of the process is the precipitation of $Al(OH)_3$ as pH is reduced by NaOH extraction
  - Solids formation may affect phase separation
  - Potential accumulation of solids
  - Need/desire to separate solids from raffinate
- Precipitate formation <u>may</u> drive equipment selection
- Problem may be mitigated by choice of process and equipment
  - Ion exchange vs solvent extraction
  - Batch vs continuous
  - In SX, contactors vs mixer-settlers vs columns

Processing options and considerations

- Ion Exchange
  - Resistance of resin to chemical, radiological degradation
  - Configuration
    - Fixed bed
    - Fluidized bed
    - Resin-in-pulp
  - Plugging of pore structure by precipitate
  - Plugging of bed by precipitate
  - Resin loading/elution frequency
- Solvent Extraction
  - Na extraction kinetics
  - Solids accumulation in equipment
  - Continuous, high throughput

Ion exchange issues and options

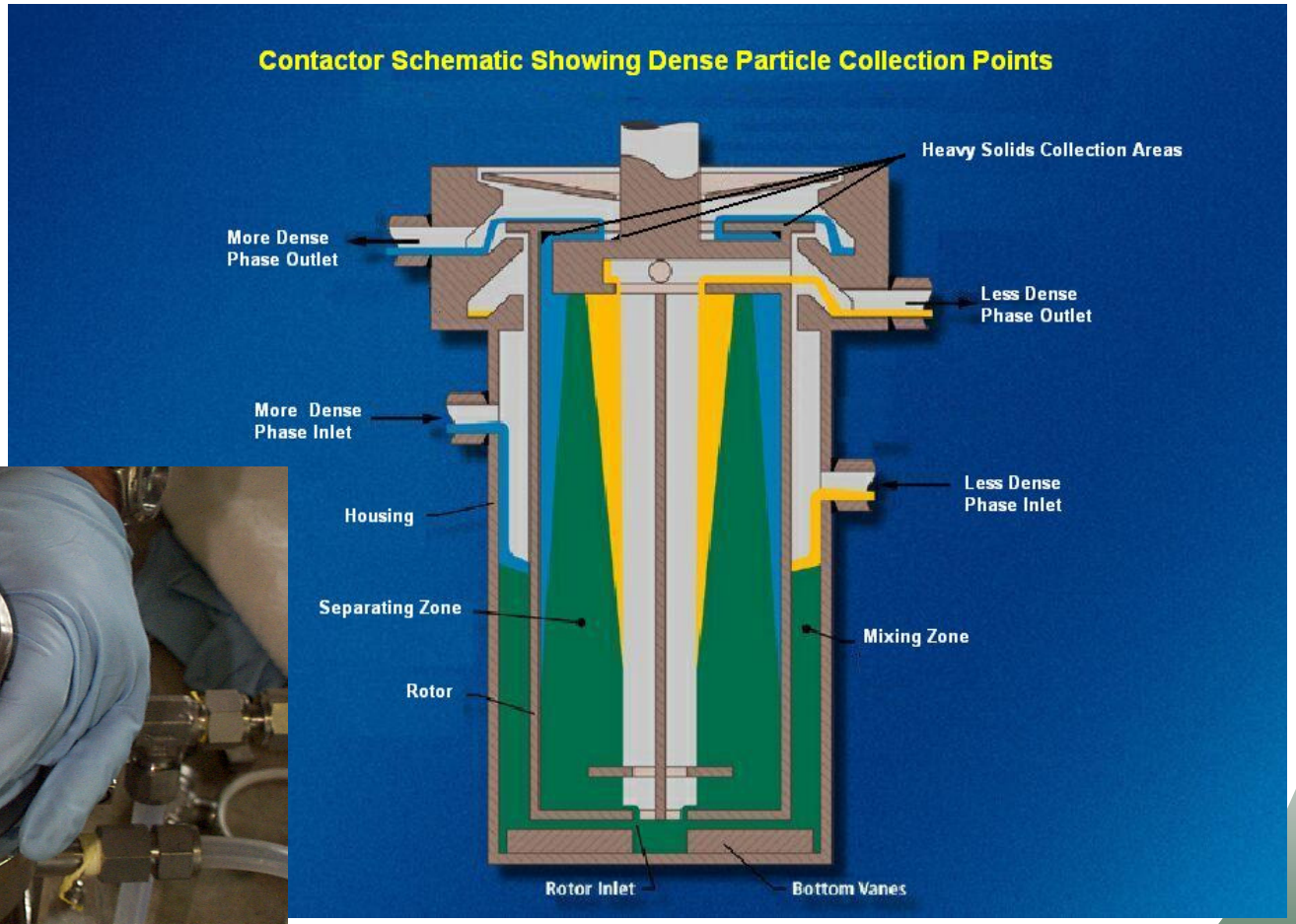
- Fixed bed not feasible due to precipitate formation
- Fluidized bed possible if precipitate can be separated from resin due to density, size difference
- Resin-in-pulp commonly used in solid/liquid applications
  - Commonly used to recover metal ions from slurries
  - Dilute slurry of resin in solution facilitates exchange
  - Difference in solids/resin sizes allows retention of resin in separator
  - Limited to recovery from low-concentration feeds
  - Typically, entering solids are sized; are not produced in situ
- Ion exchange problematic for removal of NaOH at high concentrations

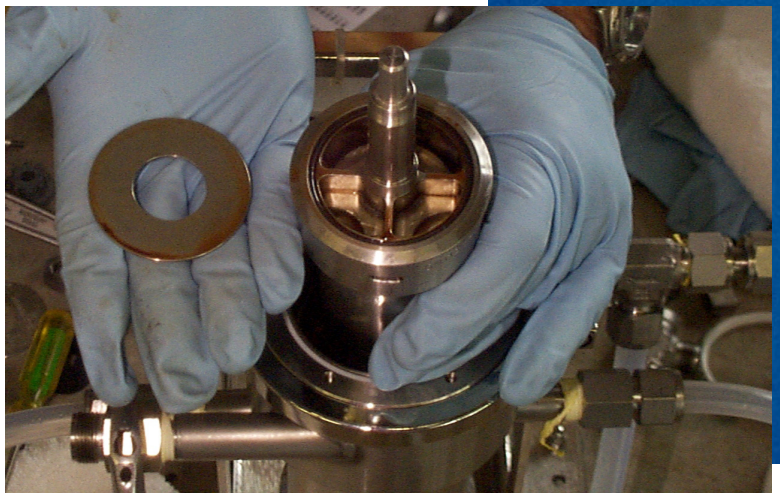
Solvent extraction issues and options

- Precipitation issue determines feasibility of SX and selection of equipment
  - Centrifugal contactors, mixer/settlers not amenable to the presence/formation of solids
  - Kinetic considerations, extraction vs precipitation
- SX better suited than IX for application due to limited D_{Na}, high NaOH concentrations
- Phase separation behavior
  - Separation of dispersed liquids
  - Partitioning of solids between phases
- Solvent stability
- Water solubility

Solids in Centrifugal Contactors

- **Accumulation occurs at critical points**





Process/equipment selection

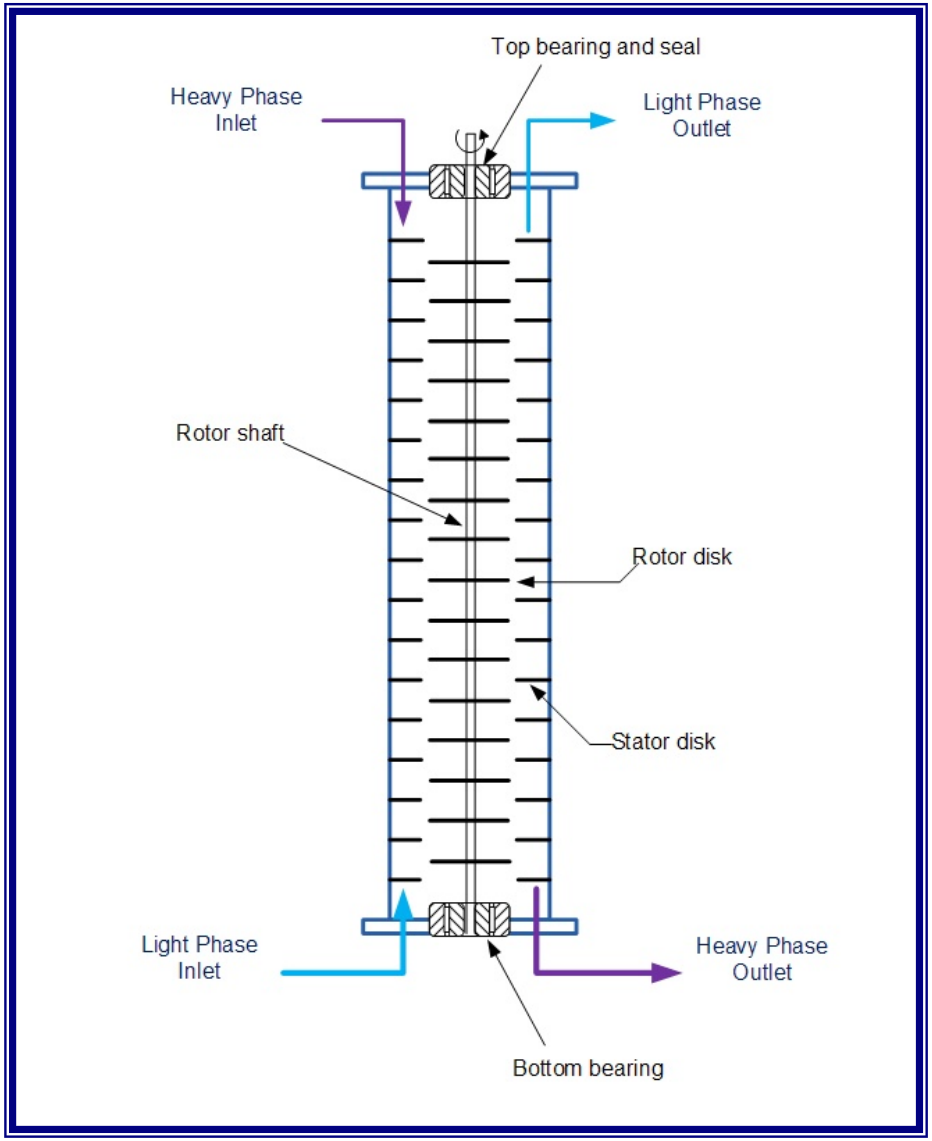
- Determine rate of precipitate formation
  - IX residence time is long; process must handle precipitate
  - If precipitation formation is rapid (seconds) SX equipment must process solids
  - If precipitation is “reliably” slow, extraction process may be designed to be solids-free
    - “Reliably” slow, i.e., slow over a wide range of process conditions
    - Solids-free extraction is possible if extraction kinetics are fast relative to precipitation
    - Requires careful design to control residence time
    - Anticipate off-normal conditions that could result in precipitation

Process/equipment selection

- Combination of fast extraction and slow precipitation would facilitate use of centrifugal contactors
  - Extraction performed at high throughput, low residence time
  - Precipitation in raffinate holding vessel
- Fast precipitation:
  - Must design for the presence of solids in SX
  - Centrifugal contactors, mixer/settlers not feasible

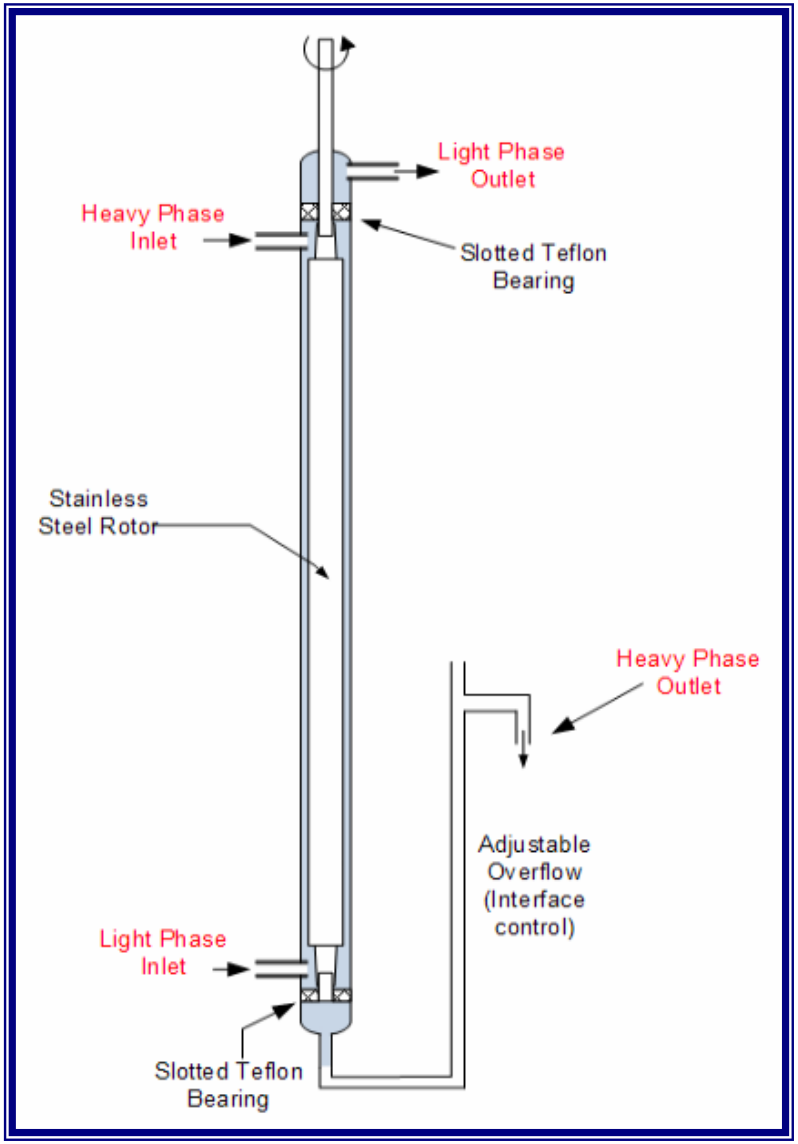
Process/equipment selection

- Rotating disc column
  - Similar to conventional pulsed column
  - Addresses precipitation if solids partition to one phase
  - Extraction not limited by kinetics



Process/equipment selection

- Couette column
  - Combines features of pulsed column and centrifugal contactor
  - Dispersion created by shear (similar to centrifugal contactor)
  - Lower residence time than pulsed column
  - Dispersion separates by gravity



Processing concept

- Prerequisite Cs removal to mitigate coextraction
- NaOH (actually Na^+) extraction using hydroxy acid in diluent (Isopar L®) with modifier (Exxal 8®)
- Stripping with H_2O to recover NaOH
- Concentration of NaOH for recycle
- Recycle of solvent
- Filtration to remove precipitated $Al(OH)_3$

Advantages include:

- High throughput
- Continuous NaOH recovery—no back flushing, no membrane fouling