Removal of Trace Contaminants

An Introduction to
How Ion Exchange Resins Really Work

Peter Meyers, March 2021

ResinTech Inc.
INNOVATIONS IN ION EXCHANGE

Author's Introduction

- Modern ion exchange resins provide a relatively simple and cost effective way to make purified or deionized water

- A new and exciting area of ion exchange is in the removal of trace contaminants from a sea of ordinary salts

  - Today I will show you how the principle of concentration difference permits a relatively simple but quantifiable way of looking at how resins really work

- I hope you all enjoy this presentation

Agenda

- The Uniqueness of Water
- The Basics of Ion Exchange
- Ion Exchange Theory & Essential Calculations
- Trace Contaminants
- Wrap Up

Part 1: The Uniqueness of Water

- The four basic elements as told by our ancestors
- The uniqueness of water
- Salts dissolved in water
- The difference between bulk and trace contaminants

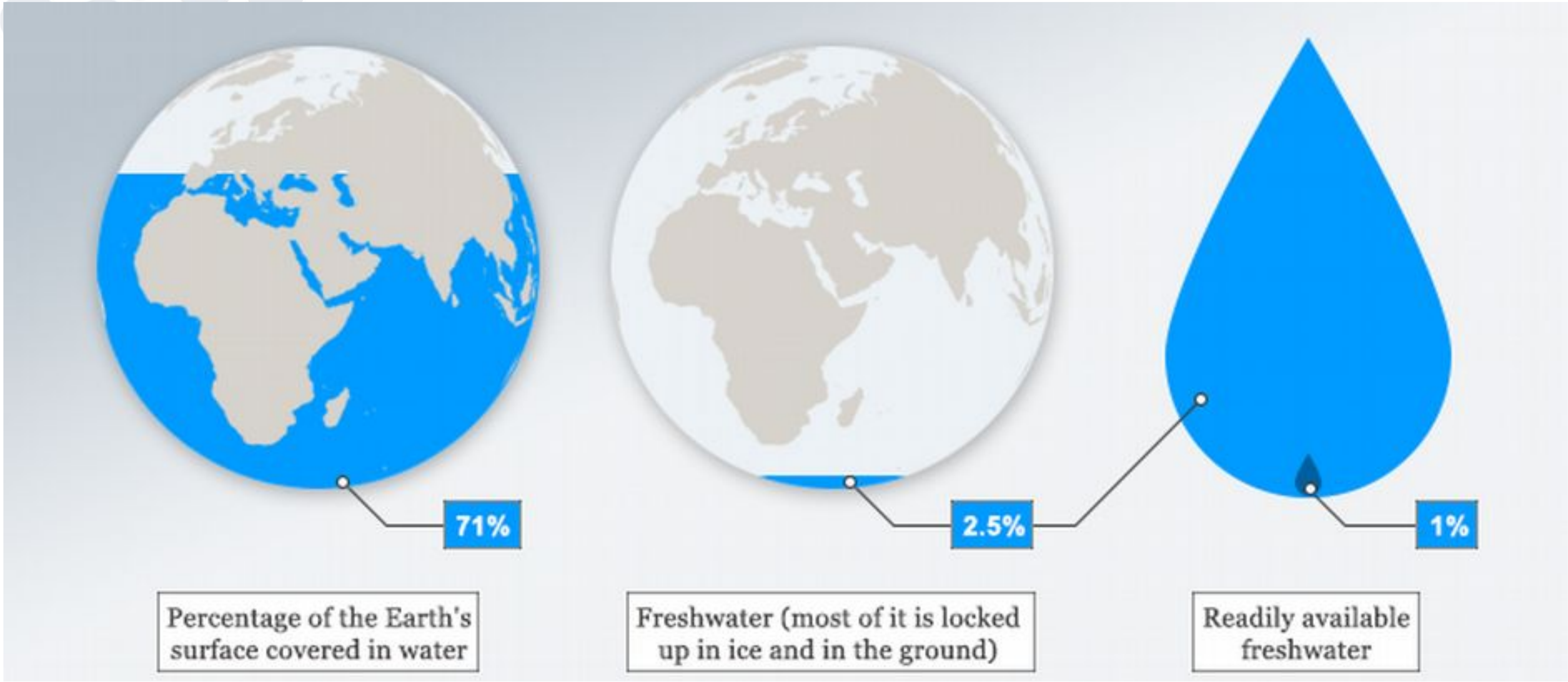
Earth, the Water Planet

The Four Original Elements

- Earth
- **Water**
- Air
- Fire

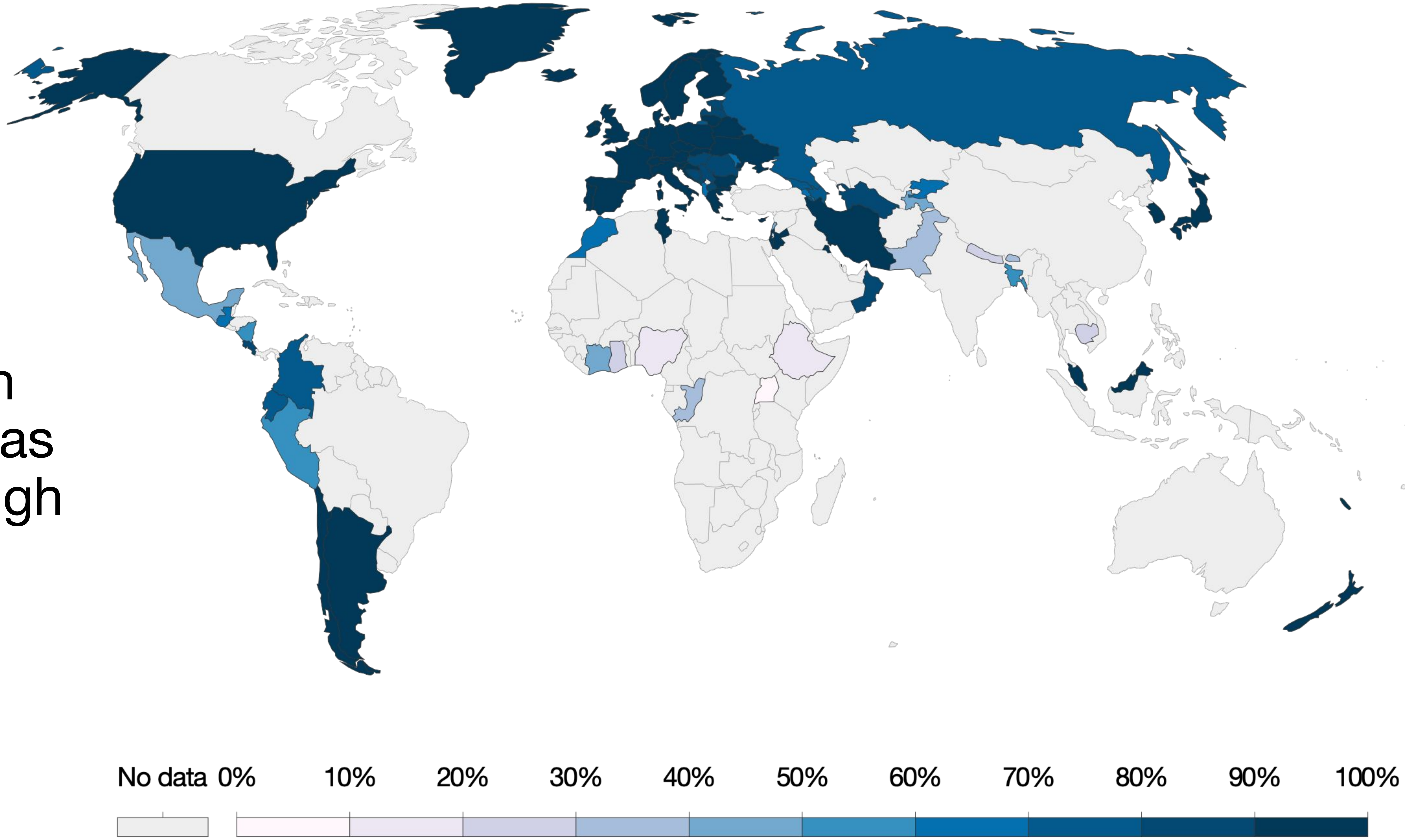
Uniquely Water. But . . .

Most fresh water is contained in ice fields, relatively little in lakes and rivers



Uniquely Water. But . . .

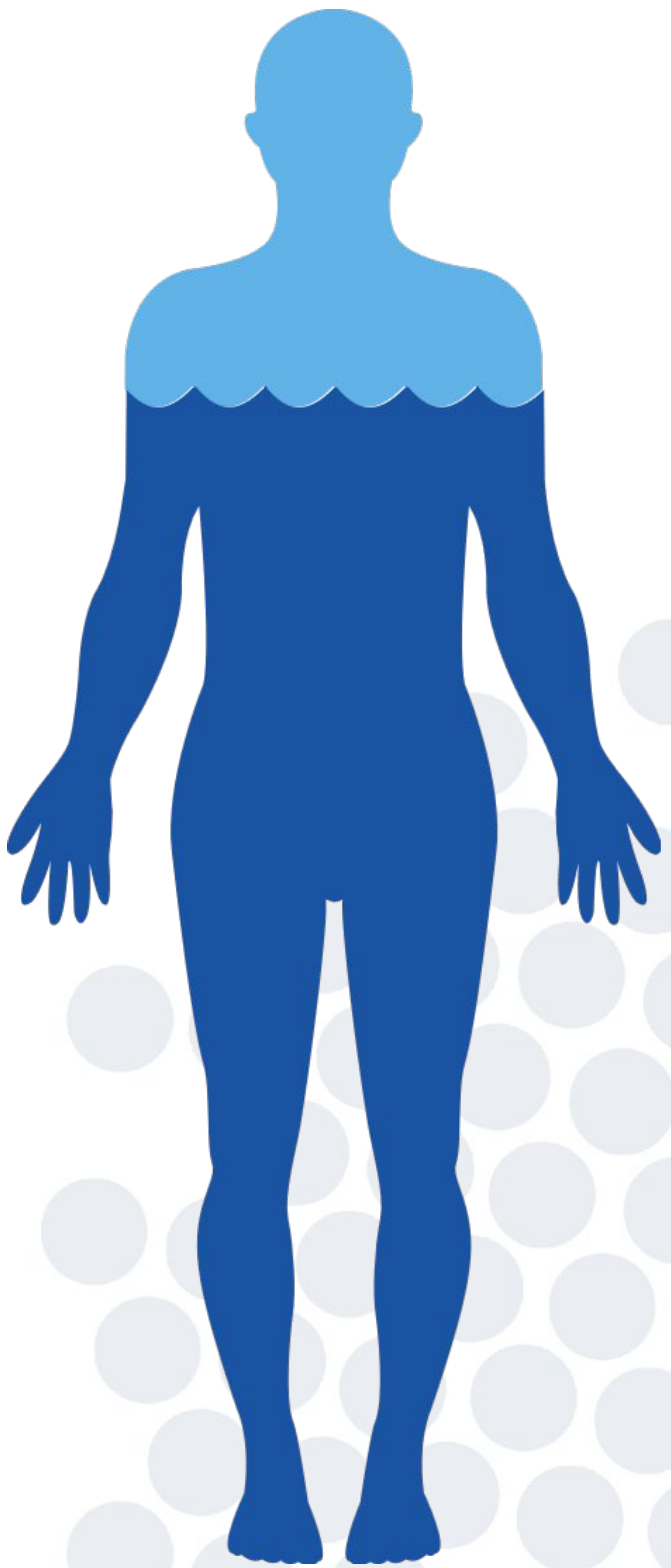
Most of earth's human population lives in areas that do not have enough fresh water



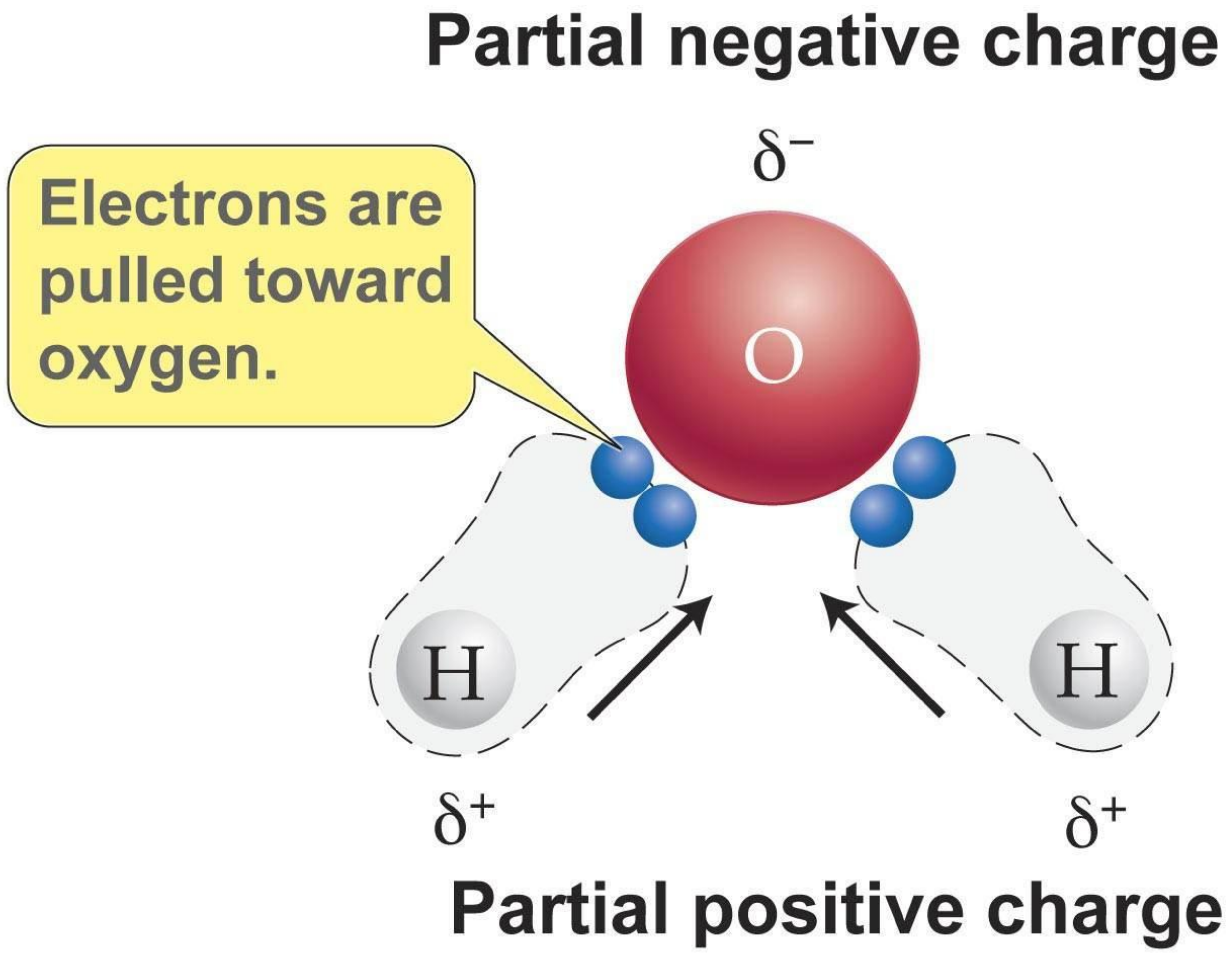
Source: WHO/UNICEF Joint Monitoring Programme for Water Supply, Sanitation and Hygiene (JMP)

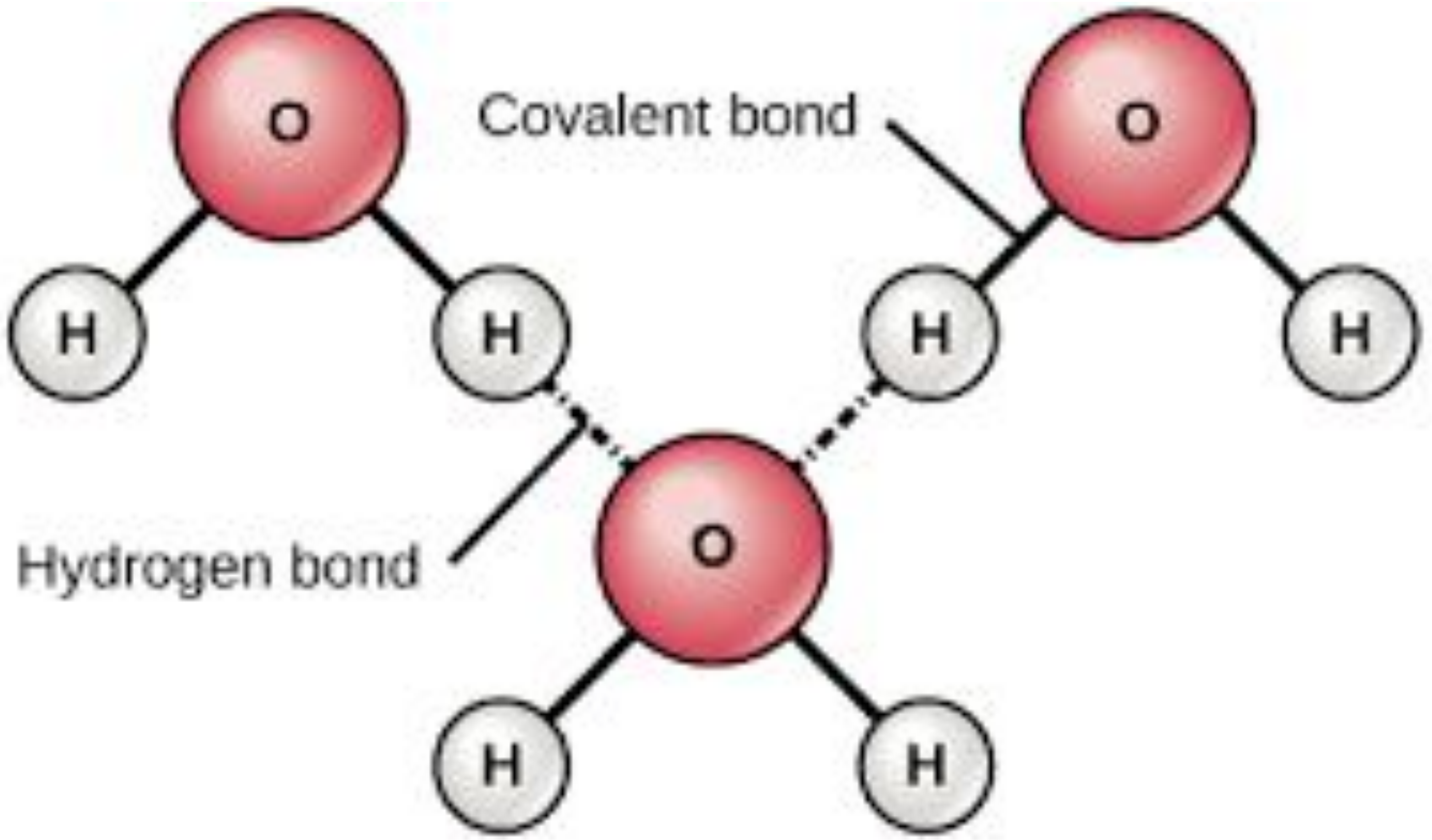
Uniquely Water. But . . .

Our bodies are approximately 65% water. Without it… we will die within a few days.



The Unique Chemistry of Water



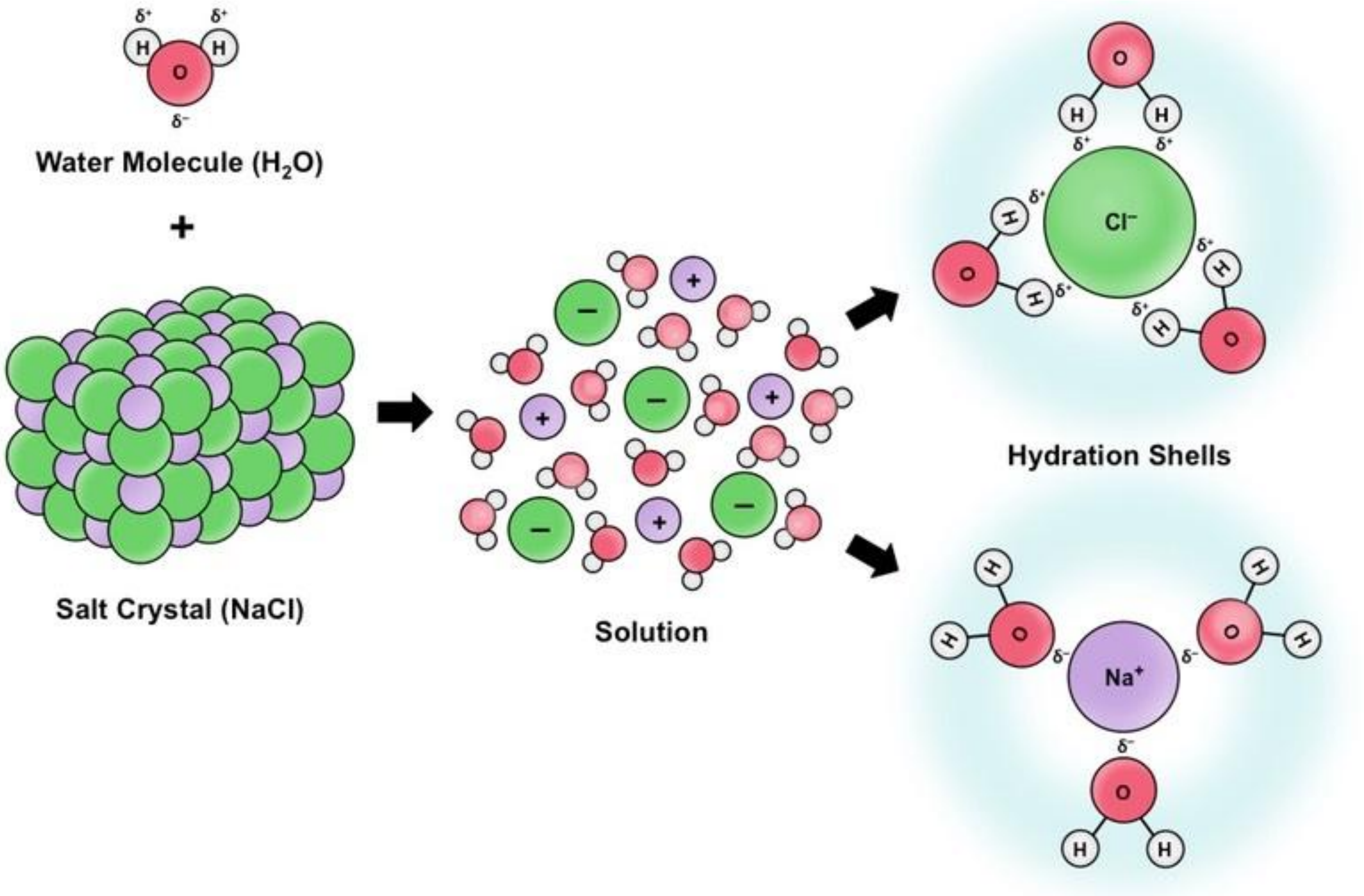


The Unique Chemistry of Water

- **Boiling Point and Freezing Point**
  - Water really should be a gas at room temperature
  - Water should freeze at a much lower temperature
- **Surface Tension, Heat of Vaporization, and Vapor Pressure**
  - Unusually high surface tension
  - Unusually high heat of vaporization
- **Viscosity and Cohesion**
  - Water is relatively thick and sticky compared to other liquids with similar mwt.

Water - the Universal Solvent

More substances dissolve in water than in any other liquid!



Salts Dissolved in Water

"Total Dissolved Solids" or TDS

- For the most part, these bulk dissolved solids are present as ions.
- They are not poisonous except at very high concentrations.
- Ion exchange resins are commonly used to remove some or all of these bulk ions. Examples include:
    - water softeners
    - nitrate removal units
    - deionizers

Molecules Also Dissolve in Water

Not all substances that dissolve in water turn into ions.

- Not all substances that dissolve in water turn into ions.
- Some molecules have covalent bonds that are too strong to permit ionization. Others partially ionized with some or all remaining molecular when they dissolve
- Water still is able to dissolve these substances by using the polar ends of the water molecules
- Examples of molecular or weakly ionized substances dissolved in water include:
  - Sugar (always molecular)
  - Silica (molecular except at high pH)
  - Carbon dioxide (often present in both molecular and ionic forms)

Part 2: Basics of Ion Exchange

- Importance of Ion Exchange Resins
- Differences between molecules and ions
- Early ion exchange materials
- Modern ion exchange resins
- IX selectivity
- Equilibrium vs kinetics

Importance of Ion Exchange Resins

Our modern world would not be possible without ion exchange resins

- No computers or other electronic gadgets (such as cell phones)
- Almost no plastics
- No cheap and plentiful electricity
- No way to remove many toxic contaminants from our drinking water
- Almost all manufacturing processes depend on the availability of pure water

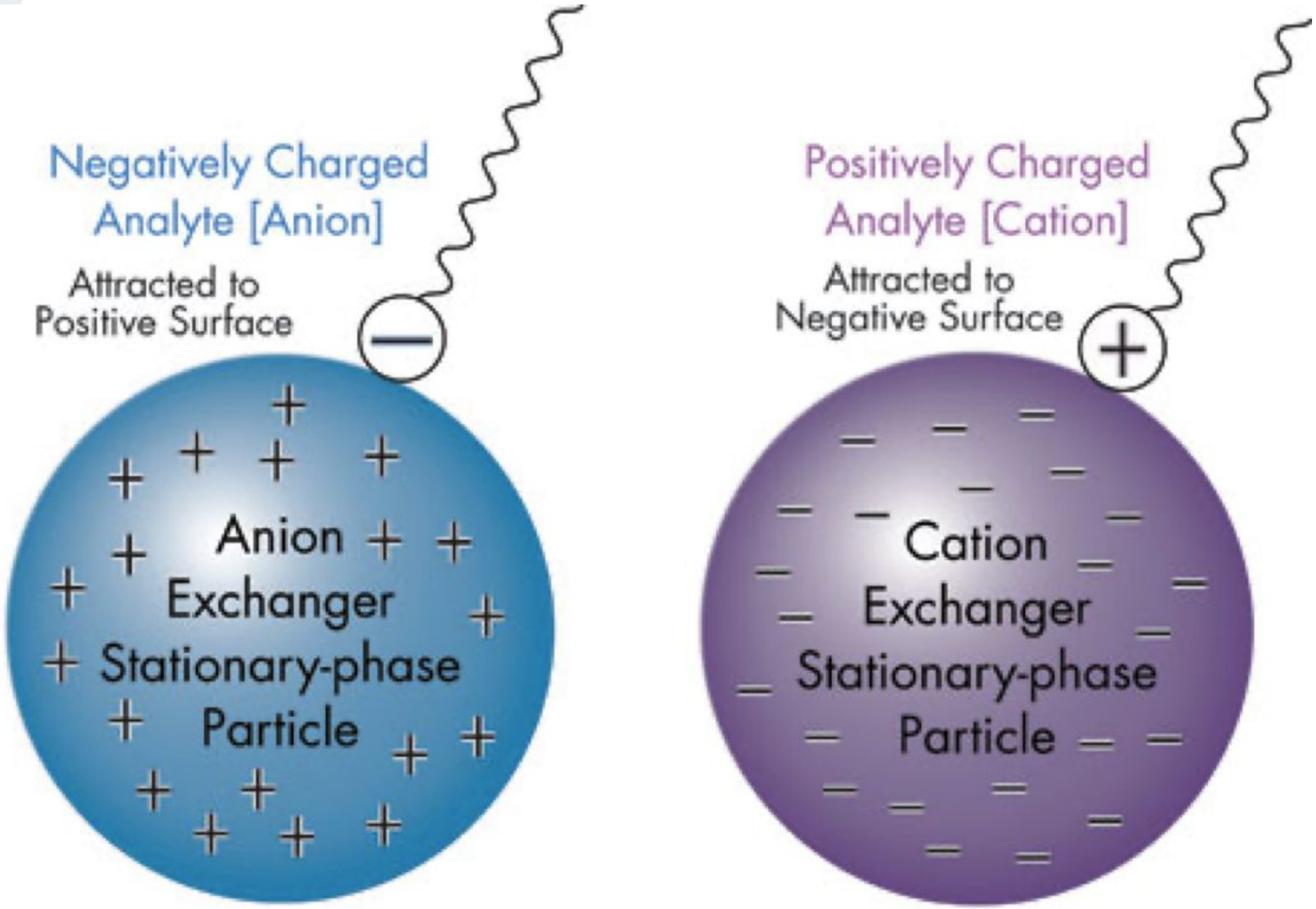
Molecules vs. Ions

What's the difference?

- Although both may contain groups of atoms, ions *steal* electrons from each other:
    - The "Robber" becomes an anion (negative charge)
    - The "Robbie" becomes a cation (positive charge)
- Atoms in molecules *share* electrons (but not always equally). Unequal sharing results in polar molecules

Remember… Ion Exchange Resins only remove ions ... except for the exceptions

The Ion Exchange Process



Evolution of Ion Exchangers

- **Aluminosilicates** (Gradually dissolve)
- **Sulfonated Coal** (Stable at any pH)

- **Sulfonated styrene DVB polymers** (modern softening resin)
- **Chloromethylation**
  - First strongly basic resins
  - Basis of most chelating resins
- **Acrylic DVB polymers**
  - First weakly acidic resins

- **Natural Zeolites** (alumino silicates)

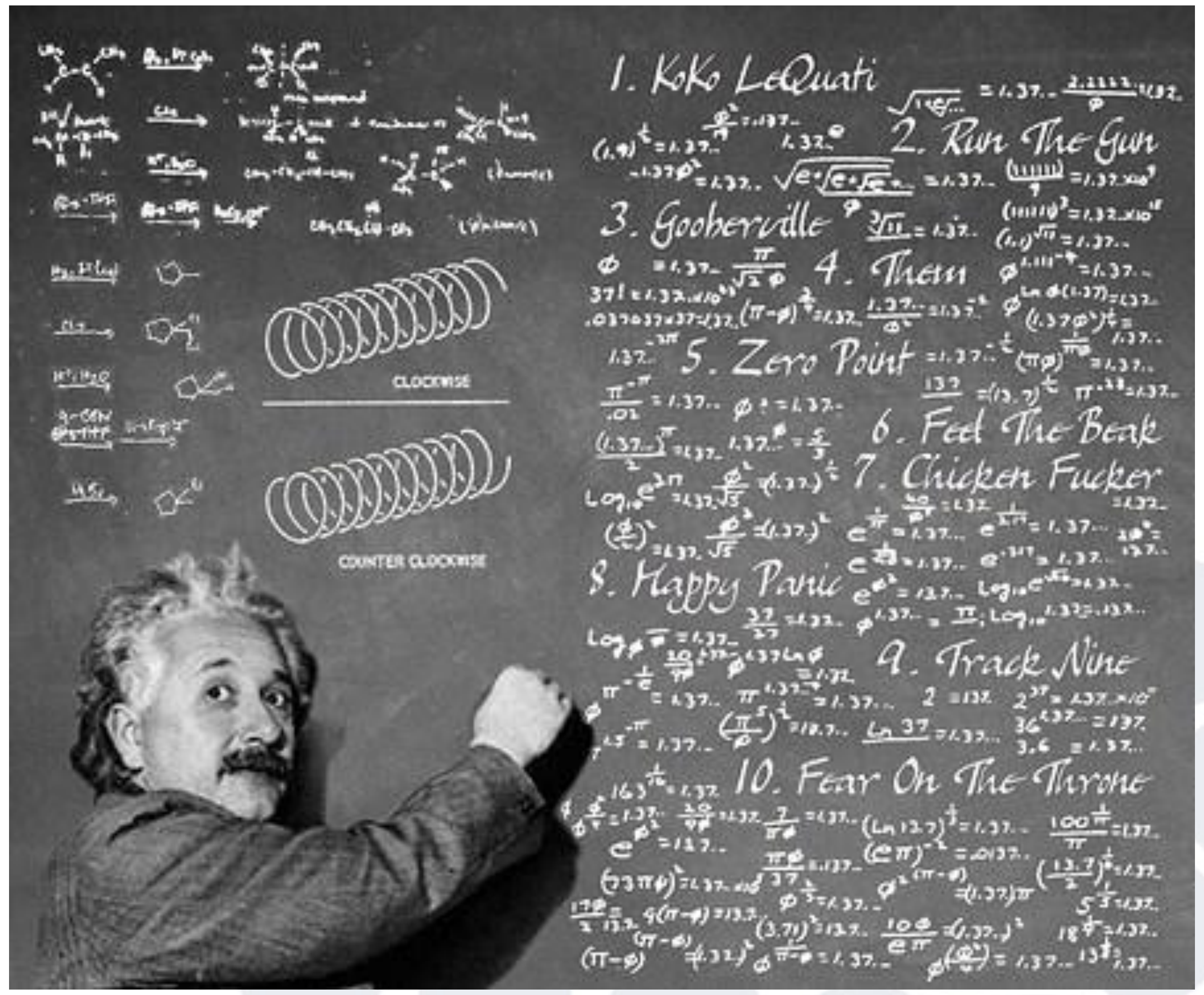
Phenolic condensation polymers (First weak base anion medias)

Modern Ion Exchange Resins

- Almost all based on Styrene Divinylbenzene copolymer
- Balance mostly acrylic Divinylbenzene copolymer
- Strong acid cation resins all sulfonated copolymer
- Weak acid cation resins all acrylic DVB with carboxylic functional groups
- Weak and Strong Base anion resins mostly Styrene DVB but with some Acrylic DVB and various amine functional groups

Part 3: Ion Exchange Theory

- Simplified Ion Exchange theory
- Ion Exchange Resins Physical Characteristics
- Ion Exchange Selectivity
- Small and Fast vs Big and Slow
- Crowding Changes Selectivity
- A brief note regarding units of measure



Simplified Ion Exchange Theory

Ion exchange resins are *plastic beads*
that *take salt out of water*
and *put other salts back in.*

Ion Exchange Resins

Physical Characteristics

- Solid plastic spheres approximately 0.6 mm diameter
- Plastic is functionalized to become
  - Solid cation = anion resin
  - Solid anion = cation resin
- The solid phase includes a mobile "counter ion" of opposite charge that is free to move in and out of the solid plastic according to the laws of ion exchange

What Ion Exchange Resins Look Like

Gel
Resin

Macroporous
Resin

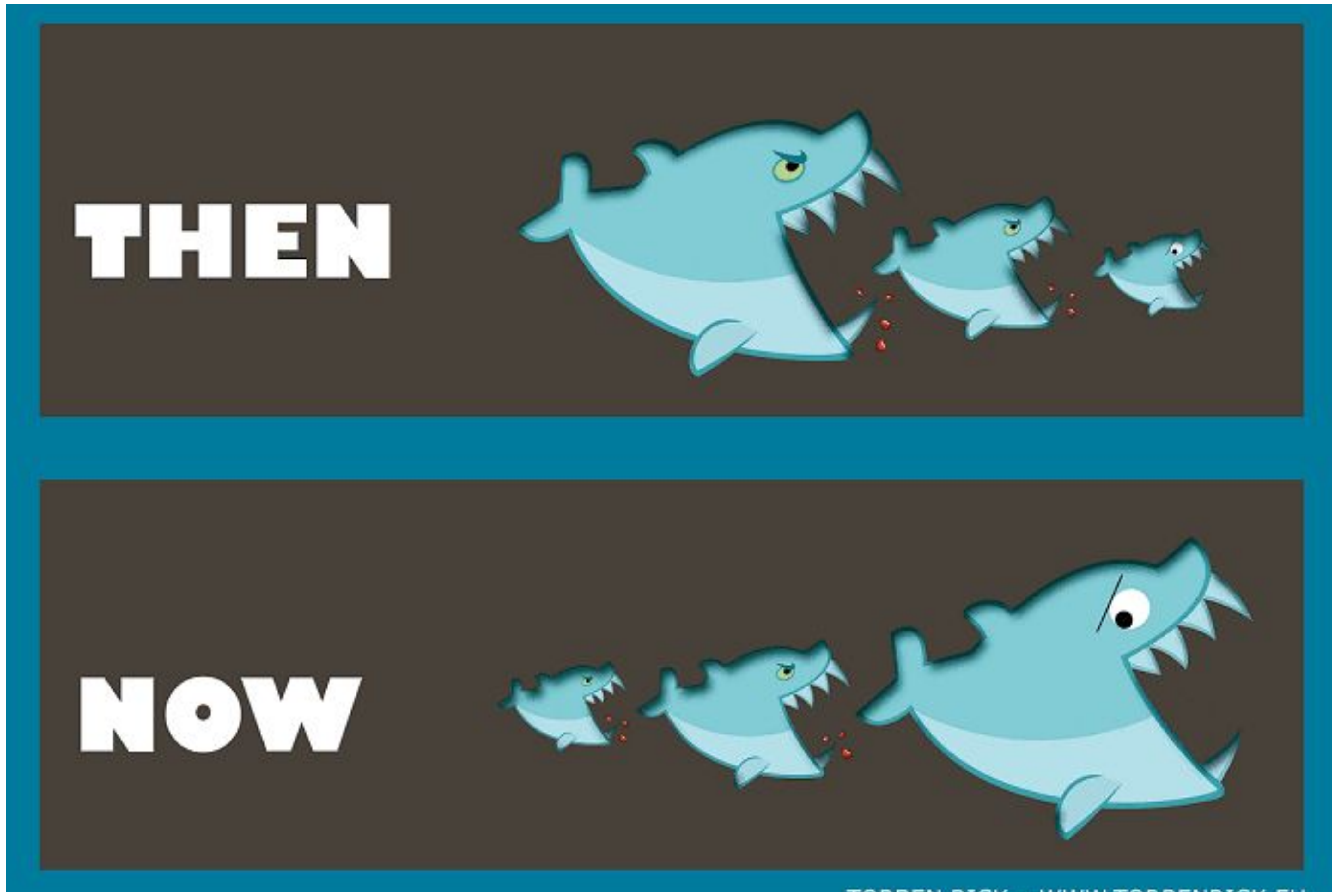
Ion Exchange “Selectivity”

Some ions fit better than others

- Mathematical concept to explain how much resins prefer one ion over another
- Hellferich attributed selectivity to swelling pressure
    - Most swollen form equals least preferred form
- A simpler theory is that some ions simply fit better
- Valence (number of charges) important because for divalent ions, selectivity changes with concentration

Small and Fast vs Big but Slow

No one wins all the time



- **Conditions that favor small and fast**
  - High space velocities (short EBCT)
  - High ionic strength (low TDS)
- **Conditions that favor big and slow**
  - Low space velocities
  - Low ionic strength

Crowding changes apparent selectivity

But only for some ions

- Divalent ions need two ion exchange sites
  - In uncrowded solutions divalent ions can find two adjacent sites easily
  - Crowding makes it more difficult
- Divalent ion selectivity decreases as concentration increases
- Monovalent ion selectivity does not change with concentration

A Brief Note About Units of Measure

Milli-equivalents are so much easier to use than kilograins

- Kilograins per cu ft is about as convenient as expressing the speed of light in furlongs per fortnight
- A milli-equivalent is simply the ions concentration (milligrams per liter) divided by the equivalent weight (molecular weight divided by valence)
- This is sooo much easier to work with once you get used to it
- For the record
  - 1 meq/L = 50 ppm as $CaCO_3$
  - 1000 meq/L = 21.8 kilograins per cu ft
  - 1 BV (bed volume) = 7.5 gallons per cu ft

Part 4: Trace Contaminants

The needle in the haystack

- A Working Definition
- Principles of Concentration Difference
- Simplified Mathematics
  - Equal Preference
  - Low selectivity
- Common attributes of long life resins

What is a Trace Contaminant?

A Working Definition

A very small concentration of an ionized but undesirable element or compound

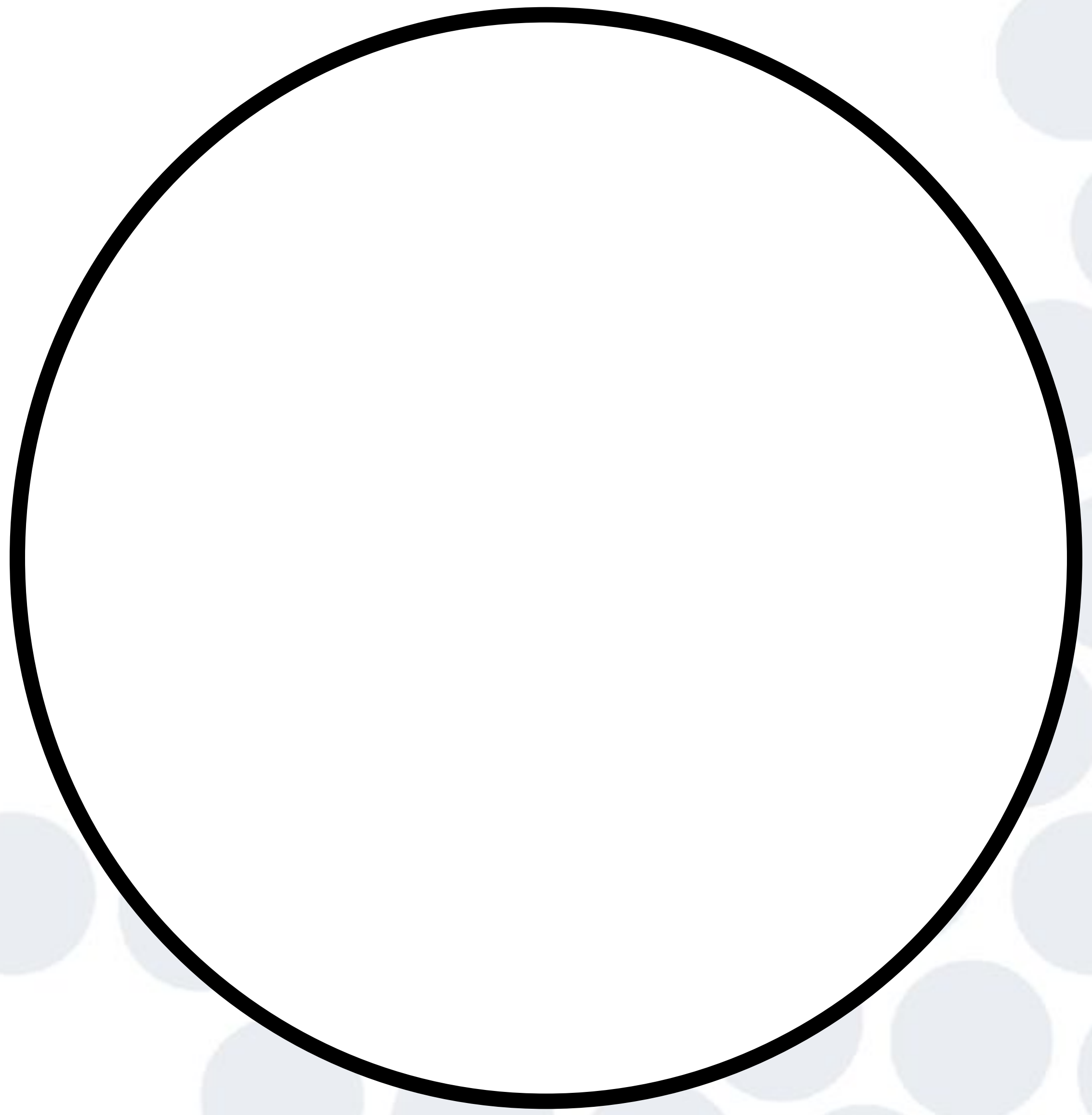
- Generally much less than 1 mg/L
- Generally less than 1% of the total ions present

Bulk Ions vs. Trace Ions

- Bulk ions accumulate to a significant fraction of an IX resins capacity, while trace ions do not.
  - **Throughput calculations for bulk ions is complicated**
- Bulk ions are often present in new resins, while trace ions (hopefully) are not.
- Removal of a trace ion and replacement with a bulk ion does not significantly alter the water or resin composition
  - **This allows a simple calculation of throughput capacity**

Trace ion vs Bulk ion Behavior

Transitioning from trace to bulk



Resin bead

When there are no trace ions in the resin, the resin properties and behavior with respect to the trace ion are determined by the starting ionic form of the resin

Trace ion vs Bulk ion Behavior

Transitioning from trace to bulk

With very little of the trace contaminant in the water and almost none in the resin, the resin properties and behavior with respect to the trace ion are still determined by the starting ionic form of the resin.

Trace ion vs Bulk ion Behavior

Transitioning from trace to bulk

As the concentration of trace ions in the water and resin increases, the resin properties begin to change. At first the resin properties and behavior are mostly determined by the starting ionic form of the resin

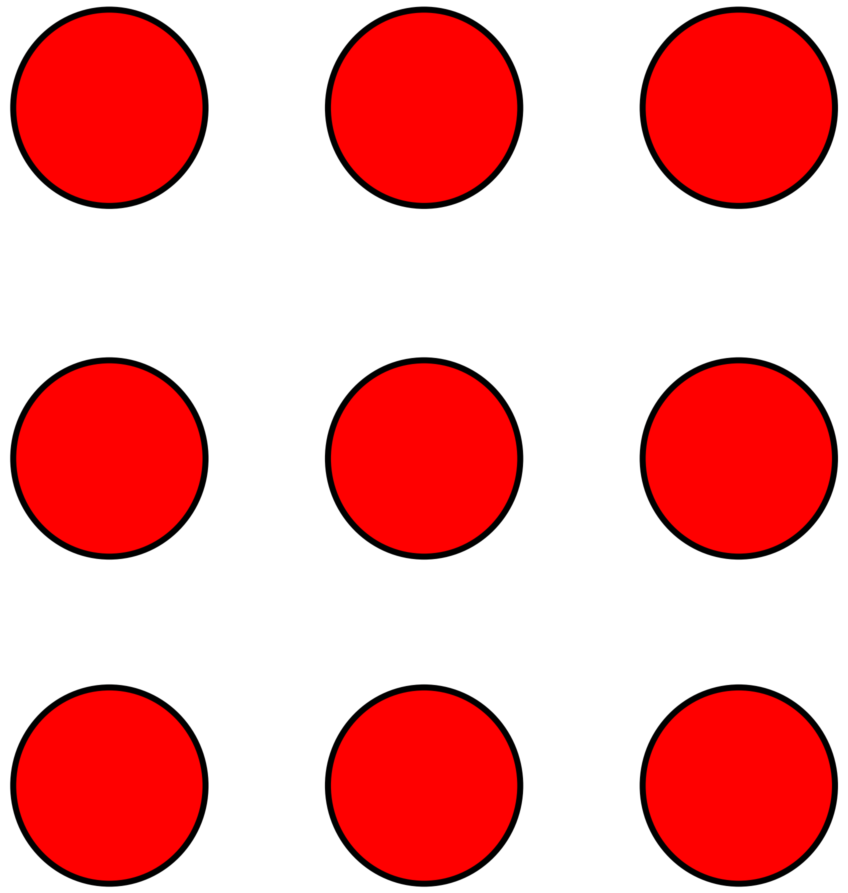
Trace ion vs Bulk ion Behavior

Transitioning from trace to bulk

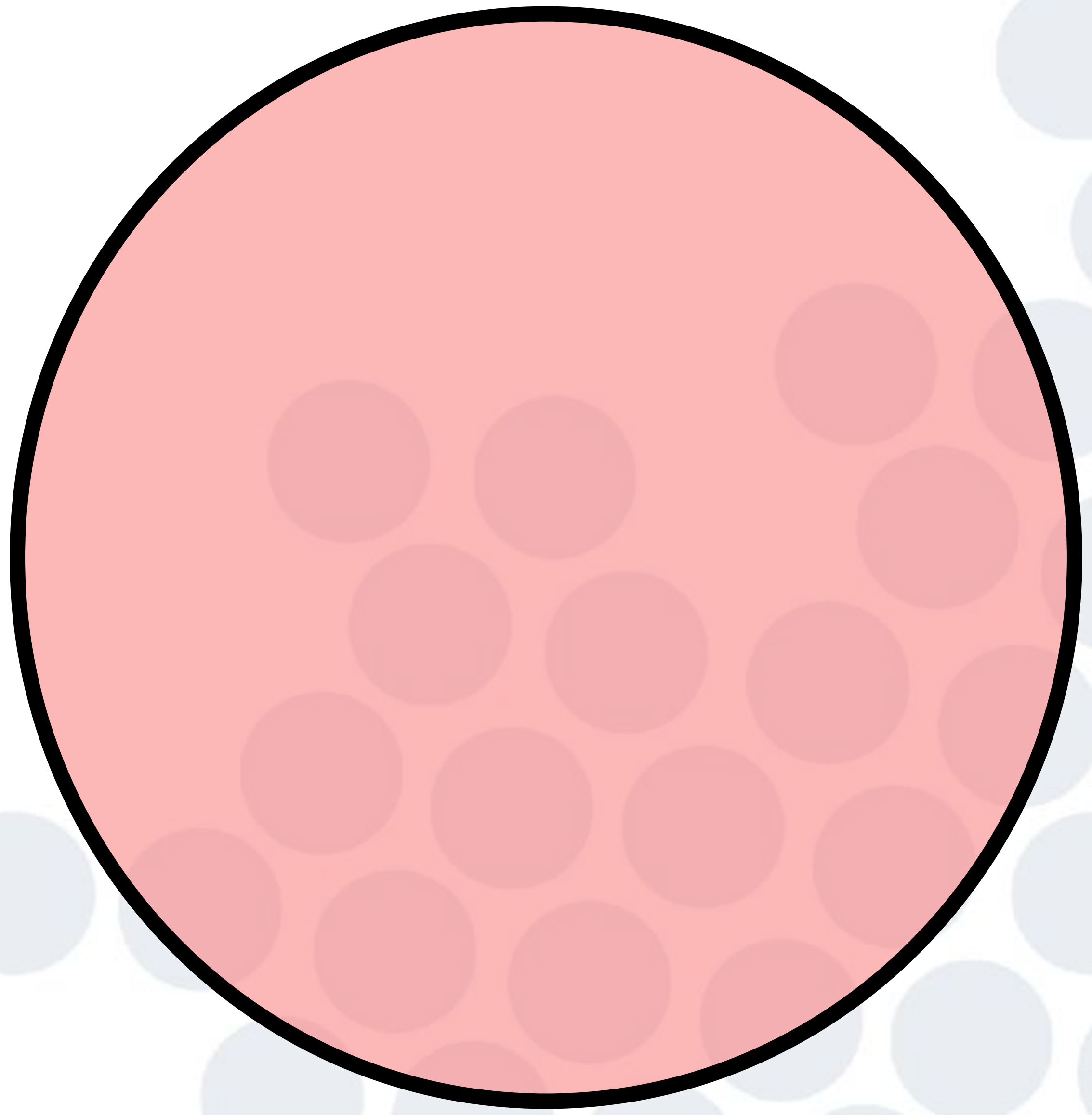
As the trace ion concentration continues to increase in the water and resin, the resin increasingly takes on properties intermediate between the starting ionic form of the resin and the form of the trace contaminant. However, the resin properties and behavior are still dominated by the starting ionic form of the resin

Trace ion vs Bulk ion Behavior

Transitioning from trace to bulk



(Is this still a)
Trace Contaminant
ions in the water



Resin bead

Past some point, the simplifying assumption that the properties and behavior of the resin are governed by the starting ion in the resin is no longer valid. The resin properties and behavior are in between that of the starting ion and the (no longer) trace ion, and the simplifying assumption is inaccurate.

Trace ion vs Bulk ion Behavior

Transitioning from trace to bulk

From this point on, the principles of trace contaminants being controlled by concentration difference no longer apply and interaction between water and resin enters the realm of bulk contaminants. The simplifying assumption for trace ion behavior becomes wildly inaccurate and no longer applies.

Principle of Concentration Difference

Conditions where the simplified calculations are valid

- The total ionic concentration in the resin is much higher than the ionic concentration (TDS) of water.
- At equilibrium, the equivalent fraction of the trace ion in the resin will be equal to the equivalent fraction of that ion in the water, times the resins preference for the trace ion.
- The trace ions remains a small fraction of the resins total capacity such that the resin behavior toward the trace does not change very much.
- When these three conditions are met, we can use a simple calculation to predict the behavior of any trace ion.

Setting the Stage for Simplified Calculations

Examples of Trace Contaminants

- **Resin Concentration**
    - Cation resins roughly 100,000 mg/L as CaCO3 (2000 meq/L)
    - Anion resin roughly 70,000 mg/L as CaCO3 (1400 meq/L)
- **Water concentration (TDS)**
    - Typically less than 1000 mg/L as CaCO3 (20 meq/L)
        - *NOTE: the resin concentration is typically at least 70 to 100 times greater than the water.*

The following examples use 100 mg/L as CaCO3 (2 meq/L) — 1000 times greater.

Simplified Capacity Calculations*

Variables & Formulas

FRACTION IN WATER	x	PREFERENCE	=	FRACTION IN RESIN

FRACTION IN THE RESIN	x	RESIN TOTAL CAPACITY	=	CAPACITY FOR TRACE

RESIN CAPACITY	÷	TRACE CONCENTRATION	=	THROUGHPUT CAPACITY

**Assumes the trace contaminant is less than 10% fraction in the resin, less than 1% in the water*

Trace Contaminant Example

Metallium (Me)

Assumptions:

Resin capacity	Me concentration	TDS Concentration	Resin's numerical preference for Me
100,000 mg/L as $CaCO3$ (20 meq/L)	1 mg/L as $CaCO3$ (0.02 meq/L)	100 mg/L as $caCO3$ (2 meq/L)	1.0*

**All other ions are equally preferred.*

History of Metallium

- Mythical contaminant with undefined mass or charge
- Named after Zelas **Metallium**, also known as Lord Beastmaster, a Japanese anime Slayer (approx 457 BC)
- Used in this presentation as a substitute for any real ion
- Any perceived disparagement of real ions is unintentional

Resin Capacity for Metallium

FRACTION IN WATER		x PREFERENCE	= FRACTION IN RESIN
Concentration (mg/L Me as CaCO3)	÷ TDS concentration (mg/L as CaCO3)		numerical fraction
1 (0.02 meq/L)	100 (2.0 meq/L)	1	0.01

FRACTION IN THE RESIN	x RESIN TOTAL CAPACITY	= RESIN CAPACITY
numerical fraction	(mg/L as CaCO3)	(mg/L as CaCO3 in resin)
0.01	100,000 (2000 meq/L)	1000 (20 meq/L)

RESIN CAPACITY	÷ CONCENTRATION	= THROUGHPUT CAPACITY
mg/L Me as CaCO3	(mg/L Me as CaCO3)	(bed volumes)
1000 (20 meq/L)	1 (0.02 meq/L)	**1000**

Three Principals of Trace Ion Removal

1. It is not necessary for the trace to be preferred, only that there be a significant concentration *difference* between the water and resin.

Impact of Trace Concentration

What happens to throughput if trace concentration drops in half?

Resin Capacity for Metallium

At ***half*** the original concentration

FRACTION IN WATER		x	PREFERENCE	= FRACTION IN RESIN
Concentration (mg/L Me as CaCO3)	÷ TDS concentration (mg/L as CaCO3)			fraction
0.5 (0.01 meq/L)	99.5 (1.99 meq/L)		1	0.005025

FRACTION IN THE RESIN	x	RESIN TOTAL CAPACITY	= RESIN CAPACITY
fraction		(mg/L as CaCO3)	(mg/L as CaCO3 in resin)
0.005025		100,000 (2000 meq/L)	502.5 (10.05 meq/L)

RESIN CAPACITY	÷	Me CONCENTRATION	= THROUGHPUT CAPACITY
(mg/L as CaCO3)		(mg/L Me as CaCO3)	Bed volumes
502.5 (10.05 meq/L)		0.5 (0.01 meq/L)	**1005**

Three Principals of Trace Ion Removal

1. It is not necessary for the trace to be preferred, only that there be a significant concentration *difference* between the water and resin.

2. **The concentration of the trace ion is almost completely irrelevant as far as throughput is concerned.**

Impact of TDS

What happens to throughput if TDS concentration doubles?

Resin Throughput Capacity for Metallium

At ***double*** the original TDS in the water

FRACTION IN WATER		x	PREFERENCE	= FRACTION IN RESIN
Concentration (mg/L Me as $CaCO_3$))	÷ TDS concentration (mg/L as $CaCO_3$)			fraction
1 (0.02 meq/L)	200 (4.0 meq/L)		1	0.005

FRACTION IN THE RESIN	x	RESIN TOTAL CAPACITY	= RESIN CAPACITY
(numerical fraction)		(mg/L as $CaCO_3$)	(mg/L as $CaCO_3$ in resin)
0.005		100,000 (2000 meq/L)	500 (10 meq/L)

RESIN CAPACITY	÷	Me CONCENTRATION	= THROUGHPUT CAPACITY
mg/L as $CaCO_3$		(mg/L Me as $CaCO_3$)	(bed volumes)
500 (10 meq/L)		1 (0.02 meq/L)	**500**

Three Principals of Trace Ion Removal

1. It is not necessary for the trace to be preferred, only that there be a significant concentration *difference* between the water and resin.

2. The concentration of the trace ion is almost completely irrelevant as far as throughput goes.

3. **The TDS of the water has a *profound* effect on throughput.**

Trace Contaminant Example for Fluoride

Fluoride (F) an ion with hugely unfavorable selectivity

Assumptions

Resin Total capacity (mg/L as CaCO3)	Fluoride concentration (mg/L as CaCO3)	TDS Concentration (mg/L as CaCO3)	Resin preference for F (compared to chloride)
70,000 (1400 meq/L)	1 (0.02 meq/L)	100 (2 meq/L)	0.05

Resin Throughput Capacity for Fluoride

FRACTION IN WATER			x	PREFERENCE	=	FRACTION IN RESIN
Concentration (mg/L F as CaCO3	÷	TDS concentration (mg/L as CaCO3)				numerical fraction
1 (0.02 meq/L)		100 (2 meq/L)		.05		0.0005

FRACTION IN THE RESIN	x	RESIN TOTAL CAPACITY	=	RESIN CAPACITY
numerical fraction		(mg/L as CaCO3)		(mg/L of CaCO3)
0.0005		70,000 (1400 meq/L)		35 (0.7 meq/L)

RESIN CAPACITY	÷	CONCENTRATION	=	THROUGHPUT CAPACITY
(mg/L F as CaCO3))		(mg/L F as CaCO3)		(bed volumes)
35 (0.07 meq/L)		1 (0.02 meq/L)		**35**

Common Attributes of Long Life Resins

- Resins removing trace contaminants are almost always kinetically limited
  - Needle in the haystack problem
- High ionic strength limits kinetics still further
  - Crowding reduces the apparent selectivity of certain ions
- Volume throughputs are often high, increasing risk of fouling

Trace Contaminants that IX resins remove well

This is only a partial list

Inorganic

• Vanadium (as vanadate)	SIR-700-HP
• Perchlorate	SIR-110-HP (SIR-100-HP)
• Arsenic (as arsenate)	ASM-10-HP (SBG2-HP)
• Chromate	SIR-700-HP (SBG2-HP)
• Lead	WACG-HP (CG8 and CG10)
• Mercury	SIR-200 (SIR-300)
• Selenium (as selenite)	CHM-20 (ASM-10-HP)
• Thallium	CG10 (SACMP)
• Heavy metals (Cd, Cu, Ni, etc)	SIR-300 (WACMP-Na

Trace Contaminants that IX resins remove well

Man made Radioactives

- Iodine SIR-110-HP (CHM-20)
- Strontium CG10 (SACMP)
- Cesium SIR-600 (CG10)
- Antimony ASM-125
- Cobalt ASM-125

Naturally Occurring Radioactives

- Radium RSM-50 (RSM-25, CG8)
- Uranium SBG2-HP (SBG1)

Organic

- PFAS SIR-110-HP

Wrapping up

Take aways about trace contaminants

- The concentration of the trace contaminant is relatively unimportant
- The TDS of the water is profoundly important
- It is not necessary for the trace to be the most preferred ion in order to obtain useful throughputs

Questions?


ResinTech Inc.

THANK YOU

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INNOVATIONS IN ION EXCHANGE