

Fluoridation

Limited Treatment Short Course



MICHIGAN DEPARTMENT OF
ENVIRONMENT, GREAT LAKES, AND ENERGY

Outline

- What is Fluoride
- Public health
- Fluoride compounds used for water treatment
- Common feeders and design
- Safety
- Residual testing
- Operator Math

What is Fluoride?

Periodic Table of the Elements

Atomic Number Atomic Mass

Symbol

Name

Electron Shells

Electron Configuration

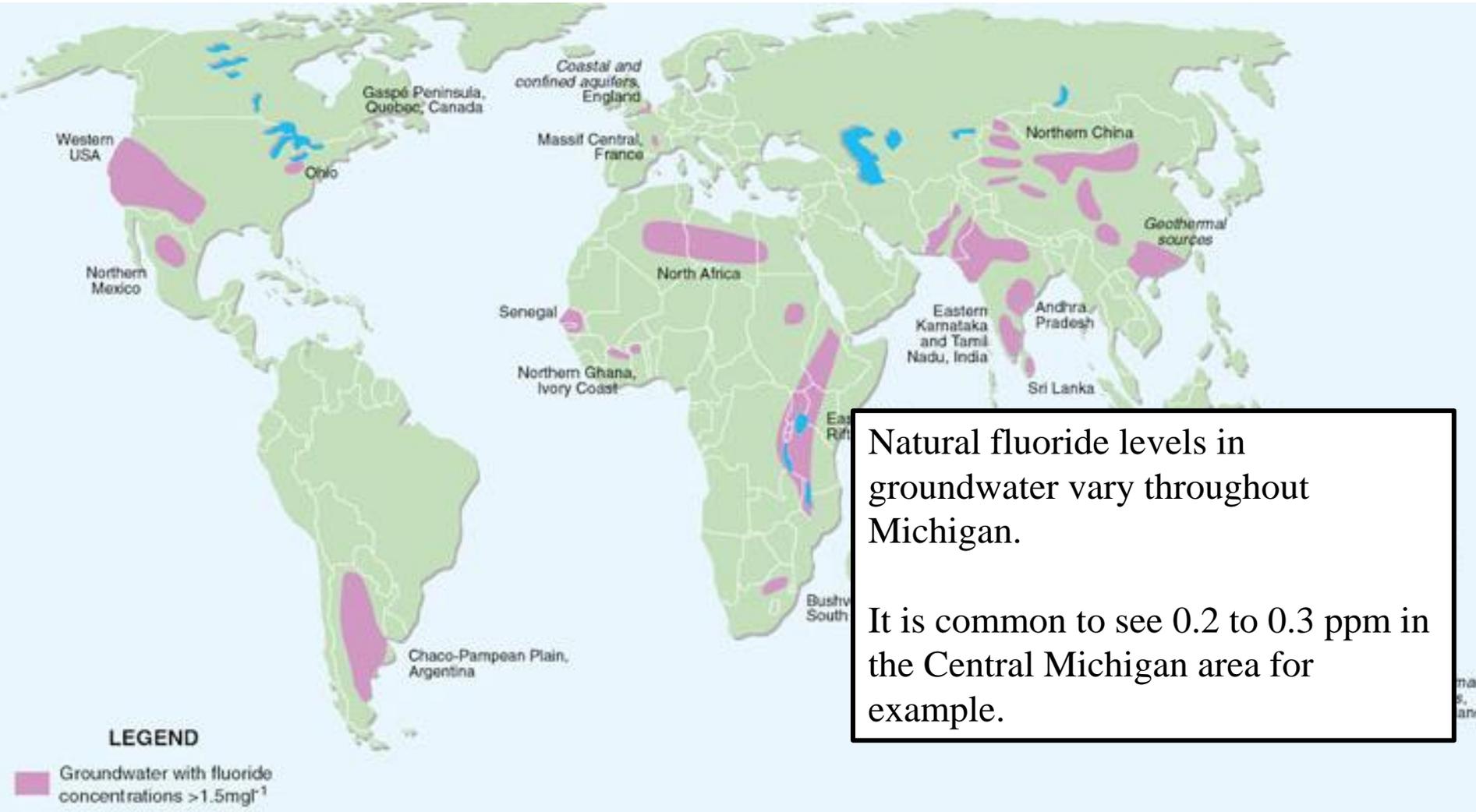
Element symbol represents state at room temperature.
Solid, Liquid or Gas

1	2											13	14	15	16	17	18		
1A	2A											3A	4A	5A	6A	7A	8A		
1	2											5	6	7	8	9	10		
H	He											B	C	N	O	F	Ne		
1s ¹	1s ²											[He]2s ² 2p ¹	[He]2s ² 2p ²	[He]2s ² 2p ³	[He]2s ² 2p ⁴	[He]2s ² 2p ⁵	[He]2s ² 2p ⁶		
3	4											13	14	15	16	17	18		
Li	Be											Al	Si	P	S	Cl	Ar		
[He]2s ¹	[He]2s ²											[Ne]3s ² 3p ¹	[Ne]3s ² 3p ²	[Ne]3s ² 3p ³	[Ne]3s ² 3p ⁴	[Ne]3s ² 3p ⁵	[Ne]3s ² 3p ⁶		
11	12	3	4	5	6	7	8	9	10	11	12								
Na	Mg	IIIB	IVB	VB	VIB	VII B		VIII		IB	IIB								
3B	4B	5B	6B	7B		8		8		1B	2B								
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
[Ar]4s ¹	[Ar]4s ²	[Ar]3d ¹ 4s ²	[Ar]3d ² 4s ²	[Ar]3d ³ 4s ²	[Ar]3d ⁴ 4s ²	[Ar]3d ⁵ 4s ²	[Ar]3d ⁶ 4s ²	[Ar]3d ⁷ 4s ²	[Ar]3d ⁸ 4s ²	[Ar]3d ⁹ 4s ¹	[Ar]3d ¹⁰ 4s ²	[Ar]3d ¹⁰ 4s ² 4p ¹	[Ar]3d ¹⁰ 4s ² 4p ²	[Ar]3d ¹⁰ 4s ² 4p ³	[Ar]3d ¹⁰ 4s ² 4p ⁴	[Ar]3d ¹⁰ 4s ² 4p ⁵	[Ar]3d ¹⁰ 4s ² 4p ⁶		
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
[Kr]5s ¹	[Kr]5s ²	[Kr]4d ¹ 5s ²	[Kr]4d ² 5s ²	[Kr]4d ³ 5s ²	[Kr]4d ⁴ 5s ²	[Kr]4d ⁵ 5s ²	[Kr]4d ⁶ 5s ²	[Kr]4d ⁷ 5s ²	[Kr]4d ⁸ 5s ²	[Kr]4d ⁹ 5s ¹	[Kr]4d ¹⁰ 5s ²	[Kr]4d ¹⁰ 5s ² 5p ¹	[Kr]4d ¹⁰ 5s ² 5p ²	[Kr]4d ¹⁰ 5s ² 5p ³	[Kr]4d ¹⁰ 5s ² 5p ⁴	[Kr]4d ¹⁰ 5s ² 5p ⁵	[Kr]4d ¹⁰ 5s ² 5p ⁶		
55	56	57-71			72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba				Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
[Xe]6s ¹	[Xe]6s ²				[Xe]4f ¹⁴ 5d ² 6s ²	[Xe]4f ¹⁴ 5d ³ 6s ²	[Xe]4f ¹⁴ 5d ⁴ 6s ²	[Xe]4f ¹⁴ 5d ⁵ 6s ²	[Xe]4f ¹⁴ 5d ⁶ 6s ²	[Xe]4f ¹⁴ 5d ⁷ 6s ²	[Xe]4f ¹⁴ 5d ⁸ 6s ²	[Xe]4f ¹⁴ 5d ⁹ 6s ¹	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ³	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶
87	88	89-103			104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra				Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
[Rn]7s ¹	[Rn]7s ²				[Rn]5f ¹⁴ 6d ² 7s ²	[Rn]5f ¹⁴ 6d ³ 7s ²	[Rn]5f ¹⁴ 6d ⁴ 7s ²	[Rn]5f ¹⁴ 6d ⁵ 7s ²	[Rn]5f ¹⁴ 6d ⁶ 7s ²	[Rn]5f ¹⁴ 6d ⁷ 7s ²	[Rn]5f ¹⁴ 6d ⁸ 7s ²	[Rn]5f ¹⁴ 6d ⁹ 7s ²	[Rn]5f ¹⁴ 6d ¹⁰ 7s ²	[Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ¹	[Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ²	[Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ³	[Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁴	[Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁵	[Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁶

Lanthanide Series	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
	[Xe]5d ¹ 6s ²	[Xe]4f ¹ 5d ¹ 6s ²	[Xe]4f ² 6s ²	[Xe]4f ³ 6s ²	[Xe]4f ⁵ 6s ²	[Xe]4f ⁶ 6s ²	[Xe]4f ⁷ 6s ²	[Xe]4f ⁷ 5d ¹ 6s ²	[Xe]4f ⁹ 6s ²	[Xe]4f ¹⁰ 6s ²	[Xe]4f ¹¹ 6s ²	[Xe]4f ¹² 6s ²	[Xe]4f ¹³ 6s ²	[Xe]4f ¹⁴ 6s ²	[Xe]4f ¹⁴ 5d ¹ 6s ²
Actinide Series	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
	Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrencium
	[Rn]6d ¹ 7s ²	[Rn]6d ² 7s ²	[Rn]5f ¹ 6d ¹ 7s ²	[Rn]5f ³ 6d ¹ 7s ²	[Rn]5f ⁴ 6d ¹ 7s ²	[Rn]5f ⁶ 7s ²	[Rn]5f ⁷ 7s ²	[Rn]5f ⁷ 6d ¹ 7s ²	[Rn]5f ⁹ 7s ²	[Rn]5f ¹⁰ 7s ²	[Rn]5f ¹¹ 7s ²	[Rn]5f ¹² 7s ²	[Rn]5f ¹³ 7s ²	[Rn]5f ¹⁴ 7s ²	[Rn]5f ¹⁴ 6d ¹ 7s ²

- Alkali Metal
- Alkaline Earth
- Transition Metal
- Basic Metal
- Metalloid
- Nonmetal
- Halogen
- Noble Gas
- Lanthanide
- Actinide

Groundwater Levels



Natural fluoride levels in groundwater vary throughout Michigan.

It is common to see 0.2 to 0.3 ppm in the Central Michigan area for example.

Colorado Brown Stain: The Fluoride Discovery

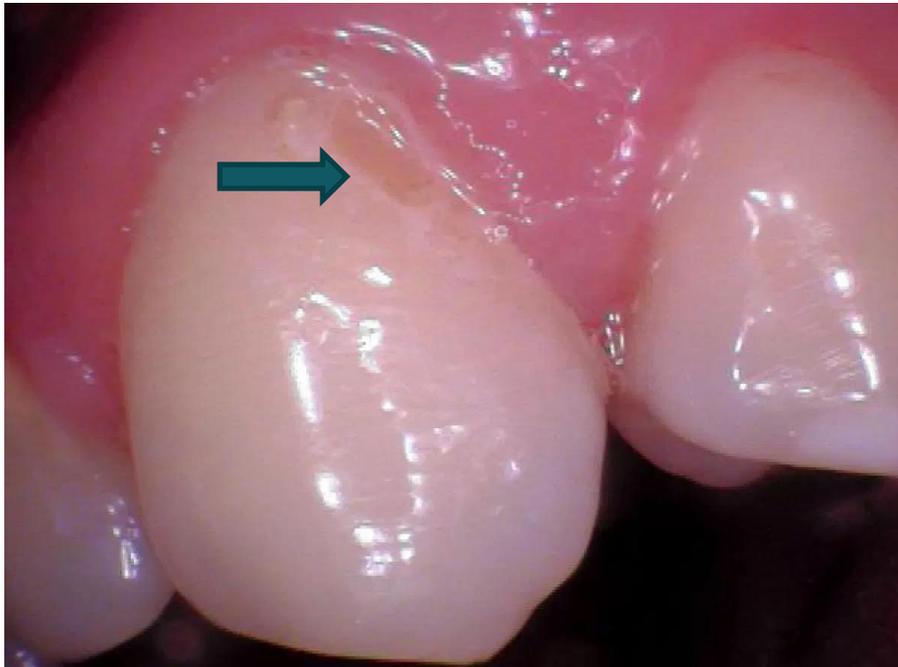
“Colorado brown stain” caused
by high levels of fluoride



Dr. Fredrick McKay

Fluoride and Tooth Enamel

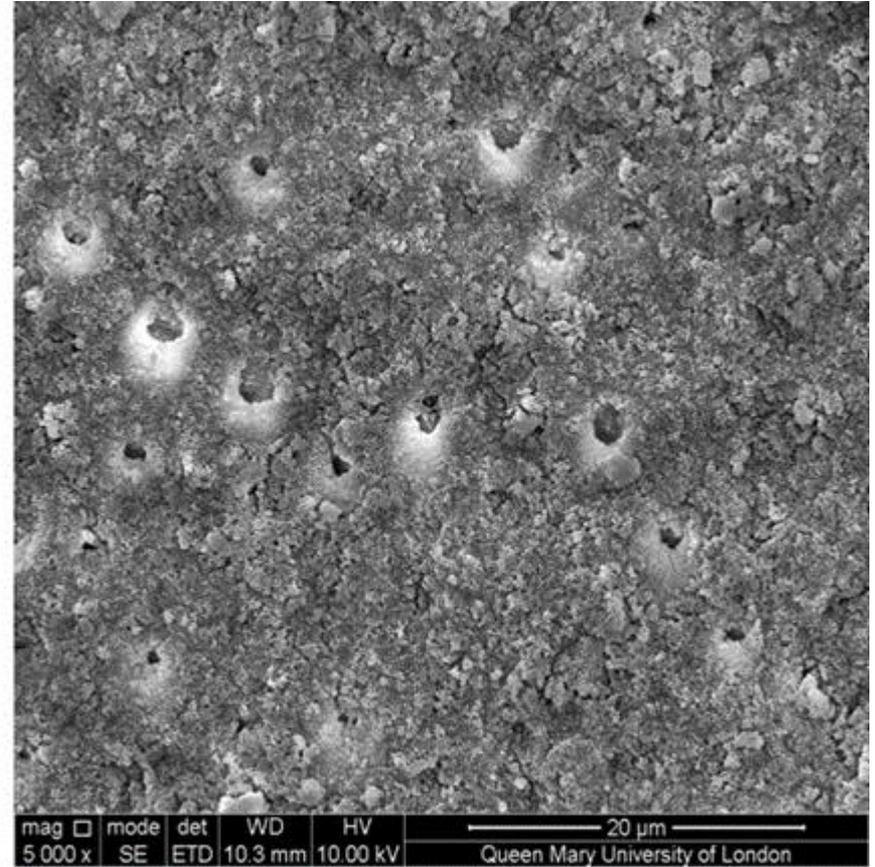
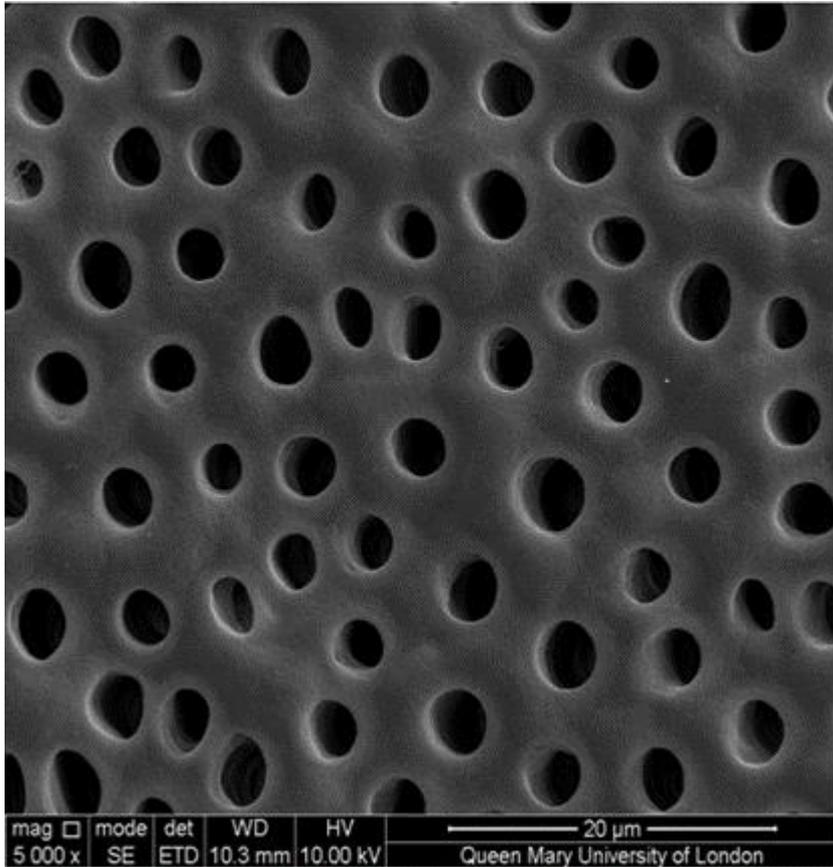
Acid Erosion



Filling in the imperfections



How Fluoride Works



Optimal Fluoride Levels

- New Optimal Level for US: 0.7 mg/L (ppm)
 - Lowered from 1.0 mg/L in 2015
- Target Dose Range: 0.6 - 0.8 mg/L
 - Under 0.6 mg/L provides no benefits
- Regulations
 - *Primary Standard MCL: 4.0 mg/L*
 - *Secondary Standard MCL: 2.0 mg/L*

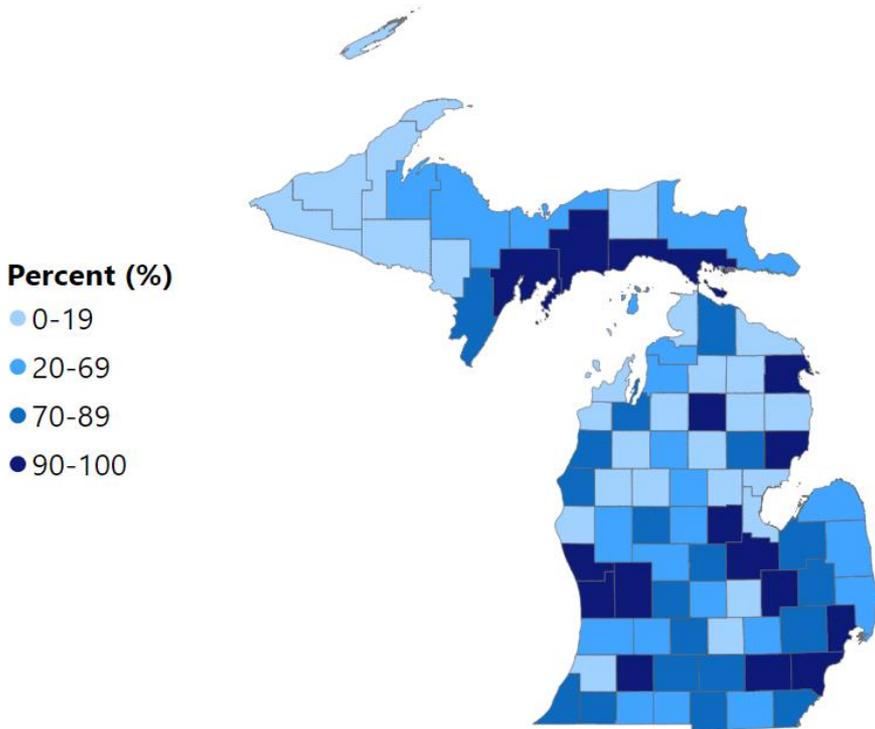
Health Benefits

- Makes teeth more resistant to tooth decay caused by bacteria.
- Proven to strengthen bones in the older population, reducing bone fractures.
- Every dollar spent on fluoride saves an average of \$38 on dental care.
- Costs between cities between \$0.11 to \$1.50 per person per year.
- Optimal fluoride levels have no known negative impacts.



Michigan Statistics

Percent on Community Water System with Access to Optimally Fluoridated Water



- 1450 total water systems.
- 622 systems are currently fluoridating.
- 91% of Michigan's 10,077,331 people use fluoridated water.

Types of Fluoride

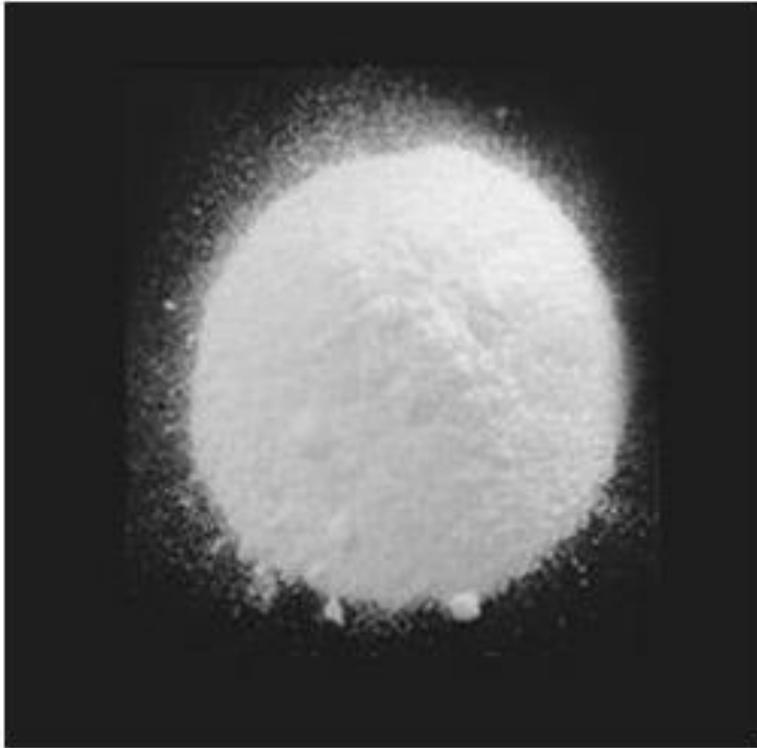


Hydrofluorosilicic Acid (H₂SiF₆)

- Straw Colored Liquid (Acid)
- 79.1% F⁻ in pure acid
- Typical acid concentration is 23% or 25% pure Fluoride
- Yielding **18.2% or 19.8% F⁻**

Types of Fluoride

Sodium Fluorosilicate (Na_2SiF_6)



- Powder
- 60.6% F^- in pure compound
- Typically 98% pure
- Yielding **59.4% F^-**

Types of Fluoride



Sodium Fluoride (NaF)

- Powder or crystal
- 45.2% F⁻ in pure compound
- Typically grade 98% pure
- Yielding **44.2% F⁻**

Fluoride Storage and Use

- Fluoride material being used must meet:
 - **NSF/ANSI Standard 60.**
- Plants that accept large shipments of fluoride should feed from a day tank.
- Spill containment should be provided.
- Feed point should be on the downstream side of the well check valve.
- Isolation valve closed when plant shut down.
 - Ex: Close fill water valve on saturator.

Fluoride Safety

- Gloves, apron, face shield, eye wash, etc. should be provided for operator safety.
- Fluoride chemicals should be isolated from other chemicals, inside a building, vented to outside.
- Plan in place for fluoride spills.
- Hydrofluorosilicic acid off-gases and can be corrosive often etching glass of chemical rooms.
- This mixing of hydrofluorosilicic acid with sodium hypochlorite can cause catastrophic damage through extreme chemical oxidation and can be toxic.

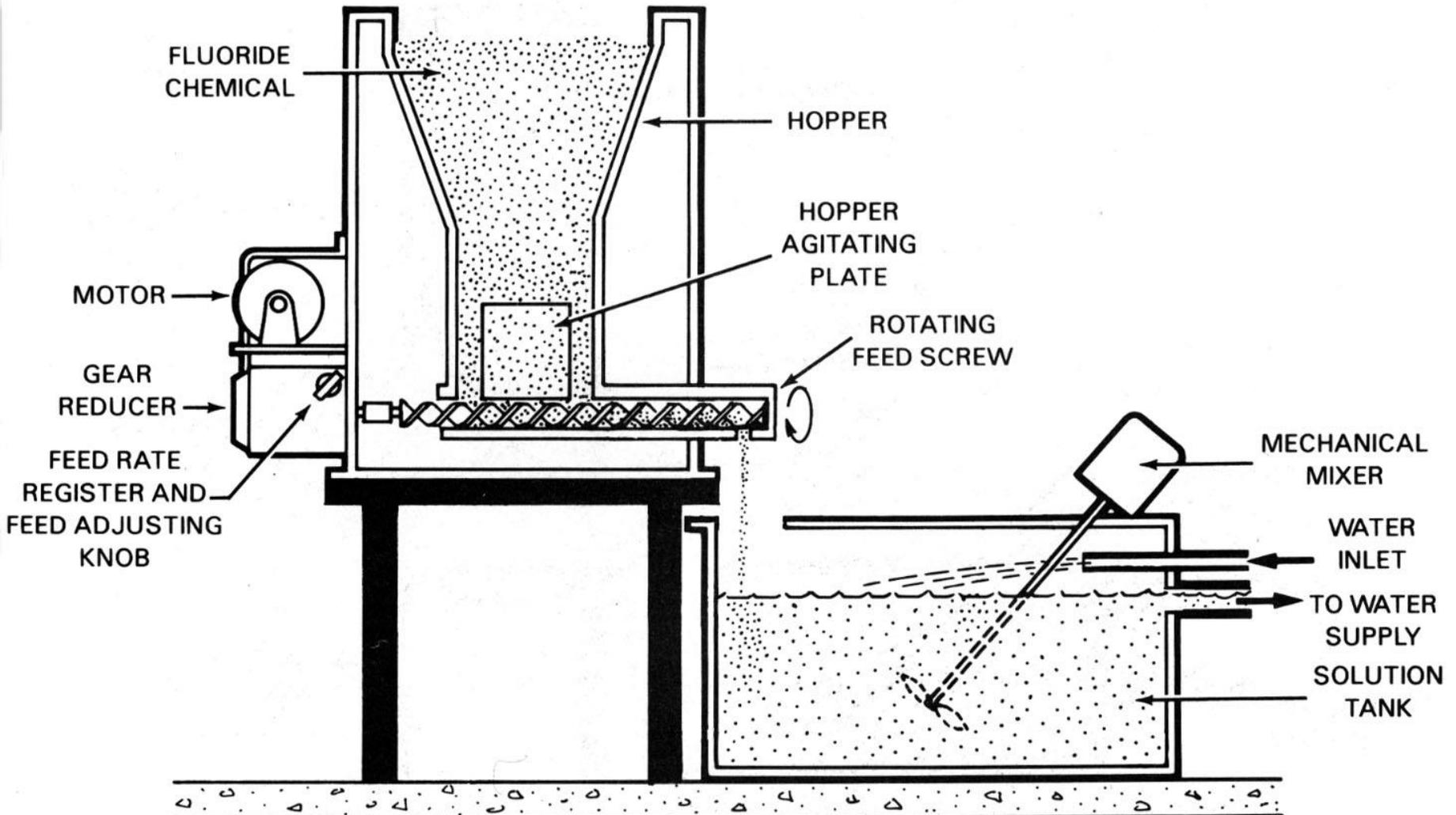


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Types of Feeders

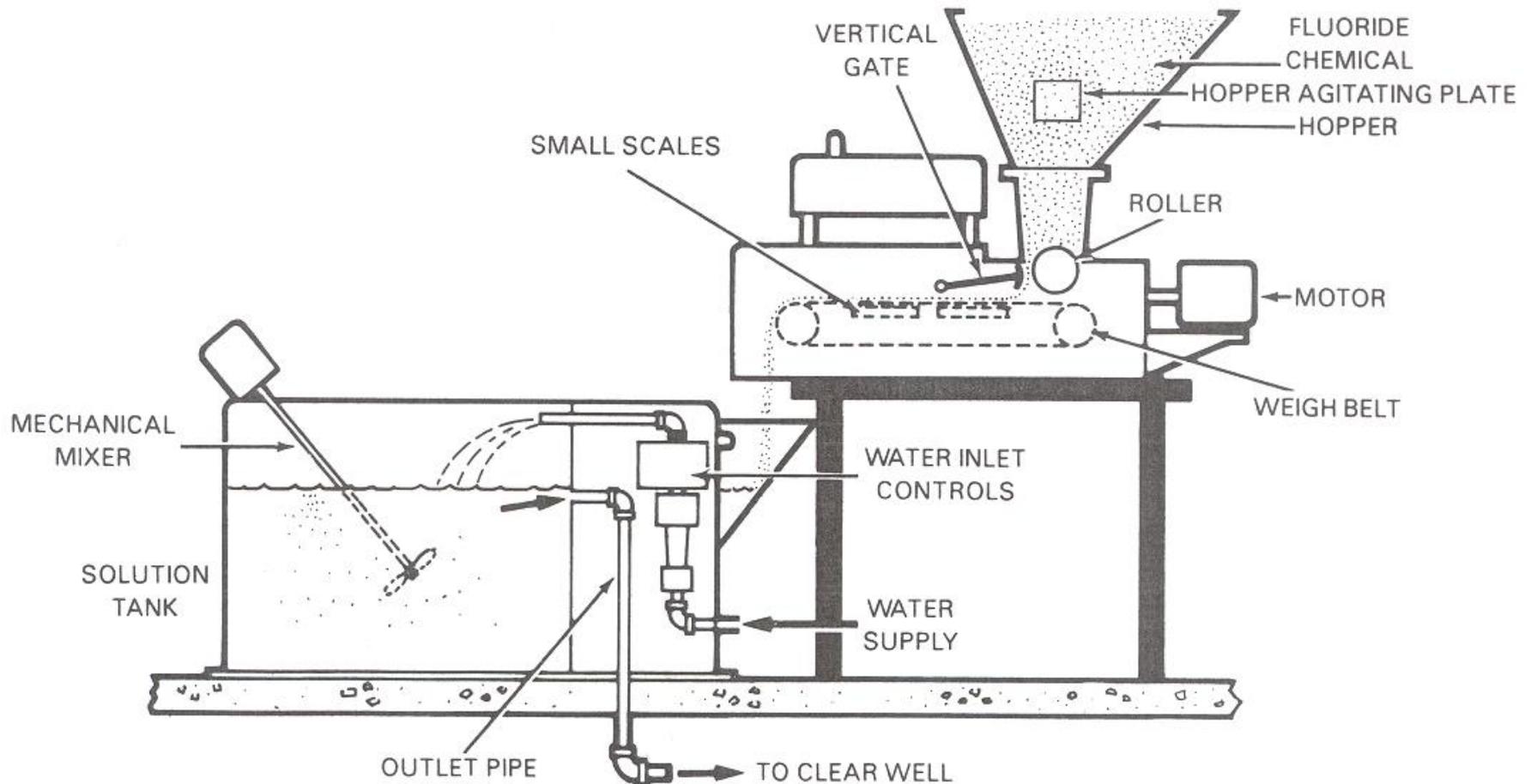
- Volumetric
 - Delivers a certain volume of chemical over time
 - Used for powder.
- Gravimetric
 - Delivers a certain weight of chemical over time.
 - Used for powder.
- Positive Displacement Pump
 - Used for liquids.
 - Most common in Michigan.
- Upflow Saturator
 - Used for powder.
 - “Safest” used with NaF.

Volumetric Feeders



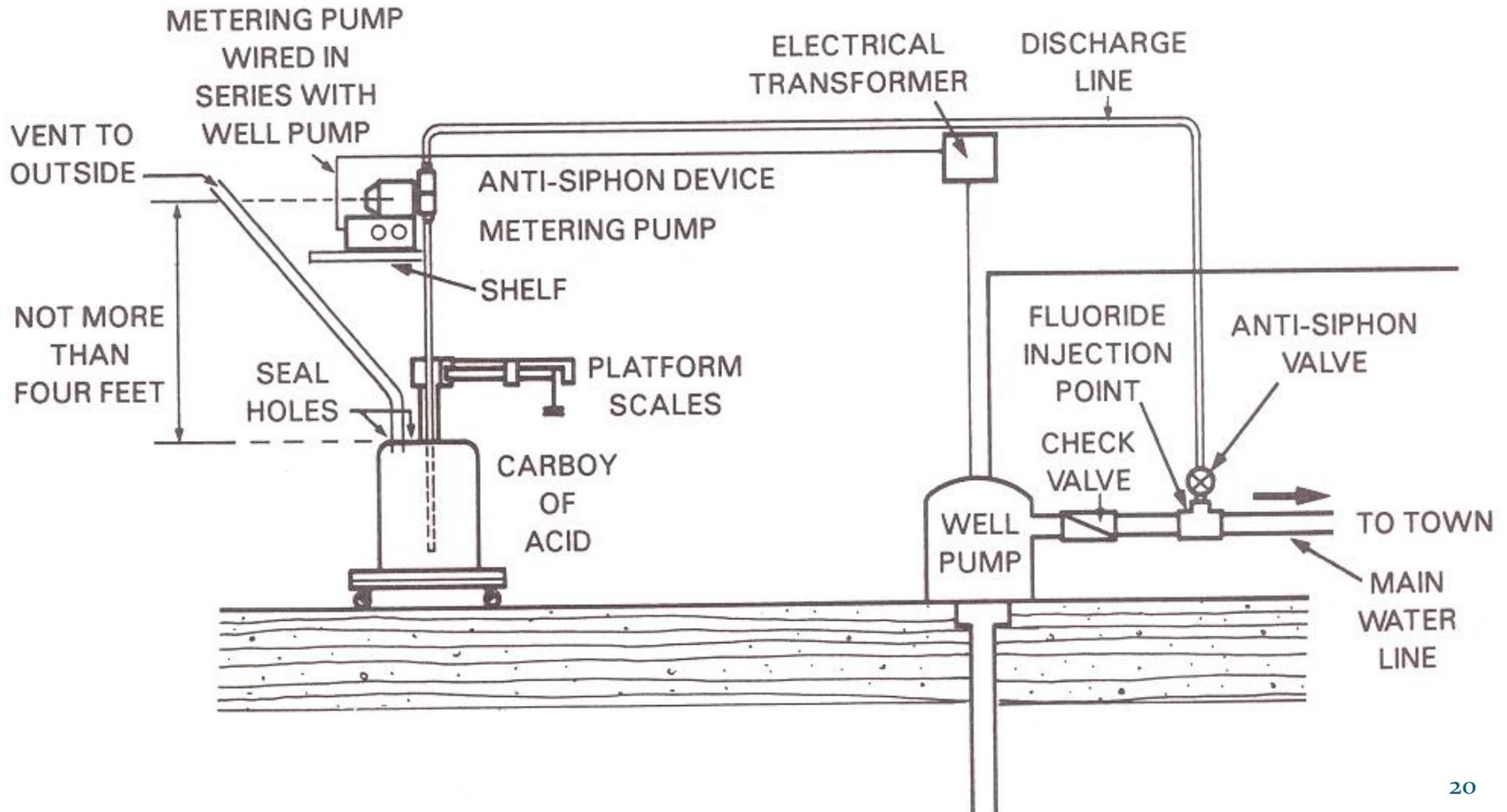
Gravimetric Feeders

GRAVIMETRIC FEEDER, BELT-TYPE

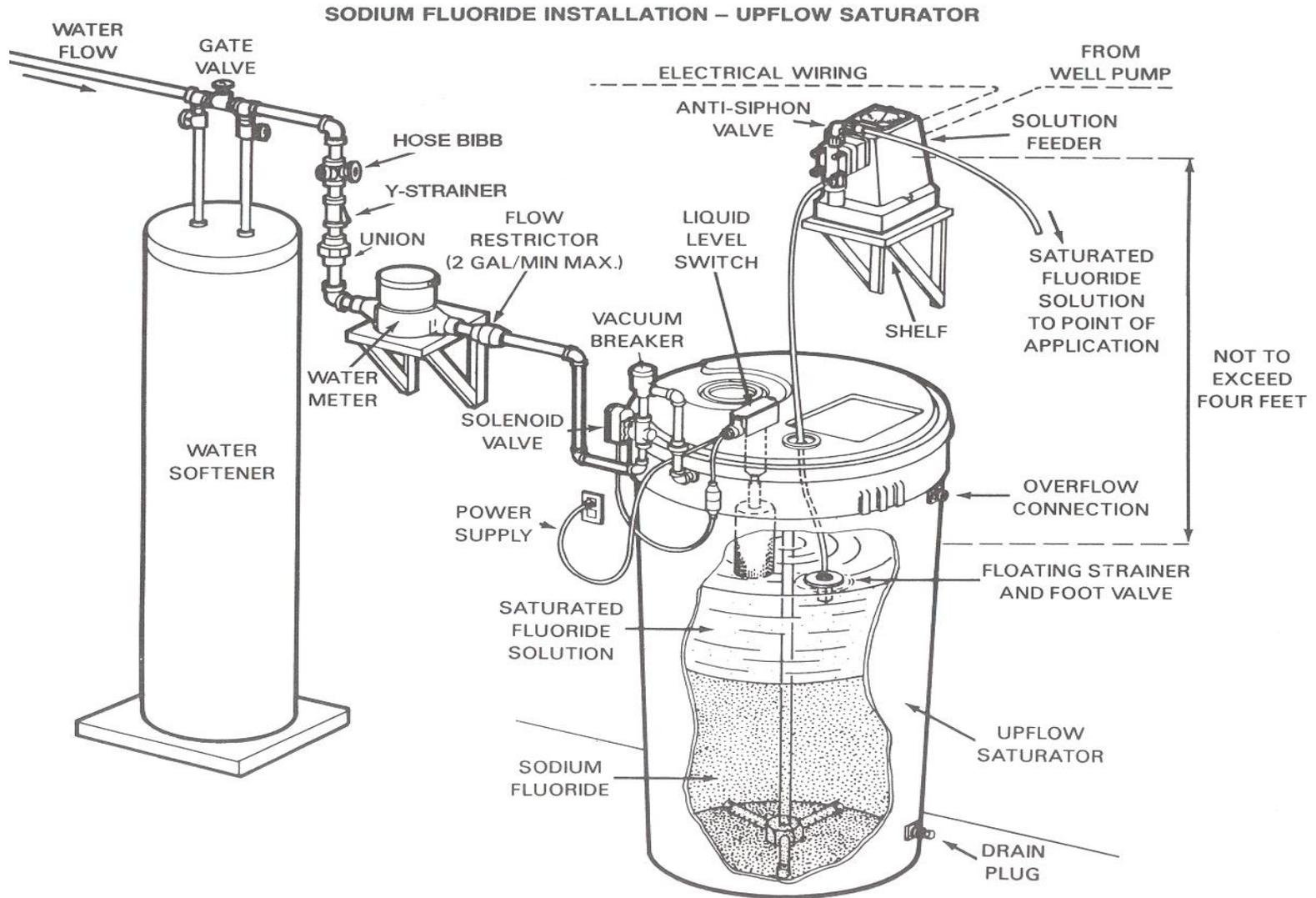


Positive Displacement Pump Feeders

HYDROFLUOSILICIC ACID INSTALLATION — CARBOY (DRUM) STORAGE

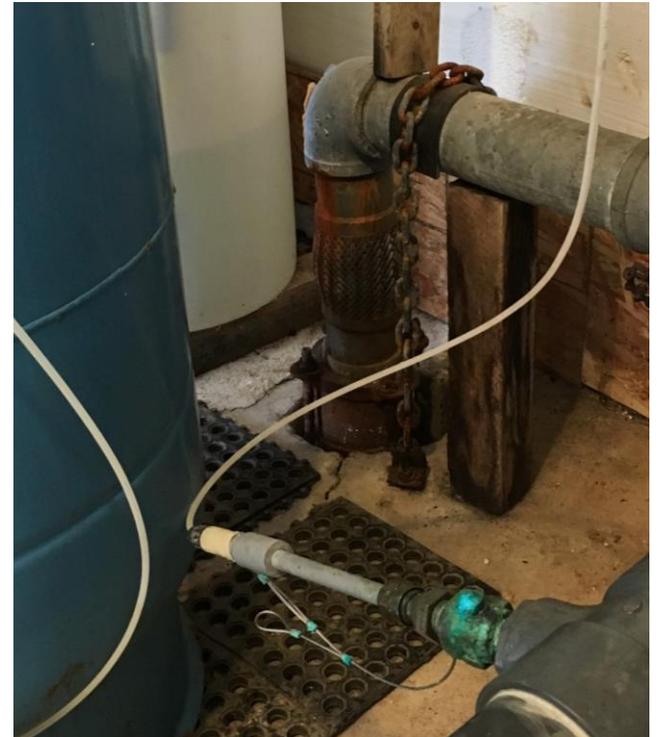


Upflow Saturator Feeders



Injecting Fluoride Solution

- Injection quill should be positioned at 4 o'clock or 7 o'clock to prevent corrosion from any leaks.
- If injecting into a pressurized pipeline, redundant anti-siphon valves are required.
(Not required if into open basin).
- Electrical outlet must be wired so feed equipment is energized only when well pump is energized.



Fluoride Testing Frequency

Basic Testing for Both Groundwater and Surface Water Supplies:

Location	Frequency
Raw Water	Monthly
Plant Tap	Daily
Distribution	Weekly

Surface Water Supplies may sample raw water more frequently due to variability of the source water.

Fluoride Testing Methods

SPADNS

- A dye turns sample red; Any F^- present decreases the intensity of the color.
- Measured using a spectrophotometer.



Fluoride Testing Methods

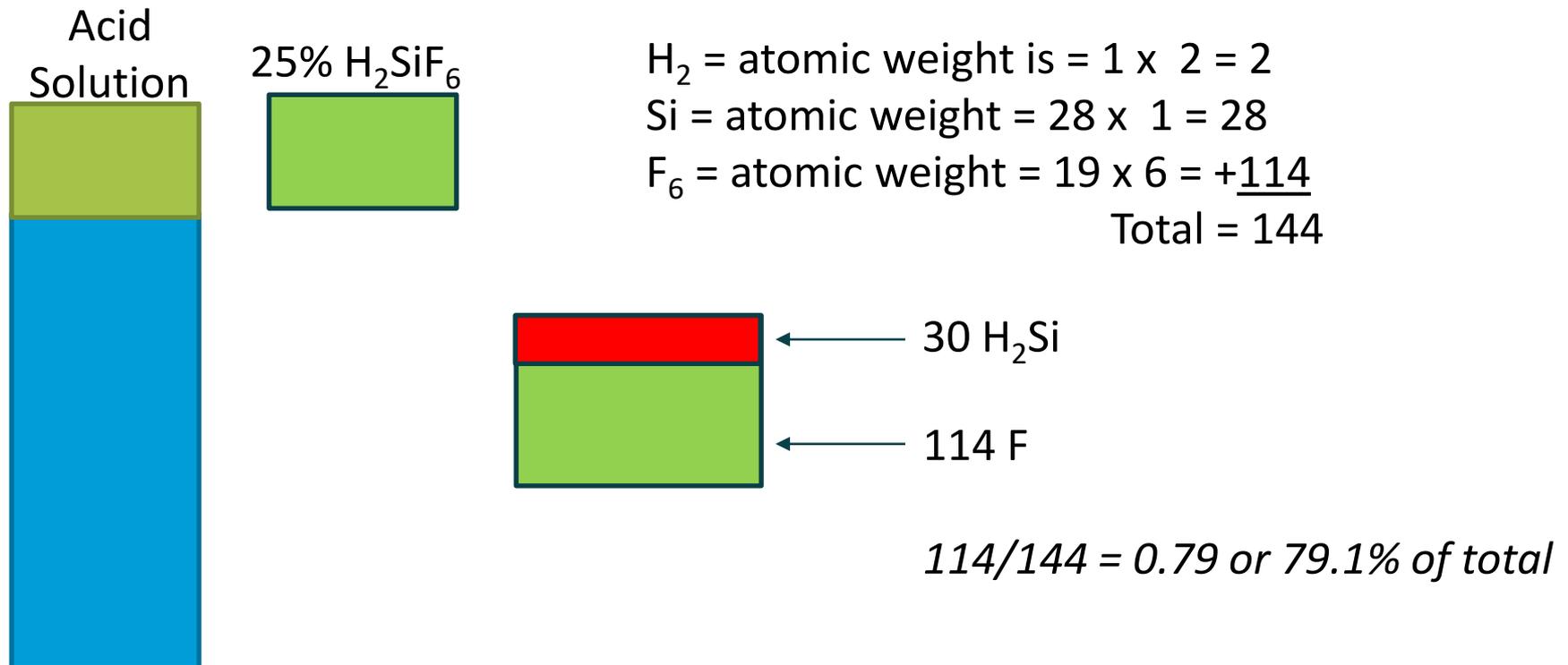
Electrode

- Voltage Potential - proportional to the difference between F^- in electrode and F^- in water.
- More accurate than SPADNS



Hydrofluorosilicic Acid Concentration

Hydrofluorosilicic acid solution is made with compound H_2SiF_6 . The solution concentration is generally 22%-25% H_2SiF_6 .



Total solution is 25% compound H_2SiF_6 , which is 79.1% F; $25\% \times 79\% = 19.8\%$
So the amount of fluorine is 19.8 % in the acid solution

Example 1: How many gallons of 25% (19.8% actual fluoride) hydrofluorosilicic acid will be required to apply 1.0 ppm of fluoride to 1 million gallons of water? Assume that 1 gallon of acid weighs 10.4 pounds.

$$1) 1 \text{ million gallons H}_2\text{O} \times \frac{8.34 \text{ lbs}}{\text{gal}} = 8.34 \text{ million lbs H}_2\text{O}$$

$$2) 1 \text{ ppm} = \frac{? \text{ lbs F}}{8.34 \text{ M lbs H}_2\text{O}}$$

$$3) 1 \text{ ppm} \times 8.34 \text{ M lbs} = 8.34 \text{ lbs F}^-$$

4) However, we want to find gallons of acid solution, not pure F lbs, so, we need to continue on to the next slide.

Solving for the lbs of F in solution;

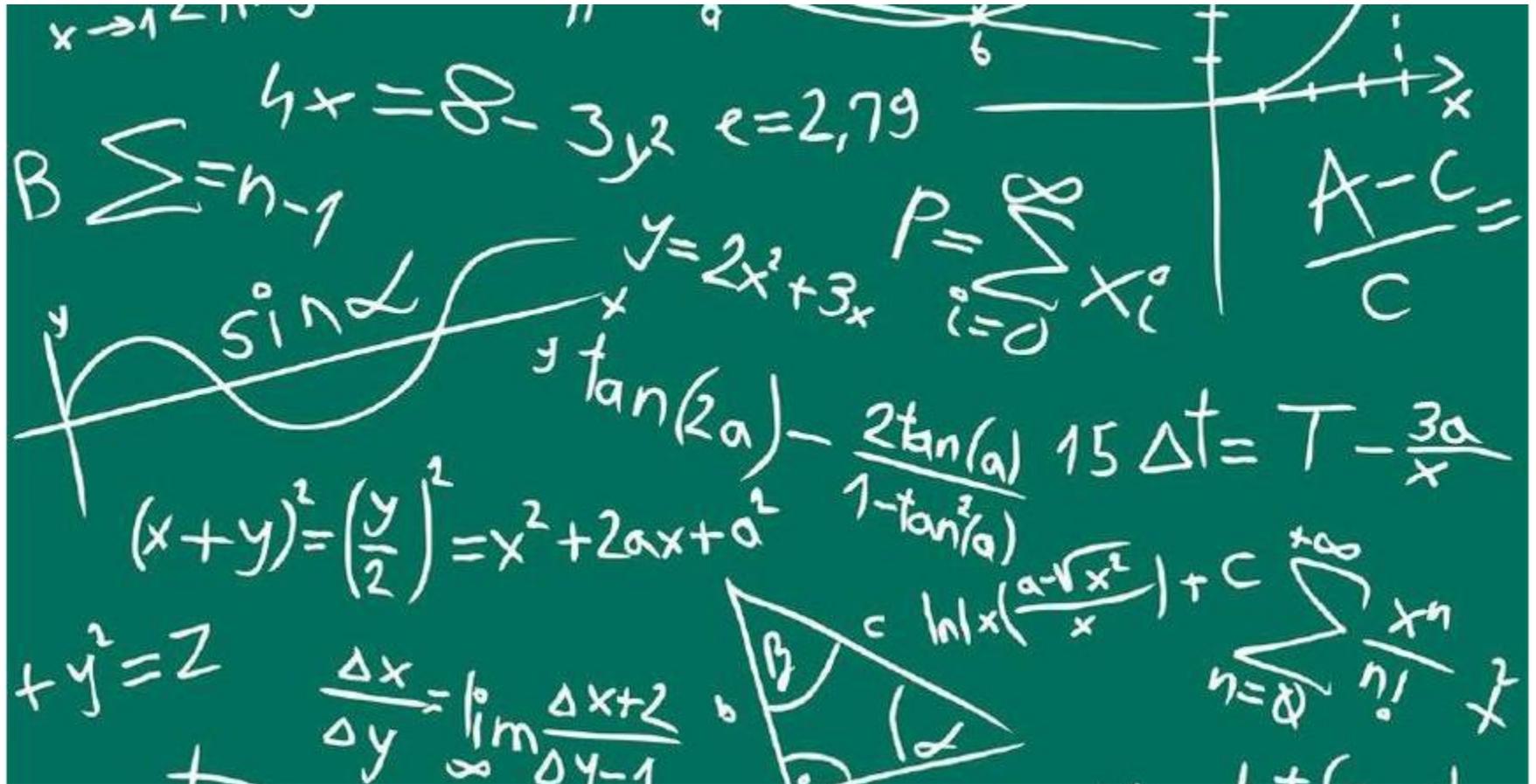
$$5) \frac{8.34 \text{ lbs } F^-}{0.198} = 42.2 \text{ lbs solution}$$

Question was for gallons of solution:

$$6) 42.2 \text{ lbs solution} \times \frac{1 \text{ gal}}{10.4 \text{ lbs}} = 4 \text{ gal soln fluorosilicic acid}$$



Problems

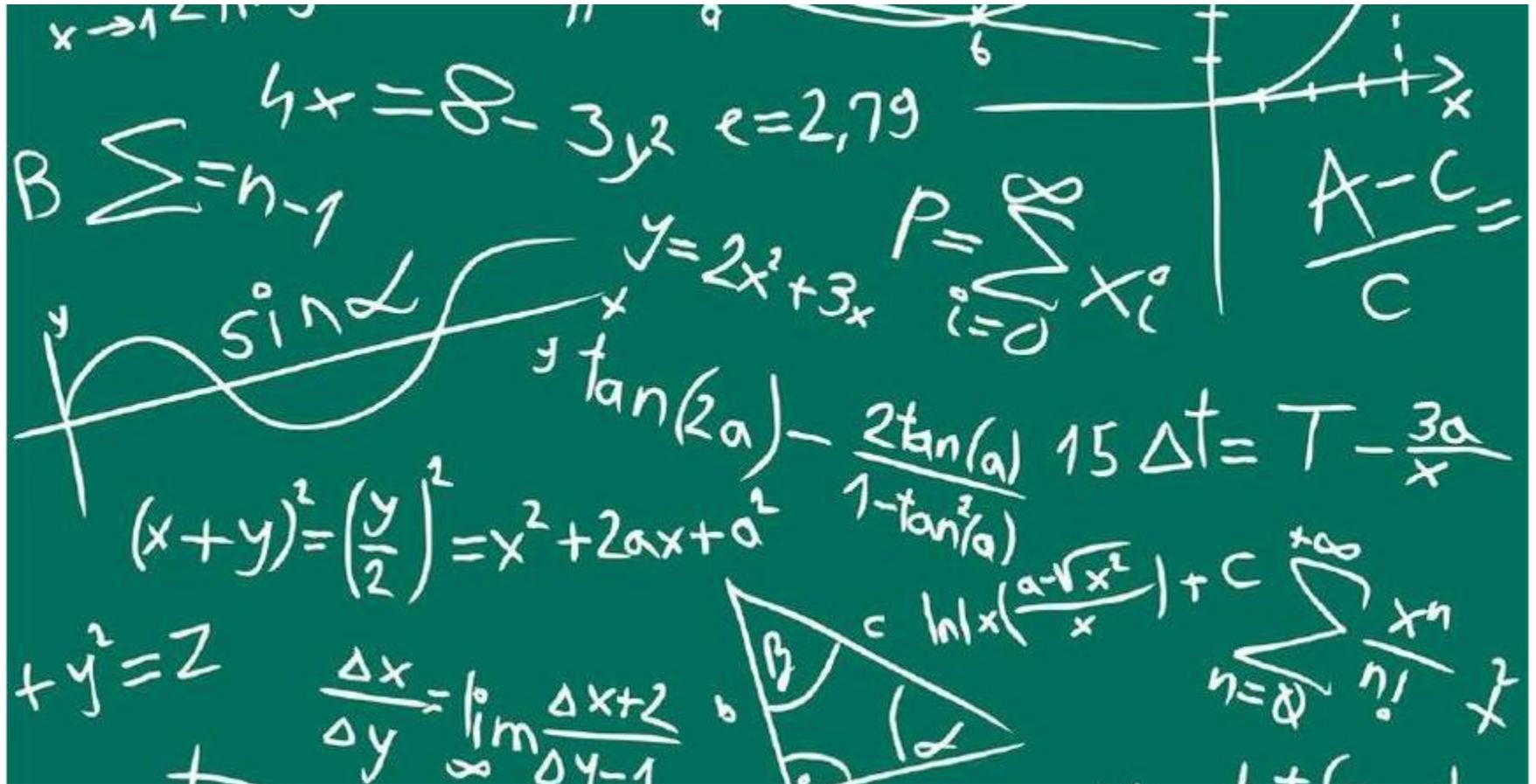


1. How many gallons of 25% fluorosilicic acid (10.4 lbs/gal) is required if the average pumping rate is 400 gpm for 4 hours, the natural fluoride concentration is 0.4 mg/L, and the final desired concentration is 1.0 mg/L?

2. How many gallons of 25% hydrofluorosilicic acid will be required for a period of 30 days if the average daily pumping rate is 700 gpm, the natural fluoride concentration is 0.45 mg/L, and the fluoride concentration desired is 0.95 mg/L. Acid solution weighs 10.4 lbs/gal.

3. Sodium fluoride is sometimes applied by means of a saturator. In this treatment, excess sodium fluoride is added to the solution container, and is applied as a 4% solution (maximum solubility). The amount of fluoride used can be determined by measuring the number of gallons of the 4% solution used in a given period of time. If the city pumps 480,000 gallons of water per day, and 26.4 gallons of 4% solution made from 98% sodium fluoride was used, what was the concentration of the applied fluoride? Assume the weight of 4% solution is 8.4 pounds per gallon.

Problem Solutions



1. How many gallons of 25% fluorosilicic acid (10.4 lbs/gal) is required if the average pumping rate is 400 gpm for 4 hours, the natural fluoride concentration is 0.4 mg/L, and the final desired concentration is 1.0 mg/L?

Solution contains 25% H_2SiF_6 . H_2SiF_6 is 79.1% F.

So solution contains 19.8% F.

$$\text{ppm} = \frac{\text{lbs F}}{\text{Mlb H}_2\text{O}}$$

$$\frac{400 \text{ gal H}_2\text{O}}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times 4 \text{ hrs} \times \frac{8.34 \text{ lbs}}{\text{gal}} \times \frac{1 \text{ Mlbs}}{1,000,000 \text{ lbs}} = 0.8 \text{ M lbs H}_2\text{O}$$

$$1 \text{ mg/L} - 0.4 \text{ mg/L} = 0.6 \text{ mg/L} \text{ or } \mathbf{0.6 \text{ ppm}}$$

$$0.6 \text{ ppm} = \frac{? \text{ lbs F}}{0.8 \text{ M lbs H}_2\text{O}} = \mathbf{0.48 \text{ lbs pure F}}$$



Question asked for gallons of solution...

$$0.48 \text{ lbs F} \times \frac{100\% \text{ soln}}{25\% \text{ H}_2\text{SiF}_6} \times \frac{100\% \text{ soln}}{79\% \text{ F}} = 2.43 \text{ lbs solution}$$

or

$$0.48 \text{ lbs F} \times \frac{1}{0.198} = 2.43 \text{ lbs solution}$$

Now to convert to gallons:

$$2.43 \text{ lbs solution} \times \frac{1 \text{ gal}}{10.4 \text{ lbs}} = \mathbf{0.23 \text{ gallons}} \text{ of solution}$$

2. How many gallons of 25% hydroflourosilicic acid will be required for a period of 30 days if the average daily pumping rate is 700 gpm, the natural fluoride concentration is 0.45 mg/L, and the fluoride concentration desired is 0.95 mg/L. Acid solution weighs 10.4 lbs/gal.

$$\text{ppm F} = \frac{\text{lbs F}}{\text{Mlb H}_2\text{O}}$$

$$\frac{700 \text{ gal H}_2\text{O}}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{24 \text{ hr}}{\text{day}} \times 30 \text{ days} \times \frac{8.34 \text{ lbs}}{\text{gal}} \times \frac{1 \text{ Mlb}}{1,000,000 \text{ lbs}} = 252.2 \text{ M lbs H}_2\text{O}$$

$$0.95 \text{ mg/L target} - 0.45 \text{ mg/L raw} = 0.5 \text{ mg/L F or } 0.5 \text{ ppm F}$$

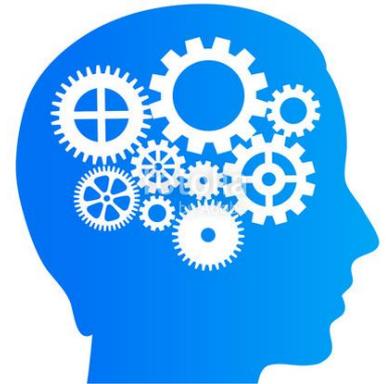
$$0.5 \text{ ppm} = \frac{? \text{ lbs F}}{252.2 \text{ M lbs H}_2\text{O}} \quad 0.5 \text{ ppm} \times 252.2 \text{ M lbs} = 126.1 \text{ lbs F}$$

Question asked for gallons of solution...

$$126.1 \text{ lbs F} \times \frac{100\% \text{ soln}}{25\% \text{ H}_2\text{SiF}_6} \times \frac{100\% \text{ soln}}{79\% \text{ F}} = 637 \text{ lbs solution}$$

or

$$126.1 \text{ lbs F} \times \frac{1}{0.198} = 637 \text{ lbs solution}$$



Now to convert to gallons:

$$637 \text{ lbs solution} \times \frac{1 \text{ gal}}{10.4 \text{ lbs}} = \mathbf{61.25 \text{ gallons of solution}}$$

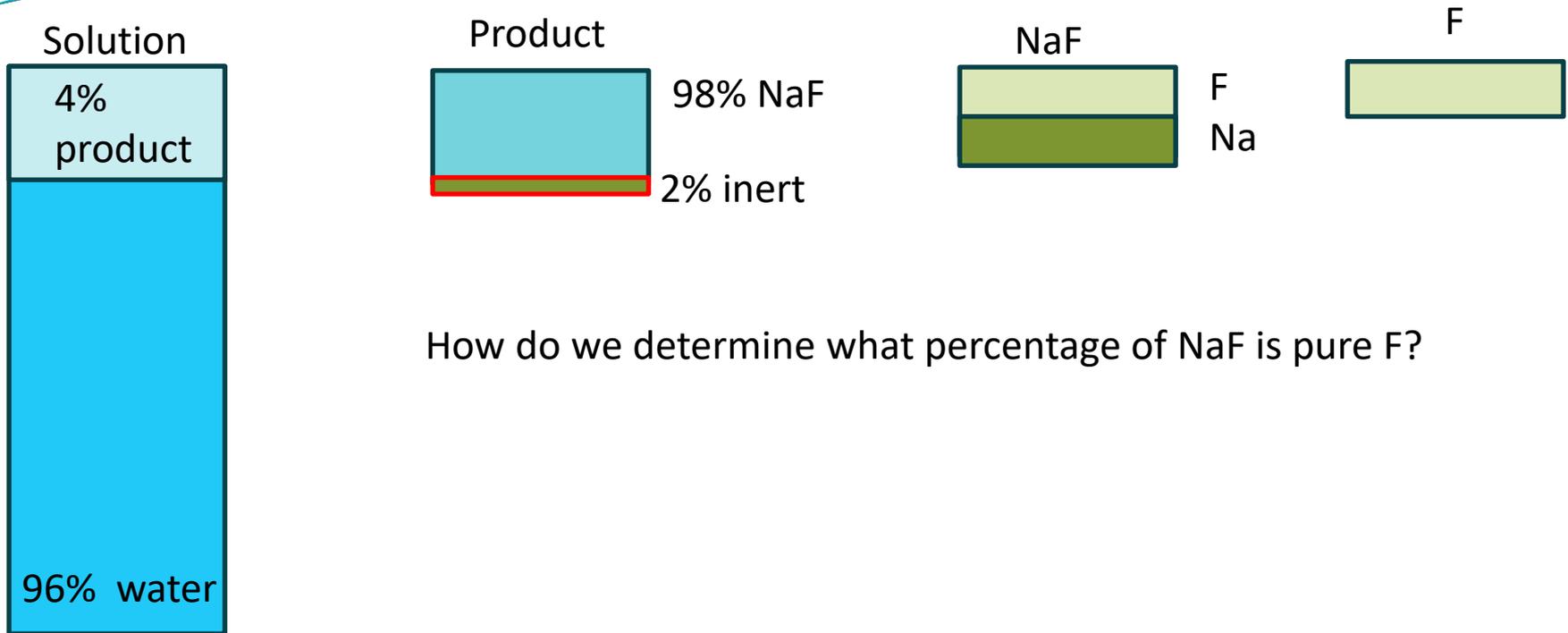
3. Sodium fluoride is sometimes applied by means of a saturator. In this treatment, excess sodium fluoride is added to the solution container, and is applied as a 4% solution (maximum solubility). The amount of fluoride used can be determined by measuring the number of gallons of the 4% solution used in a given period of time. If the city pumps 480,000 gallons of water per day, and 26.4 gallons of 4% solution made from 98% sodium fluoride was used, what was the concentration of the applied fluoride? Assume the weight of 4% solution is 8.4 pounds per gallon.

So we are given the volume of water pumped (convert to M lbs), the amount of solution used (convert to F), and must determine concentration in ppm.

$$\text{ppm} = \frac{\text{lbs F}}{\text{Mlb H}_2\text{O}}$$

$$\frac{480,000 \text{ gal H}_2\text{O}}{\text{day}} \times \frac{8.34 \text{ lbs}}{\text{gal}} \times \frac{1 \text{ M lbs}}{1,000,000 \text{ lbs}} = 4.0 \text{ M lbs H}_2\text{O per day}$$

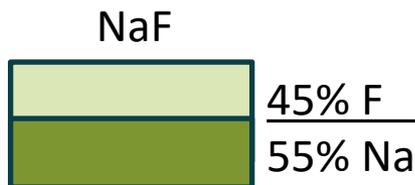
26.4 gallons of 4% solution, made from 98% Sodium Fluoride (NaF) product



How do we determine what percentage of NaF is pure F?

From the period table we see that Na weighs 23 and F weighs 19, so NaF weighs 42.

So the percent of NaF compound occupied by F is $\frac{19 \text{ lbs F}}{42 \text{ lbs NaF}}$ or 45%



We were given 26.4 gallons of solution and need to convert to lbs F to use our equation; Solution weight of 8.4 lbs/gal was provided

$$26.4 \text{ gallons soln} \times \frac{8.4 \text{ lbs}}{\text{gallon}} \times \frac{4\% \text{ product}}{100\% \text{ soln}} \times \frac{98\% \text{ NaF}}{100\% \text{ product}} \times \frac{45\% \text{ F}}{100\% \text{ NaF}} = ? \text{ lbs F}$$
$$= 3.93 \text{ lbs F}$$

Now we know the amount in lbs of F applied, so we can use our equation to determine the concentration of F.

$$\text{ppm F} = \frac{\text{lbs F}}{\text{Mlb H}_2\text{O}}$$
$$\frac{3.93 \text{ lbs F}}{4.0 \text{ Mlb H}_2\text{O}} = ? \text{ ppm}$$
$$= 0.98 \text{ ppm F}$$





Questions?