Ion Exchange for Water Treatment:

Challenges, Solutions and Developments

Wolfgang H. Höll

Forschungszentrum Karlsruhe, Germany

KIT – die Kooperation von
Forschungszentrum Karlsruhe GmbH
und Universität Karlsruhe (TH)

ntroduction

ldest documentation of an ion exchange process:

ible, 2. Book Mose (Exodus) Chapter 15, 23 – 25:

Exodus 15:23

When they came to Marah, they could not drink the waters of Marah, for they were bitter; therefore it was named Marah.

Exodus 15:24

So the people grumbled at Moses, saying, "What shall we drink?“

Exodus 15:25

Then he cried out to the LORD, and the LORD showed him a tree; and he threw it into the waters, and the waters became sweet. There He made for them a statute and regulation, and there He tested them

ntroduction

odern interpretation:

ituation: No potable water available

hallenge: Production of potable water from saline raw water

ntroduction

odern interpretation:

hallenge: Production of potable water from saline raw water

olution: Application of ion exchange

ntroduction

odern interpretation:

hallenge: Production of potable water from saline raw water

olution: Application of ion exchange

Use of a biosorbent

ntroduction

odern interpretation:

hallenge: Production of potable water from saline raw water

olution: Application of ion exchange

Use of a biosorbent

Application in batch reactor

ntroduction

odern interpretation:

hallenge: Production of potable water from saline raw water

olution: Application of ion exchange

Use of a biosorbent

Application in batch reactor

One-time application, no regeneration

ntroduction

odern problem:

hallenge: Production of product water of a desired composition

ituation: Raw water of a given composition

olution: Application of ion exchange

- suitable exchangers
- suitable technology

spects:

- Efficiency
- Health issues
- Ecology
- Economic operation

ontents

- Ion exchanger materials
- Industrial water treatment
- Drinking water treatment
- Waste water treatment
- Prediction of plant performance

- Ion exchanger materials
- Industrial water treatment
- Drinking water treatment
- Waste water treatment
- Prediction of plant performance
- Conclusions

vailable ion exchange materials:

- Polymeric exchangers
- Inorganic materials
- Biosorbents
- Hybrid materials
- Magnetic micro exchangers
- further kinds

on Exchangers

xchangers: Usually porous materials

Functional groups distributed across the volume / surface

on Exchange: Interdiffusion of ions across an external film and within the porous phase

accompanied by an „immobilisation“ of target ions at functional groups

anufacturing of new exchangers:

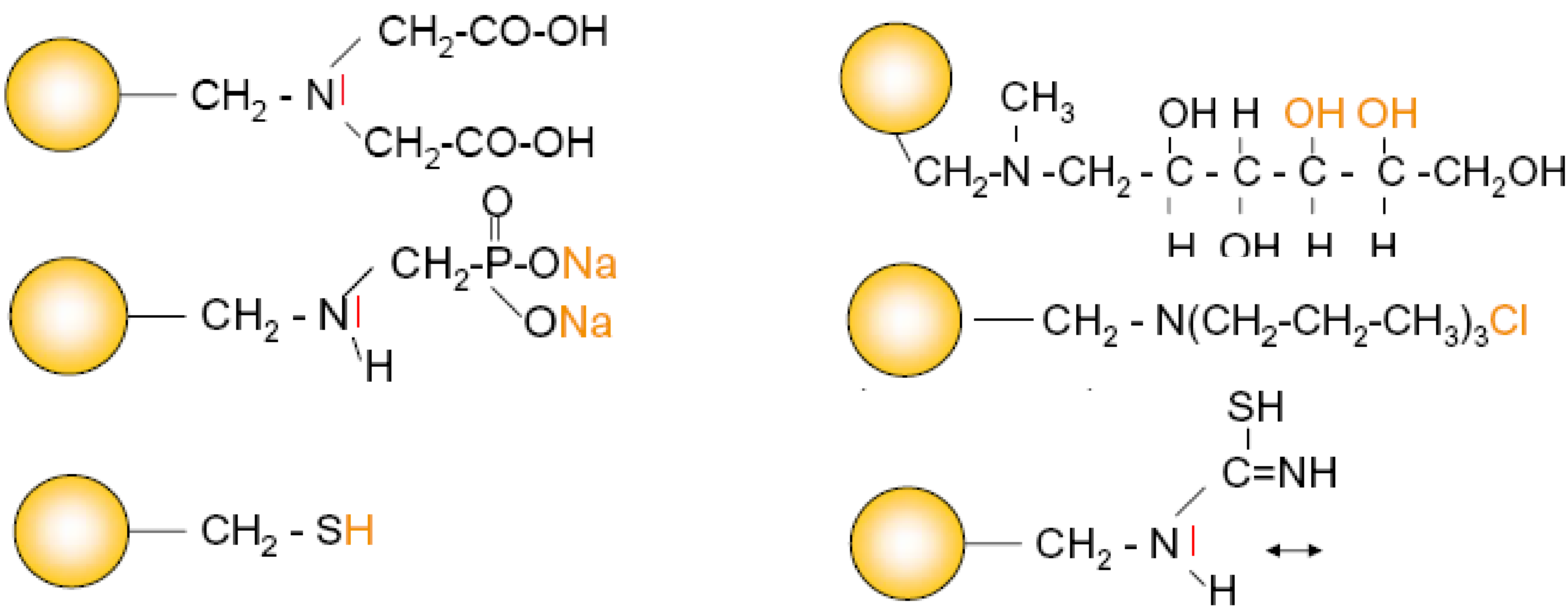
hallenges:

- physically and chemically stable
- fast internal diffusion
- preferred sorption of target ions, however, reversible immobilisation
- reasonable price
- ....

on Exchangers

hallenge: **Developing selectivity for target ions**

olution: **Synthesis of a spectrum of selective polymeric exchangers, e.g.:**



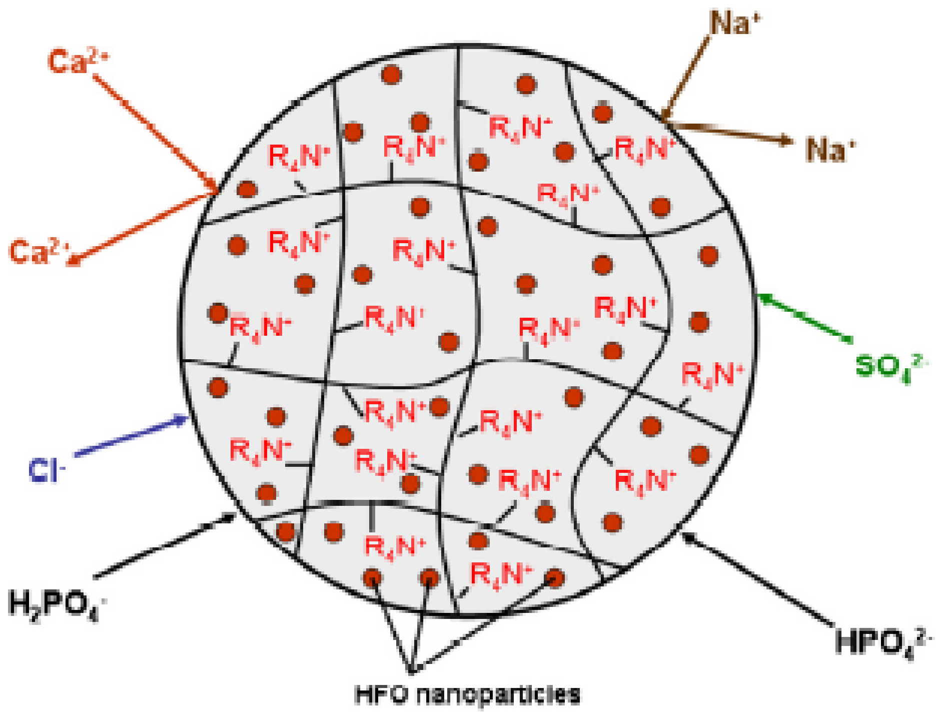
urce: S. Neumann, Lanxess Comp.: Green Environment through Lewatit, Recycling, Istanbul, 2007

urther attempts: **Solvent-impregnated exchangers**

Conventional exchangers pre-loaded with dystuff materials, like

- naphtol blue-black
- congo-red
- alizarin-red
- crystal violet

olution: **Synthesis of hybrid organic / inorganic exchangers:**



urces: S. Neumann, Lanxess Comp.: Green Environment through Lewatit, Recycling, Istanbul, 2007

L.M. Blaney, S. Cinar, A.K. Sengupta, Water Research 41 (2006), 1603 - 1013 olution: Novel inorganic exchangers, e.g.:

- Ferrocyanides
- Titanates, Silico-titanates
- Zr Phosphates, etc.
- Metal (hydr)oxides (FeOOH-, TiO_2, MnO_2-, CeO_2-based)
- …

- Al tungstate,
- Zr tungstate molybdate
- Ti iodovanadate

on Exchangers

hallenge: Selectivity for further species (F^-, …)

erhaps: targetted modification of existing (standard) exchangers ???

Application of molecular modeling methods ??

on Exchangers

hallenge: Acceleration of kinetics at trace concentration levels

roblem: Mass flux according to Fick‘s first law:

$$\frac{\dot{N}}{V_R} = a_S D_{eff} \frac{\partial c}{\partial r}$$

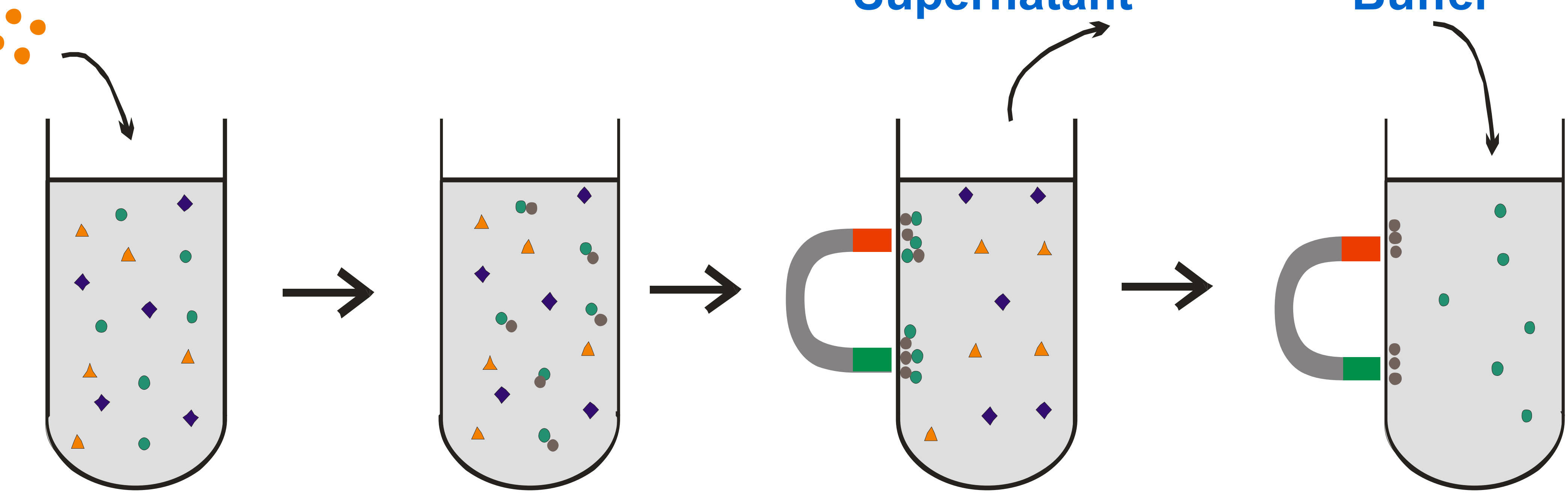
olution: Increase of specific surface = application of smaller resin beads,

Magnetic properties needed for handling

dvantages: Fast kinetics, simple process design

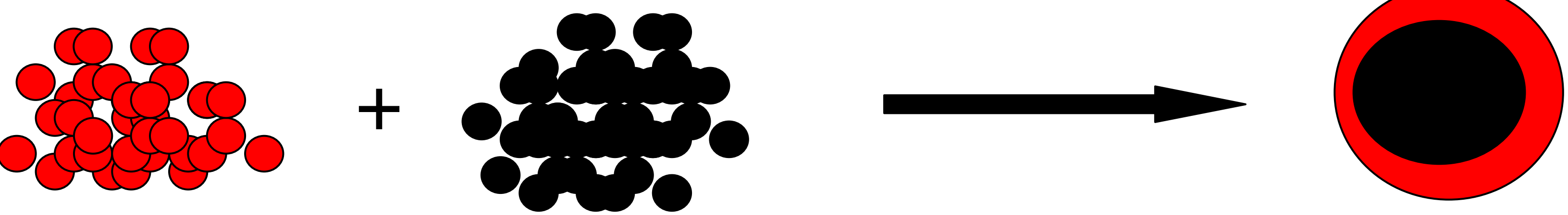
on Exchangers

agnetic fishing:



urce: M. Franzreb

urther developments: „Magnetic“ inorganic exchangers



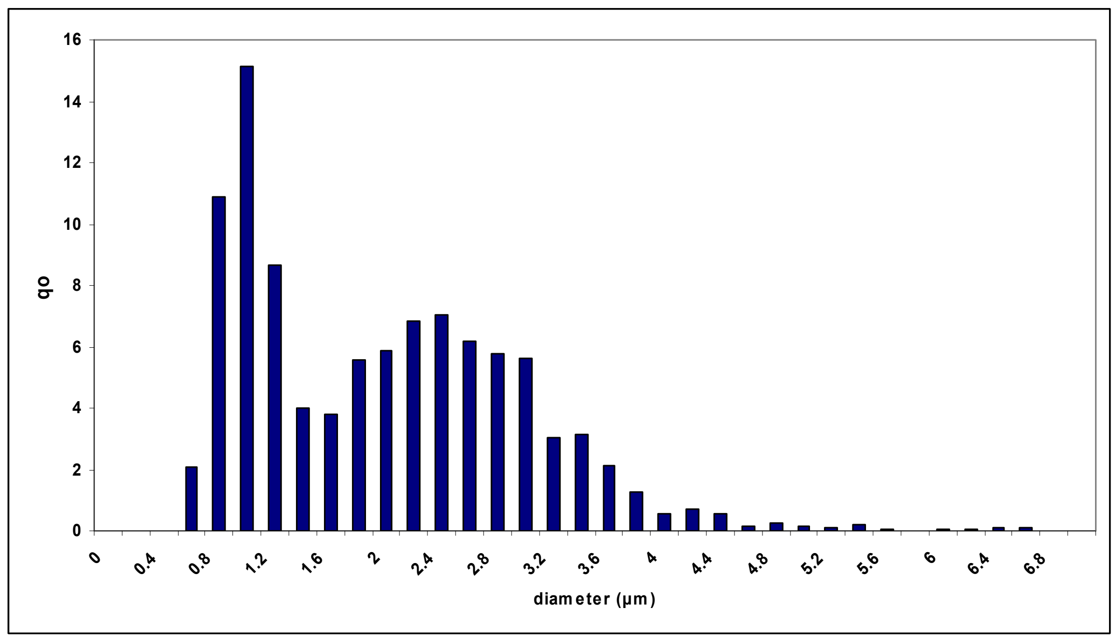
$Al(OH)_3$ Magnetite / Magnetic

MnO_2 Maghemite Micro exchanger

TiO_2

Ca-Silicate

....



urce: C. Salinas, Thesis, Karlsruhe Research Center (under preparation)

on Exchangers

hallenge: Cheap sorbents (for one-time application)

olution: a) Biosorbents = dead biomass:

Materials containing acetamido, alcoholic, carbonyl, phenolic, carboxy, amido, amino, imidazol, phosphate, sulphydryl groups

Examples: bacteria, algae, yeast, fungii, peat, bark, hulls of peanuts and beans, leaves, rice husks, jatropha husks, straw, Chinese reed, bagasse, coir pith, chitin, chitosan, …

b) Inorganic waste materials:

Examples: red mud, Cr(III)/Fe(III) waste, fly ash, …

art 2

- Ion exchangers
- **Industrial water treatment**
- Drinking water treatment
- Waste water treatment
- Prediction of plant performance
- Conclusions

ndustrial Water Treatment

hallenge: **Production of boiler feed water from tap / salt-bearing water**

ypical Requirements:

Parameter	Required	
Conductivity	< 0.1 µS/cm	- < 0.06 µS/cm
Sodium	< 3 µg/kg	
Chloride	< 3 µg/kg	
Sulfate	< 3 µg/kg	- < 0.5 µg/kg
Silica	< 10 µg/kg	- < 4 µg/kg
TOC	< 200 - 300 µg/kg	

urce: J. Belles-Baumann, PowerPlant Chemistry 7 (2005), 4 – 12, Purolite comp., Condensate purification, techn. Bull., 1999

ndustrial Water Treatment

olution:

- smart combination of weakly and strongly electrolyte exchangers,
- suitable technology
- optimum operation during service and regeneration

roblems remaining:

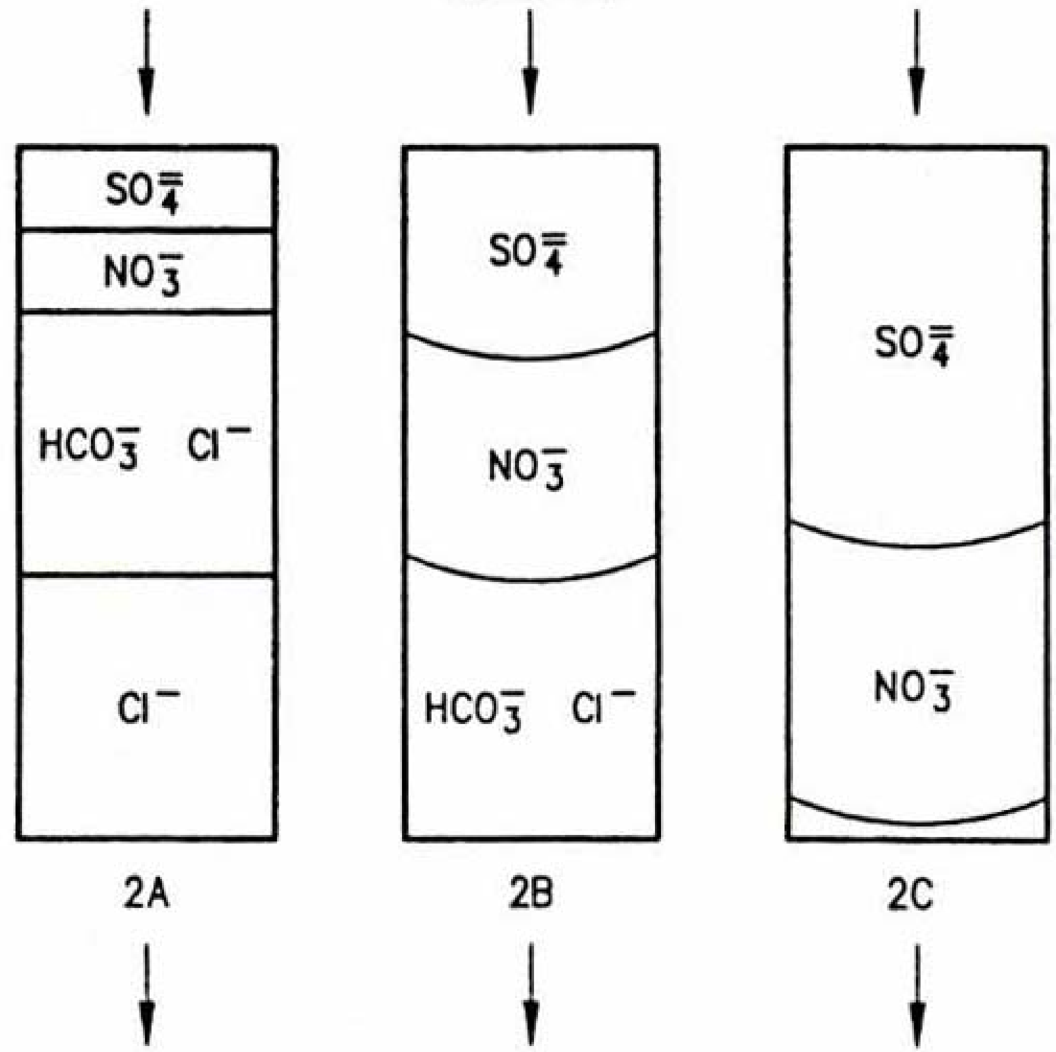
- performance of NOM
- elimination of silica

evelopment of Ion Exchange

ulticomponent systems: Formation of loading zones

xample:

-Cl⁻ + SO_4^{2-}, NO_3^-, HCO_3^-

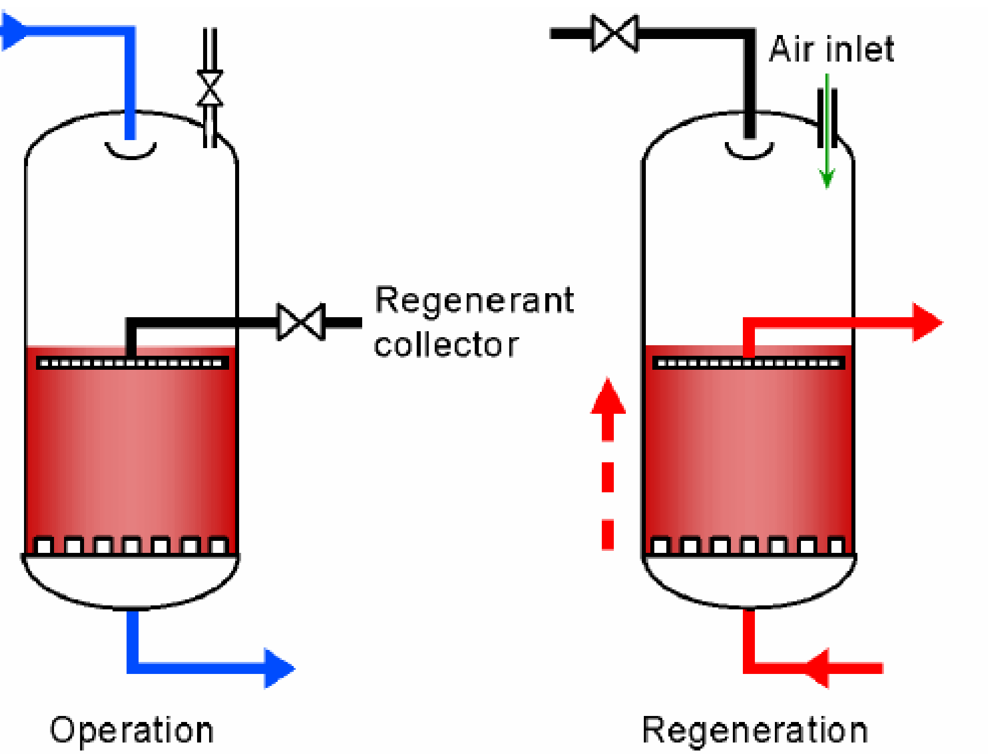


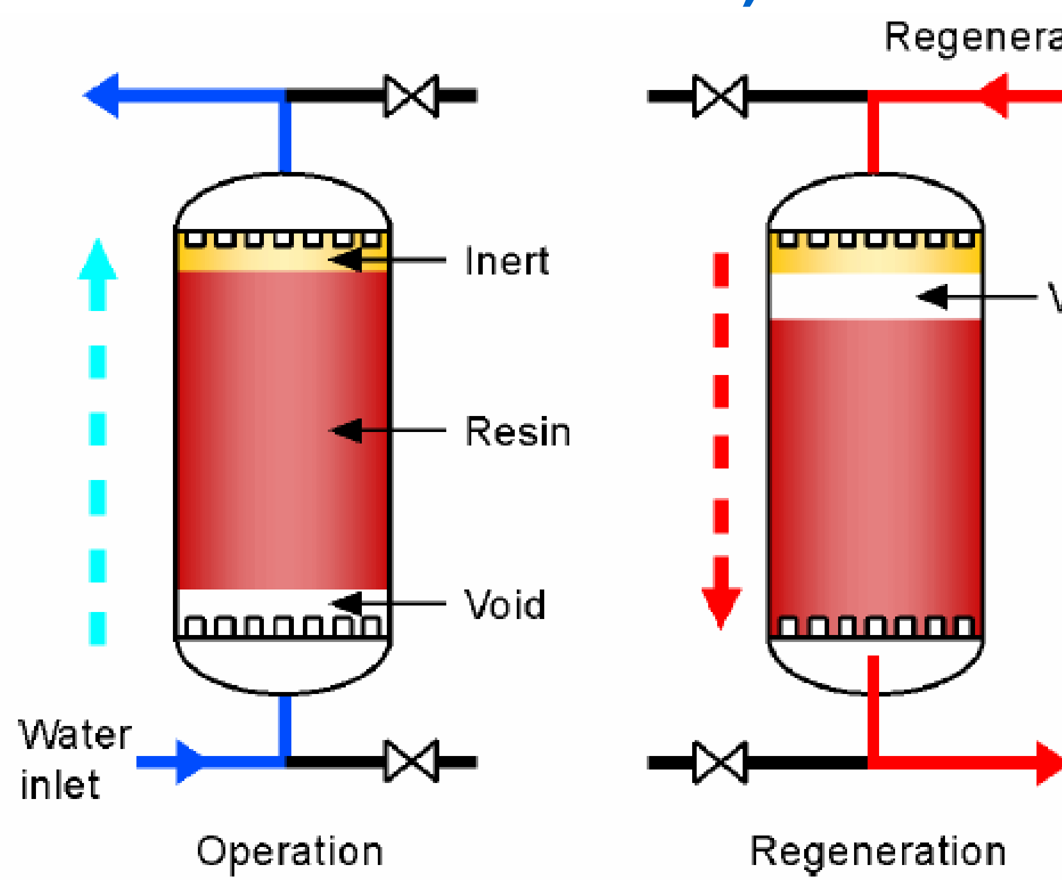
urce: G. Guter, Ion Exchange Technolgy, A. Sengupta (Ed.), 1995

evelopment of Ion Exchange

onsequences:

) Counterflow regeneration (different modifications)





Air hold down

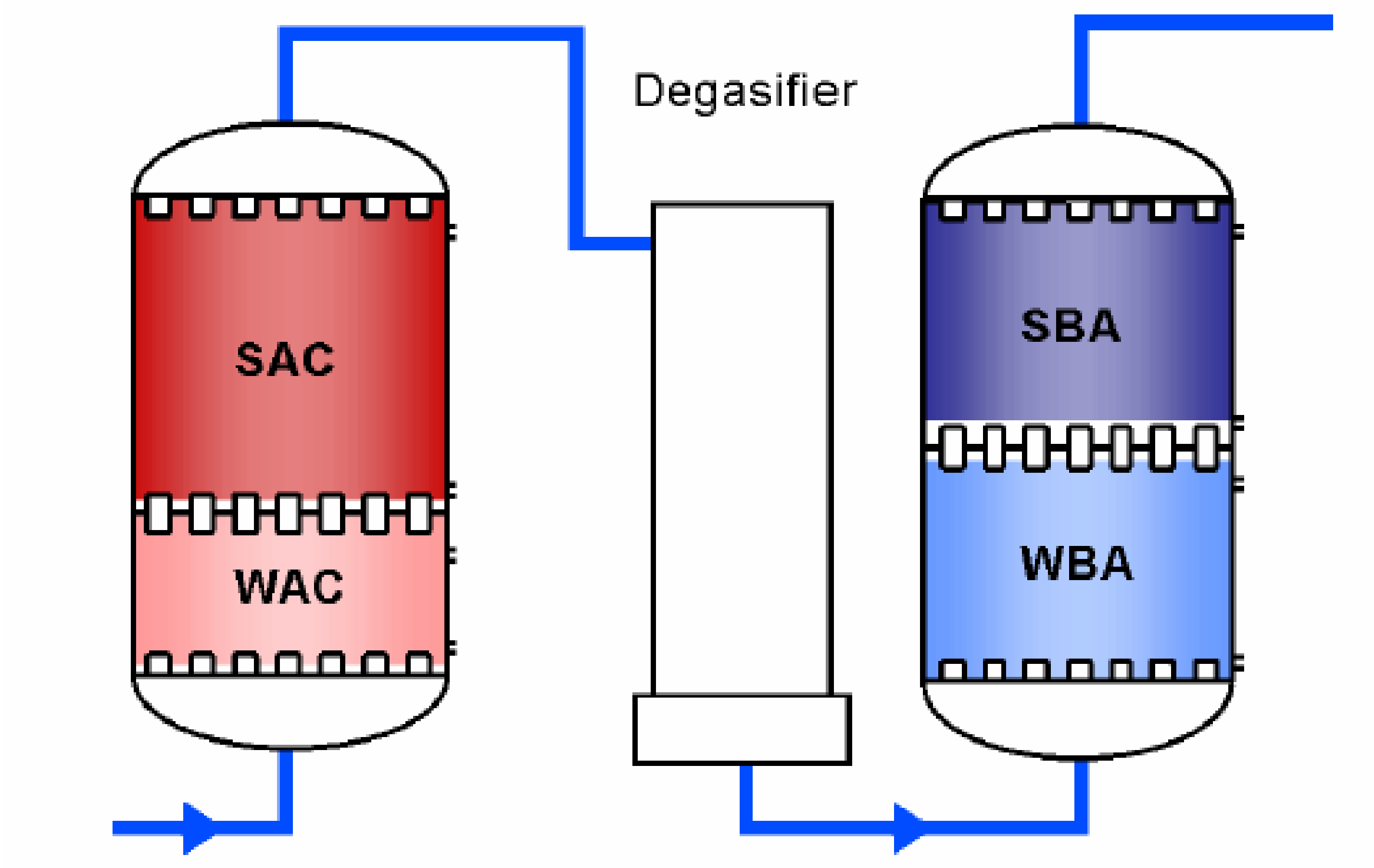
Packed bed

urce: J. Belles-Baumann, PowerPlant Chemistry 7 (2005), 4 - 12

evelopment of Ion Exchange

onsequences:

) Combination weakly / strongly electrolyte exchanger



urce: J. Belles-Baumann, PowerPlant Chemistry 7 (2005), 4 - 12

ondensate Polishing: Elimination of corrosion products

roblem: Usually low concentration of ions

asic fact: Ion exchange develops if the exchanger material is not in equilbrium with liquid phase composition

Driving force = distance to equilibrium

small

ndustrial Water Treatment

ondensate Polishing:

hallenge: - Elimination at high flow rates

- High temperature, > 90 °C

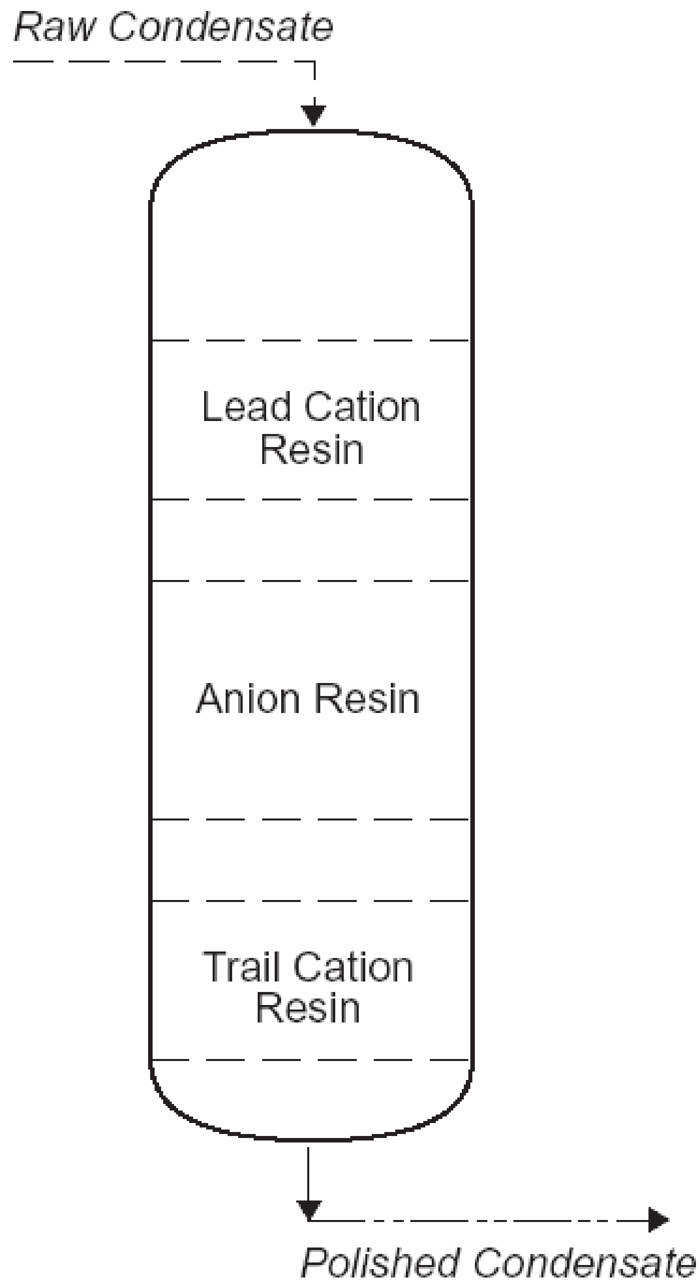
- No release of impurities from resins

olution: Smart combination of exchangers / operatio of plants

ndustrial Water Treatment

olution:

ripol bed



urce: DOW, Guide to Condensate Polishing, 2003

ndustrial Water Treatment

hermal stability of olymeric resins:

otal and strongly basic apacities as a function f temperature and perating time esin: Type 2

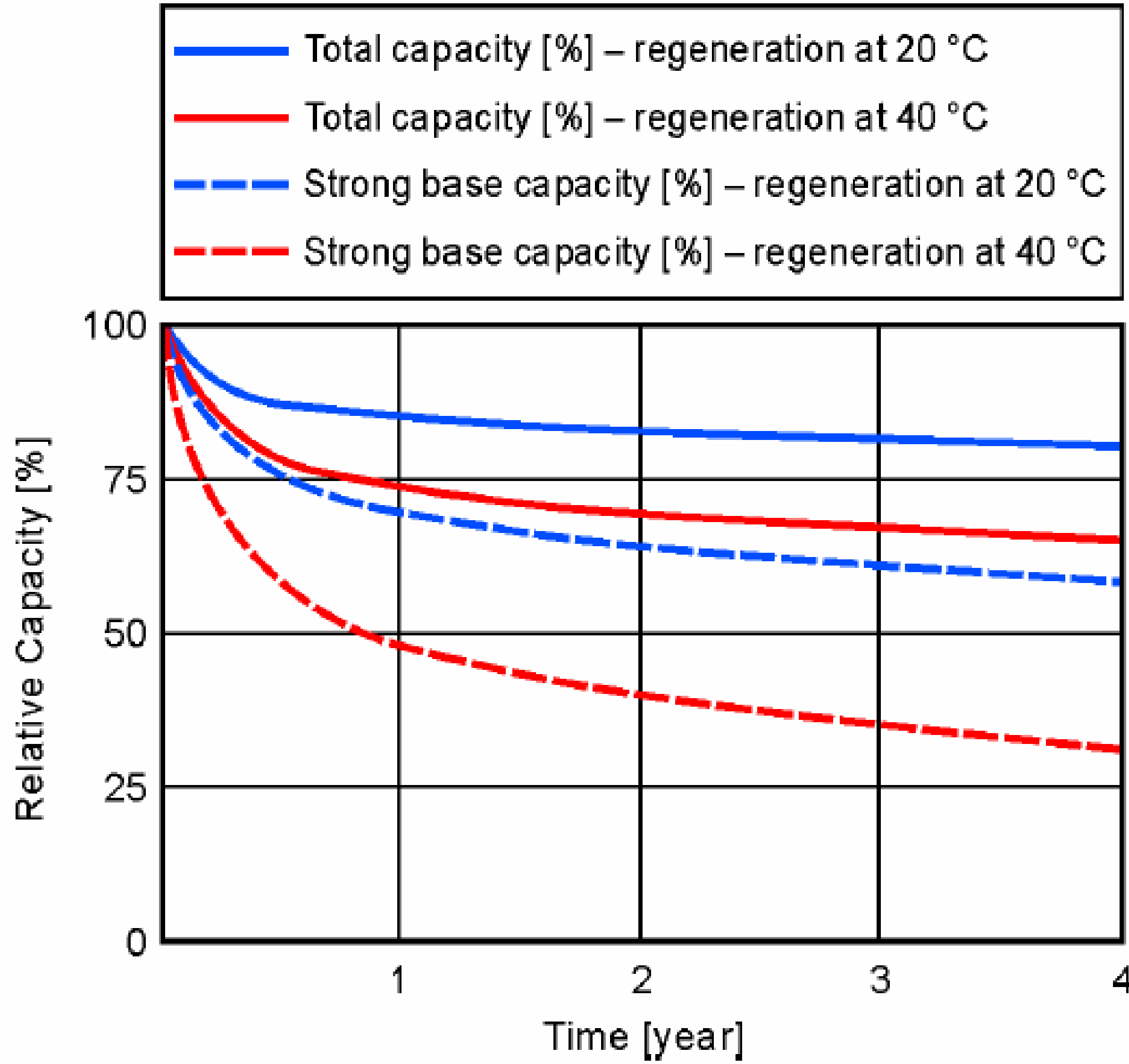


table anion exchangers ?‘

ource: J. Belles-Baumann, PowerPlant Chemistry 7 (2005), 4 – 12

ndustrial Water Treatment

ltrapure Water:

hallenges: - to demineralize water which is already demineralized water

roblem: Distance to equilibrium very small,
again: small driving forces

ltrapure Water:

hallenges:

- master the limited stability of resins
- master the regeneration problem <u>if applied</u> (trace contaminations in chemicals)
- elimination of silica and boron down to low levels

ltrapure Water:

esired Rinsing Water Quality:

Memory Size	256M	1G	4G	16 G	64G
TOC, ppb	> 1	< 1 – << 0.5	< 1 - < 0.5	< 1 - <0.5	<0.5 ?
B, ppt	< 100	< 50	< 50	10 – 50	10 – 50 ?
Na^+, ppt	< 7	< 5	< 2	< 2	< 1
F^-, ppt	30	30	< 10	< 10 ?	< 5 ?
Cl^-, ppt	< 20	< 20	< 10	< 5	< 5 ?

ource: J. Hutcheson, Filtration + Separation, June 2006, 22-25

olutions:

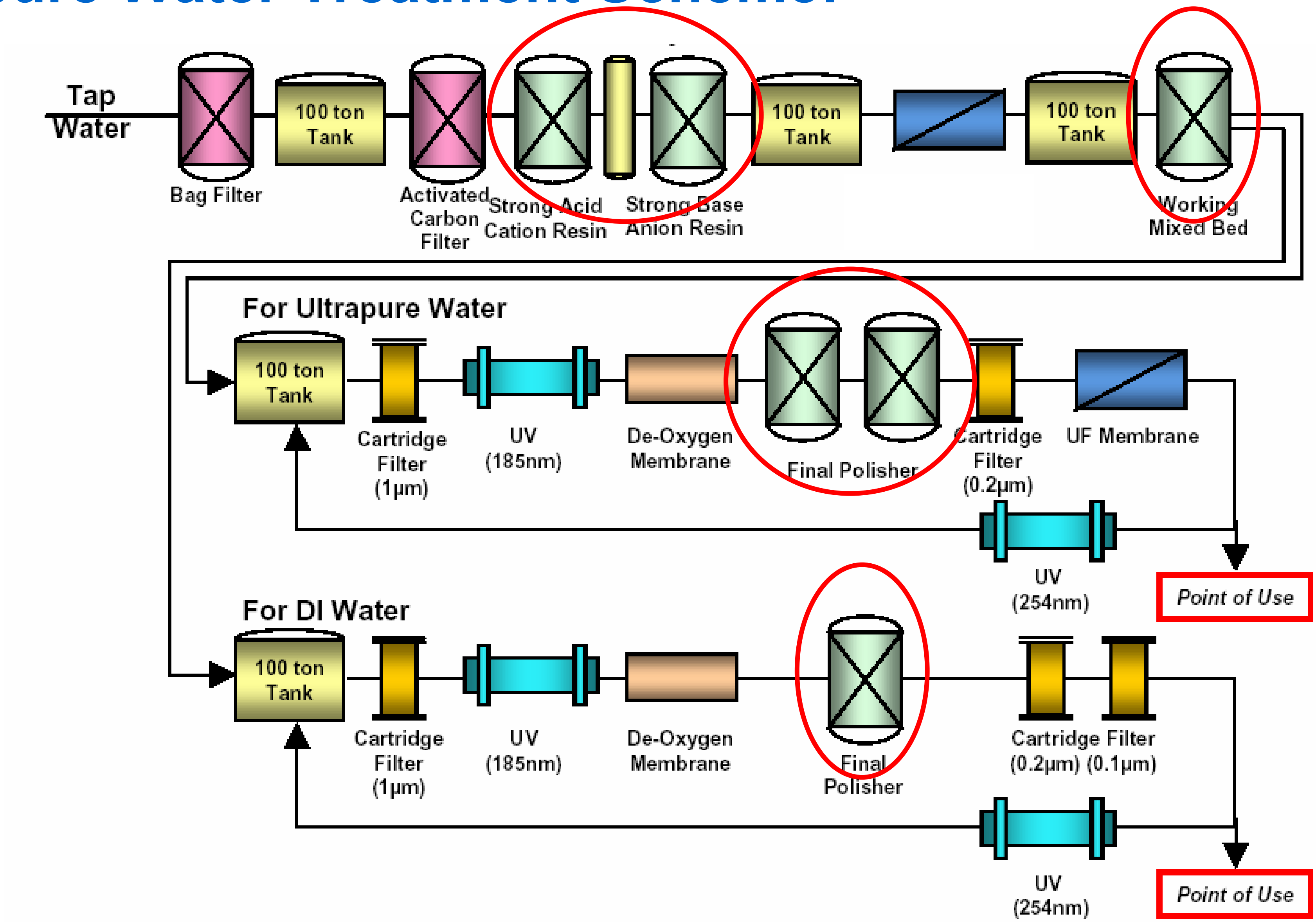
- carefully pre-treated or regenerated exchangers or exclusive use of fresh exchangers (elution of organics)

- physically stable exchangers (decomposition, release of fine beads)

- application of selective exchangers (boron

ndustrial Water Treatment

ltrapure Water Treatment Scheme:



urce: **DOW, DOWEX™ Ion Exchange Resins, Case History, Form No. 177-02021-0704**

art 3

- Ion exchangers
- Industrial water treatment
- **Drinking water treatment**
- Waste water treatment
- Prediction of plant performance
- Conclusions

rinking Water Treatment

hallenges:

Removal of bulk components (Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, HCO_3^-, NOM) below desired concentrations

Standards for nitrate:

< 50 mg/L , or < 10 mg/L NO_3-N

No complete elimination needed

Removal of hazardous trace contaminants (heavy metals, arsenic, fluoride, …) below standards

Almost complete elimination is compulsory

rinking Water Treatment

ealth-related and ecological constraints:

Negligible release of organic compounds from the exchangers

No increase of amount of bacteria in product water

Minimum discharge of effluents/salts from regeneration

rinking Water Treatment

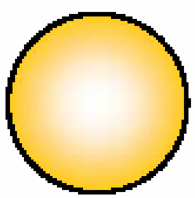
hallenge: **Nitrate Removal:**

rocess: **Exchange for chloride**

$$\overline{R{-}N^{+}(R_a)_3\,Cl^{-}} + (NO_3^{-}, SO_4^{2-}, HCO_3^{-}) \Leftrightarrow \overline{R{-}N^{+}(R_a)_3\,(NO_3^{-}, SO_4^{2-}, HCO_3^{-})} + Cl^{-}$$

roblem: **Sulphate preferred by conventional exchangers**

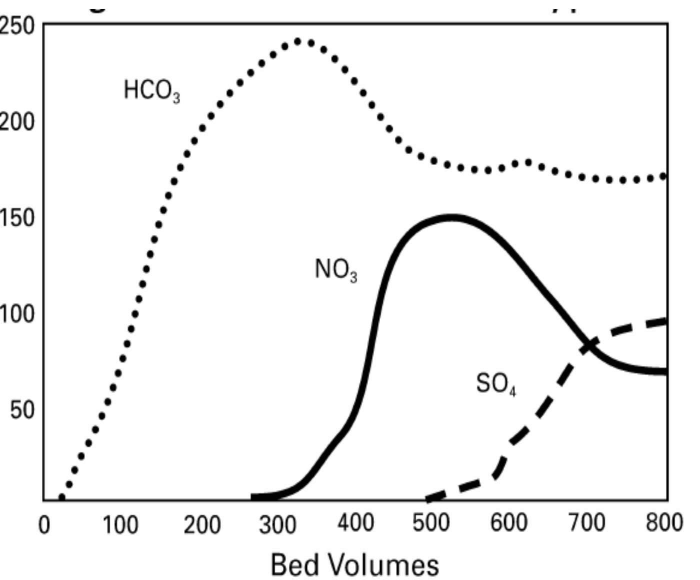
olution: **Development of „selective“ anion exchangers**

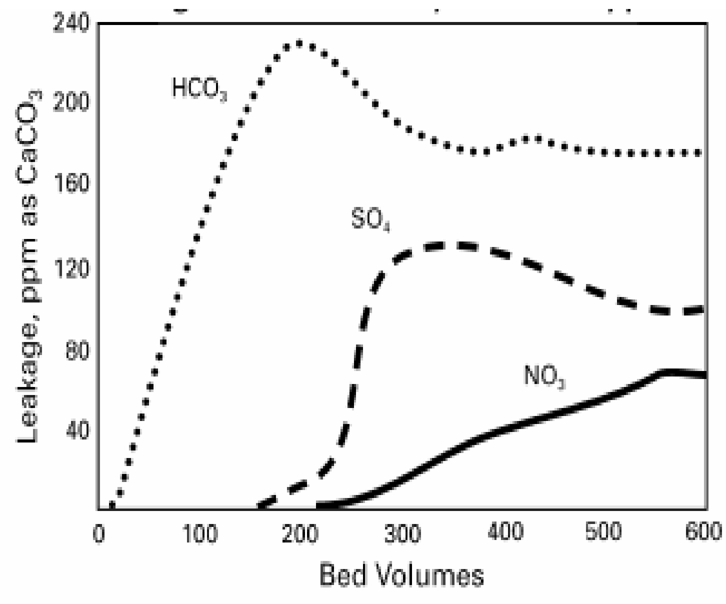


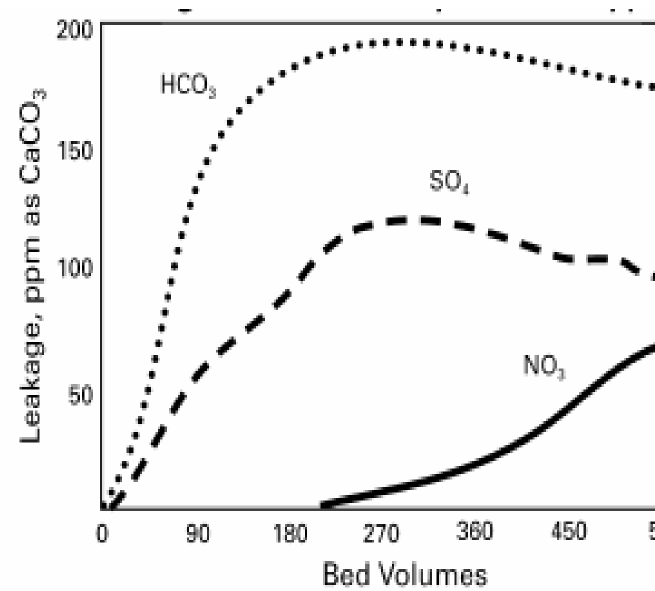
$$—CH_2 - N(CH_2\text{-}CH_2\text{-}CH_3)_3Cl$$

urce: **J. Neumann, Lanxess, Green Environment through Lewatit**

reakthrough Performance:







Conventional Type 2 **Tri-ethyl** **Tri-butyl**

urce: F.J. de Silva, ResinTech. Inc., www.waterinfocenter.com, 2003

rinking Water Treatment

hallenge: Decrease of amounts of unused NaCl

olution:
- Elimination of nitrate from spent regenerant
- Re-use of regenerant after spiking

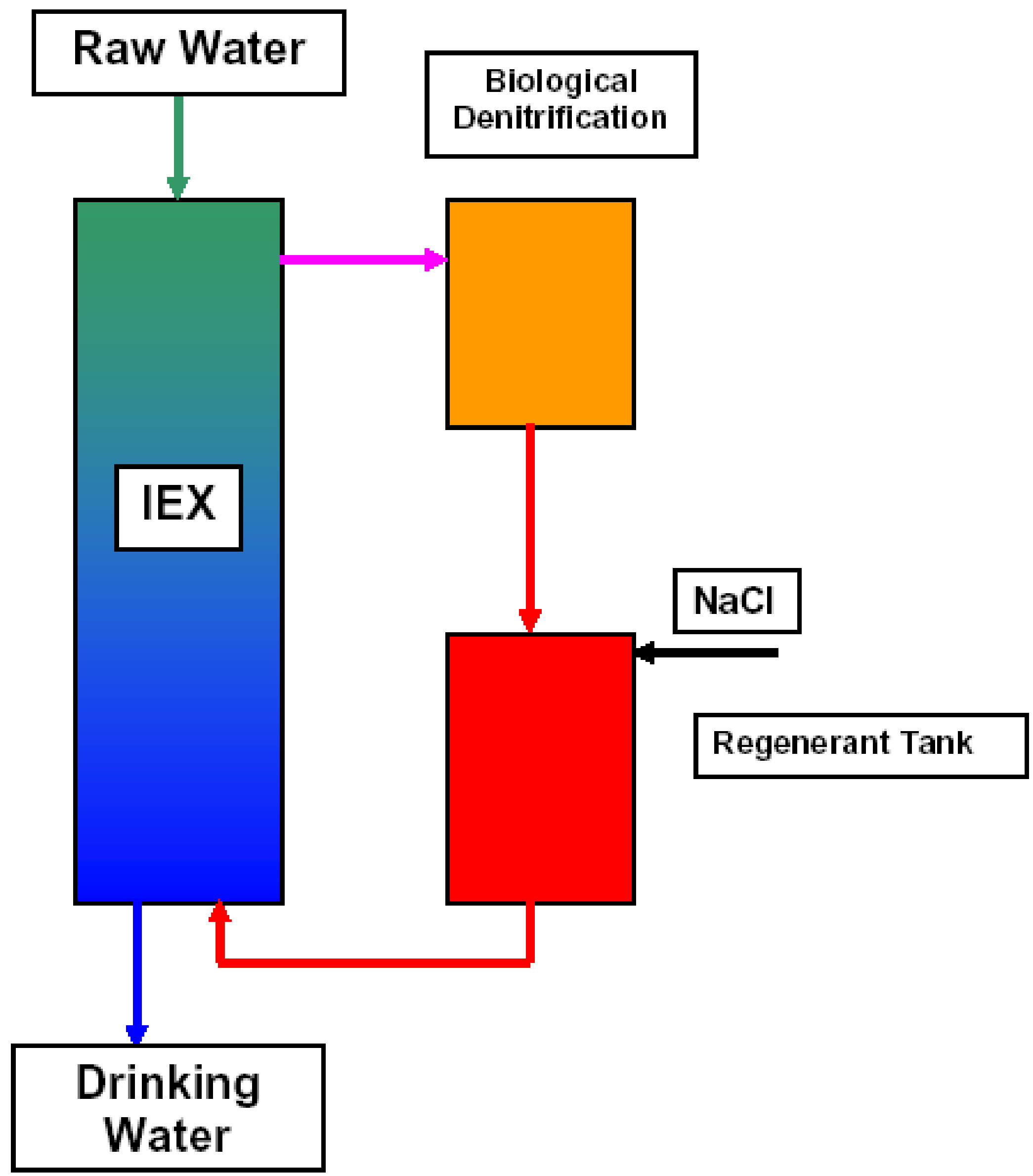
pproaches:
- Biological denitrification (Van der Hoek, 1988)
- Electrochemical denitrification (NITROUT process)

Drinking Water Treatment

Nitrate elimination coupled with biological denitrification in spent regenerant

Pilot plant tests in The Netherlands

Conventional strongly basic resin

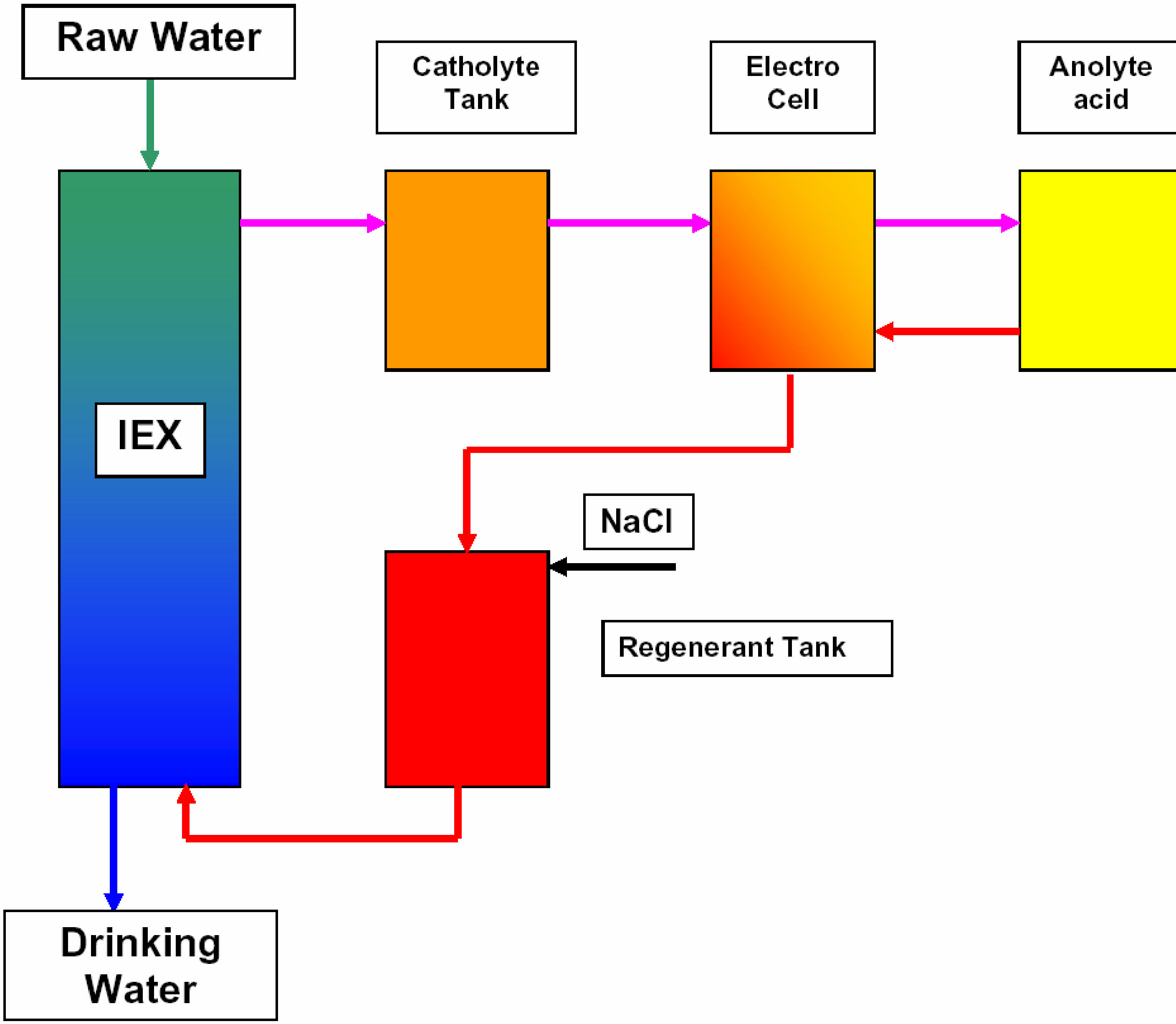


Drinking Water Treatment

NITROUT Process

Application of nitrate-selective resin,

Successful demonstration campaign in Germany



Drinking Water Treatment

Nitrate removal through partial demineralization:

Problem:

- Two different regenerants always double the quantity of salt equivalents in the effluent

Solution:

- the product of the service cycle has to regenerate both exchangers at the same time.

Approaches:

- SIROTHERM process (dissociation of H_2O)
- CARIX process (carbonic acid cycle)

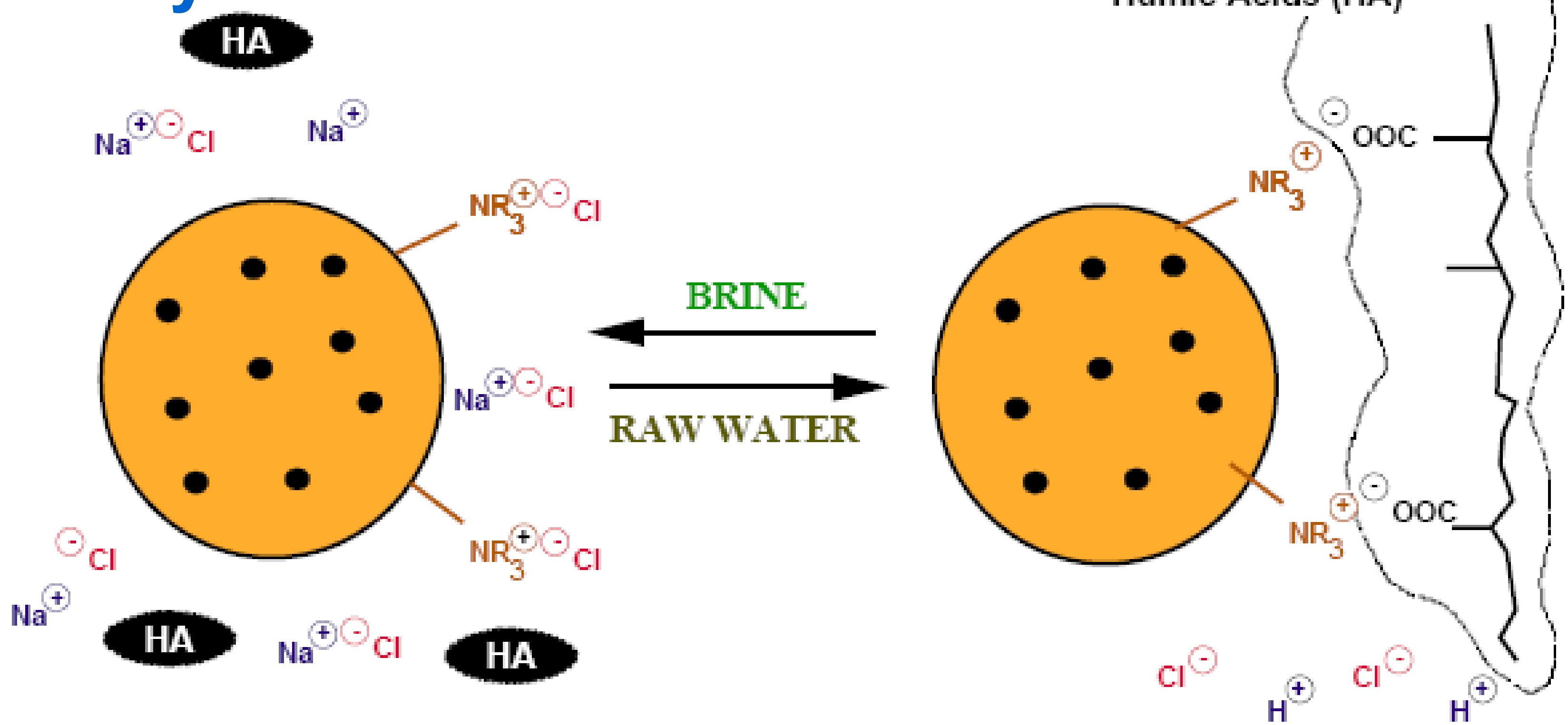
rinking Water Treatment

hallenge: Reduction of unacceptable levels of NOM

olution: Application of strongly basic anion exchangers

ew approach:

- Application of magnetic strongly basic exchangers in chloride form
- Regeneration by means of brine solutions



ourtesy of ORICA Comp.

Problem/Challenge: Unacceptable amounts of NaCl in wastewater

Solution: Removal of NOM from spent regenerant by means of micro/ultrafiltration rinking Water Treatment

imination of Trace Contaminants:

nallenge: **Far-reaching elimination in the presence of a background composition with much higher concentrations**

olution: **Selective elimination by means of suitable exchangers / processes is compulsory**

hemical Parameters of EU for Trace contaminants: :

Mercury	1 µg/L
Antimony	5 µg/L
Cadmium	5 µg/L
Arsenic	10 µg/L
Lead	10 µg/L
Selenium	10 µg/L
Chromium	50 µg/L
Nickel	20 µg/L
Fluoride	1.5 mg/L

urce: EU Drinking Water Directive

rinking Water Treatment

imination of Trace Contaminants:

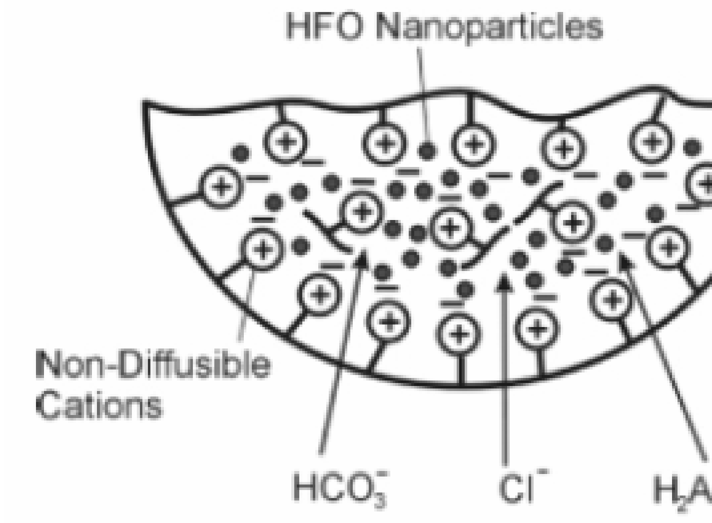
arget Species	Suitable Exchanger
rsenic	Iron (hydr)oxide-based materials
valent heavy metals	- IDA resins in Ca^{2+} form - Weakly basic resins in free base form - Hydrous metal oxides / hybrid resins
xy anions	Weakly basic resins in free base form
	…

rinking Water Treatment

xample 1: Arsenic sorption by eans of iron (hydr)oxides:

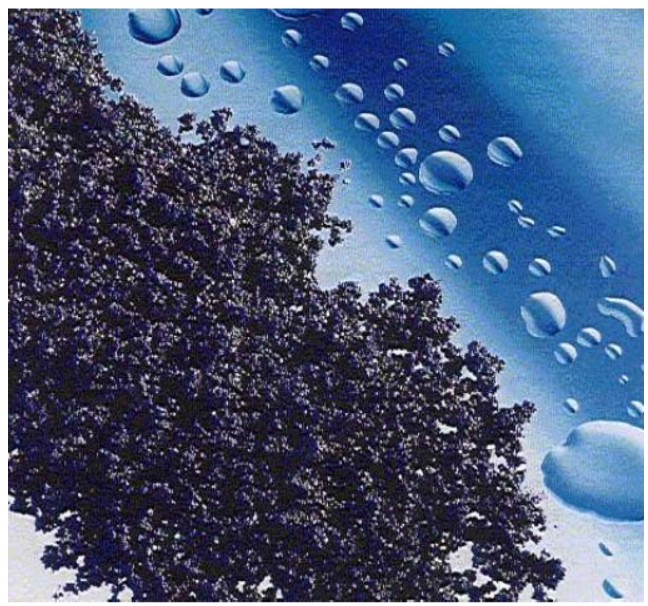
$$\overline{>Fe-OH} + H^+ \Leftrightarrow \overline{>Fe^+} + H_2O$$

$$\overline{>Fe^+} + H_2AsO_4^- \Leftrightarrow \overline{>Fe-H_2AsO_4}$$



ifferent Materials:

- GFH
- Bayoxide E 33 (GFO)
- GTO (Adsorbsia, TiO_2)
- Hydrous ferrous oxide nanoparticles in polymer structure



urce:, GEH Wasserchemie, ARSENEX®, L Cumbal, AR Sengupta, Env. Sci. Techn. 2005, 39, 6508

rinking Water Treatment

xample 2: Nickel removal, application of chelating ion exchangers:

$$\overline{-\mathbf{N}\{(\mathbf{CH_2COO^-})_2\}\mathbf{Ca}^{2+}} + \mathbf{Ni}^{2+} \Leftrightarrow \overline{\mathbf{R}-\mathbf{N}\{(\mathbf{CH_2COO^-})_2\}\mathbf{Ni}^{2+}} + \mathbf{Ca}^{2\cdot}$$

xample 2: Nickel removal, application of chelating ion exchangers:

$$\overline{-N\{(CH_2COO^-)_2\}Ca^{2+}} + Ni^{2+} \Leftrightarrow \overline{R-N\{(CH_2COO^-)_2\}Ni^{2+}} + Ca^{2\cdot}$$

xample 3: Application of weakly basic anion exchangers:

$$\overline{R-NH_2} + Me^{2+} + SO_4^{2-} \Leftrightarrow \overline{R-NH_2(Me^{2+}, SO_4^{2-})}$$

le = Hg, Cu, Pb, Cd, Zn, Ni,

no Ca, Mg

rinking Water Treatment

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le = Hg, Cu, Pb, Cd, Zn, Ni,

no Ca, Mg

xample 4: Elimination of oxy anions (Chromate):

$$\overline{R-N(R')_2 \bullet H_2O} + (CrO_4^{2-}) \Leftrightarrow \overline{R-NH(R')_2^+ (CrO_4^{2-})} + OH^-$$

art 4

- Ion exchangers
- Industrial water treatment
- Drinking water treatment
- **Waste water treatment**
- Prediction of plant performance
- Conclusions

/astewater Treatment

Challenges in industrial wastewater treatment:

renovation of concentrated process liquors

recovery of components (acids, metals, organics) for re-use

removal of heavy metals (after neutralization and precipitation), fluoride, phosphate, borate, organic components

radioactive species

recovery of water

Solutions:

Application of standard ion exchangers,

Application of chelating resins usually for polishing

Application of inorganic exchangers

Application of biosorbents

xamples: Application of Cerium hydroxide inorganic exchangers for treatment of semiconductor wastewaters:

- elimination of fluoride:
  ~30 mg/L to < 1 mg/L pH = 3

- elimination of boron
  ~120 mg/L to < 10 mg/L pH = 7 - 9

urce:, READ-F, Shin Nihon Salt Co. Ltd, Japan, 2006

/astewater Treatment

hallenge: Removal of radioactive spieces

equired: extreme selectivity

physical / chemical stability against radiation

olution: (Pyridine-based) polymeric exchangers

Inorganic materials (titanates, silico-titanates, zeolites, hexacyanoferrates, e.g. SrTreat, CoTreat, CsTreat)

electivity Coefficients:

Ion Exchange Material	Concentration of Na (mol/L)	Selectivity coefficient, $k_{Cs/Na}$
Sulphonic acid resin	not known	<10
Resorcinol-formaldehyde resin	6.0	11,400[a)]
Zeolite (mordenite)	0.1	450
Silicotitanate (CST)	5.7	18,000
CsTreat®	5.0	1,500,000

urce:, R. Harjula et al. Nucl. Technol. 127, 1999, 81

/astewater Treatment

iosorbents and inorganic waste materials:

echanisms of sorption:

- Ion (cation) exchange
- Ligand exchange onto hetero atoms (N, S, O)

dvantage: easily available at low cost

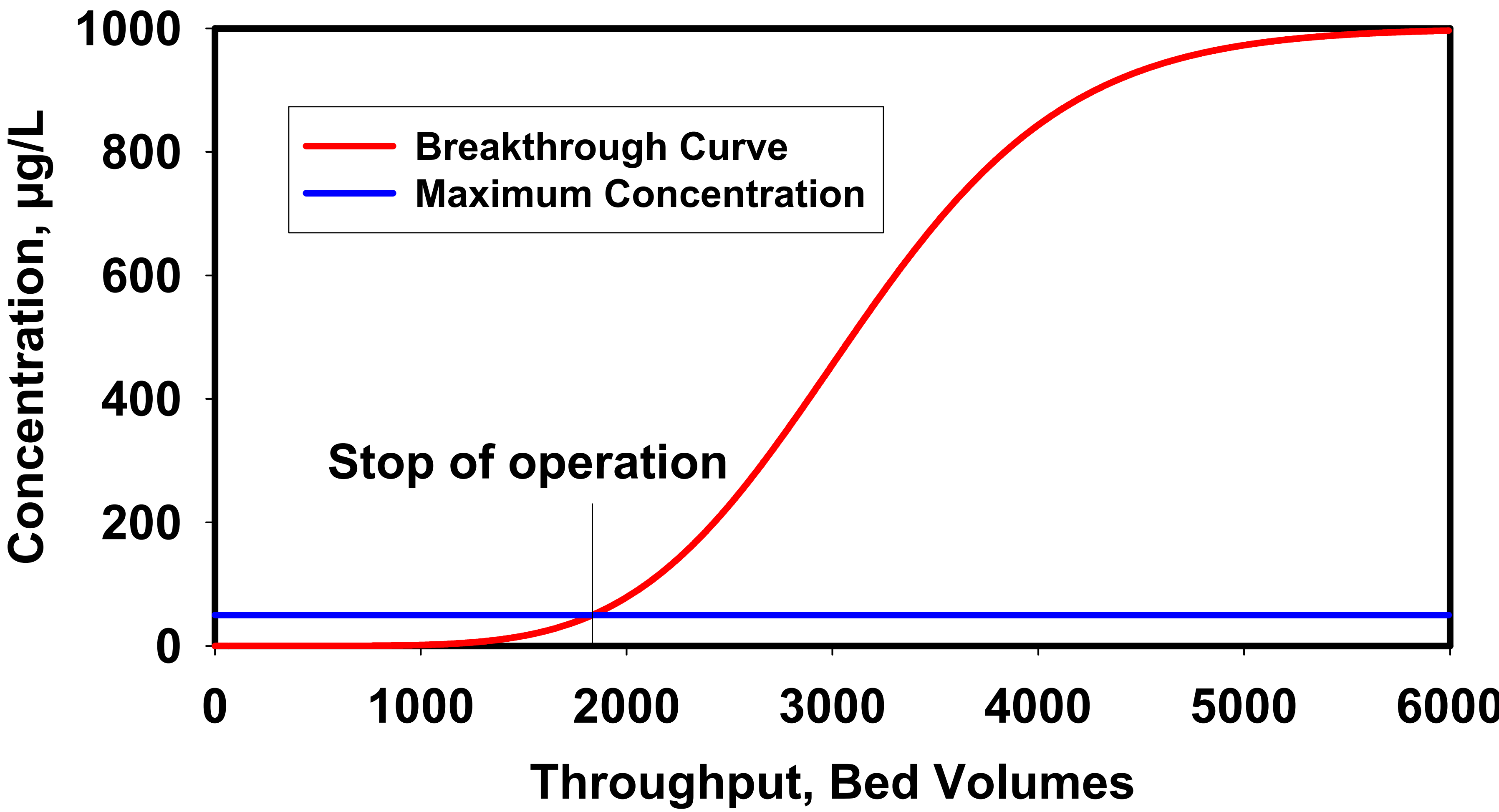
roblems: sometimes pre-treatment required,
„bleeding“,
poor immobilization of metals,
safe discharge / storage

art 5

- Ion exchangers
- Industrial water treatment
- Drinking water treatment
- Waste water treatment
- **Prediction of plant performance**
- Conclusions

rediction of Performance of Plants

hallenge: **Prediction of breakthrough performance**



rediction of Performance of Plants

esired: - Volume of water that can be passed until a preset column effluent concentration is exceeded

acts: Column performance depends on

- exchange equilibrium
- dispersion due to kinetics and hydrodynamics

undamentals

asis: - Knowledge of the fundamental facts of ion exchange and of the chemistry of the system

acts: - ions bear electrical charges (e.g. Cu^{2+}, not Cu(II), $HCrO_4^-$, not Cr(VI))

- there is electroneutrality at any point and any time

limination of ions is only possible:

ither: by exchange of equivalent amounts of ions of the same charge sign

r: by simultaneous sorption of equivalent amounts of cations and anions

undamentals

h. basis (1): Description of ion exchange equilibria

roblems:
- usually multicomponent systems
- equilibria with weakly dissociated exchangers depend on pH
- chemical reactions in liquid phase have to be considered (e.g. carbonic acid)

ools:
- separation factors
- equilibrium constants
- Langmuir (Freundlich) relationship(s)
- surface complexation approaches

undamentals

asis (3): - Description of ion exchange / sorption kinetics

eminder: - ion exchange / sorption processes are **mass transfer-controlled**:

- by liquid-phase diffusion of ions across the NERNST film around the sorbent particles, $F \sim r_P^{-1}$

and/or

- by interdiffusion of ions in the exchanger phase, $F \sim r_P^{-2}$

undamentals

asis (3): - Description of ion exchange / sorption kinetics

ools:
- NERNST-PLANCK equations
- FICK‘s relationships
- Linear-Driving-Force approaches
- …

rediction of Performance of Plants

olution: **Numerical Solution of the differential column mass balance equation:**

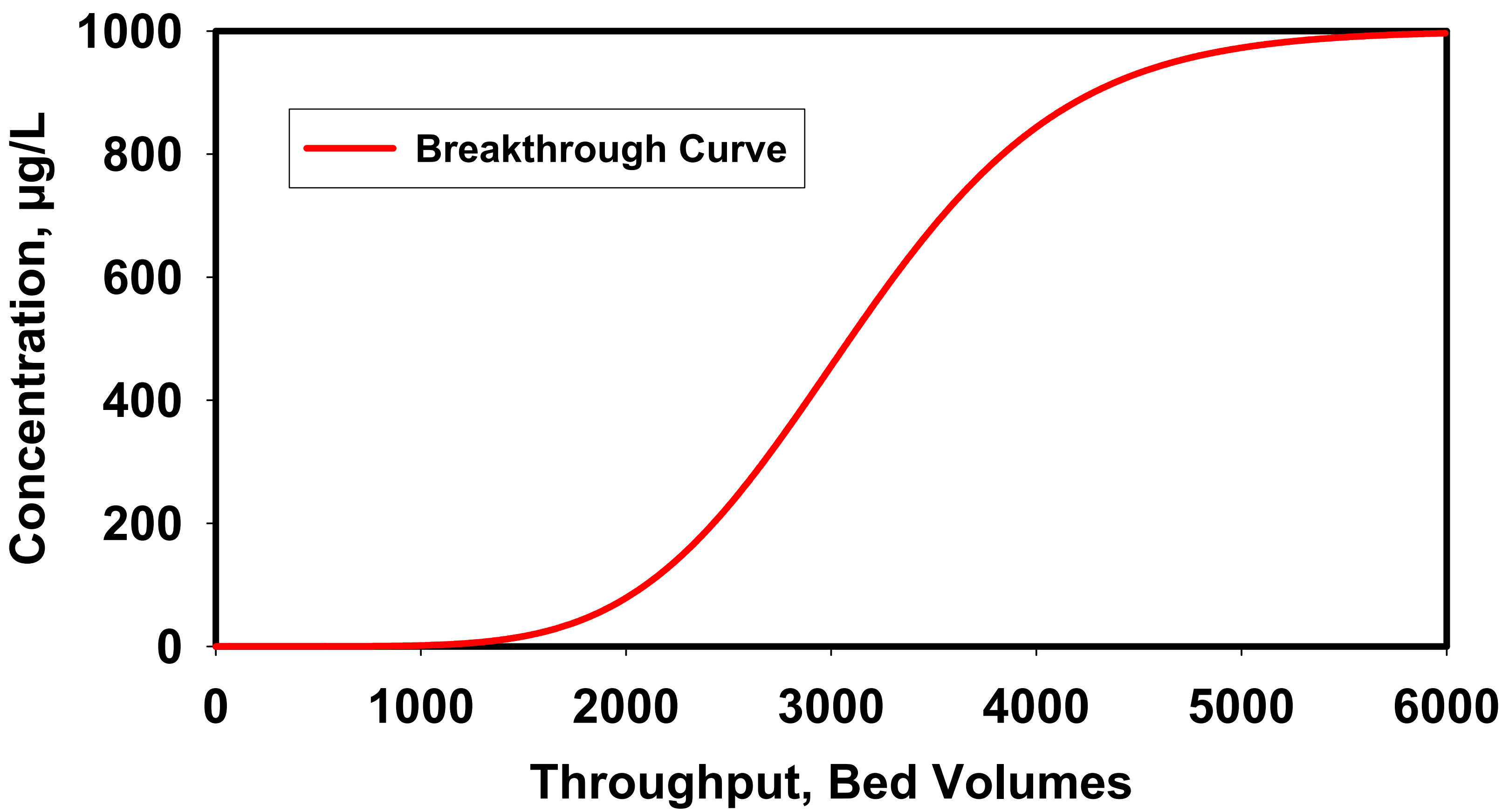
$$\varepsilon \frac{\partial c_i}{\partial t} + v_F \frac{\partial c_i}{\partial z} + (1-\varepsilon)\frac{\partial \bar{c}_i^{av}}{\partial t} = 0$$

The third term contains the kinetics of exchange which considers the distance to equilibrium

(Multicomponent) exchange equilibrium is assumed at the surface of the exchanger beads.

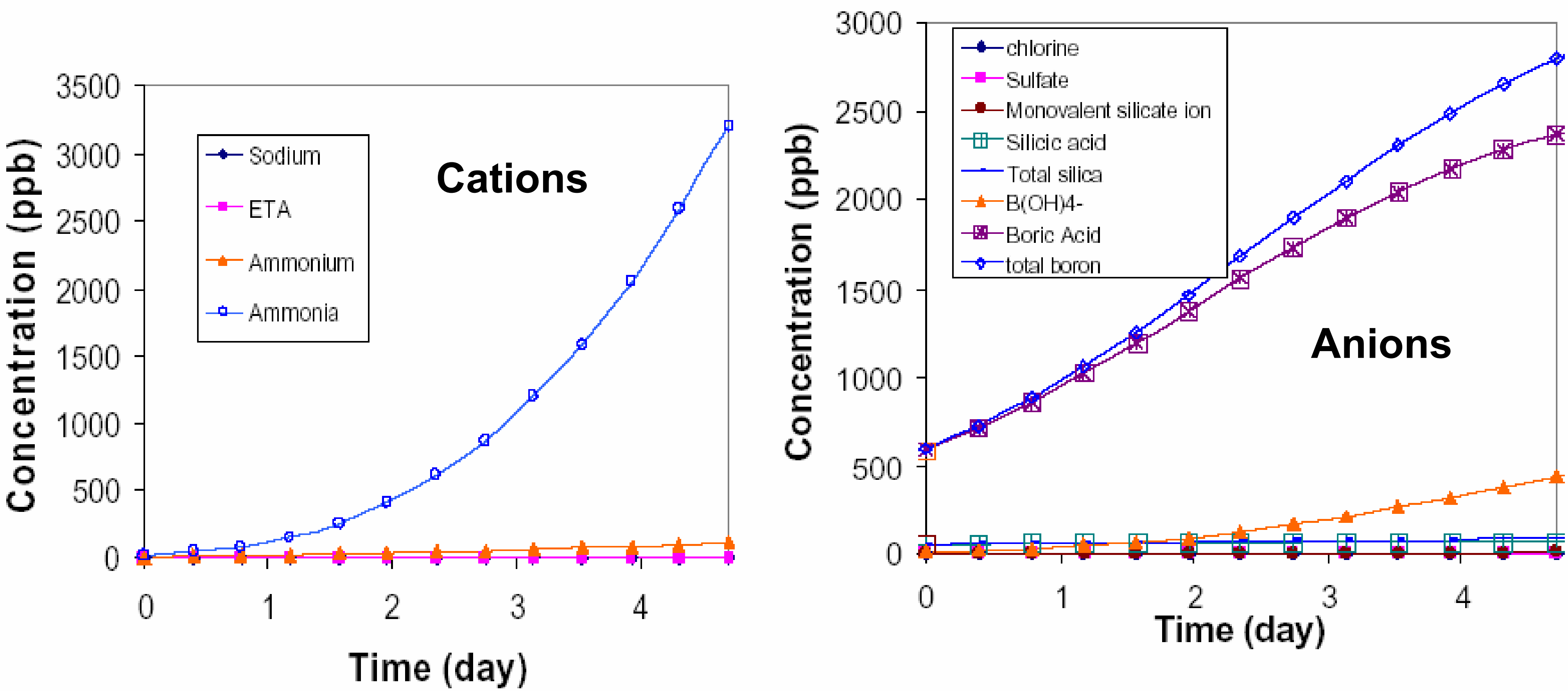
rediction of Performance of Plants

esult: Concentration profiles in the column and breakthrough curve based on properties of ion exchangers, feed composition, throughput, kind of regeneration, temperature



rediction of Performance of Plants

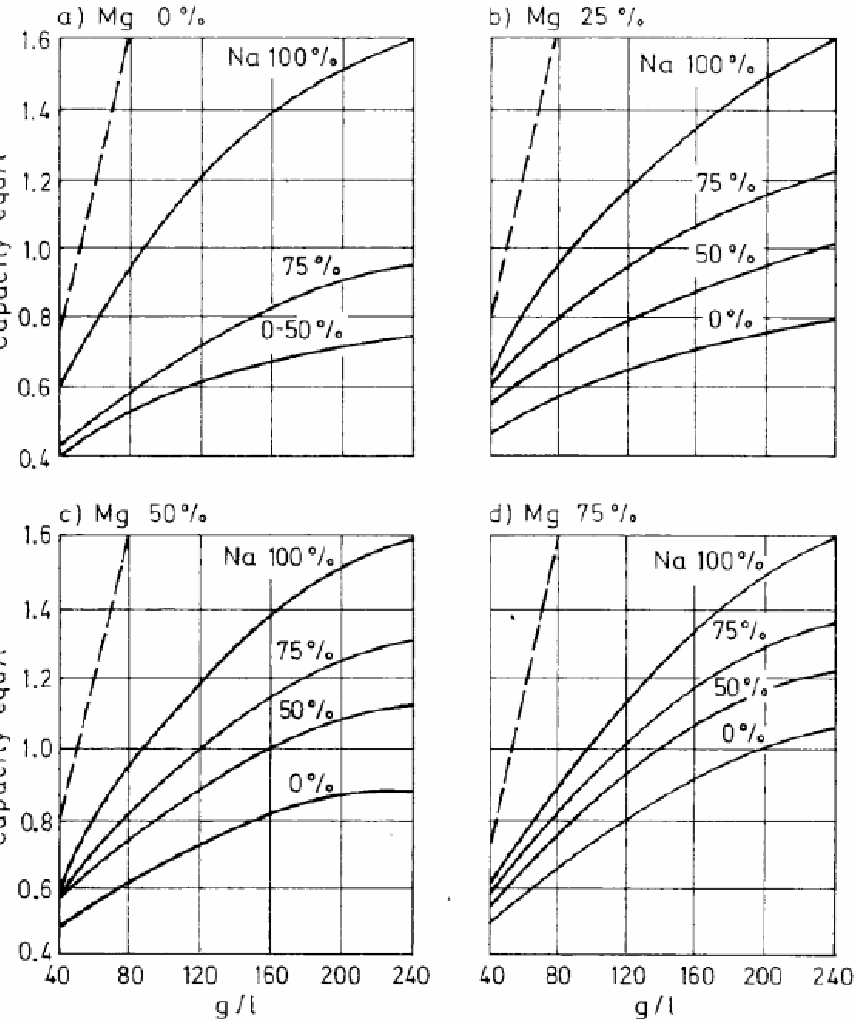
ealized: **For prediction of multicomponent exchange in mixed beds, condensate polishing / ultrapure water: OSUMBIE Simulator**



urce:, J H Lee, G Foutch, Progress in integrating silica and borate into the simulator, Presentation OSU 2001

rediction of Performance of Plants

eality: **Entirely empirical prediction based on manufacturers' calculation programs:**



- PureDesign™
- CADIX
- IXCalc
- Lanxess Design Software
- DIAION WATER TREATMENT SUPPORT PROGRAM

Effective capacity of a strongly acidic exchanger after regeneration by means of H_2SO_4

rediction of Performance of Plants

vailable: - Powerful computers
- Advanced numerical methods

hallenge: Prediction of column performance based on mathematical solutions of the differential filter column mass balance

eeded: - Equilibrium data for exchange resins
- Suitable consideration of liquid-phase chemical reactions
- Suitable consideration of exchange kinetics

onclusions

irst Challenge: Preparation of potable water

odern challenges: Efficient and economic treatment of

- Industrial water
- Potable water
- Wastewater

equiring:

- suitable exchangers
- suitable technologies
- reliable prediction

onclusions

ompetitors:
- Membrane processes
- Chemical precipitation
- ...

trengths:
- Flexibility with respect to throughput
- Selectivity towards target species

ossible progress:
- Molecular modeling for exchanger development
- Theory-based prediction of plant performance

Thank you !