Removal of Bulk Ionic Contaminants

Introduction to How Ion Exchange Resins Actually Work

Peter Meyers, March 2021

ResinTech Inc.

INNOVATIONS IN ION EXCHANGE

Author’s Introduction

- By far the biggest uses of IX resins are for bulk contaminant removal such as water softening, nitrate removal, and deionization.
- In our first webinar we discussed the basics of trace ion removal and why this is different than the removal of bulk ions
- In this second introductory webinar we take up some of the basic concepts related to bulk ion removal.
- I hope you all enjoy this presentation

Agenda for the Bulk Contaminants Webinar

- Bulk Ionic Contaminants
- Ionic Equivalents & Equivalent Concentrations
- The Selectivity Equation (Products over Reactants)
- Setting the Stage (a little more resin theory)
- Salt form exchanges (hardness, nitrate, and alkalinity)

Part 1: One tiny typo and Bulk becomes . . .

Bulk ions

- Greater than 1% of TDS
- Soluble
- Not easily separated from each other
- Not really “contaminants”
- Sensitive processes/applications

More about Bulk Ions

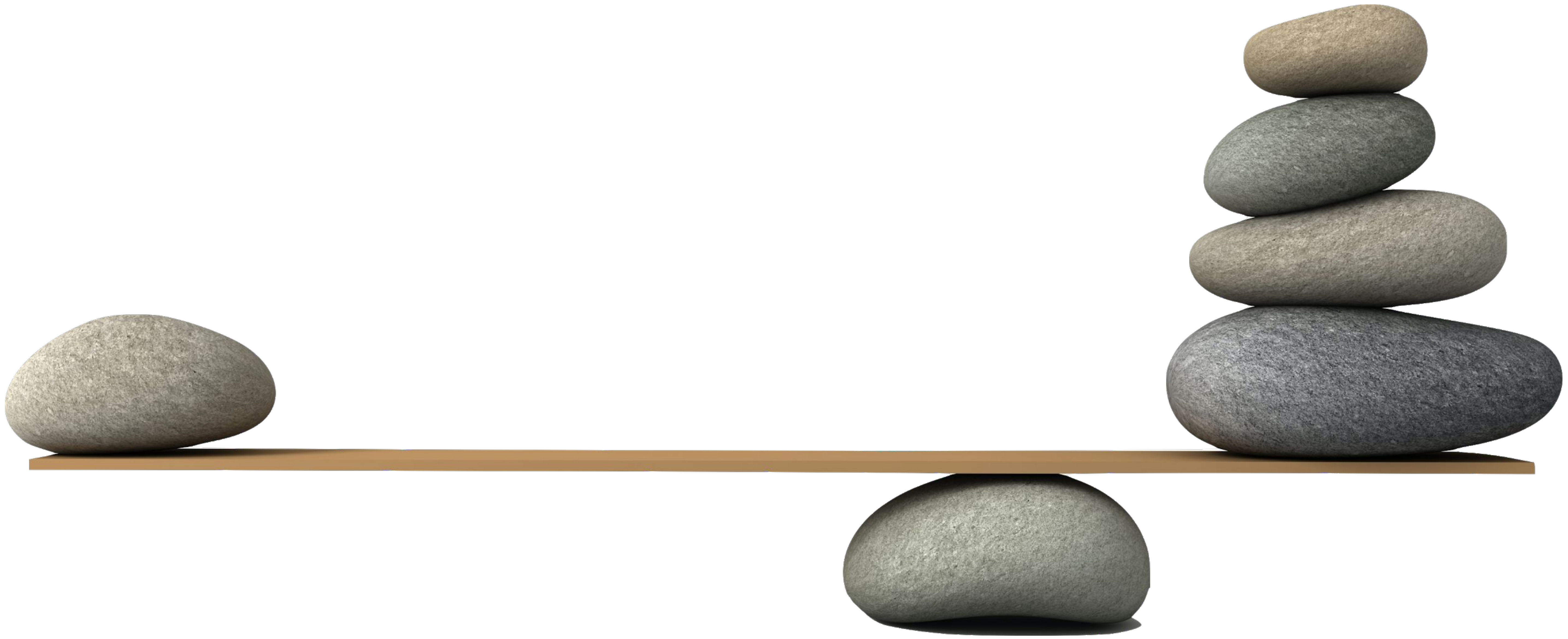
- Accumulate in IX resins much greater than 1%
- Removed from resin using regeneration (though not completely)
- Use of IX significantly alters the water and resin compositions

Part 2: Ionic Equivalents

A. Ionic Equivalents

B. Ionic Equivalents in water

C. Ionic Equivalents in Resin



A. Ionic Equivalents

Avagadro's number (6.02×10^{23}) of electrical charges

Electrons are negatively charged

- Ions that have gained electrons are anions
- Ions that have lost electrons are cations

Equivalent weight (eqwt) = molecular weight (mwt) / valence

- All IX is on the basis of an equal number of charges

B. Ionic Equivalents in Water

- Calcium carbonate mwt is 100 g/L
  - Valence is 2 (divalent)
  - Equivalent weight is 100/2 = 50 g/L (as $CaCO_3$) ← very convenient # to multiply and divide
- Water Concentrations typically reported mg/L or meq/L, not g/L or eq/L
- Resin Concentration and Water Concentration must use same units


ONE DOES NOT SIMPLY
DO Equillibrium Calculations WITHOUT CONVERTING
TO Equivalents [redacted]

C. Ionic Equivalents in Resin

Total capacity and concentration are the same thing

Resin concentrations usually expressed as eq/L

(eq/L x 1000 = meq/L) or (eq/L x 21.8 = kilograins/cu ft)

Resin Types	Form	Approx. concentration* (meq/L)
Strong Acid Cation (i.e. CG8)	Na	2000
Weak Acid Cation (i.e. WACG)	H	4000
Strong Base Anion (i.e. SBG2)	Cl	1400
Weak Base Anion (i.e. WBMP)	FB	1400

*Considerable variation due to X-link, porosity, etc.

Part 3: The Selectivity Equation

- The Selectivity Equation (products over reactants)
- Le Chatelier's Principle
- Neutralization Reactions
- The big picture is made up from many little pictures

Products over Reactants

Just like solubility product equations

$$K(Y^a/X^b) = (R\text{-}Y)^b(X)^a \,/\, (R\text{-}X)^a(Y)^b$$

Products Reactants

$K(Y^a/X^b)$ = constant for ion Y going into resin and ion X coming out

R = resin concentration

X = water concentration for ion X with valance “b”

Y = water concentration for ion Y with valence “a”

When both **X** and **Y** have the same valence **b** and **a** can be ignored

Validating the assumption used in our last Webinar

- 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 contaminant example

Perchlorate against Chloride

$$K(ClO_4/Cl) = (Cl)(RX\text{-} ClO_4) / (ClO4)(RX\text{-}Cl)$$

Products Reactants

Assumptions:

SBG1 (Strong base gel Type 1) **$K(ClO_4/Cl)$** = 125 **(RX-Total Cap)** = 1500 meq/L

Initial Conditions	meq/L	Final Conditions	meq/L
$RX\text{-}ClO_4$	1	$RX\text{-}ClO_4$	2.0
RX-Cl	**1499***	RX-Cl	**1498***
ClO_4	1	ClO_4	0.016
Cl	**1499***	Cl	**1500***

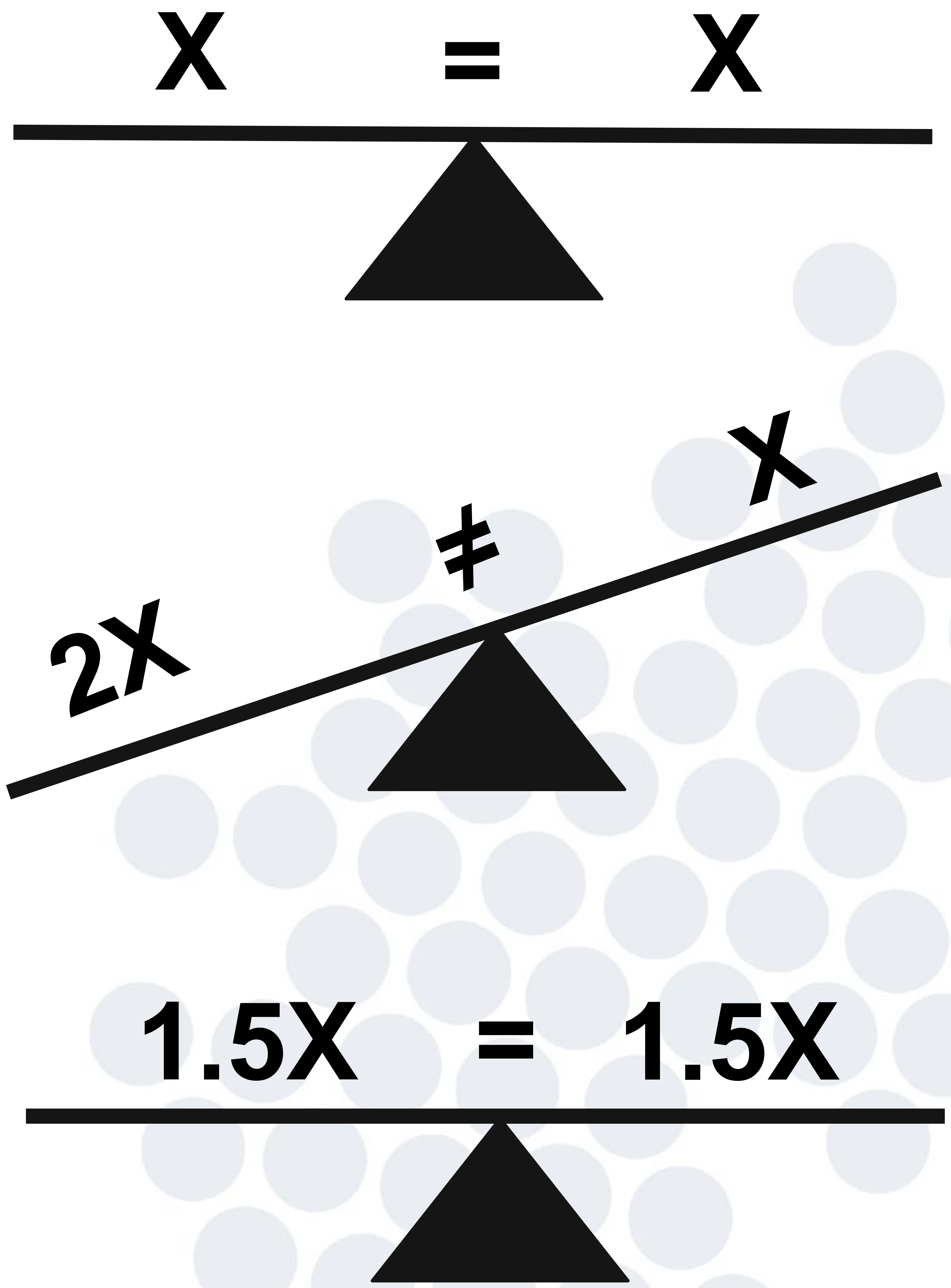
*Note: assumptions used in the last webinar for trace ion removal (that neither resin nor water composition changes significantly), hold true for perchlorate against chloride

Le Chatelier's Principle

Restoring balance

With any reversible chemical reaction, a change in concentration on one side of the equation results in a change on the other side to restore balance.

Henry Louis Le Chatelier



An unfavorable bulk exchange

Alkalinity Against chloride

$$K(HCO_3/Cl) = (Cl)(RX\text{-}HCO_3) / (HCO_3)(RX\text{-}Cl)$$

Products Reactants

Assumptions:

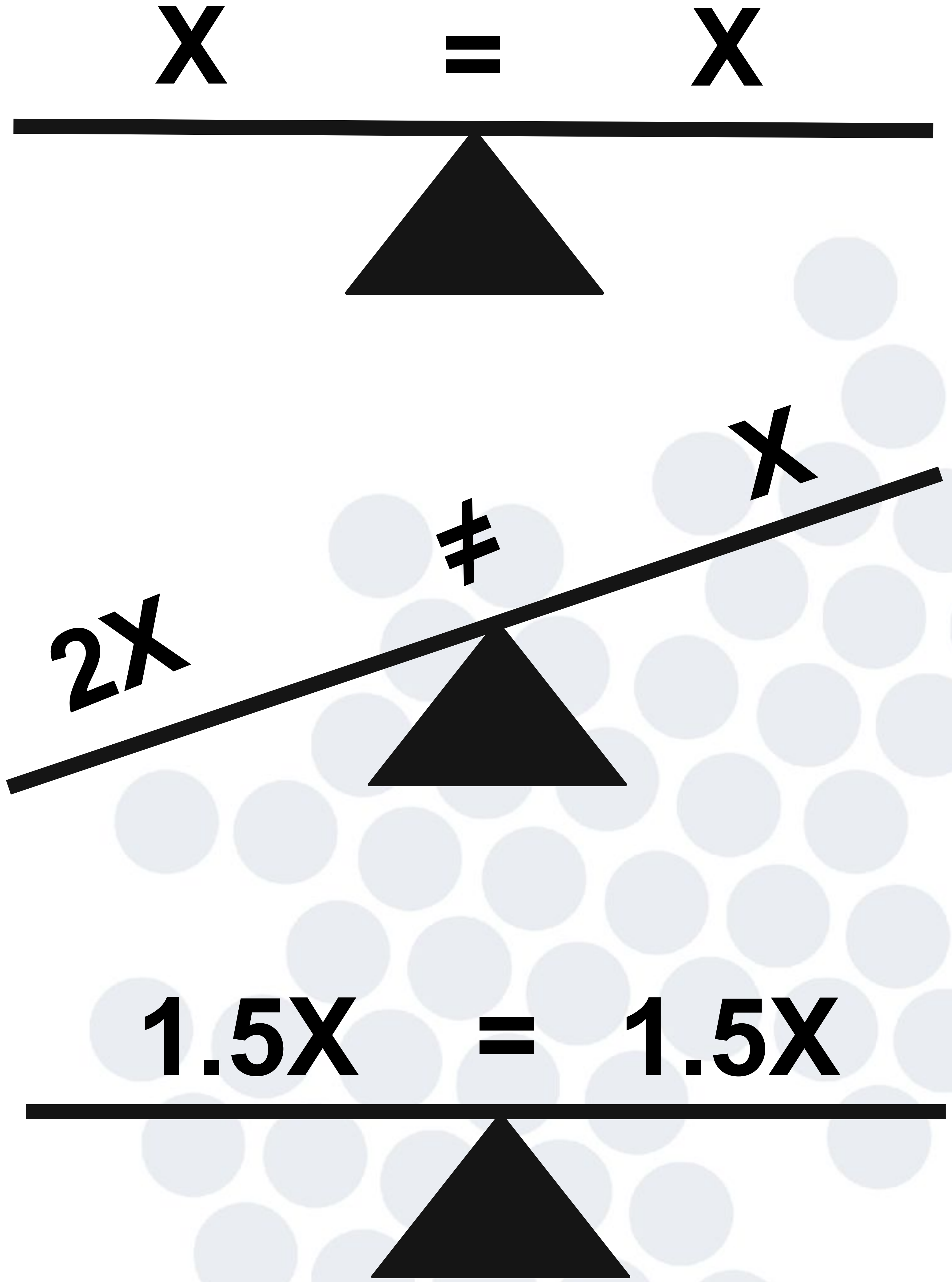
SBG2 (Strong base gel Type 2) **K(HCO3/Cl)** = 0.25 **(RX-Total Cap)** = 1400 meq/L

Initial Conditions	meq/L	Final Conditions	meq/L
$RX\text{-}HCO_3$	10	$RX\text{-}HCO_3$	**467***
RX-Cl	1390	RX-Cl	933
HCO_3	1390	HCO_3	933
Cl	10	Cl	467

*For the old timers: 467 meq/L = 10 kilograins per cu ft

The alkalinity balancing act

Restoring balance



Neutralization Reactions

What happens when one of the products is removed?

Example: Hydrogen form cation resin with sodium chloride

$$RX^{-}\text{-}H^{+} + Na^{+} + Cl^{-} \rightarrow RX^{-}\text{-}Na^{+} + H^{+} + Cl^{-}$$

As Na^{+} is removed, H^{+} is added to the product side to balance

Neutralization Reactions

What happens when one of the products is removed?

Example: solution contains sodium hydroxide rather than sodium chloride

$$RX^{-}\text{-}H^{+} + Na^{+} + OH^{-} \rightarrow\rightarrow\rightarrow RX^{-}\text{-}Na^{+} + H_2O + Cl^{-}$$

Hydrogen ions do not build up and the reaction proceeds much further

Part 4: Setting the stage (a little more IX theory)

- Selectivity is a double edged sword
- The big picture is made up from many little pictures
- The IX working zone (Importance of bed height)

Selectivity is a Double Edged Sword

A big "K" is not always a good thing

High Selectivity

- gives higher throughput capacity
- lower leakage for virgin resin, but...
- makes regeneration problematic
  - if K is 3:1 for X:Y
  - it takes 3Y remove 1X

Regeneration of ions with high selectivity

Ways of dealing with the double edged sword problem

- Chemicals
- Divalent to monovalent exchanges (e.g. Water softeners)
- Intermediate regenerants (Bisulfate vs. chloride, hydroxide vs. sulfate)
- Decomposing Regenerants (Ferric chloride against perchlorate)
- Salt form weak resins
- Neutralization reactions

Animate slide with each bullet point shown separately

The big picture is made up from many little pictures

Each selectivity calculation defines a reaction between water and resin.

The introductory examples include all the water reacting with all the resin.

This is like dumping all the resin into a lake and hoping it will remove everything, all at once

Fixed beds of resin provide opportunities to divide the work up into smaller pieces

In a tank full of resin there may be thousands or millions of individual interactions between water and resin

These multiple equilibriums provide much larger capacity and lower leakage than is accomplished by simply reacting all the water with all the resin

Cromatogrqphic programs such as ResinTech MIST-X use the power of computers to solve these millions of little calculations to paint the bigger picture.

The big picture

Millions of “small” calculations can be assembled into complete effluent profiles for any water and resin.

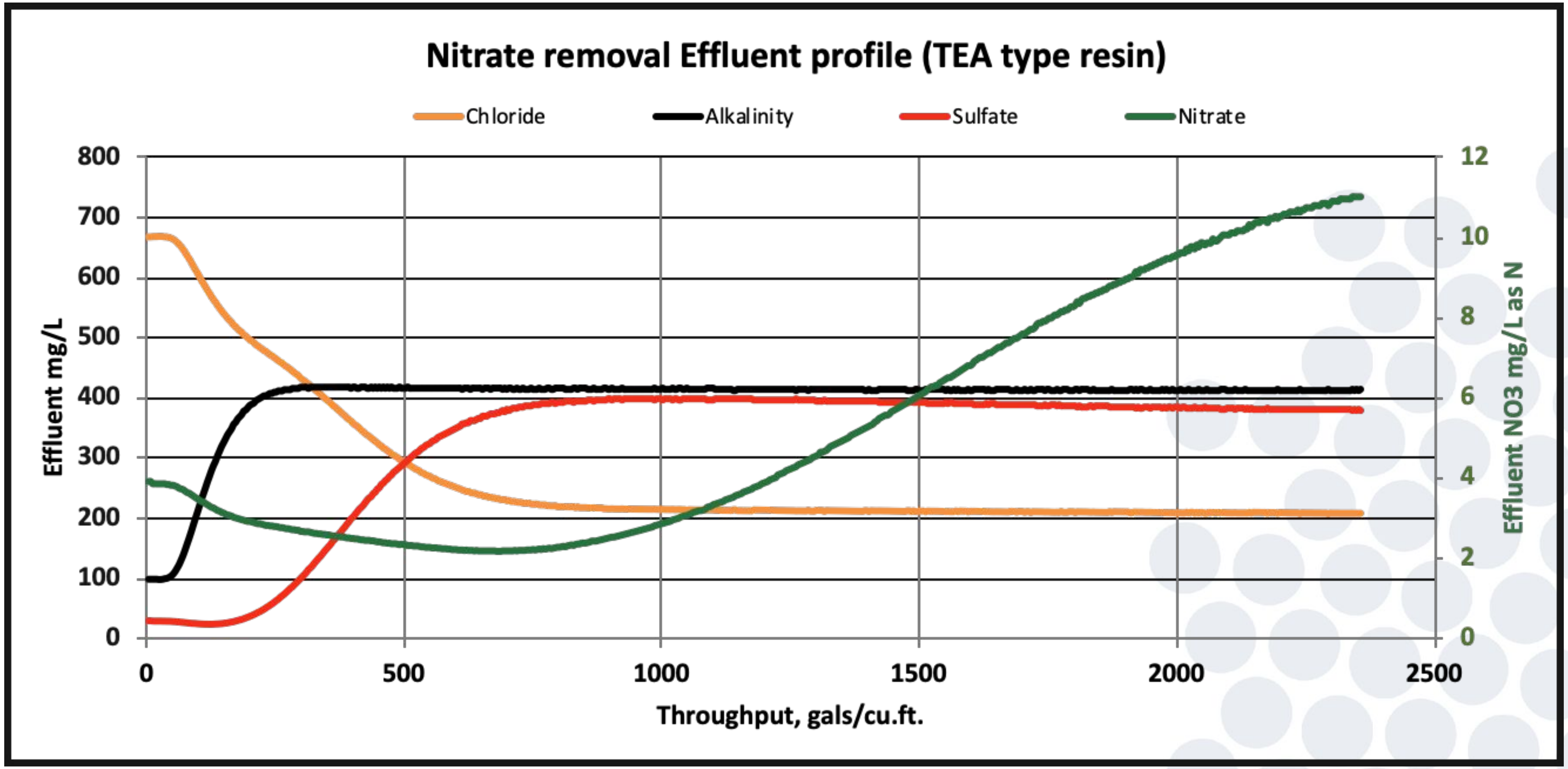
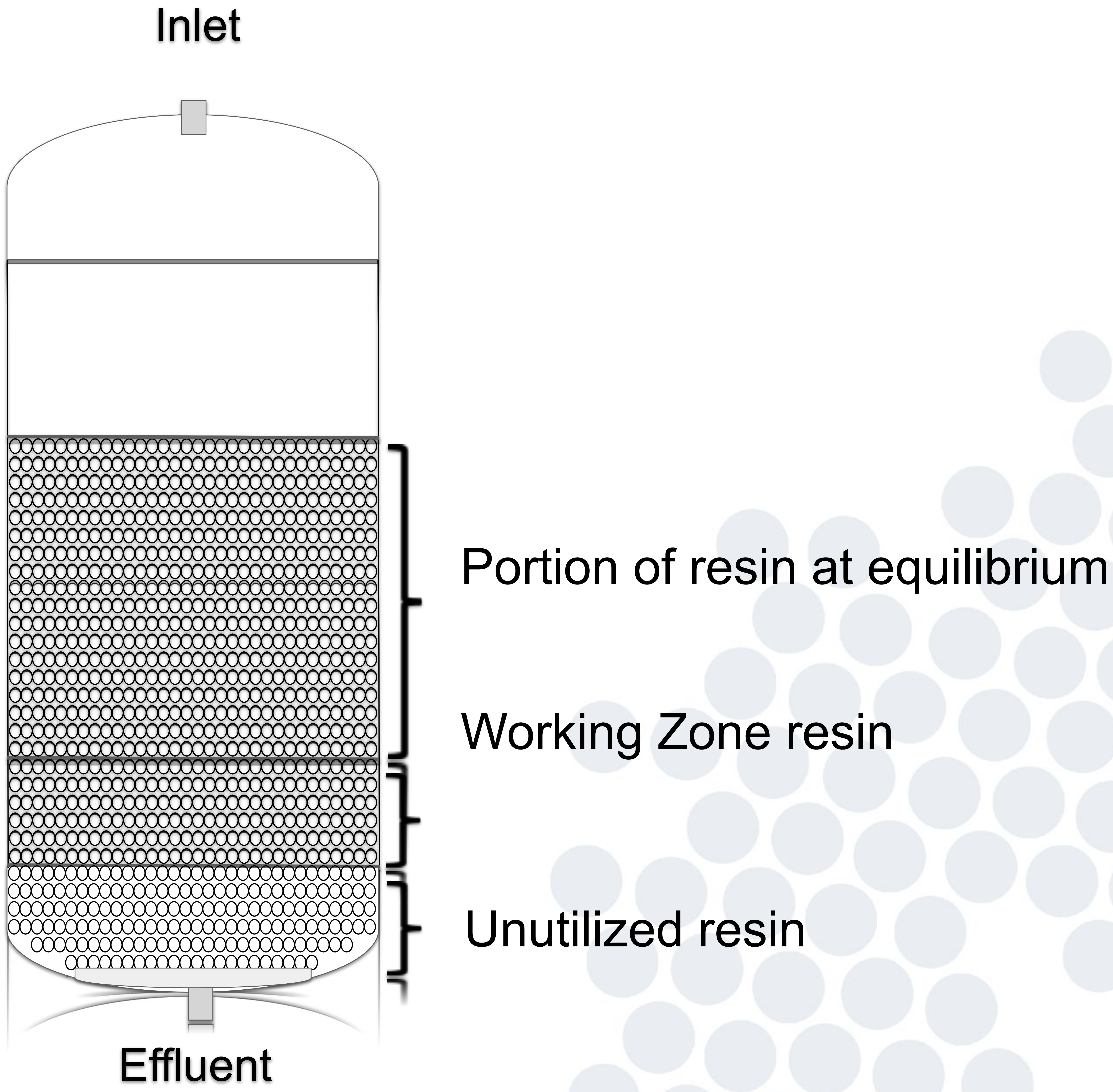
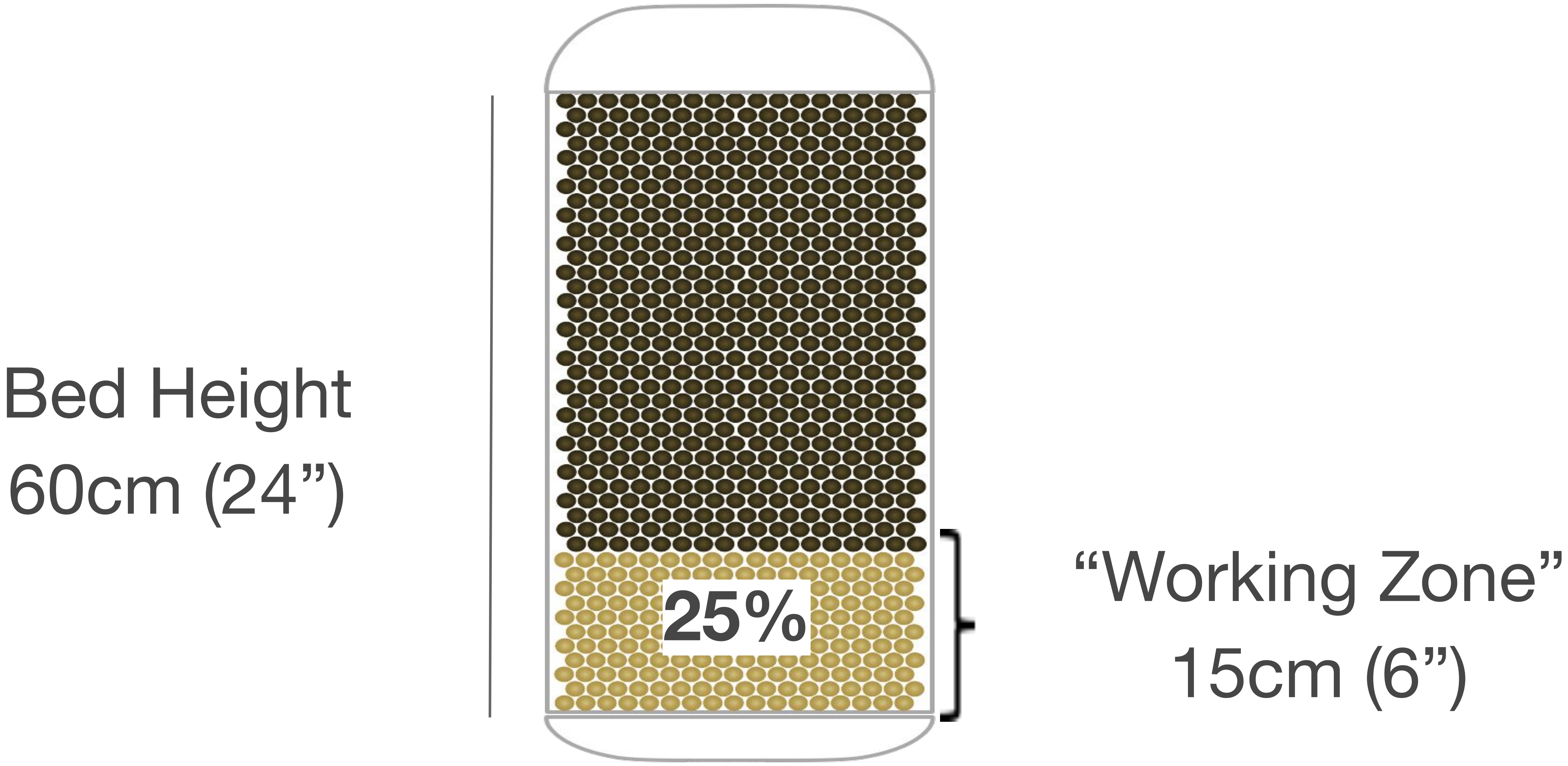


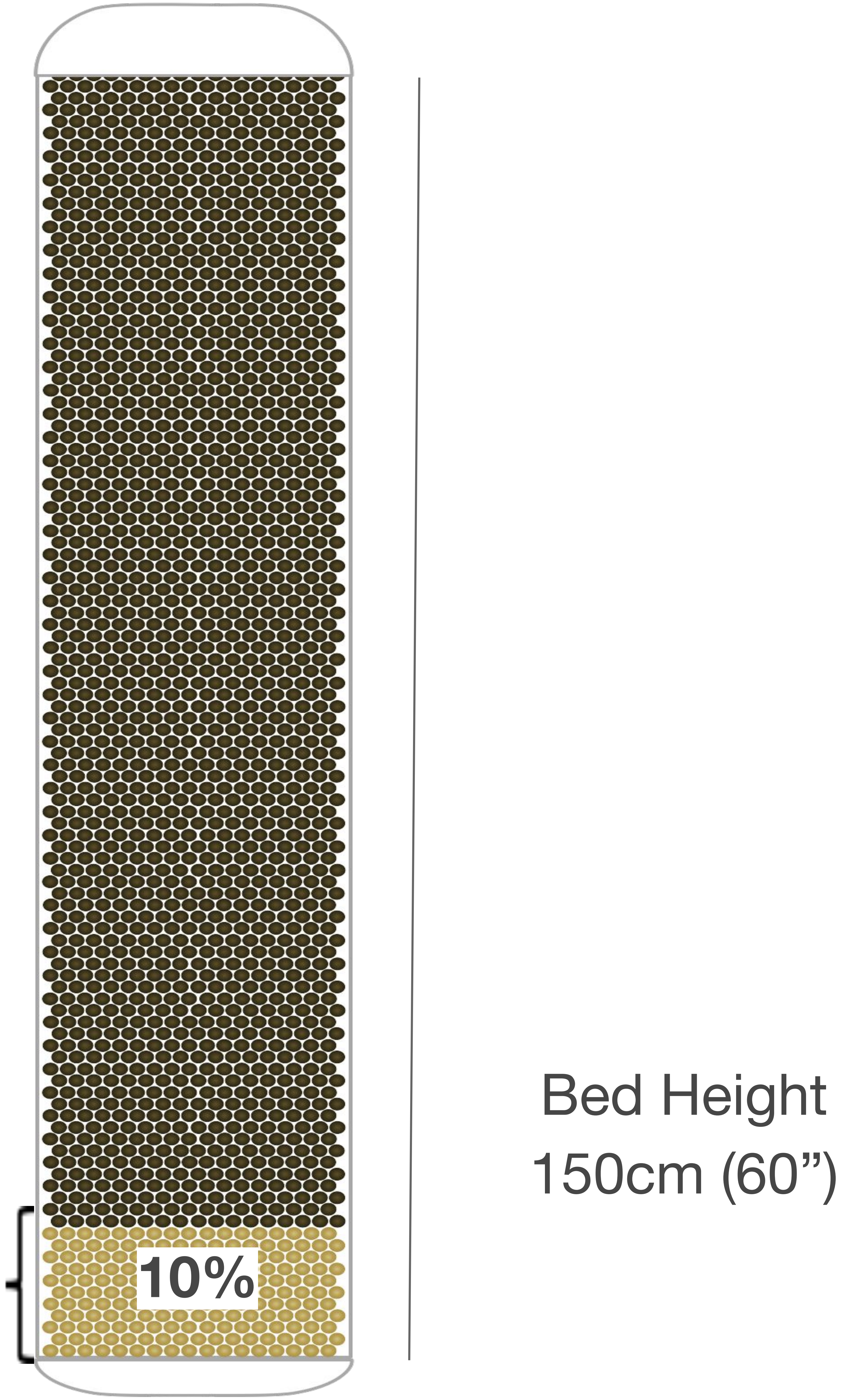
Illustration of Various Zones within an Ion Exchange Column



Importance of bed height

Deeper is almost always better





Part 4: Salt Form Bulk Exchanges

- Hardness Removal (AKA Water Softening)
- Nitrate Removal
- Alkalinity Removal

Hardness Removal (AKA Water Softening)

An exchange where concentration matters

Type of cation resin	"K" (Ca/Na)	"K" (Mg/Na	Capacity meq/L
CG8*	3.7	1.0	2000

*CG8 is a strong acid gel cation

*Capacities and "K" values appropriate for ResinTech products

Flash back to Apparent Selectivity

"Apparent Selectivity ("AK") for divalent to monovalent ion relationships depends on the concentration difference between resin and water

NOTE: *If unsure go back and review previous lecture about trace contaminants.*

"AK" (Mg^{+2}/Na^{+1}) = "K" (Mg^{+2}/Na^{+1}) x resin concentration / water concentration

Hardness Removal calcium against sodium

An exchange where concentration matters

Ca vs Na	100 ppm as $CaCO_3$	1000 ppm as $CaCO_3$	100,000 ppm as $CaCO_3$
	2 meq/L	20 meq/L	2000 meq/L
CG8	3700	370	3.7

*CG8 selectivity for calcium against sodium is very high when TDS is low, but declines sharply as TDS increases

Hardness Removal magnesium against sodium

An exchange where concentration matters

Mg vs Na	100 ppm as $CaCO_3$	1000 ppm as $CaCO_3$	100,000 ppm as $CaCO_3$
	2 meq/L	20 meq/L	2000 meq/L
CG8	1000	100	1.0

*CG8 selectivity for magnesium against sodium, although not as high as calcium, is high when TDS is low, but declines sharply as TDS increases

Hardness Removal by softeners is TDS limited

- Above approx 10,000 ppm TDS as $CaCO_3$, softeners no longer remove hardness very well at all.   But...
- softening is a classic example of an equilibrium process that is efficient in both the exhaustion and regeneration sides of the equilibrium equation

Why Water Softening is so Efficient

- Apparent selectivity for hardness is **very favorable** when TDS is relatively **low**
- **low leakage** can be obtained even when resin is significantly in **Hardness form**
- **High brine concentration** during regeneration greatly reduces apparent selectivity for hardness ions
- **Chemical efficiency** can exceed **90%** (5500 grains per pound of salt) when brine concentration exceeds **10%** (roughly 100,000 ppm as CaCO3)

Nitrate Removal

An example of bulk exchange where selectivity matters but sulfate is king

Type of anion resin	K (NO_3/Cl)	K (SO_4/Cl)	Capacity (meq/L)
SBG2*	3	0.15	1400
SIR-100*	5	0.02	950
SIR-110*	23	0.003	760

*SBG2 contains DMEA (Dimethyl ethanolamine)
*SIR-100 contains TEA (Triethylamine)
*SIR-110 contains TBA (Tributylamine)


Where do nitrates come from?

*Capacities and "K" values appropriate for ResinTech products

Selectivity for nitrate against chloride doesn't change with concentration

NO_3 vs Cl	100 ppm as $CaCO_3$	1000 ppm as $CaCO_3$	10,000 ppm as $CaCO_3$
	2 meq/L	20 meq/L	200 meq/L
SBG2	3	3	3
SIR-100	5	5	5
SIR-110	23	23	23

Nitrate selectivity compared to chloride remains constant as TDS increases because nitrate and chloride are both monovalent

"Selectivity for sulfate against chloride changes with concentration

SO_4 vs Cl	100 ppm as $CaCO_3$	1000 ppm as $CaCO_3$	10,000 ppm as $CaCO_3$
	2 meq/L	20 meq/L	200 meq/L
SBG2	105	10.5	1.05
SIR-100	9.5	0.95	0.01
SIR-110	1.14	0.11	0.001

Sulfate selectivity compared to chloride changes rapidly as TDS increases because sulfate is divalent and chloride is monovalent

Against nitrate, sulfate is king

Increasing TDS dramatically changes sulfate to nitrate selectivity

NO_3 vs SO_4	100 ppm as $CaCO_3$	1000 ppm as $CaCO_3$	10,000 ppm as $CaCO_3$
	2 meq/L	20 meq/L	200 meq/L
SBG2	0.03	0.29	2.9
SIR-100	0.53	5.3	53
SIR-110	20	200	2000

Sulfate selectivity compared to nitrate changes rapidly as TDS increases because sulfate is divalent and chloride is monovalent

Why Nitrate removal is not nearly as efficient as water softening

- Apparent selectivity for nitrate against chloride remains constant for both the exhaustion and regeneration cycles
- **Salt brine (chloride ions) are not efficient to remove nitrate during regeneration**
- **Substantial nitrate leakage occurs because reasonable salt doses do not completely strip nitrate from the resin during regeneration**
- **Chemical efficiency** seldom approaches even 50%, despite the best techniques (deep beds, countercurrent regeneration, etc)

Alkalinity Removal by Chloride Cycle Dealkalizers

An Example of an Unfavorable Exchange

Type of anion resin	"K" (HCO_3/Cl)	"K" (SO_4/Cl)	Capacity meq/L
SBG2*	0.25	0.15	1400

*SBG2 is a strong base gel type 2 anion

*Capacities and "K" values appropriate for ResinTech products

The Softeners (foreground) are much smaller than the Dealkalizers (background)

Alkalinity Removal by Chloride cycle Dealkalizers

Apparent Selectivity Bicarbonate against chloride

HCO_3 vs Cl	100 ppm as $CaCO_3$	1000 ppm as $CaCO_3$	10,000 ppm as $CaCO_3$
	2 meq/L	20 meq/L	200 meq/L
SBG2*	0.25*	0.25*	0.25*

*Apparent Selectivity for bicarbonate against chloride doesn't change because both ions have the same valence)

Alkalinity Removal by Chloride cycle Dealkalizers

Apparent selectivity for sulfate against chloride

SO_4 vs Cl	100 ppm as $CaCO_3$	1000 ppm as $CaCO_3$	10,000 ppm as $CaCO_3$
	2 meq/L	20 meq/L	200 meq/L
SBG2*	105*	10.5*	1.05*

*Apparent Selectivity for sulfate against chloride changes with concentration because sulfate is divalent and chloride is monovalent

Alkalinity Removal by Chloride Cycle Dealkalizers

Putting it all together for bicarbonate against sulfate

HCO_3 vs SO_4	100 ppm as $CaCO_3$	1000 ppm as $CaCO_3$	10,000 ppm as $CaCO_3$
	2 meq/L	20 meq/L	200 meq/L
SBG2	0.002*	0.024*	0.24*

*Apparent Selectivity for bicarbonate against sulfate changes with concentration because sulfate is divalent and bicarbonate is monovalent. Because we chose chloride as the reference ion, bicarbonate against sulfate is the ratio of the two previous calculations

“Good enough”

Alkalinity removal is a classic example of a bulk ion exchange that is unfavorable but “good enough”...

- Useful capacity despite unfavorable selectivity
- Not good for waters with lots of sulfate
- Substantial alkalinity leakage

Wrapping up

Takeaways about Bulk Contaminants and Salt Form Exchanges

It's all about equivalents

- One charge goes in, another comes out
- Products over reactants
- Le Chatelier is defeated when one of the products is neutralized

Apparent Selectivity changes with TDS for divalent to monovalent exchanges

- Selectivity is a double edged sword
- Bed height matters
- Only the ions in the middle dump

Next Webinar

Nitrates

Wednesday, March 31st at 11am ET

Keep an eye out for a separate registration link.

Questions?


ResinTech Inc.

THANK YOU

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INNOVATIONS IN ION EXCHANGE