Pacific Water Quality Association

Getting More from Your Arsenic and Fluoride Removal Systems

PWQA Annual Convention

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Introduction

There are two elements common to most water supplies that are ticking time bombs.

These are: Arsenic and Fluoride.

If we live long enough….

Why is it that Arsenic and Fluoride are so pernicious?

Both are bio-accumulative.

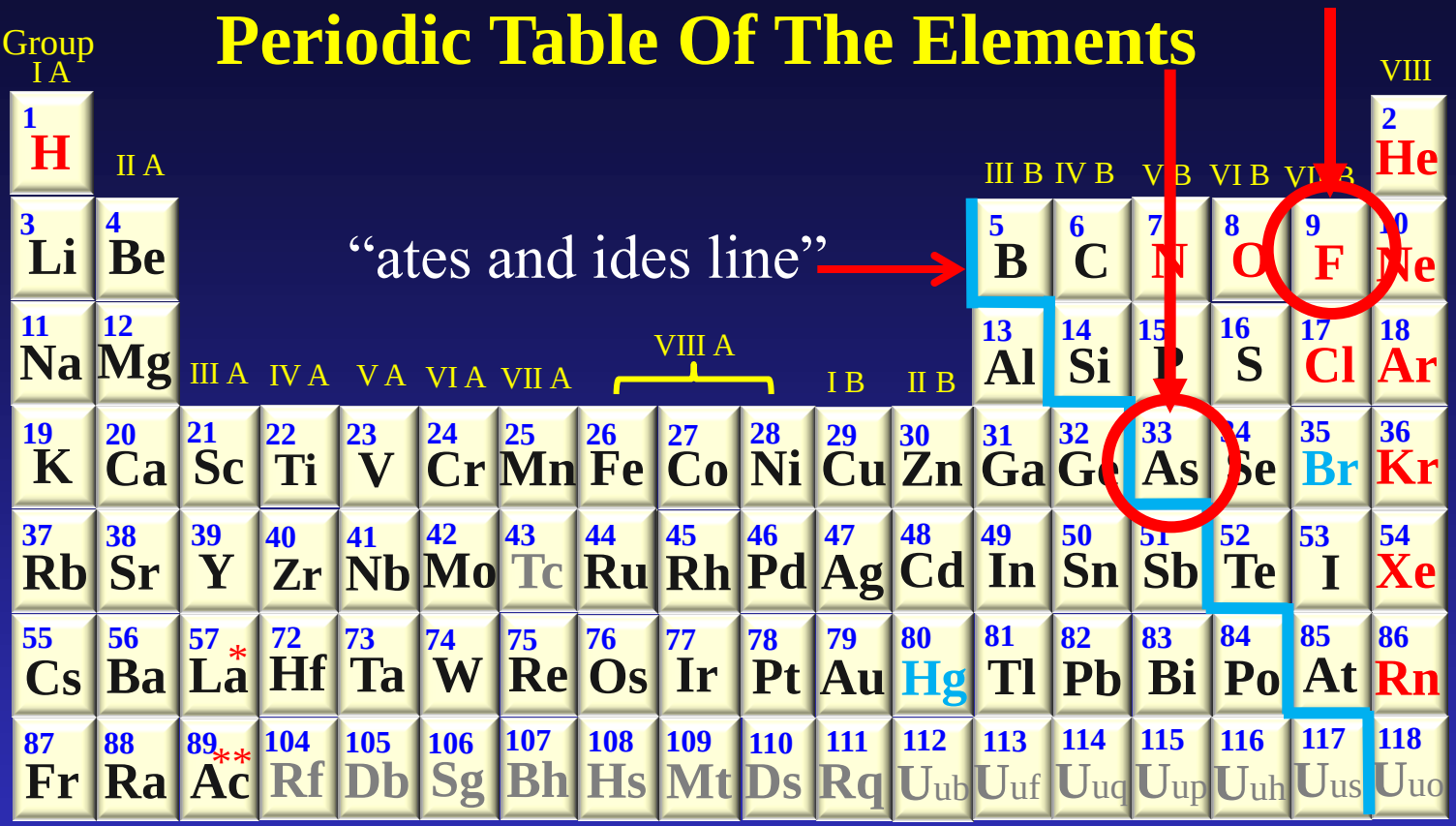
They hang around the body for a long time.

We are exposed to arsenic and fluoride through the air we breath, the food we eat as well as the water we drink.

Arsenic ***$(AsO_4)^{-3}$ can masquerade as Phosphate $(PO_4)^{-3}$ in the body and form a highly insoluble tri-calcium arsenate and even replace the tri-calcium phosphate (bone) structure.***

Fluoride ***can also react with the bone structure forming a highly insoluble calcium fluoride which can weaken both bone and tooth structure (fluorosis).***

Periodic Table Of The Elements



Lanthanide Series *	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinide Series **	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The toxicity of arsenic has been known for over 2000 years. Fluoride is a member of the halide family… all of which are known poisons. Makes a great pesticide.

Arsenic

1. *Arsenic has been a known toxin for over 2000 years.*
2. *There are trace amounts of arsenic is almost all food, water, air and soil. You can not avoid exposure to arsenic.*
3. *There are no known adverse health effects from arsenic deficiency.*
4. *Arsenic is bio-accumulative in the body. A little bit here and there over a long time still does the job.*
5. *Oxy-compounds of Arsenic [AsO_4^{-3} (arsenate) and AsO_3^{-3} (arsenite)] are far more toxic than are organic species.*
6. *Chronic arsenic exposure induces high oxidative stress.*
7. *The MCL for arsenic is now at 10 ppb. Arsenic levels in drinking water of only 0.17 μg/l (that's 170 ppt) can cause poisoning effects.*
8. *Arsenic is a known human carcinogen. Ingestion can lead to skin cancer as well as cancer of the bladder, liver and lungs.*
9. *Continuous exposure to "legal" levels of Arsenic can cost kids IQ points.*
10. *An adult person would only have to ingest about 70 milligrams of arsenic to be fatally poisoned by a single dose.*
11. *Drinking water is not the only source of arsenic in our daily lives.*

Maximum Contamination Level

Is the MCL for arsenic (10 ppb) a protective level?

The previous MCL for arsenic was reduced from 50 ppb to 10 ppb in 2006 because the 50 ppb was found to be non-protective.

The current 10 ppb does not guarantee the water is "safe" It simply represents an economic compromise between what is achievable and at what cost to do it. The MCLG (goal) is ZERO.

Therefore…… the only safe level of arsenic in drinking water is……

ZERO!!

Fluoride

1. *Fluoride is natural and can be found in the earth's crust, water and air*
2. *Fluoride, topically applied to teeth, has cavity prevention benefits that are helpful for growing children.*
3. *Humans are exposed to fluoride through food and drinking water and by breathing air..*
4. *Fluoride is bio-accumulative. I has been found to be an endocrine disrupting-neurotoxic carcinogen and is no longer considered "essential".*
5. *Consumption of fluoride at levels beyond those used in fluoridated water for a long period of time leads to skeletal fluorosis, causing dental decay and bone degradation.*
6. *A malfunctioning piece of water fluoridation equipment in Alaska in 1992 caused acute fluoride poisoning of 89 victims and one death.*
7. *The lethal dose for most adult humans is estimated at 5-10 grams.*
8. *There is enough fluoride in a tube of toothpaste to kill a child.*
9. *Drinking water is not the only source of fluoride in our diets. Most comes from food.*

Recently….

Medical Journal Designates Fluoride as Neurotoxin

by Dr. Edward Group DC, NP, DACBN, DCBCN, DABFM Published on November 8, 2014, Last Updated on November 16, 2015.

The U.S. Centers for Disease Control (CDC) in January 2011 issued a startling report that admits 2 in 5 children in America show signs of fluoride poisoning (streaking, spotting or pitting of teeth due to dental fluorosis).

The agency concluded that fluoride levels need to be lowered in municipal water supplies, reducing fluoride to 0.7 milligrams per liter (the previous recommended upper limit was 1.2 milligrams per liter).

Mike Adams, Editor of NaturalNews.com

Maximum Contamination Level

Is the MCL for fluoride (4 ppm) a protective level?

When the MCL for fluoride was established, the regulators thought the benefits of ingested fluoride were real. And the real toxicity was not known.

Fluorosis is on the rise…even in areas that do not fluoridate their municipal water.

Fluoride was recently designated a neurotoxin. Continued over exposure will cost your kids IQ points.

There is absolutely no clinical proof of any health benefit for the human body for ingested fluorid

Therefore…… The only safe level for fluoride in drinking water is…

ZERO!!

Proven Methods for Arsenic Removal

1. *Co-precipitation with Iron or Aluminum*
2. *Activated Alumina*
3. *Ion Exchange*
4. *Reverse Osmosis*
5. *Adsorbants (metal oxide based)*

Proven Methods of Fluoride Removal

- *Chemical Precipitation (CaO ~50%)*
- *Reverse Osmosis (90+%)*
- *Distillation (95+%)*
- *Adsorption (95+%)*
  - *bone char*
  - *activated alumina*
- *Ion Exchange (SBA salt regen 95+%)*

Arsenic and Fluoride Removal

Both As and F can be removed with "selective" adsorbants. However, there are a number of interfering ionic contaminants that greatly reduce the capacity of these systems.

For arsenic, this includes the arsenic specie (As^{+3} and As^{+5}), the pH of the feed, presence of oxy-ions such as phosphate, silicate, V, U, Se, Mo (all anionic).

For Fluoride, this includes bi-carbonate and pH.

How do we take some of these factors out of play with pre-treatment to maximize the performance of adsorbants?

Adsorbants

Typical arsenic media are metal oxide based

- ***Layne RT (iron)***
- ***Ferrix A33E (iron)***
- ***GFO (iron)***
- ***GFH (iron)***
- ***Metsorb (titanium)***

Typical fluoride media are aluminum oxide based which includes activated alumina and aluminum doped cation exchangers.

Activated Alumina also removes arsenic

Adsorption Media Capacity

Adsorption reactions are driven by:

Concentration and form of contaminant

pH (impacts solubilities and form)

Surface Preparation of Media

Competition from other Ions

EB Contact Time (flow rate/cu ft)

Let's look at the impact on each of these variables and see how to take them out of play.

Reducing Arsenic and Fluoride

Modern adsorbants, although highly selective for Arsenic and Fluoride, are not exclusive.

Other ions present in the water compete for sites on the adsorbant and shorten the expected life. Often these ions are not even listed in the water analysis.

Understanding their impact and making allowances for them (even when not indicated) is essential in the proper design of any arsenic removal system.

You Need a Water Analysis !!

Just because silica, phosphates, vanadium, uranium, selenium, molybdenum, et ceteranium are not included in your $20 water report…that doesn't mean they are not present.!!

To be safe, we have to assume they ARE there at some level.

ARSENIC

Arsenic V	50.0	Pre-oxydation	0		8 ppb break	2761 days
Arsenic III	0.0	EBCT	2.5	min	50% break	3840
TOTAL	50.0	gpm/cu ft	3.0			
Vanadium	0.0					
Phosphate	0.0	Volume Media	1.0	cu ft		
Silica	0.0					
pH	7.00					
Oxy-Anions	0					
Daily Usage	350					
Flowrate	3					

Capacity Calculator

2761 days = 7.56 years and 966,000 gallons

Under Ideal Conditions

Arsenic V	45.0
Arsenic III	5.0
TOTAL	50.0
Vanadium	25.0
Phosphate	75.0
Silica	30.0
pH	7.62
Oxy-Anions	15.0
Daily Usage	350
Flowrate	3

Pre-oxydation	0	
EBCT	2.5	min
gpm/cu ft	3.0	

8 ppb break	368	days
50% break	502	

Volume Media 1.0 cu ft

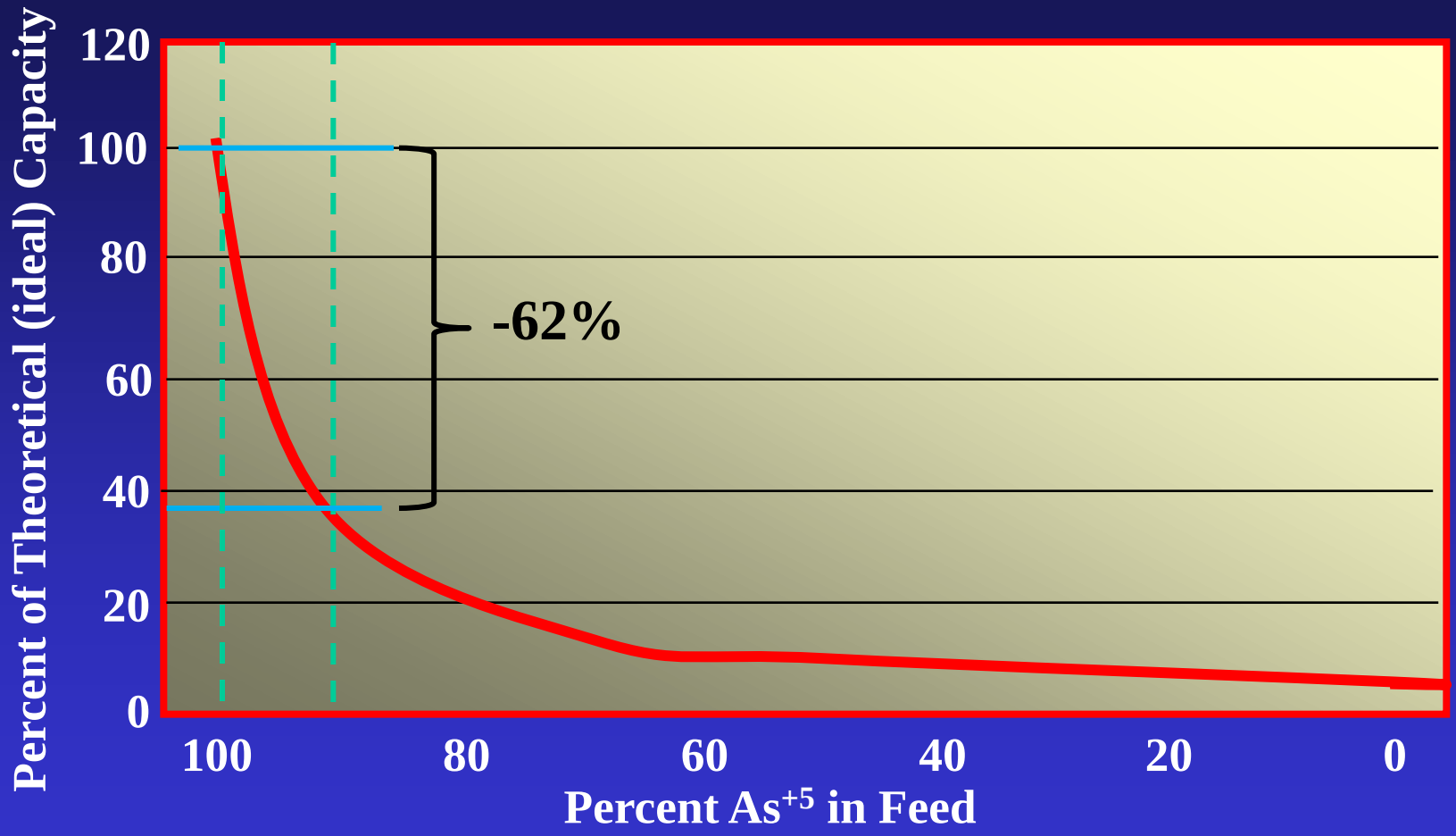
Capacity Calculator

368 days = 1 years and 128,000 gallons

Under Typical Conditions

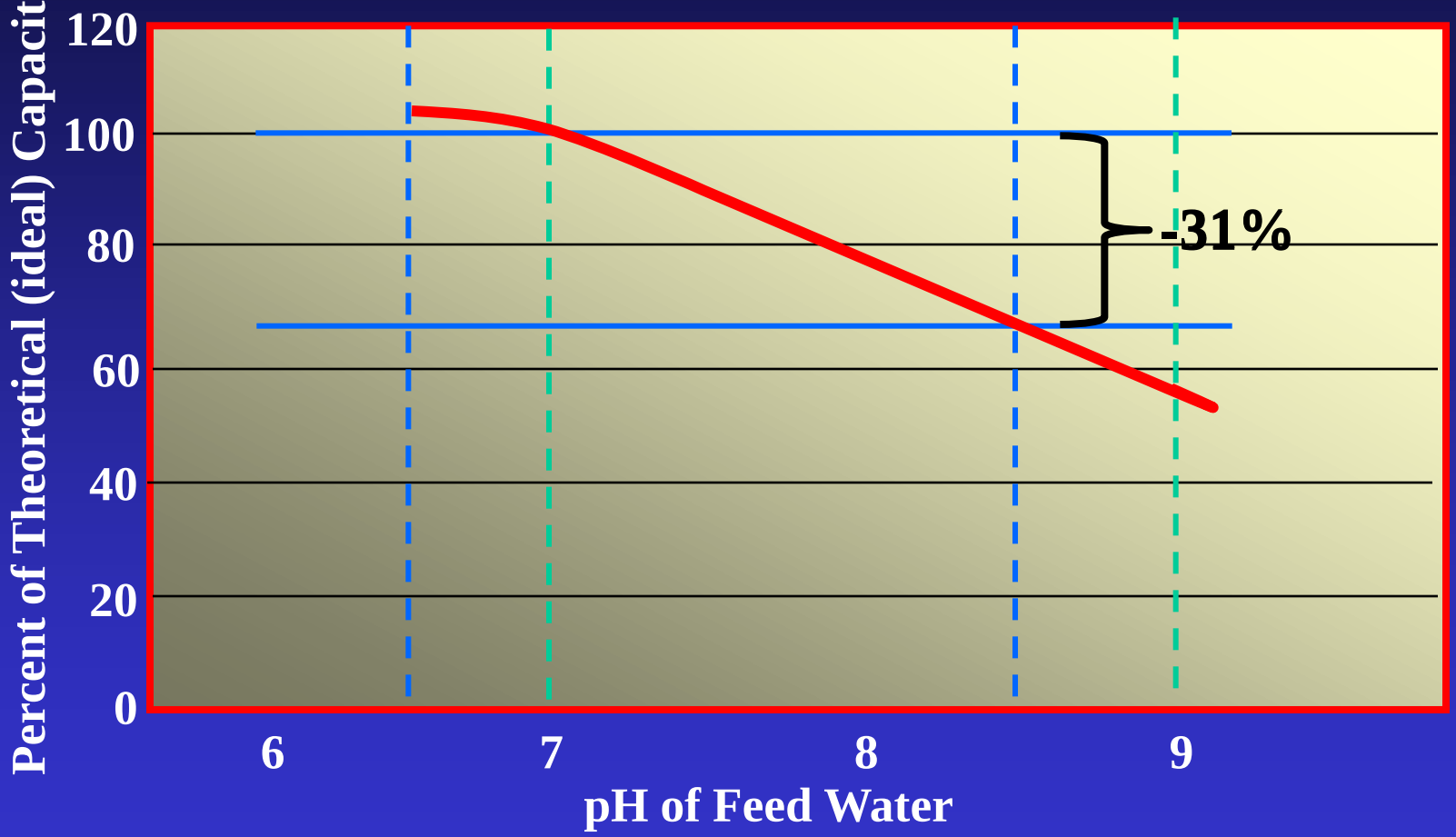
As^{+5}/As^{+3} Ratio

Basis: 50 ppb As^{+5} with 2 min EBCT at pH 7.0



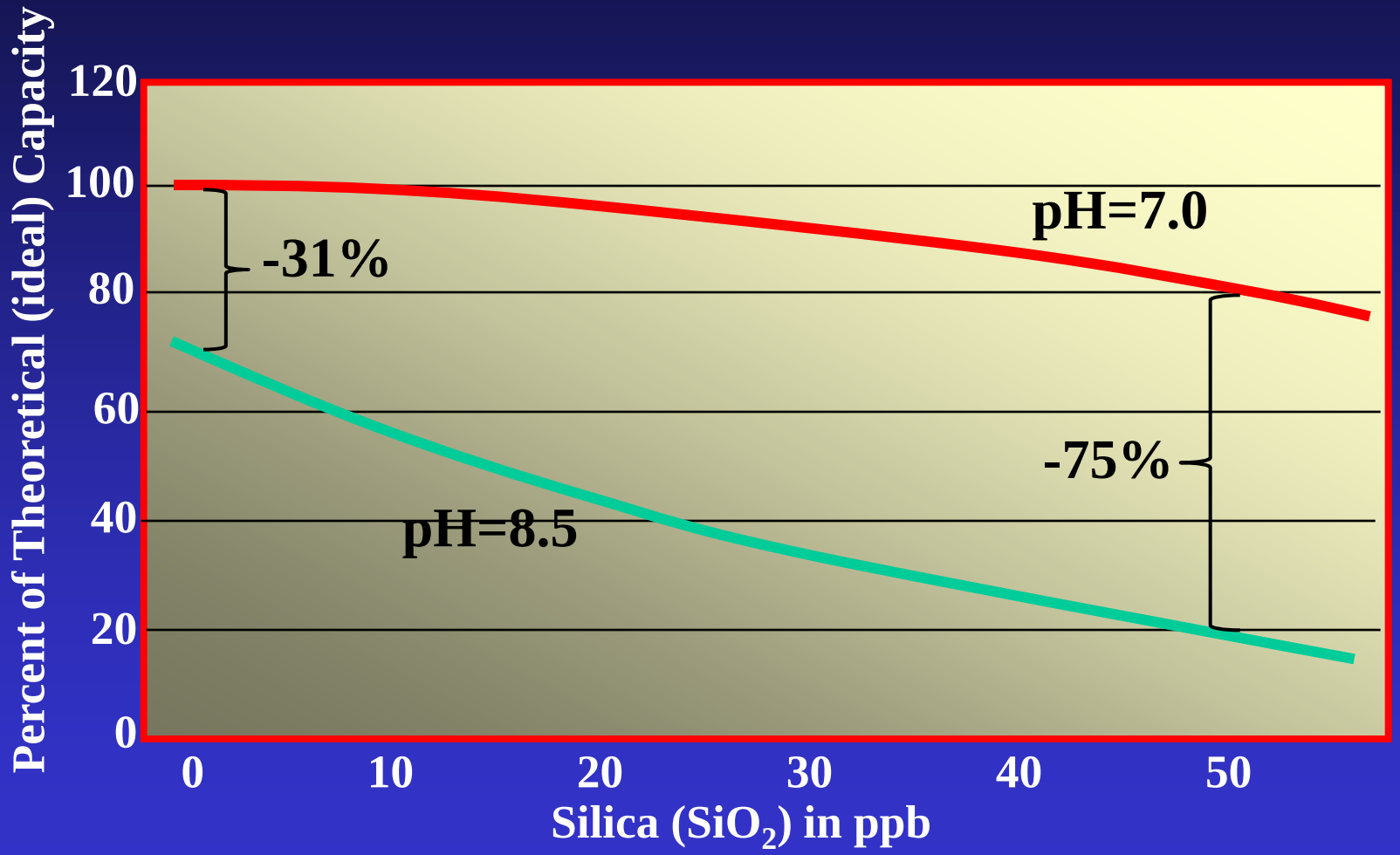
Basis: 50 ppb As^{+5} with 2 min EBCT

pH of Feed Water



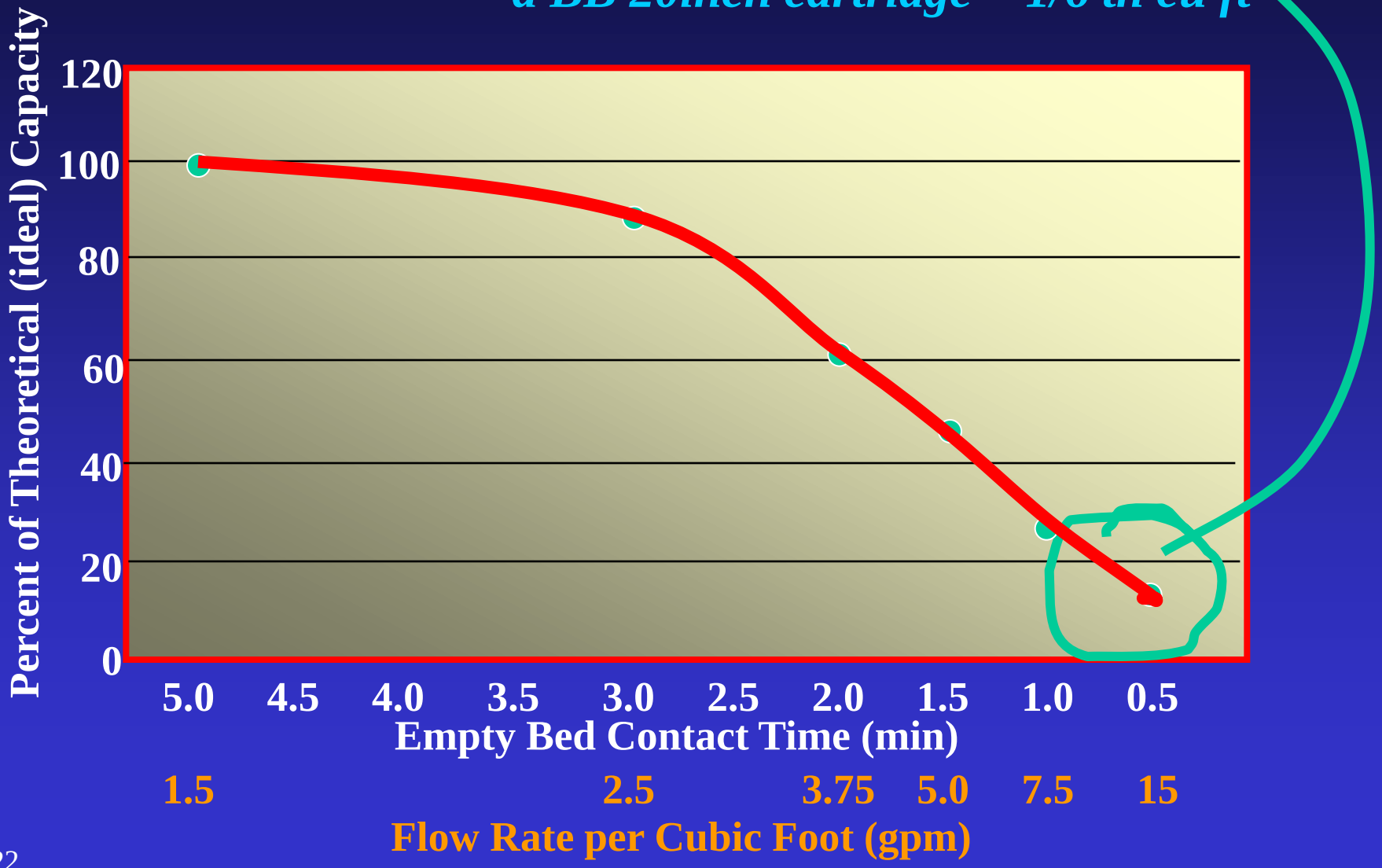
Silica

Basis: 50 ppb As^{+5} with 2 min EBCT at pH 7.0

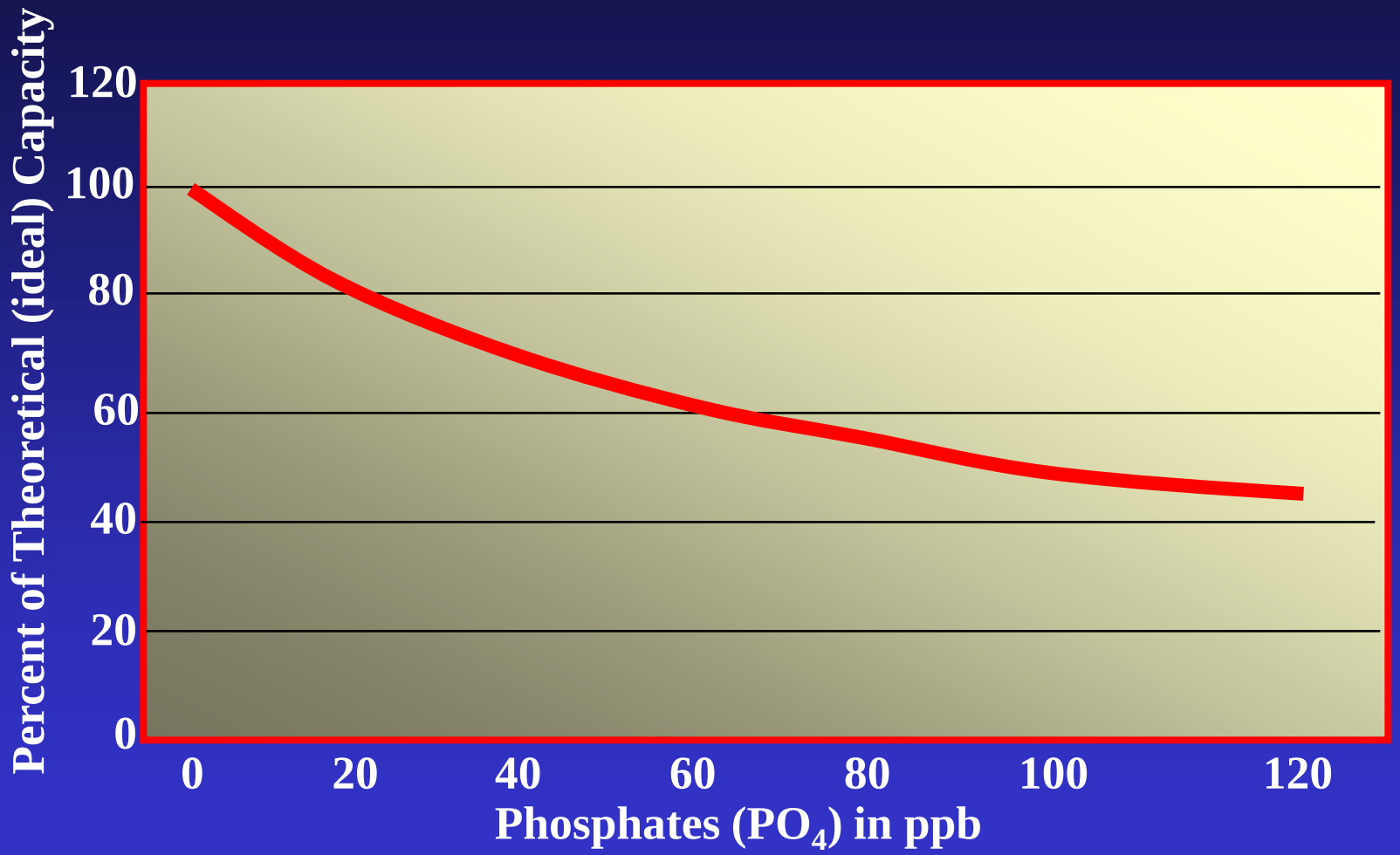


Empty Bed Contact Time (EBCT)

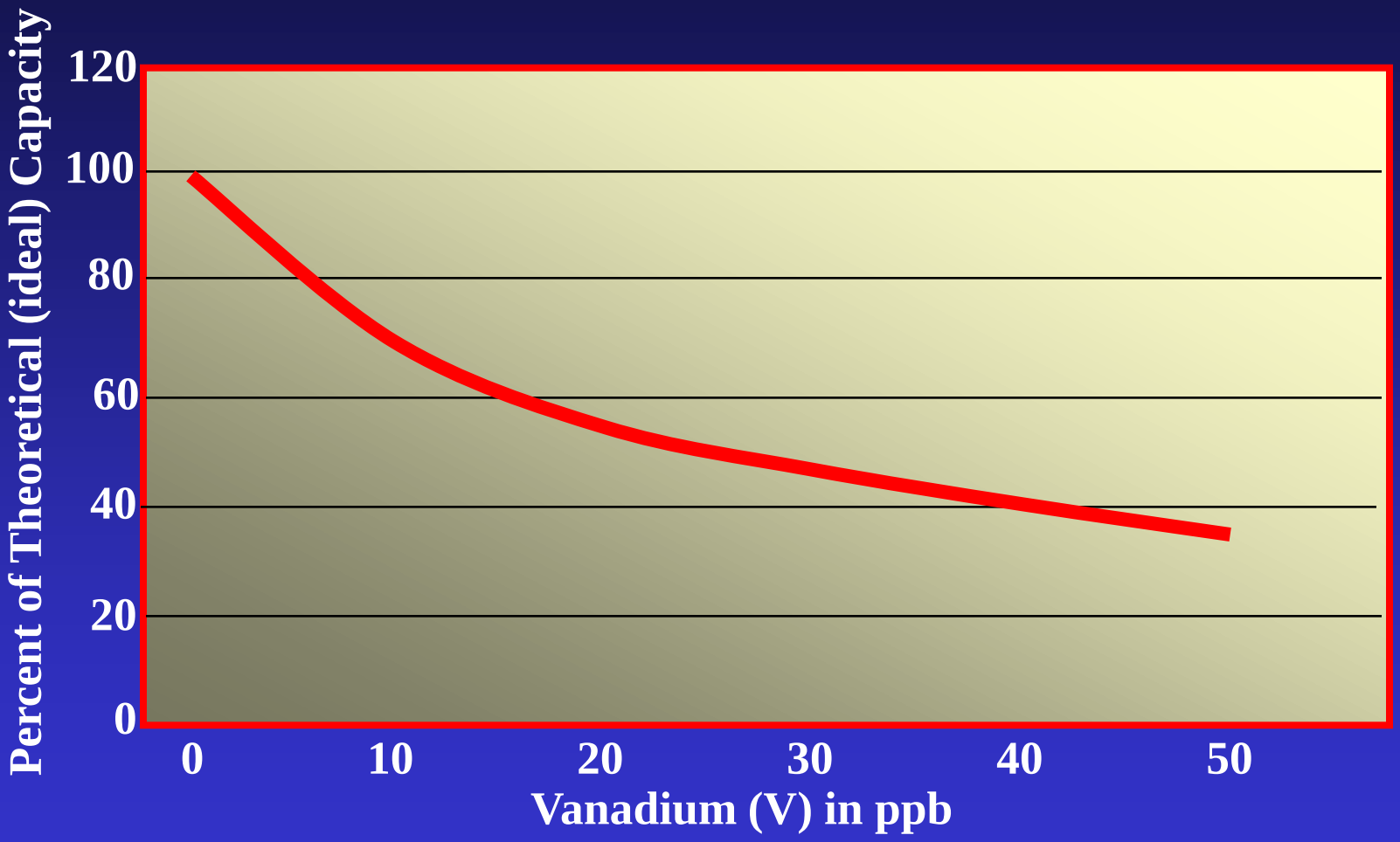
a BB 20inch cartridge = 1/6 th cu ft



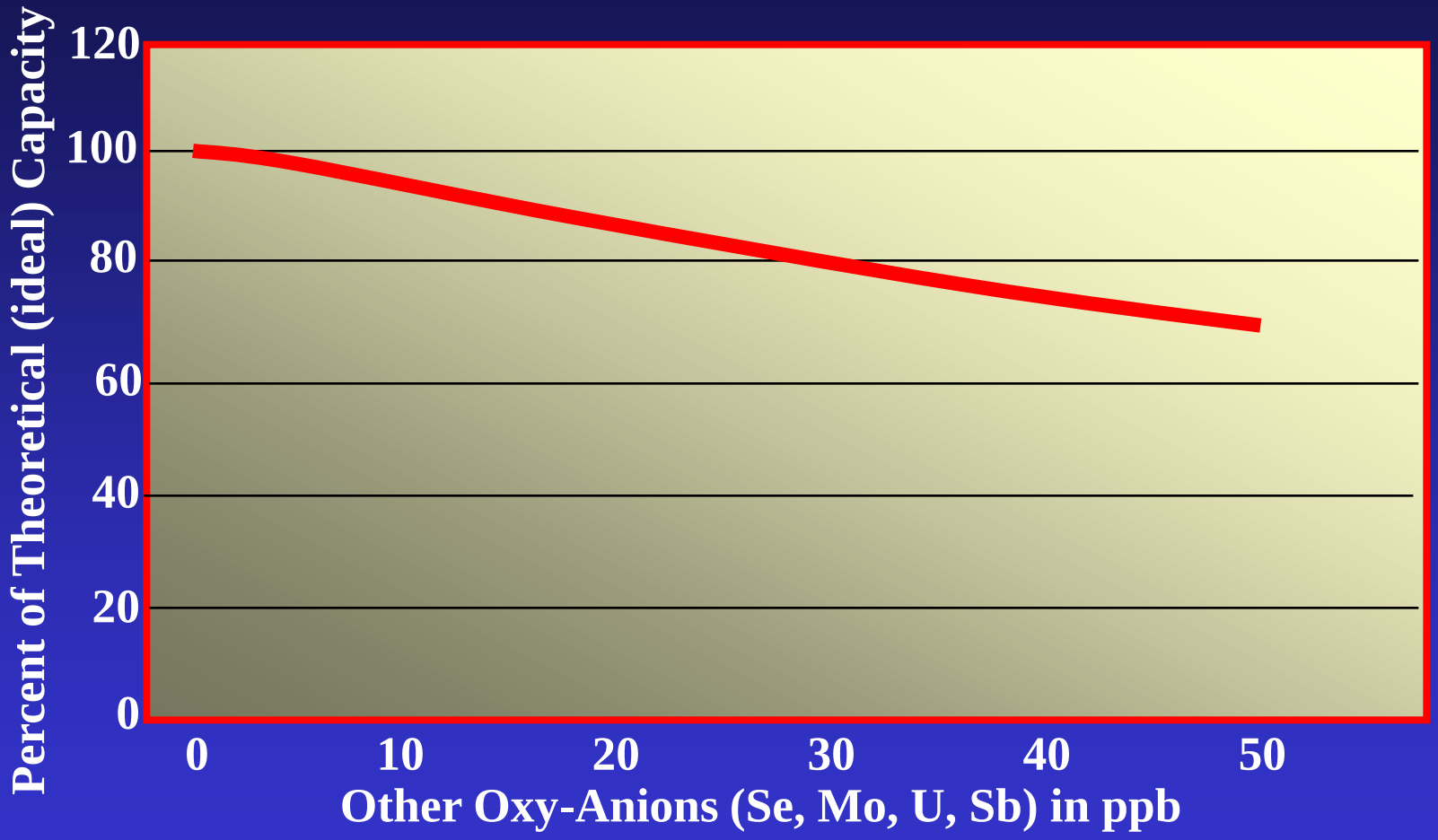
Phosphates


Percent of Theoretical (ideal) Capacity
120
100
80
60
40
20
0
0
20
40
60
80
100
120
Phosphates (PO_4) in ppb

Vanadium


Percent of Theoretical (ideal) Capacity
120
100
80
60
40
20
0
0
10
20
30
40
50
Vanadium (V) in ppb

Other Oxy-Anions



Fluoride / Activated Alumina

Yes, Activated Alumina is already ACTIVATED…..but you have to prepare its surface before use.

Properties of Activated Alumina

GRANULAR ACTIVATED ALUMINA

Chemical Properties

Al_2O_3	92%
Na_2O	0.35%
SiO_2	0.03%

Weight Loss on Ignition (1000°F) ~ 8%

Mesh Size: 14x48 US mesh

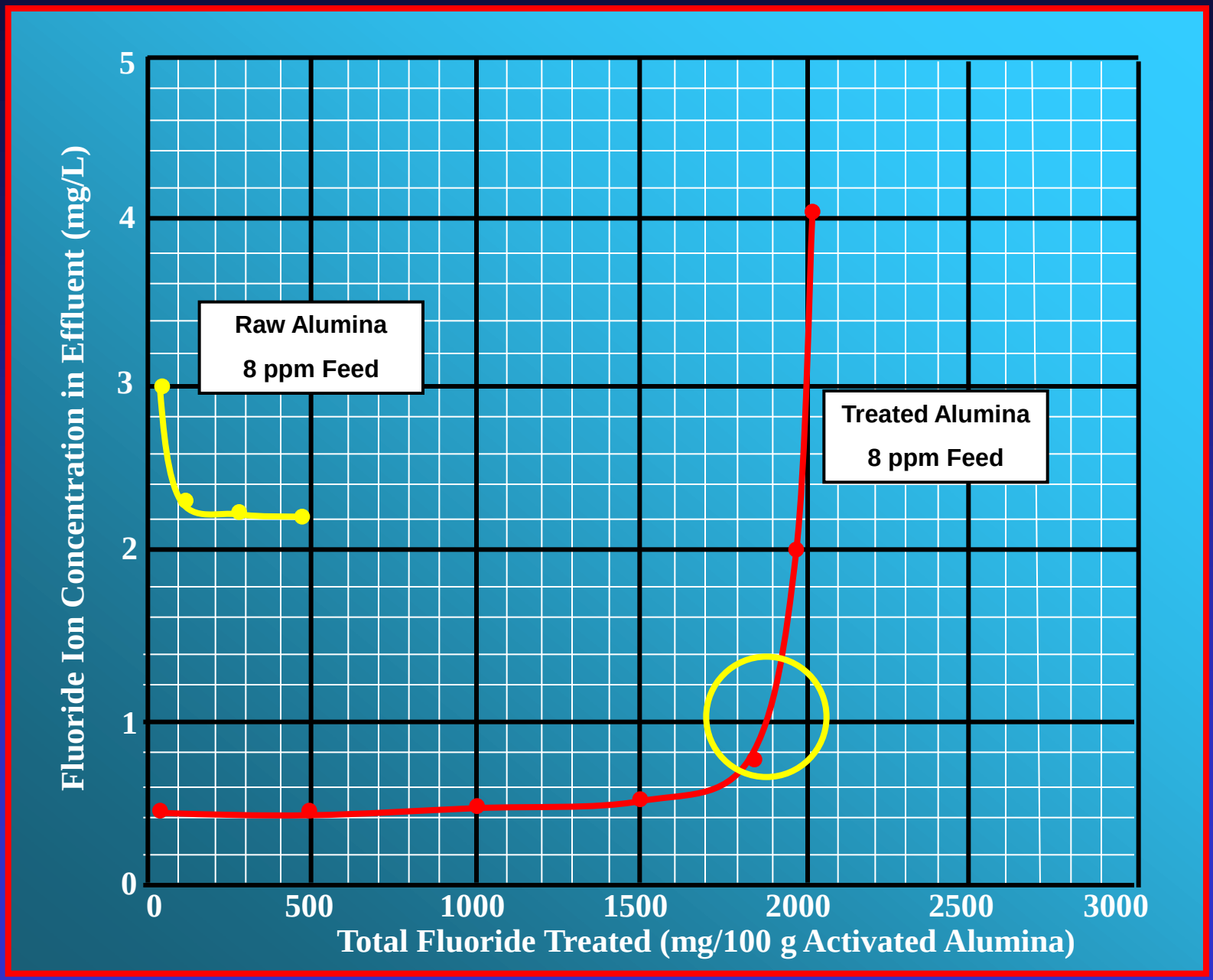
Bulk Density: 40 lbs/cu ft

Surface Area: 380 M^2/g

Pore Volume: 0.52 cc/g

MSDS: NSF-61 listed

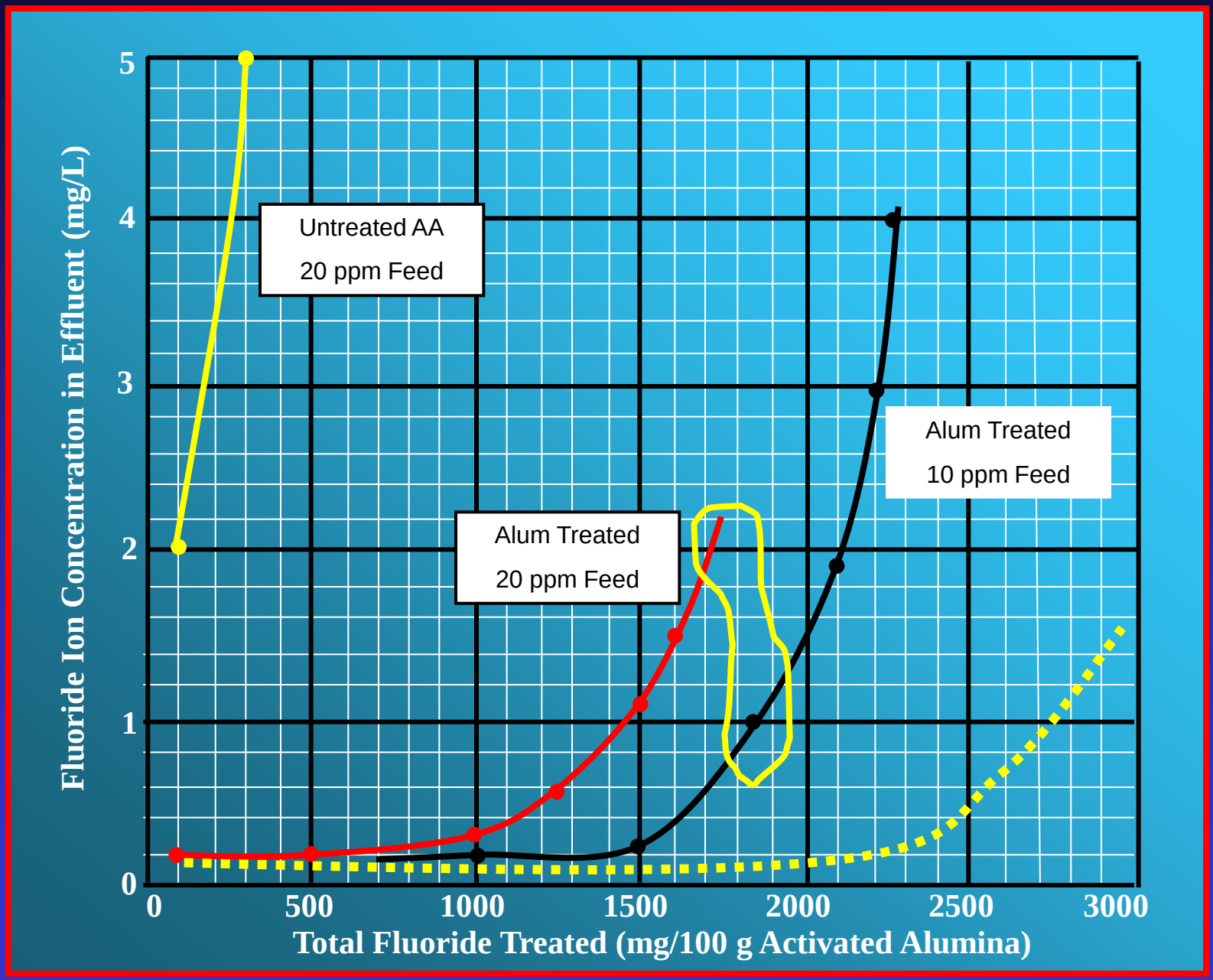
Fluoride Removal by AA from Saturated (8 ppm) CaF_2 Feed



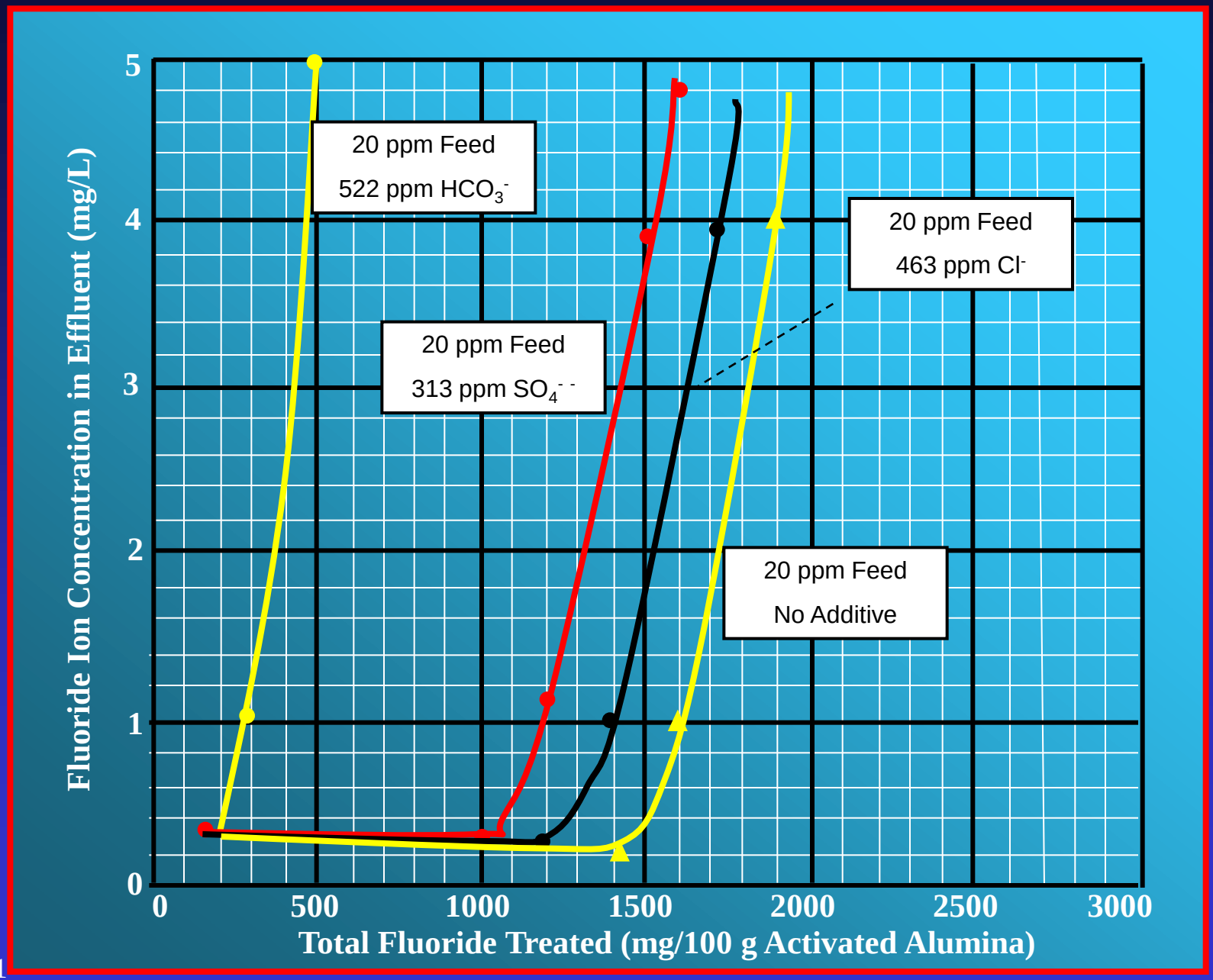
Raw Capacity of Activated Alumina

- *1900 mg F/100 gm of Activated Alumina*
- *AA = 40 lbs/cu ft ~ 18160 gms*
- *1900 mg x 181 (100 gm units) = 345,000 mg F*
- *345K mg = 1 ppm in 345K liters = 91,000 gal*
- *Typical municipal levels = 1.2 ppm*
- *Raw capacity ~ 75,000 gal to 0.1 ppm residual*
- *A 1.5 cu ft unit will treat the average home 1 yr*

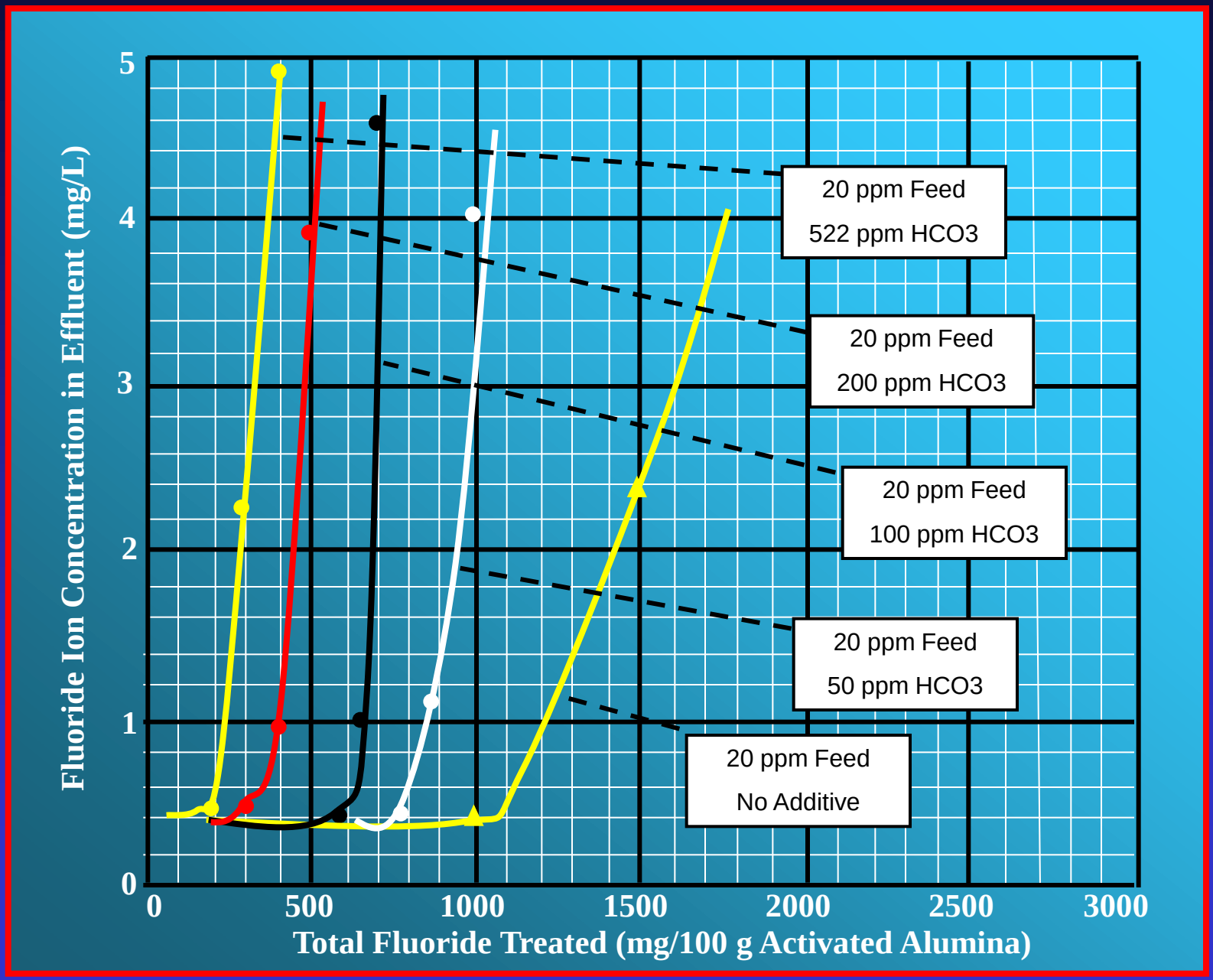
Fluoride Removal by Activated Alumina



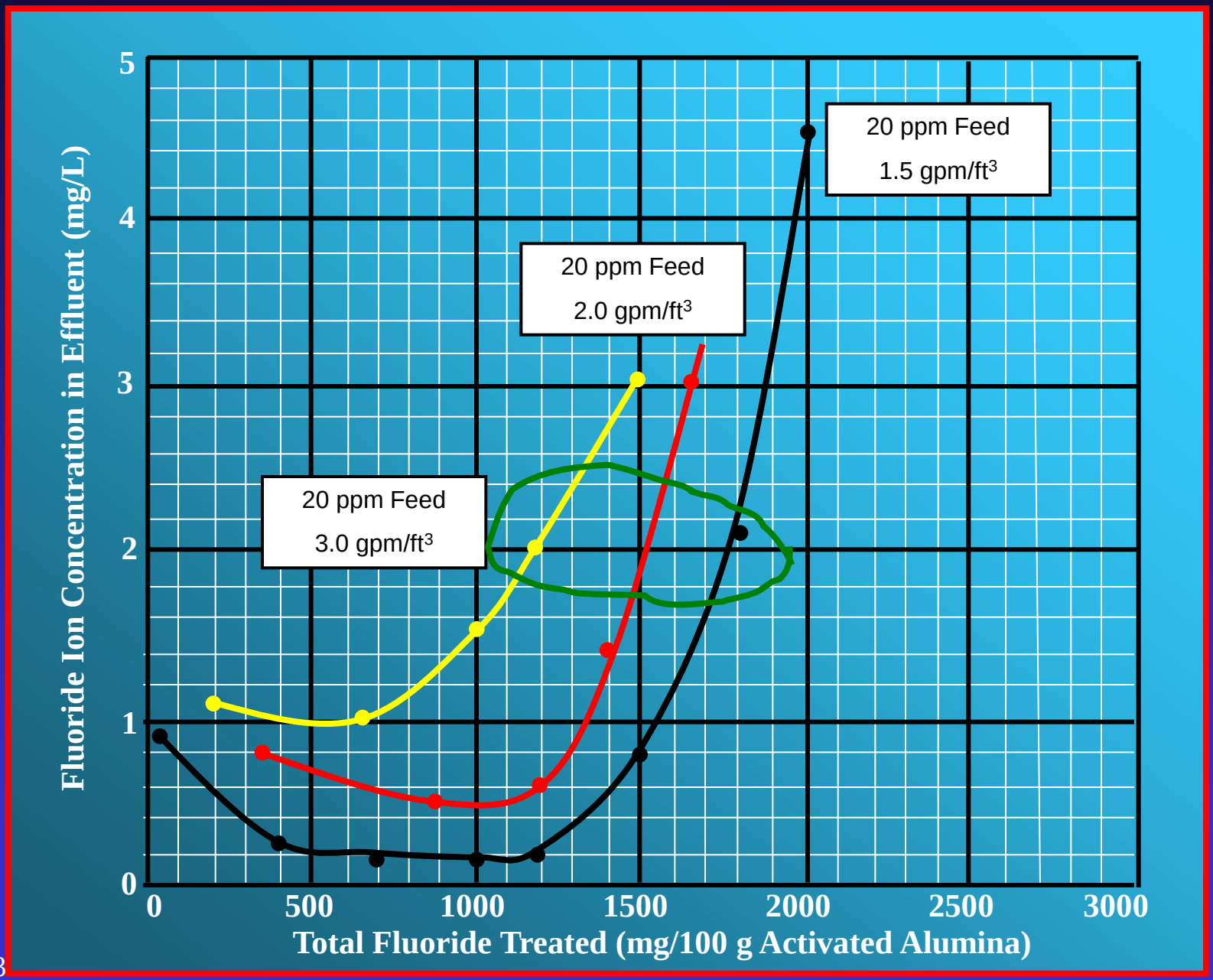
Fluoride Removal by AA with Other Ions



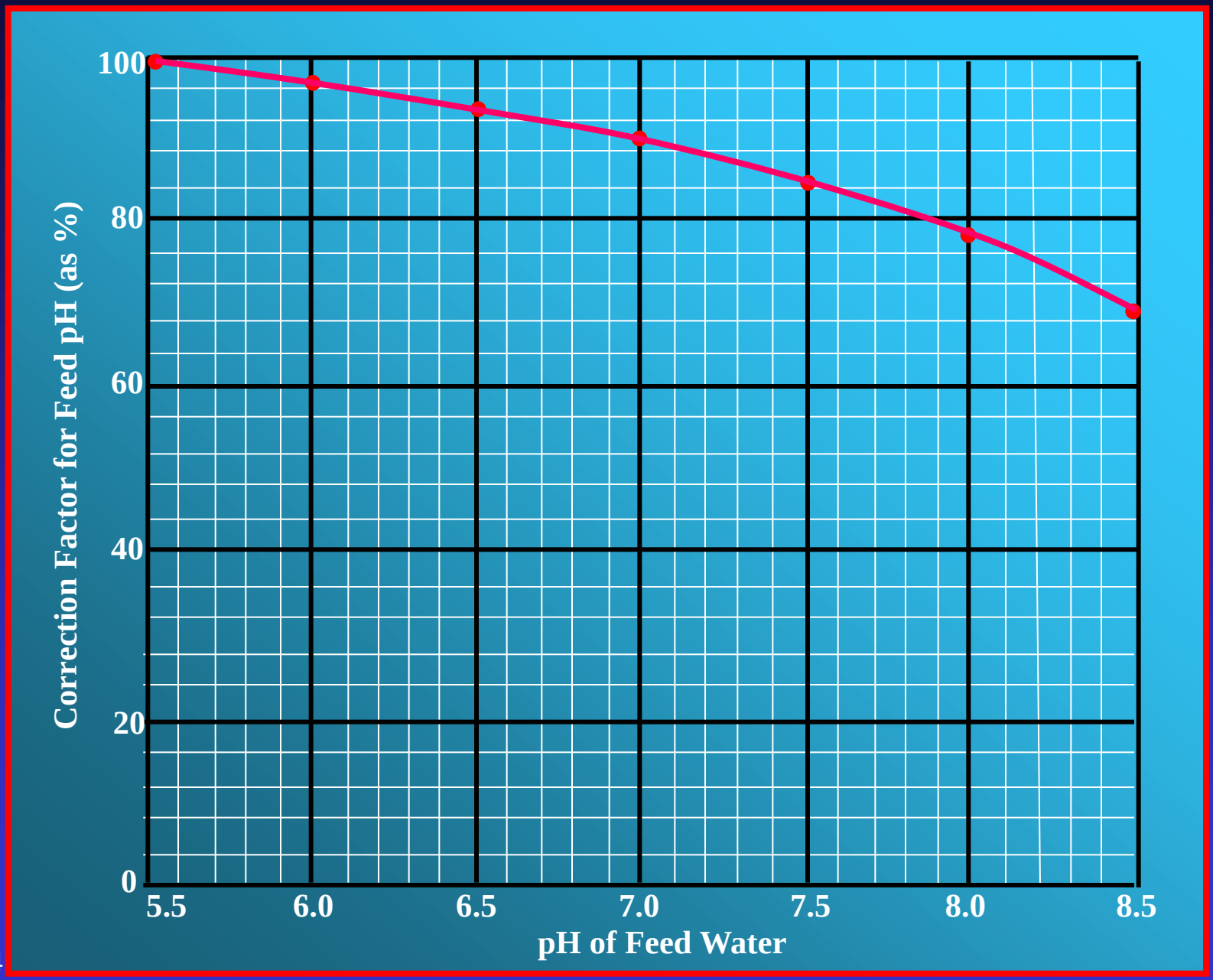
Fluoride Removal by AA with Various HCO_3 Concentrations



Fluoride Removal by Treated AA at Various Flow Rates



Fluoride Removal: Retained Capacity vs pH of Feed Water



Arsenic Specie

Pre-Oxidation of As^{+3} → As^{+5}

Most iron removal media

- ***Pyrolox***
- ***Filox***
- ***Katalox***
- ***MGS***

Disinfectants

- ***Chlorine***
- ***Ozone***
- ***Peroxide***

Not effective

- ***Aeration***
- ***Ultra Violet***

Bonus

If iron is present:

Oxidizing the iron will remove arsenic up to about 10% of the iron level. ie: 1 ppm iron will = 100 ppb As. The same appears to hold for manganese.

If bacteria are present:

Disinfection with slight excess will oxidize the arsenic.

If neither are present:

Disinfection treatment or oxidation media will convert the As^{+3} to As^{+5}.

Chemistry 101

Acids, Bases, Salts and pH

HCl H_2SO_4 & HNO_3 are strong acids—all others are weak acids

NaOH & KOH are strong bases—all others are weak bases

When an acid and a base are combined they form a salt plus water

$NaOH + HCl \rightarrow NaCl + H_2O$	*pH is neutral*
$2\ KOH + H_2SO_4 \rightarrow + K_2SO_4 + 2\ H_2O$	*pH is neutral*
$2\ NaOH + H_2CO_3 \rightarrow + Na_2CO_3 + 2\ H_2O$	*pH is alkaline*
$NH_4OH + HNO_3 \rightarrow + NH_4NO_3 + H_2O$	*pH is acidic*

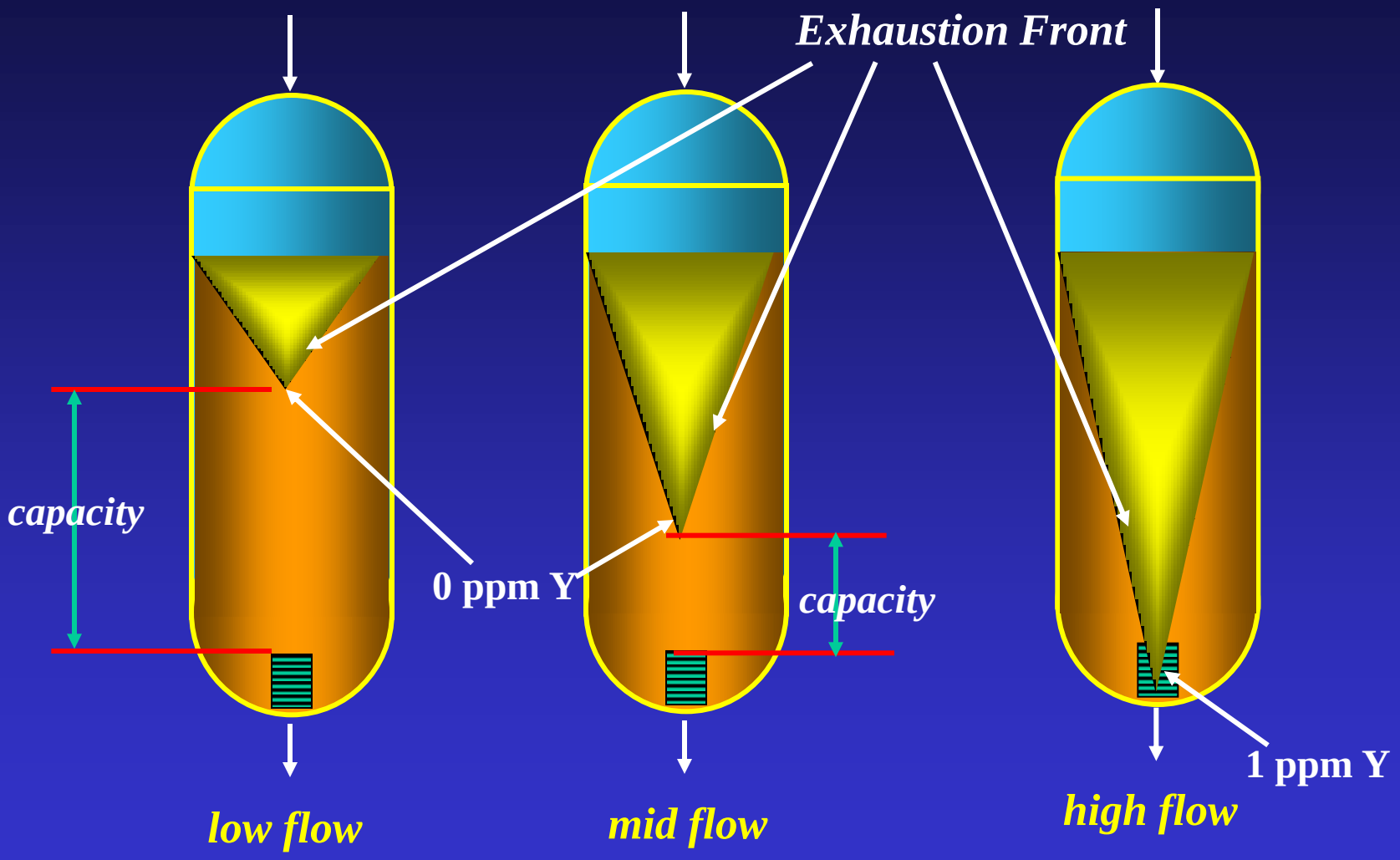
Ion exchange $NaHCO_3 + O^{-Cl} \rightarrow O^{-HCO3} + NaCl$ — *pH is reduced ~pH 7*

This is the de-alkalization reaction

A de-alkalizer also removes everything on the anion side except chlorides..*
"everything" includes nitrates, arsenic and fluoride as well as bi-carbonate.

**phosphate, oxy-metals, Se, V, Mo and uranium,*
are all anionic ~ partial to complete removal

Why is EBCT important?



Adsorption Media Capacity

Adsorption reactions are driven by:

- ✓ ~~Concentration and form of contaminant~~
- ✓ ~~pH (impacts solubilities and form)~~
- ✓ ~~Surface Preparation of Media~~
- ✓ ~~Competition from other Ions~~
- ✓ ~~EB Contact Time (flow rate/cu ft)~~

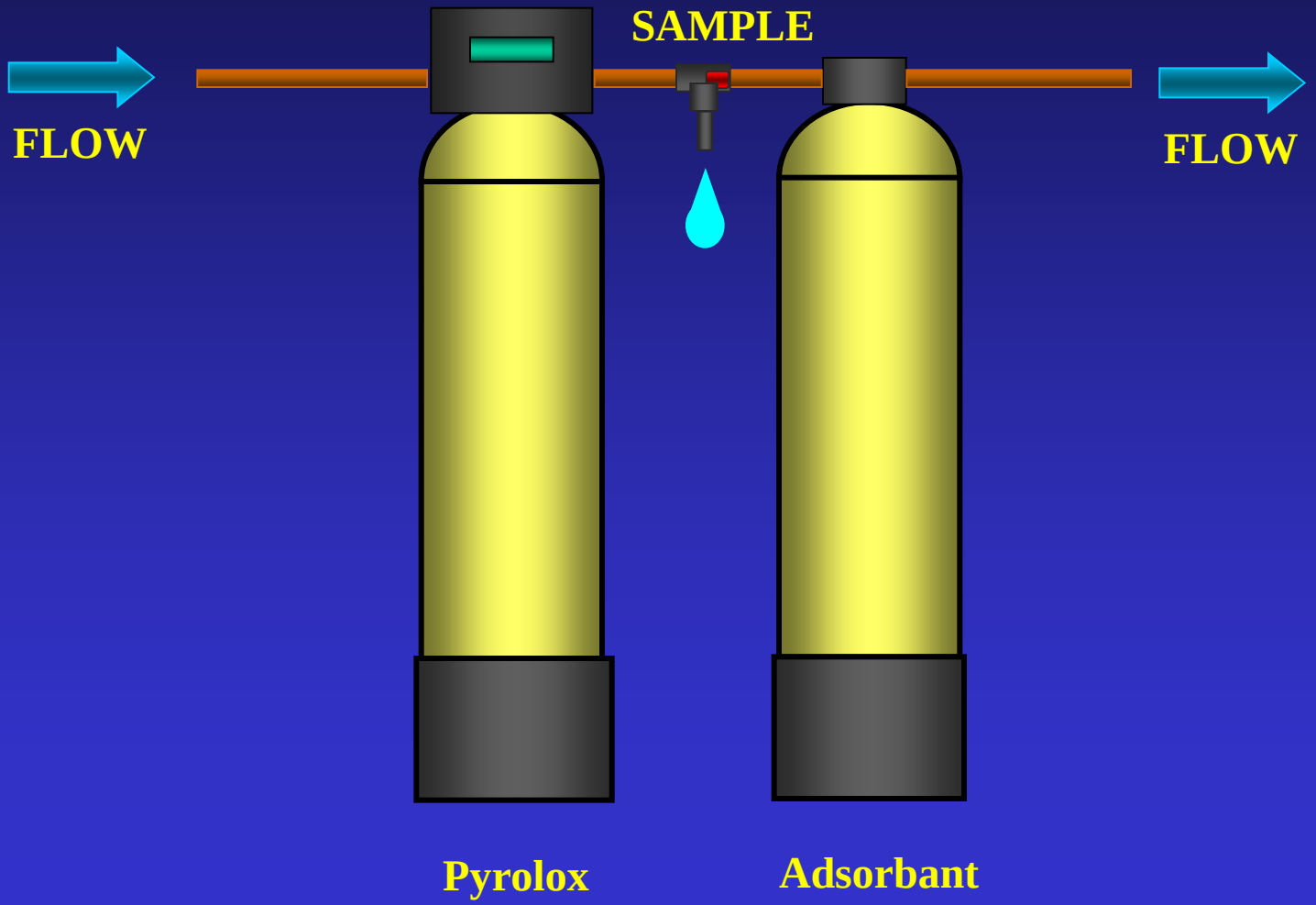
With the arsenic oxidized, the pH lowered and interfering ions reduced, the adsorbant media properly prepared and the system properly sized, you can deliver a much higher capacity AND more complete removal of either arsenic or fluoride…….

Here are some set ups that are field tested:

Designing Systems

- *typical water flow in home = 2.5-4 gpm*
- *1 cu ft unit has EBCT of 2-3 minutes POE*
- *use 1.5 cu ft if As is >200 ppb*
- *design redundant units with lead/lag*
- *down flow is preferred*
- *if system life > 1 year, use b/w on lead*
- *sample between lead/lag quarterly*
- *cartridges are not POE devices… use only as polishers post R/O*

With Oxidation Media (with iron)



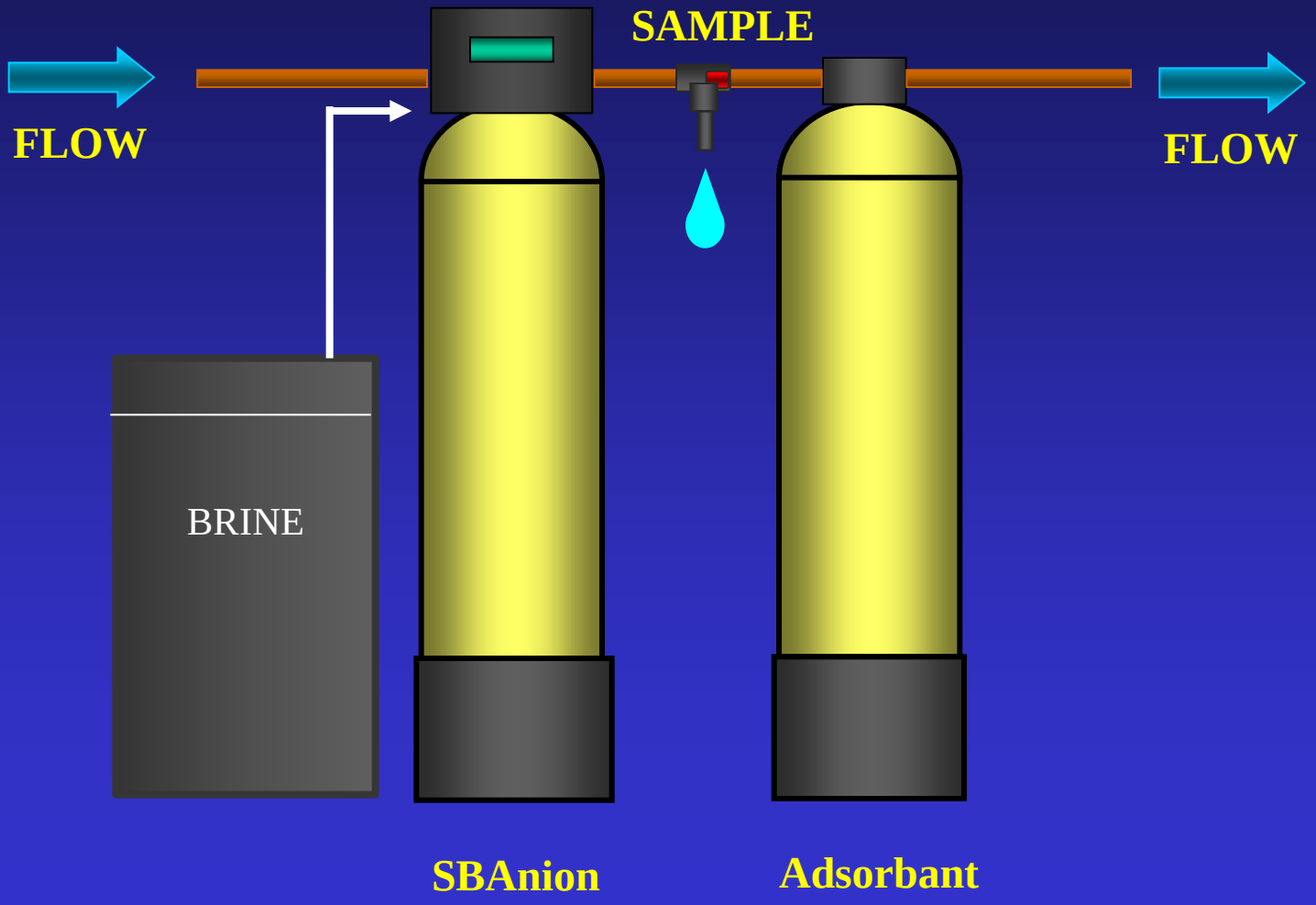
Hybrid System (As^{+3} with iron)

Property	Feed	Post Oxidizer	Post Adsorbant
Iron	1.6 ppm	0.1 ppm	0.1 ppm
As $^{+}5/^{+}3$	43/17 ppb	ND	ND

Adsorbant by itself would only have treated 73,000 gal/cu ft and lasted 183 days

As a hybrid system, it will treat >750,000 gal/cu ft and should last 5 years

With Anion/Adsorbant



Hybrid System for Fluoride

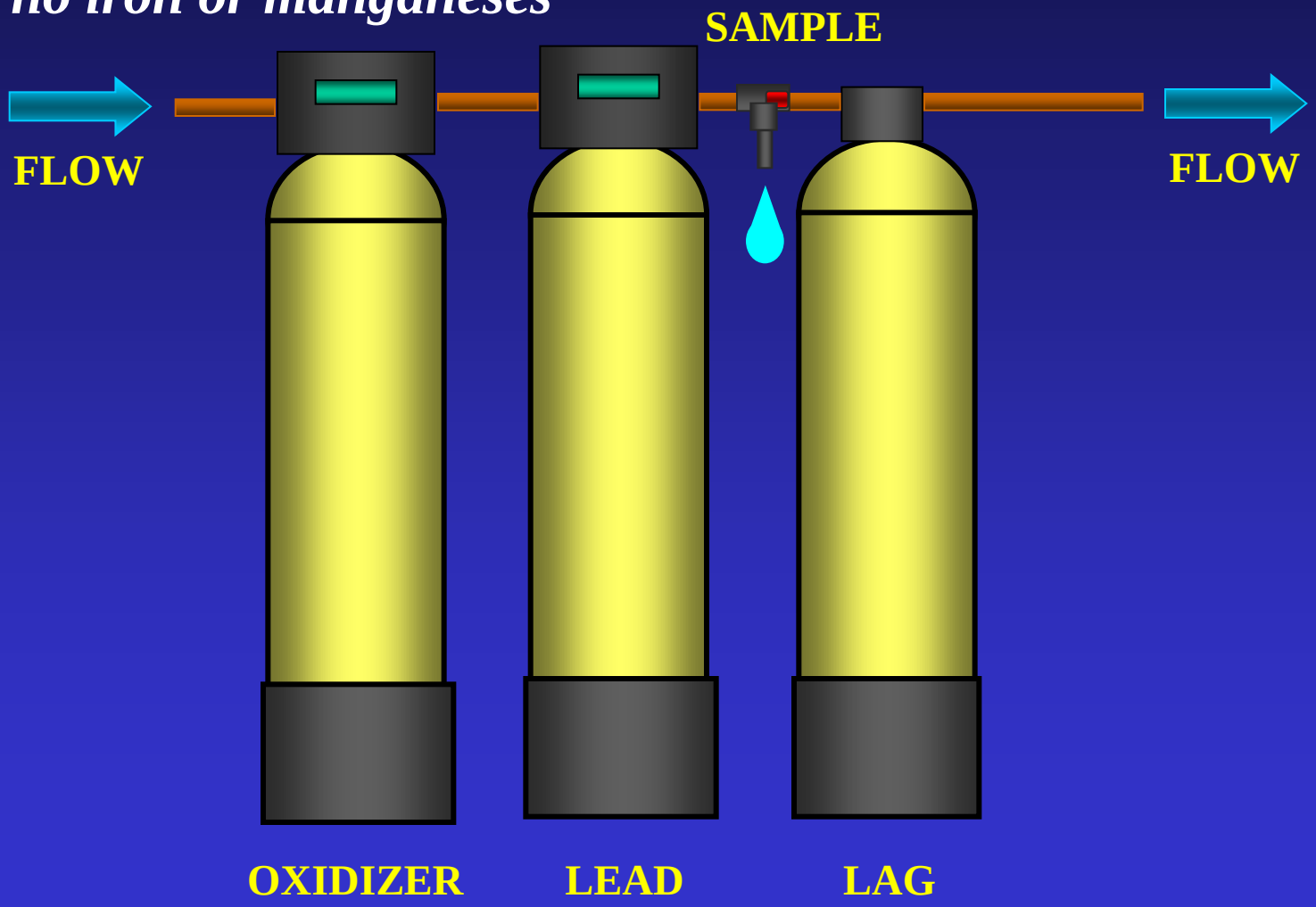
Property	Feed	Post SBA	Post AA
pH	9.8	6.4	6.5
Fluoride	14.5	1.35	0.31

Alumina by itself would only have treated 1200 gal/cu ft

As a hybrid system, it will treat >60,000 gal/cu ft

Typical Oxidizer/Lead/Lag Set Up

no iron or manganeses



Hybrid System (As^{+3} without iron)

Property	Feed	Post Oxidizer	Post Adsorbant
Iron	0.01 ppm	ND	ND
Arsenic	7/17 ppb	23 ppb	ND

Adsorbant by itself would only have treated 76,000 gal/cu ft and lasted 217 days

As a hybrid system, it will treat > 650,000 gal/cu ft and should last 5.2 years!

Fluoride Removal by Anion Exchange

Anion capacity = 13,500 gr/cu ft

13,500/22.1 = 610 gal/cycle

Component	ppm Ion	ppm $CaCO_3$
HCO_3	155	125.6
SO_4	35	36.4
Cl	140	197.2
F	7	18.4
TOTAL		377.6

use Type I (FG) w/8 lbs NaCl/ft^3 **=22.1 gpg**

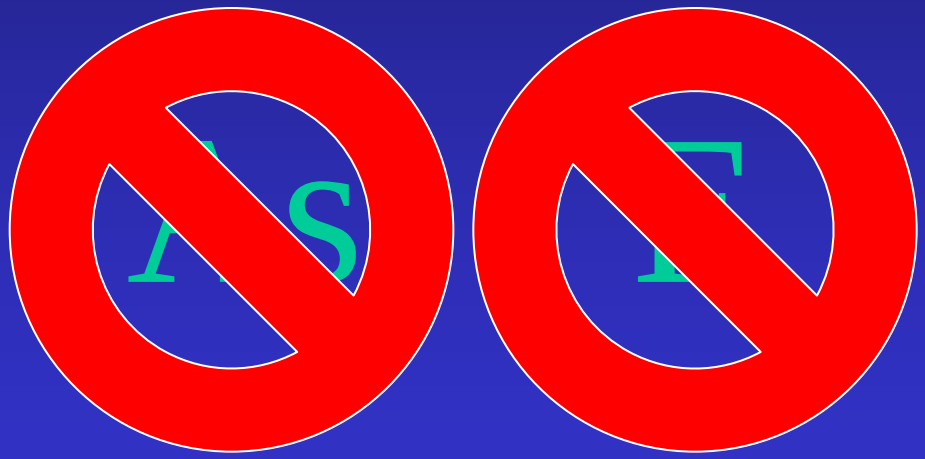
Conclusions

- ***the only safe level for arsenic and fluoride in drinking water is ZERO.***
- ***every household in the southwest is a potential customer but a water softener or carbon filter remove NEITHER. Under-the-sink RO is good. But polish it.***
- ***get a good water analysis: the better the better!***
- ***consult experts in the field for rating and design.***
- ***sample regularly and take the initiative to call customer***
- ***put a phone number on the system with instructions and dates for sampling and replacement.***
- ***spent media may be hazmat in Kalifornia but generally OK in normal states.***

Remember..

Only YOU…

YOU are the final barrier. It is YOUR responsibility to protect yourself, your family, your friends and neighbors



Be Safe!

Thank you for your participation

Pacific Water Quality Association

God Bless America

Become part of the solution

Chubb Michaud MWS

email: AskChubb@aol.com

Any Questions??