IEX 2008

The Future Application of Ion Exchange to Power Generation Systems

by

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A BRIDGE TO THE FUTURE

THE PRESSURE FOR CHANGE - 1

- Water as an Available Resource
  - Generally Diminishing Availability for Industry
  - Moving to Poorer Quality Supplies

- Water as an "Environmental Sink"
  - Receiver of Waste Products from the Process
    - Ion exchange waste water
    - Fuel /Ash and environmental clean-up waste water (metals)
    - Heat sink for steam turbine cooling

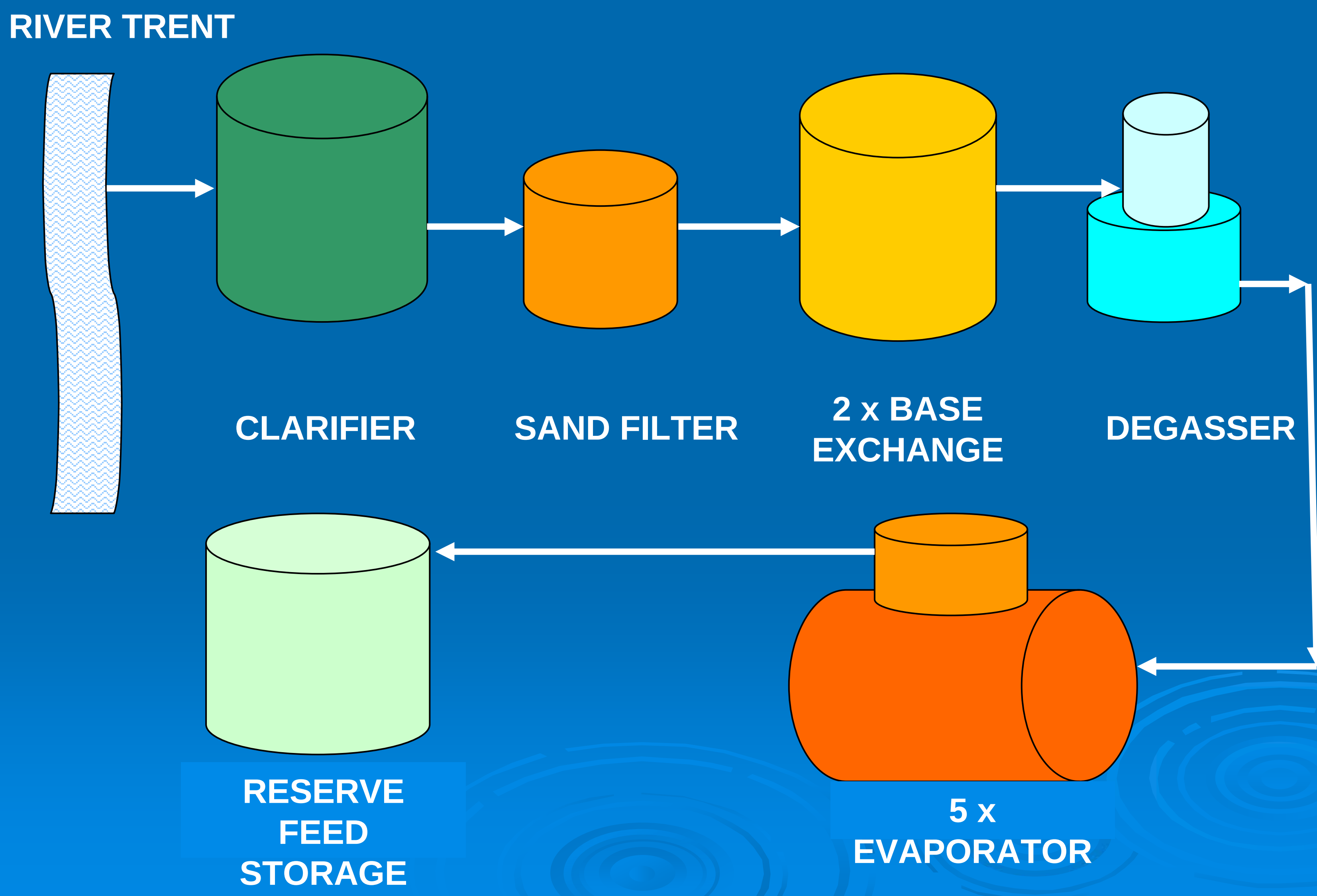
THE PRESSURE FOR CHANGE - 2

- Environmental Legislative Pressures
  - Environmental Discharges – to Air and Water
  - Classification of By-products and Wastes
  - Storage of Chemicals on Site

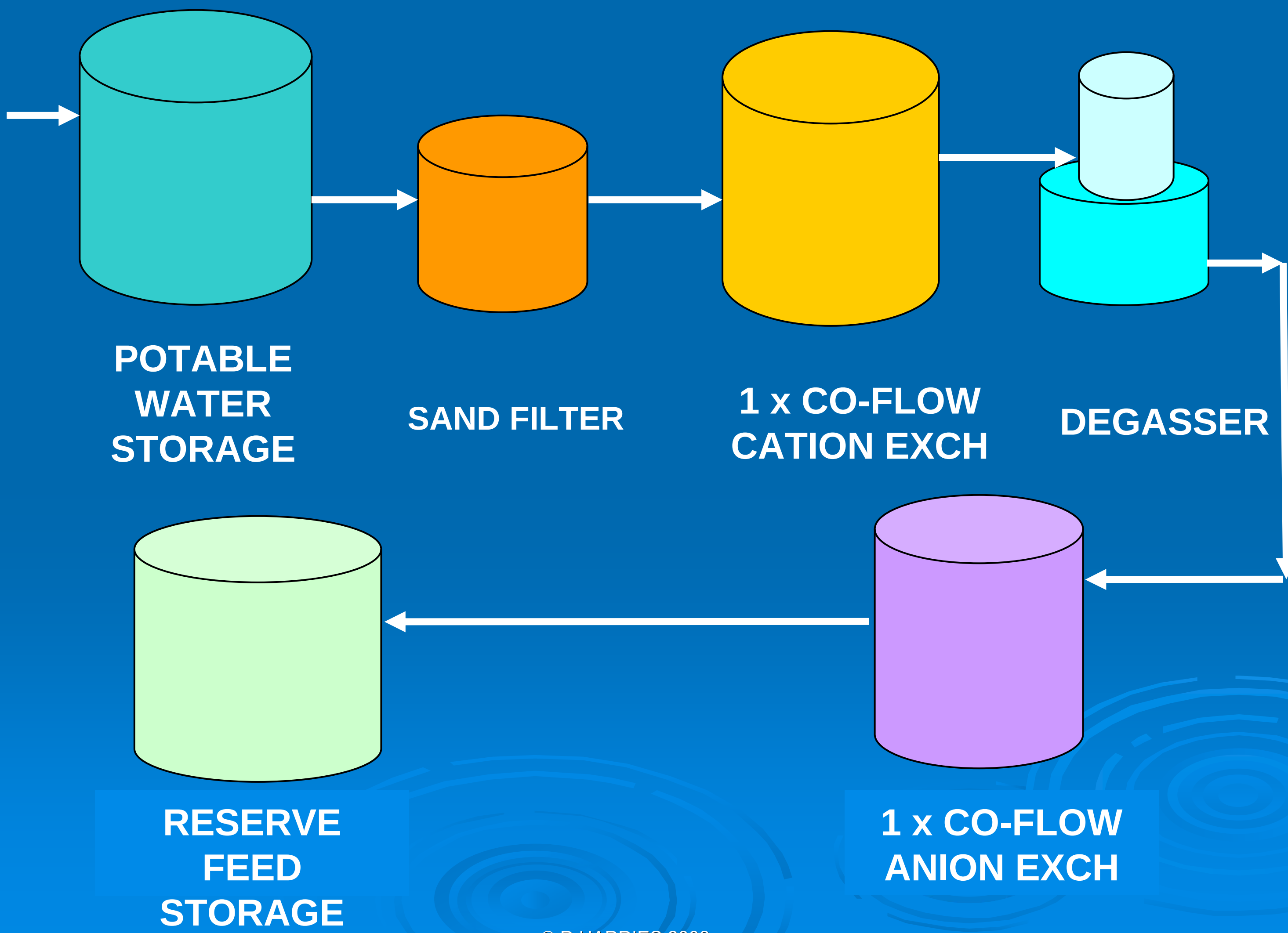
- General Economic Pressures
  - Reduce Capital Costs
  - Reduce O&M Costs

1960's TECHNOLOGY
(4 x 500MW Coal Fired Power Station)

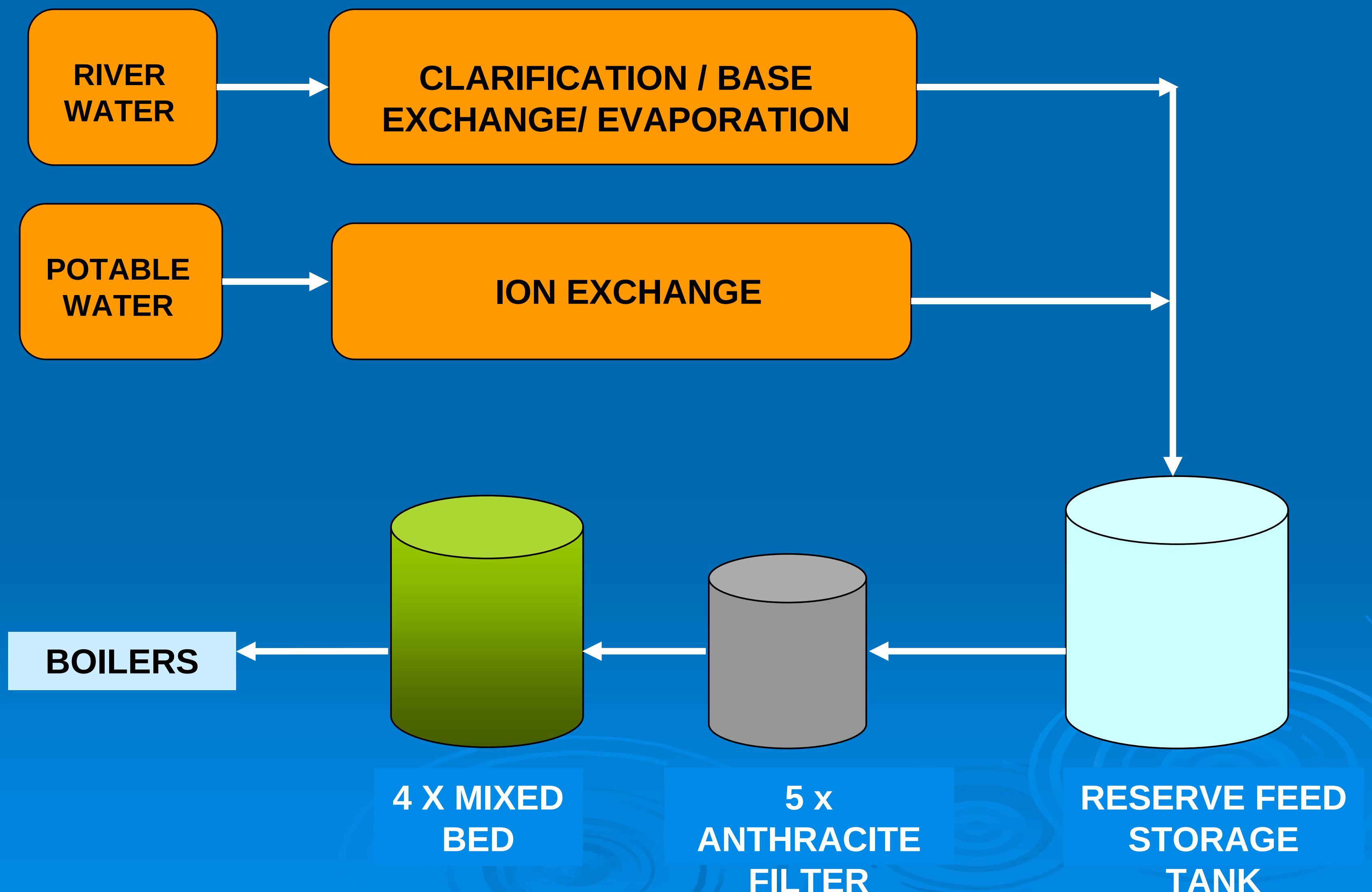
1960's BOILER MAKE-UP WATER PURIFICATION
CLARIFICATION / BASE EXCHANGE / EVAPORATION



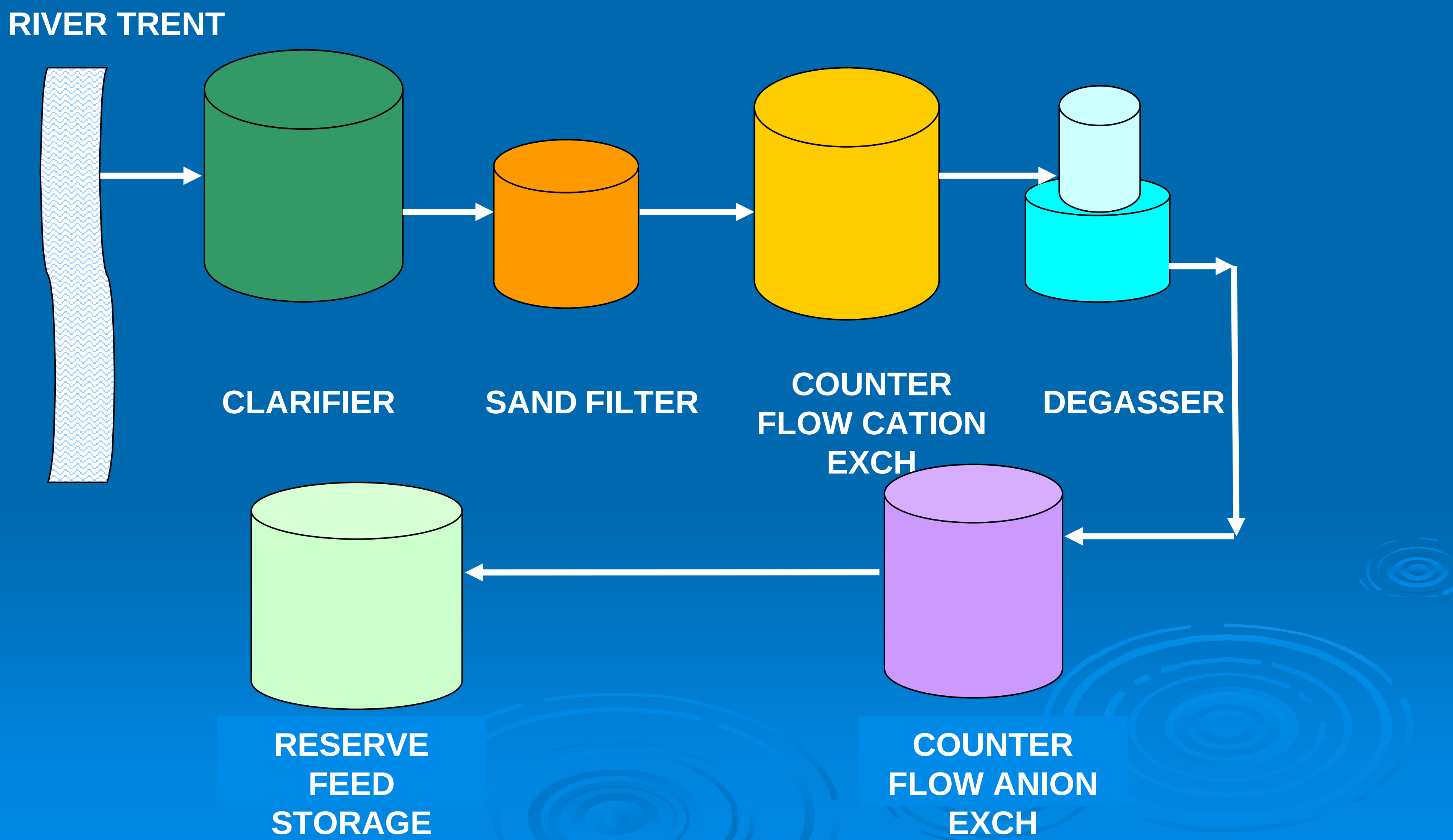
1960's BOILER MAKE-UP WATER PURIFICATION
ION EXCHANGE DEMINERALISATION



1960's BOILER MAKE-UP WATER PURIFICATION
FINAL POLISHING



1970's BOILER MAKE-UP WATER PURIFICATION
COUNTER-FLOW DEMINERALISATION



CONDENSATE POLISHING

- Ion Exchange Still the Only Practicable Option
- To Polish or Not To Polish?
  - Full Flow
  - Part Flow
  - Start-up and Emergency Polishing Only
  - Shared Polishing Between Units
  - Deep Bed or Powdered Resin
- Key Factors
  - Condenser Integrity
  - Cooling Water Source
  - Plant Design and Integrity
  - Commercial Flexibility

CONDENSATE POLISHING - 2

- Internal or External Regeneration
  - Regenerants → Resin (Internal)
  - Resin → Regenerants (External)
  - Condensate → Centralised Polishing Plant
- Design
  - Naked Mixed Bed
  - Cation + Mixed Bed
  - Separate Pre–Filtration
  - Separate Cation + Anion Beds
  - Flow Rate

CONDENSATE POLISHING – 3
Environmental Factors

- Discharge of Ammoniated Waste Liquors
  - Tighter Limits or Even Prohibition of Discharge of Ammoniated Waste Waters to Sensitive Water Courses.
- Treatment Options for Ammoniated Waste Water
  - On - Site or Off – Site
  - Recovery for Re-Use (eg Steam Stripping)
  - Micro - Biological Treatment
  - Exchange onto Zeolites (Clinoptilolite)
  - Electro-chemical Oxidation on Modified EDI

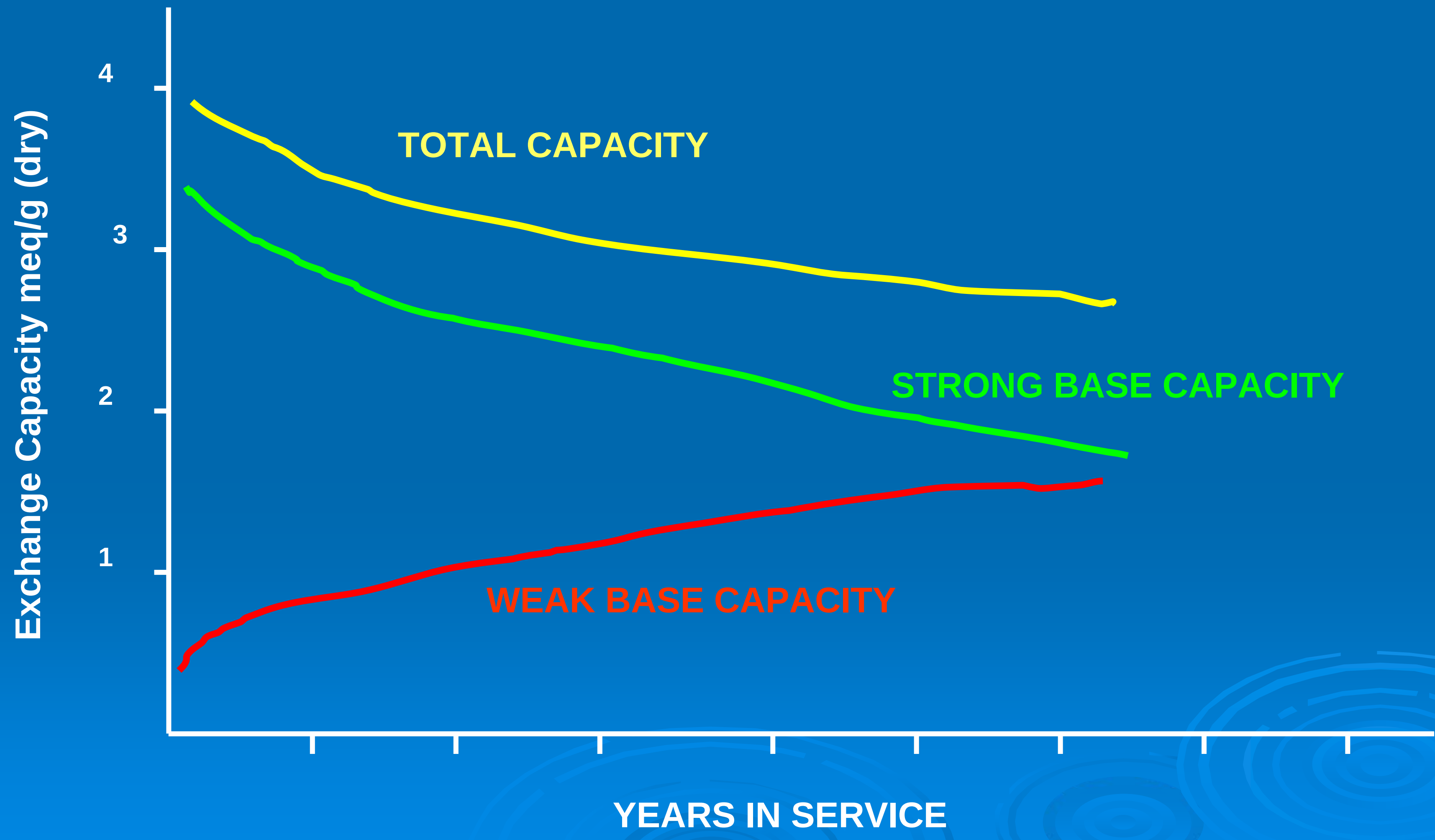
THERMALLY RESISTANT ANION RESINS
The Operational Need

- Cation Resin Thermal Resistance > 100^{o}C
- Anion Resin (Strong Base) Poorer Thermal Resistance
  - Hydroxide Form of Anion Resin Typical Limit 60^{o}C or Less
- ~20% of Steam Bypasses the Condenser
  - Improved Thermal Efficiency for Feed Heating
  - Source of Impurities and Corrosion Products
- Locate Polishing Plant Downstream in Higher Temperature Feed Water to Increase its Effectiveness.

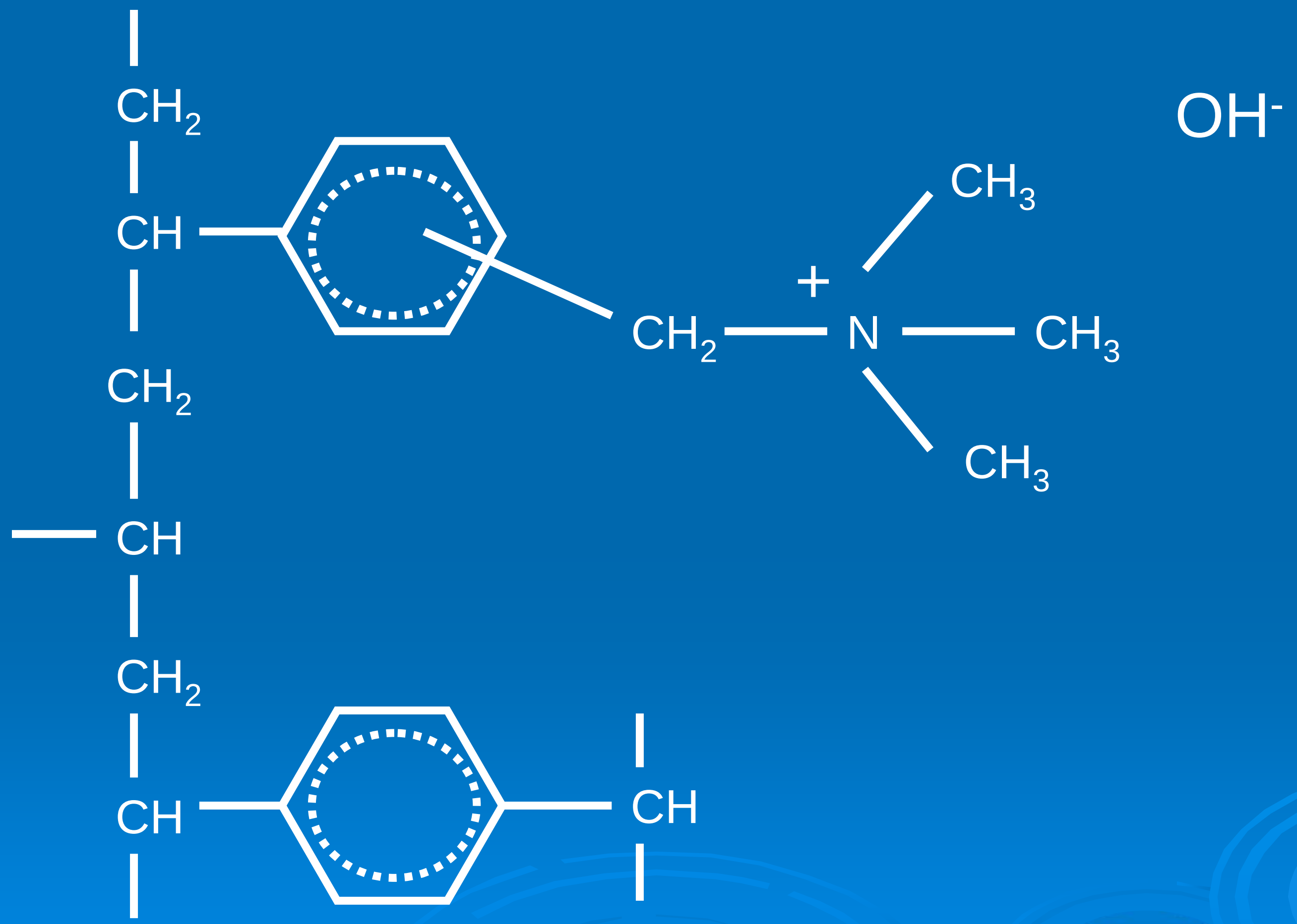
THERMALLY RESISTANT ANION RESINS – 2
The Environmental Factors

- Environmental Pressures to Reject Less Heat to Water Courses.
  - Electricity Generation Thermodynamically Inefficient
    - Current UK Coal Plant : 35-37%
    - New Generation Coal Plant : 41 – 43%
    - Gas Turbine + Heat Recovery Boiler : 55 - 58%
- Pressures to use Air Cooled Condensers in Place of Water Cooled Condensers
  - Reduces Thermodynamic Efficiency by 1 – 2%
  - Consequential Higher Condensate Temperatures
  - ACC Require Higher Ammonia in Condensate

TYPICAL INDICATIVE SERVICE CAPACITY LOSS FOR STYRENE STRONG BASE (TYPE I) ANION EXCHANGER



STRONG BASE ANION EXCHANGER
IDEALISED STRUCTURE – HYDROXYL FORM



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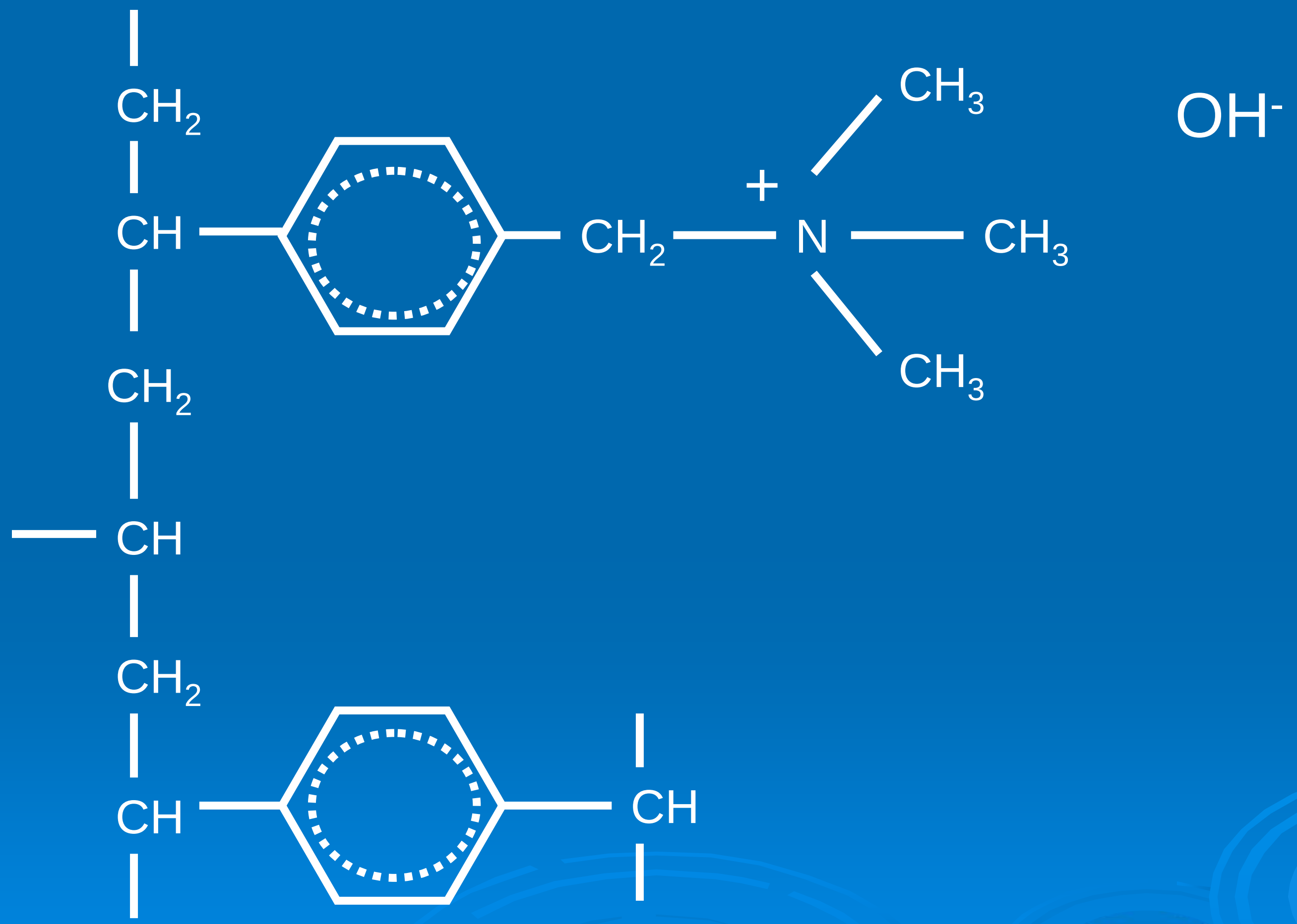


HIGH TEMPERATURE OPERATION
AIR COOLED CONDENSER – S AFRICA

- 6 X 660 MW Air Cooled Power Station
- Condensate Temperatures
  - Cool Season 50 – 55 ^{o}C
  - Hot Season 70 – 80 ^{o}C
- Condensate Polisher – Cation + Mixed Bed
- Mixed Beds Regenerated Infrequently
- Initial Charge of Macroporous Strong Base Anion Resin Operating Successfully >4 Years

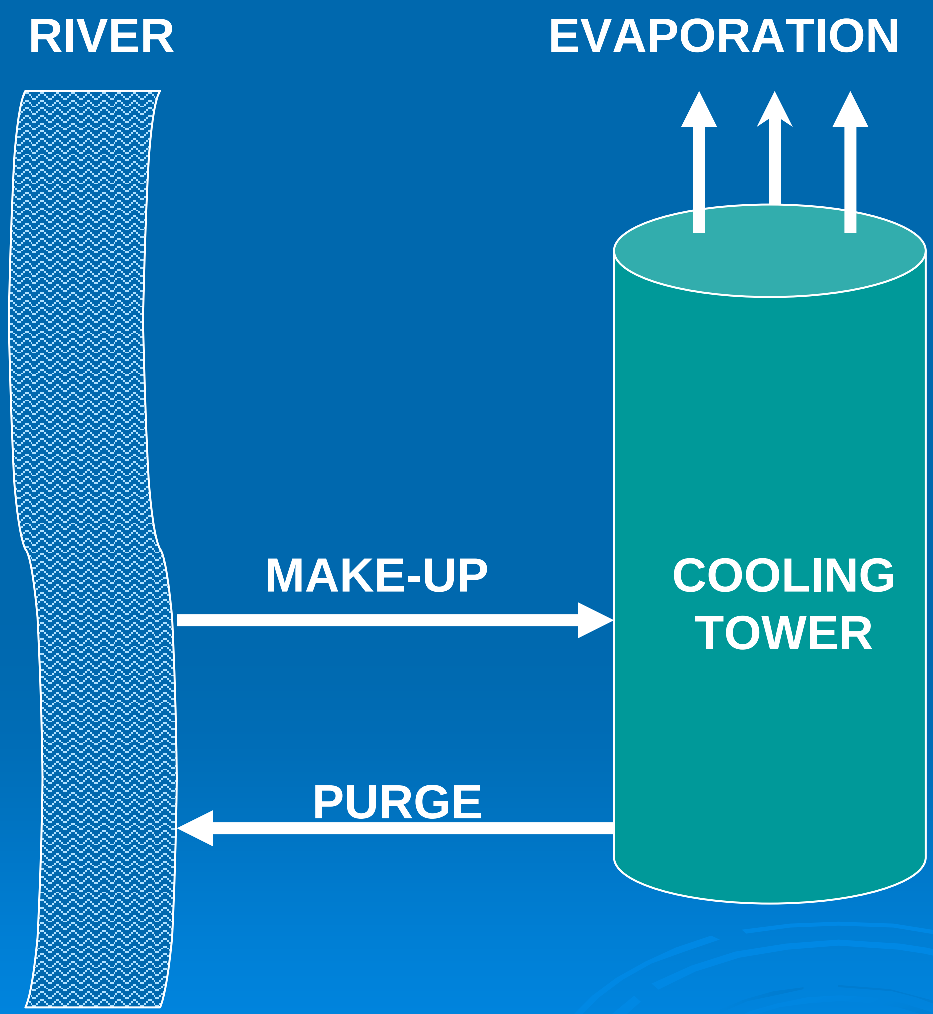
LONG TERM STAND-BY IEX PLANT

- Combined Cycle GT Power Plant
  - GT Fired on Gas or, in Emergency, on Distillate Oil
  - Use Water Injection During Distillate Firing
  - Ratio GT Water : Boiler Make-up = 10 :1
  - Regenerated IEX Streams Idle for Many Months.
- Strong Base (I) Anion Resin Tested After ~ 8 Years
  - No Significant Loss of Total or Strong Base Capacity

QUESTIONS ON HIGH TEMPERATURE OPERATION OF STRONG BASE ANION EXCHANGERS

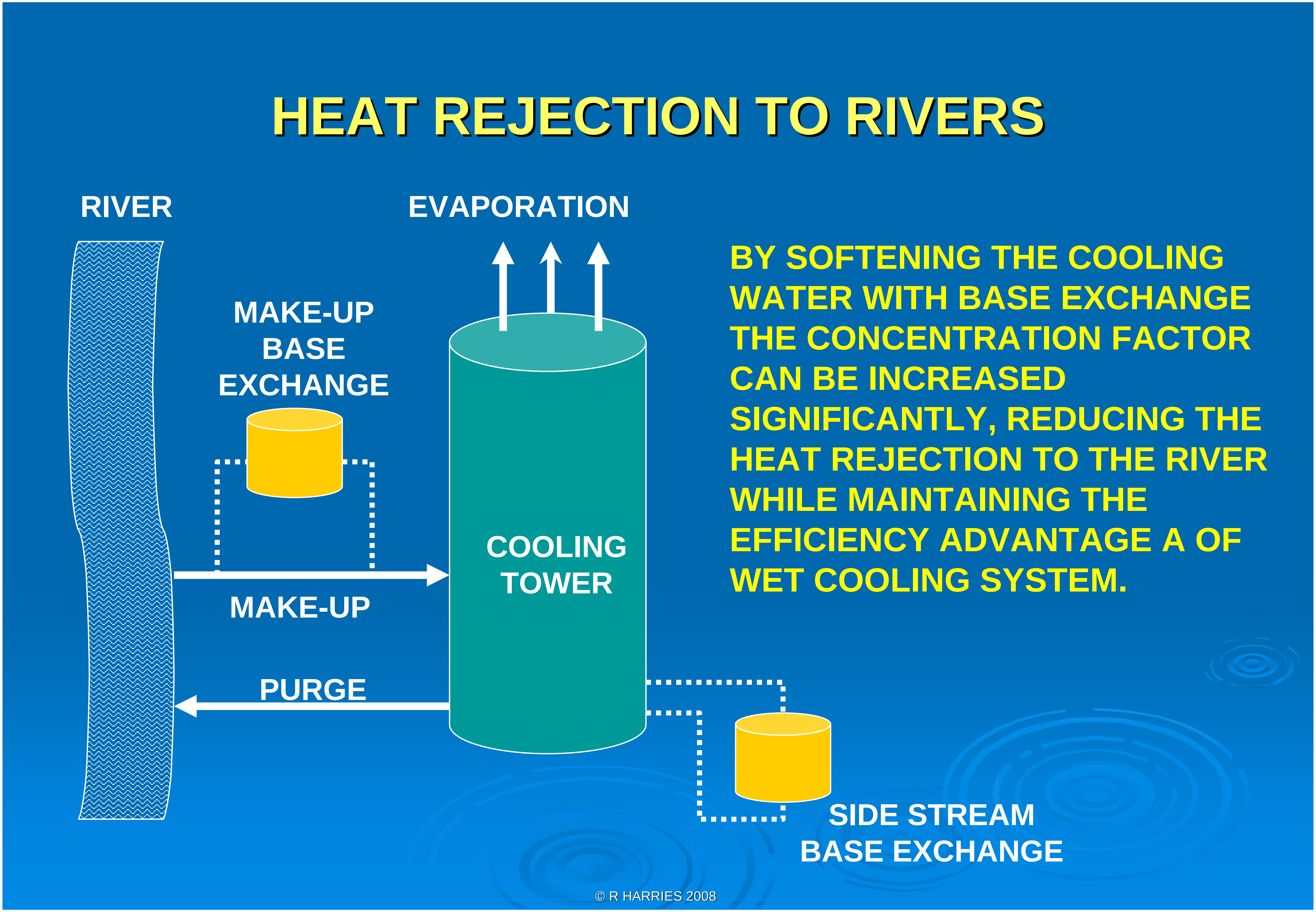
- Do the Primary “Ideal” Strong Base(I) Groups have an Inherently Good Thermal Stability?
- Is the Manufacture of the Resins (Raw Materials and Process Conditions) an Important Factor in Thermal Stability?
- Is the Frequency of Regeneration with Concentrated NaOH More Important than Time Spent in the OH^- Form in Overall Degradation.

HEAT REJECTION TO RIVERS



TYPICAL UK WET COOLING TOWER OPERATES WITH A CONCENTRATION FACTOR OF 1.5 .

INCREASING THIS FACTOR RISKS CALCIUM CARBONATE / PHOSPHATE SCALING OF THE CONDENSER TUBES.


HEAT REJECTION TO RIVERS
RIVER
EVAPORATION
MAKE-UP BASE EXCHANGE
COOLING TOWER
MAKE-UP
PURGE
SIDE STREAM BASE EXCHANGE
BY SOFTENING THE COOLING WATER WITH BASE EXCHANGE THE CONCENTRATION FACTOR CAN BE INCREASED SIGNIFICANTLY, REDUCING THE HEAT REJECTION TO THE RIVER WHILE MAINTAINING THE EFFICIENCY ADVANTAGE A OF WET COOLING SYSTEM.
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ORGANICS – THE INSOLUBLE PROBLEM?

- Removal of Naturally Occurring, Large Organic Molecules and Species.
  - Eg. Fulvic / Humic acids; Polysaccharides etc
  - Molecular weights 100's to 100,000's
- Natural Organic Species are Weakly Acidic
- Combination of Exchange and Adsorption
- Large Natural Organics are Not Fully Regenerated from the Anion Exchange Resins

DEVELOPMENTS IN ORGANICS REMOVAL

- Anion Exchange Resin
  - Dedicated Scavenger Beds or Main Beds
  - Strong Base or Weak Base Resin Styrene /dvb
  - Gel or Porous Structure
  - Iso-porous / Macroporous / Macroreticular
  - Low, Uniform Porosity Gel Type
  - Poly Acrylic / dvb Resins
    - Gel and Macroporous
    - Strong, Mixed and Weak Base Versions
- Combination of Polymer, Matrix and Basicity

1990s – THE "UK DASH FOR GAS"

- New Build Power Plants – All GT Combined Cycle
  - Functional Specification for Plant
  - New Power Plant Suppliers and Sub Suppliers
    - Often European not UK Based
  - New Water Treatment Plant Designs
    - Increased use of weak acid and weak base resins
    - Hydrochloric Acid for Regeneration
    - Lack of familiarity with UK water supplies
- Organics Leakage Problems Returned

POTABLE WATER RESOURCE AVAILABILITY

- Late1990's Demand > Supply for Potable Water
- Large Users Required to Find Alternative Supply
- For Power Plant - River Water Only Option
  - High Dissolved Solids
  - Variable and High Suspended Solids
  - Organics

REVERSE OSMOSIS

- RO Provides a Physical Barrier to Natural Organics
- Dual Function of RO
  - Reduces both Organic and Inorganic Components
- Key to Application of RO
  - Reduction in Capital and Running Costs
  - Improvement in Pre-Treatment and Pre-Filtration
  - Minimised RO Membrane Fouling
- Continuous Micro Filtration / Ultra Filtration
  - Rejects Suspended Solids
  - Rejects Bacteria
  - Robust and Backwashable

UF / RO

- Small Footprint – Easy to Retrofit
- Automatic Operation – Low Manning
- Discharges Only Influent Solids and Salts
- No Regenerants – Minimal Chemical Storage
- Dosing Limited
  - NaOCl to Protect UF Membrane
  - $NaHSO_3$ for Residual Chlorine Ahead of RO
  - Anti-scalant for RO
- Economics Favourable

UF - RO - IEX

- RO Still Requires an IEX Polishing Stage
- Retrofit to Existing Plant
  - Bypass Cation – Anion Beds and Use Mixed Beds
  - Feed RO Outlet to Front of Existing IEX Plant
    - Maintains Plant Flexibility for Alternative Water Supplies
- New Plant Options
  - UF – RO – Mixed Bed
  - UF – RO – Electro-deionisation (Zero Regenerant)
- Overall: Less Chemical Usage; Reduced Discharges

ENVIRONMENTAL CONTROL & CLEAN-UP (1)
FLUE GAS DESULPHURISATION (FGD)

- Wet Limestone – Gypsum FGD Process
- Produces a Waste Water Stream (~25 -50 m^3h^{-1})
  - High Concentration of $CaCl_2$ (up to 30,000 mg/l Cl)
  - Saturated in Gypsum ($CaSO_4.2H_2O$)
  - Trace Levels of Transition and Heavy Metals
    - Metal Cations Precipitated as Poly-sulphides to ppb Levels
  - Oxy-anions eg Borate, Arsenate, etc
    - Controlled But Not Currently Removed
    - Future Application for Ion Exchange?
    - Background Matrix Presents a Challenge!

ENVIRONMENTAL CONTROL & CLEAN-UP (2)
SELECTIVE CATALYTIC REDUCTION FOR NOx REMOVAL

- Inject Anhydrous Ammonia into Hot Flue Gas
  - NH_3 + NOx React on a Catalyst to Produce N_2
- Small Amount of Ammonia Leakage from Catalyst
  - Fouls Air Heater with $NH_4(HSO_4)$
    - Washed Off with Water
  - Accumulates in FGD Waste Water Stream
- Bulk Storage of Anhydrous Ammonia

ENVIRONMENTAL CLEAN-UP (2b)
SELECTIVE CATALYTIC REDUCTION FOR NOx REMOVAL

- Potentially Unacceptable Discharges for NH_4^+ and SO_4^{2-}
- Zeolite Clinoptilolite Removes Ammonia in the High Ca^{2+} Background Matrix
  - Slow and Poor Capacity on Granular Zeolite
  - Propose Use of Finely Ground Zeolite Slurry
    - Inject into FGD Waste Water Treatment Plant
    - Collect Reacted Zeolite in Waste Water Sludge
    - Refire Sludge with Coal

CONCLUSIONS (1)

- Ion Exchange is Likely to Dominate the Condensate Polishing Application for the Foreseeable Future
- Demineralisation Plants are Increasingly Likely to be a Combination of Membrane and Ion Exchange Processes
- There will be Continued Pressure to Reduce Storage and Consumption of Chemicals and the Disposal of Waste Regenerants

CONCLUSIONS (2)

- Abstraction and Use of Water in Power Plant will be Limited
- Water Sources will become More Difficult to Treat
- Cooling Water Softening may be Required to Limit Heat Rejection to Rivers
- Ion Exchange may need to be Developed Further for Environmental Treatment of Liquid Waste Streams

A BRIDGE TO THE FUTURE