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Innovative Resin Technologies
For
World Class PWR Chemistry Operations
Introduction

- Resins used in early PWR applications
  - Same basic properties today
  - Some changes – UPS, higher capacity
- GT focus on power utilities and unique needs
- Condensate polishing capital equipment
  - Bead & powdered resins and filter septa
- Developed & introduced many unique products and systems
- Innovations benefit PWR operations
  - ULC anion, Low sulfate cation, Specialty mixed beds, Amine form cation/mixed beds
Innovation – Ultra Low Chloride
Historical Chloride Perspective

- Contaminant
  - Increases Conductivity
  - Promotes Corrosive Reactions
  - Concentrated (100-350X) in Steam Generator

- Chemical Forms
  - Inorganic Salts
  - Organic Compounds

- Anion Exchange Resins
  - Remove Ionic Chlorides
  - Contribute Organic Chlorides – convert to ionic chlorides in reactor or steam generator
  - Contribute Ionic Chlorides, under certain conditions
Innovation – Ultra Low Chloride
Historical Chloride Perspective

• Sources of Chloride – Resin manufacture and processing
  – Copolymerization – No Cl source - Styrene/DVB/EVB
  – Chloromethylation – Cl source – Chloromethylether, metal Cl catalysts
  – Amination – No Cl source – Trimethylamine for standard anion
  – Regeneration and process chemicals and water
• “Location” of Chloride
  – Unreacted Cl sites (chlorine) in the copolymer matrix
  – Cl introduced into the copolymer matrix
  – Cl exchanged from regenerant chemical (NaOH)
Innovation – Ultra Low Chloride
Chloride Impurities in NaOH

Chloride Sites on Resin (%) vs Chloride in Caustic Regenerant (ppm) graph.
Innovation – Ultra Low Chloride Resin Specifications

- Specifications reduced – 5% Cl spec years ago
  - Westinghouse 1970’s Nuclear Grade – 3% of sites still used by some
  - Typical condensate – 0.5%
  - Nuclear Grade – 0.1%
  - Ultra Low Chloride – Too low to measure with existing methodology
Innovation – Ultra Low Chloride PWR Cond. Amine Operation

• Reduce Fe transport to Steam Generator (SG)
  – Limits IGSCC and extends SG life. Replacement cost up to ~$500M
  – Higher pH by increasing amine ETA concentration

• Cl leaches from NG anion at high pH with ETA
  – Can be >100 ppt Cl at vessel outlet – 2-5 ppb in the SG

• Need Ultra Low Chloride Anion
  – Lower than Condensate Grade (0.5%) and even Nuclear Grade (0.1%)
  – Not available in the market place
Innovation – Ultra Low Chloride PWR Condensate

- PWR determined on-site NaOH regen was Cl source
- GT developed treatment, process, and regeneration techniques to achieve ultra low chloride anion
- Dev new methods to measure Cl in NaOH and resin
- Manufactured and installed Ultra Low Chloride Anion
- First bed achieved <30ppt initial Cl. Adjusting process achieved similar and some higher results.
- Later beds achieved 20ppt, 14ppt, and <10ppt Cl and others remained in this range.
- As beds run, Cl levels continually decrease, <5ppt
Innovation – Ultra Low Chloride Benefits

- Amine form operation
  - Four years without regeneration – expect to exceed 5 years
  - Regenerant chemical cost savings
  - ETA cost savings

- Chemical cost savings ~$550,000
- Iron transport to steam generators reduced >50%
- Reduced some sludge lancing to alternate outages saved ~$650,000
- Manpower savings
- Potential for ULC in CVCS, blowdown demins, fuel pool
Innovation – Low Sulfate

• SG & reactor sulfate limits edge lower
• As manufactured cations not sufficient
• Superior quality cation needed
• Ultra low sulfate cation may be a great complement to the ULC anion
Innovation – Low Sulfate Source

- Strong acid cation – sulfonated copolymer
Innovation – Low Sulfate Source

- Polystyrene sulfonate oligomers
  - Remain in beads & diffuse out over time
- Polymer degradation/desulfonation
  - Time, temperature, oxidation
- Resin leakage through condensate system
  - Need proper particle size and strainers
Innovation – Low Sulfate SO$_4^-$ in Steam Generators

- Leachable polystyrene sulfonates pass through mixed bed to steam generator
- Can also foul anion component
- High temperature/pressure breakdown contaminants to sulfate in steam generator
- SG limits are low single digit ppb SO$_4^-$
- Leachable contaminant levels in condensate are much lower, often ppt and are not easily measured in the products
Innovation – Low Sulfate Sulfate Abatement

- Post manufacture processing needed
- Powdered resin experience helpful
  - Grinding exposes bead internals, no diffusion time
  - Refining treatments for 30 years to provide cleanest possible products
- Apply treatments to limit chance for unacceptable SO$_4$
- Currently evaluating several sources of condensate resins
  - Anticipating plant trials before end of 2008
Innovation – Low Sulfate Sulfate Abatement

- GT used low crosslinked cation for BWR Fe removal in the 90’s – significant learning experience
- $\text{SO}_4^2-$ leachables within 6-9 months after normal manufacturing treatment
- Acceptable $\text{SO}_4^2-$ performance when significant post-manufacturing process treatments applied
Innovation – Low Sulfate
Comments & Recommendations

• Fuelpool – High crosslinked cation successful in M/B – better withstand peroxide contact

• Condensate – Some partial success but may not be significantly different than normal 10% crosslinked condensate grade

• Some specs indicate a quality level need similar to electronics grade – UPW rinsed for low TOC and other contaminants
Innovation – Low Sulfate Comments & Recommendations

- Cation resins as manufactured can leach contaminants that contribute SO$_4$ to the condensate cycle
- Apply process treatments to achieve best results for bead products
- UPW grade products should be considered
- Quality is important and low price alone should not decide
Innovation – Low Sulfate Benefits

- Reduced sulfate in Steam Generators
- Reduced anion fouling – longer life
- Improved corrosion control
- Eliminate or reduce anion underlays
Innovation – SG Blowdown Demineralizers

• Condensate polishers for start-ups and condenser leaks at some PWR plants
• SGBD used to control cycle chemistry
• Specialty mixed beds for long runs
Innovation – SG Blowdown Demineralizers

• H form cation removes amine from cycle
• High ratio mixed beds
  – 3 cation:1 anion by volume or capacity
  – Longer run to amine break before regeneration or replacement
• Cation beds before mixed beds
  – Long runs and maintain H/OH mixed beds
Innovation – SG Blowdown Demineralizers

• High ratio mixed beds
  – Uniform mixing and stability important
  – Typical air mixing not always sufficient
  – Separation before packaging
Innovation – SG Blowdown Demineralizers

• Dry mixing - very consistent uniform batches
Innovation – SG Blowdown Specialty Product Benefits

• High ratios for amine and corrosion product capacity
• Dry blended for accurate uniform products
• Careful component selection and processing
• Primary secondary leak protection – radionuclide reduction
Innovation – Amine Form Cations

- Condensates
  - Ammonia, ethanolamine, hydrazine, morpholine
  - Hydrogen cation removes the amine
  - Amine can cost several $100,000
  - Operate in the amine form as described in ULC section
Innovation – Amine Form Cations

- Condensates (cont.)
  - High purity regenerant chemicals & rinses used to prepare ammonium form powdered resin
  - Same process for preparing other amine forms
  - ETA and morpholine most common
Innovation – Amine Form Cations

- Morpholine experience (2 x 1,200 MWe PWR)
  - SGBD – cation beds and mixed beds
  - Macroporous cation, high capacity gel anion
  - Excellent chemistry and minimal additional morpholine
  - Also use morpholine form powdered cation in the condensate polishing system
Innovation – Amine Form Cations

- ETA form cation possibilities
  - SGBD – cation beds and mixed beds

- Macroporous cation, high capacity gel anion
  - Condensate - Already used on-line amination

- Offer pre-treated cation
Innovation – Amine Form Cations

Benefits

• Reduced consumption and cost of amine
• More stable amine concentration in the cycle
• Reduced corrosion product transport
• Multi-year runlength
Innovation – Summary

- Ultra low Cl anion for lowest possible chlorides
- Regenerant and amine chemical cost savings with non-regenerable ULC anion
- Ultra low SO$_4$ cation for lowest SG sulfates
- Specialty SGBD mixed beds for optimal runlength and operation
Innovation – Summary

- Amine form cations for SGBD
- Amine form cations for condensates
- Significant cost savings for amine operation
- Ultimate condensate polishing – Ultra low $\text{SO}_4^-$ cation specially regenerated to the amine form and used with the ultra low Cl anion