

Manganese Treatment & Pressure Filter Optimization

IL RWA

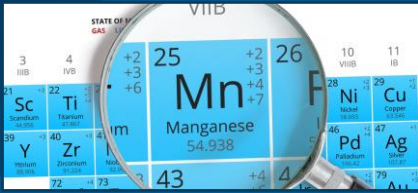
Rockford, IL

Wednesday, October 12, 2022

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Manganese (Mn)



Health & Aesthetic Issues Limits and Regulation



Removal Mechanisms Treatment Technologies



Filter Operation & Maintenance

Manganese (Mn) is a naturally occurring element

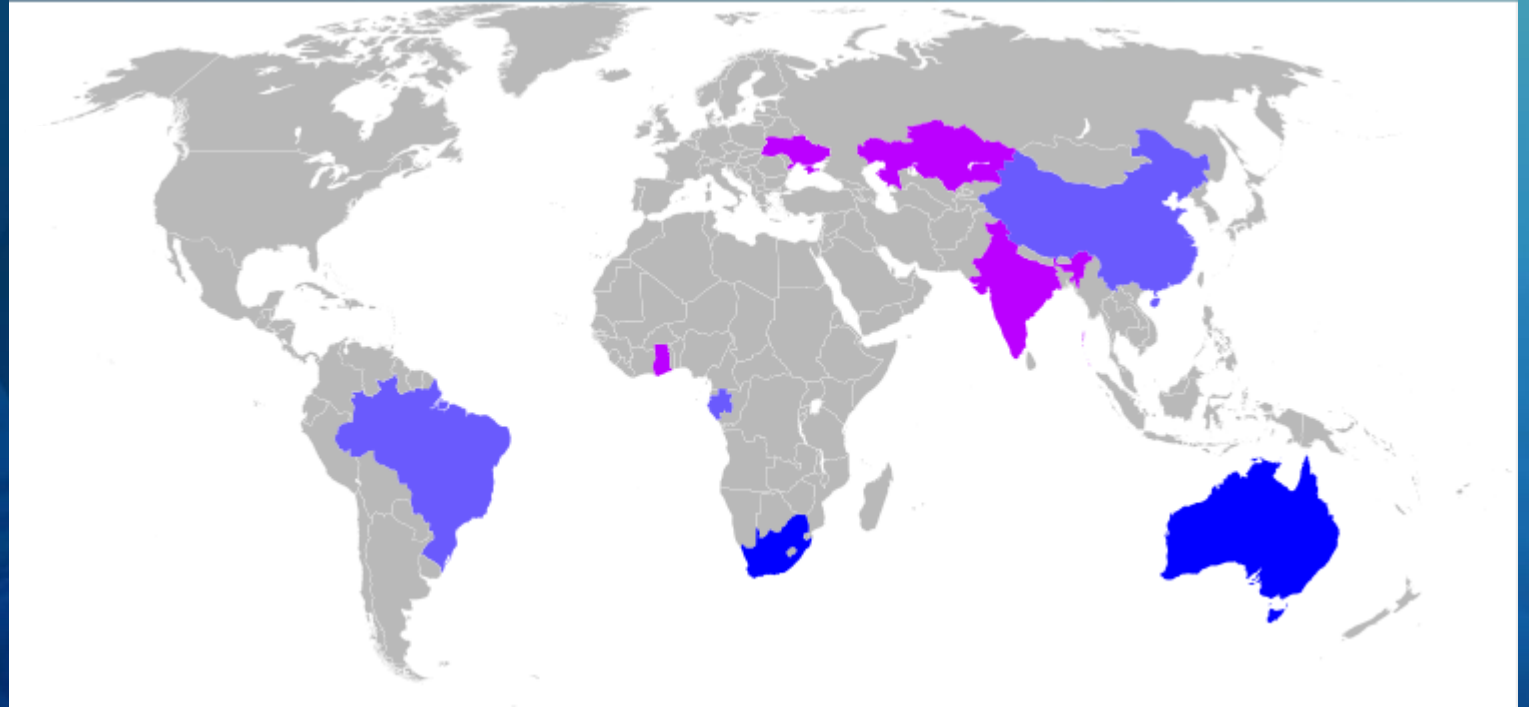
- Ranked 12th in earths crust (0.1%)
- 100+ minerals- Sulfides, oxides, carbonates, silicates, phosphates, borates

A portion of the periodic table is shown, with a magnifying glass focused on the element Manganese (Mn). The magnifying glass highlights the element's symbol 'Mn', name 'Manganese', and atomic weight '54.938'. The table also shows other elements like Scandium (Sc), Titanium (Ti), Vanadium (V), Chromium (Cr), Nickel (Ni), and Copper (Cu) with their respective atomic numbers and symbols. Oxidation states are indicated by small numbers in the top right of each element's box.

| | | | | | | | | |
|--------------------------------|---------------------------------|-------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|------------------------------|
| 3 IIIB | 4 IVB | 5 VB | 6 VIB | 7 VIIB | 8 VIIB | 9 VIIB | 10 VIII B | 11 IB |
| 21 Sc Scandium 44.956 | 22 Ti Titanium 47.867 | 23 V Vanadium 50.942 | 24 Cr Chromium 51.996 | 25 Mn Manganese 54.938 | 26 Fe Iron 55.845 | 27 Co Cobalt 58.933 | 28 Ni Nickel 58.693 | 29 Cu Copper 63.546 |
| 39 Y Yttrium 88.906 | 40 Zr Zirconium 91.224 | 41 Nb Niobium 92.906 | 42 Mo Molybdenum 95.94 | 43 Tc Technetium 98 | 44 Ru Ruthenium 101.07 | 45 Rh Rhodium 102.91 | 46 Pd Palladium 106.42 | 47 Ag Silver 107.87 |
| 72 Hf Hafnium 178.49 | 73 Ta Tantalum 180.948 | 74 W Tungsten 183.84 | 75 Re Rhenium 186.207 | 76 Os Osmium 190.23 | 77 Ir Iridium 192.222 | 78 Pt Platinum 195.084 | 79 Au Gold 196.967 | |

18.5 million tons of Mn are mined annually

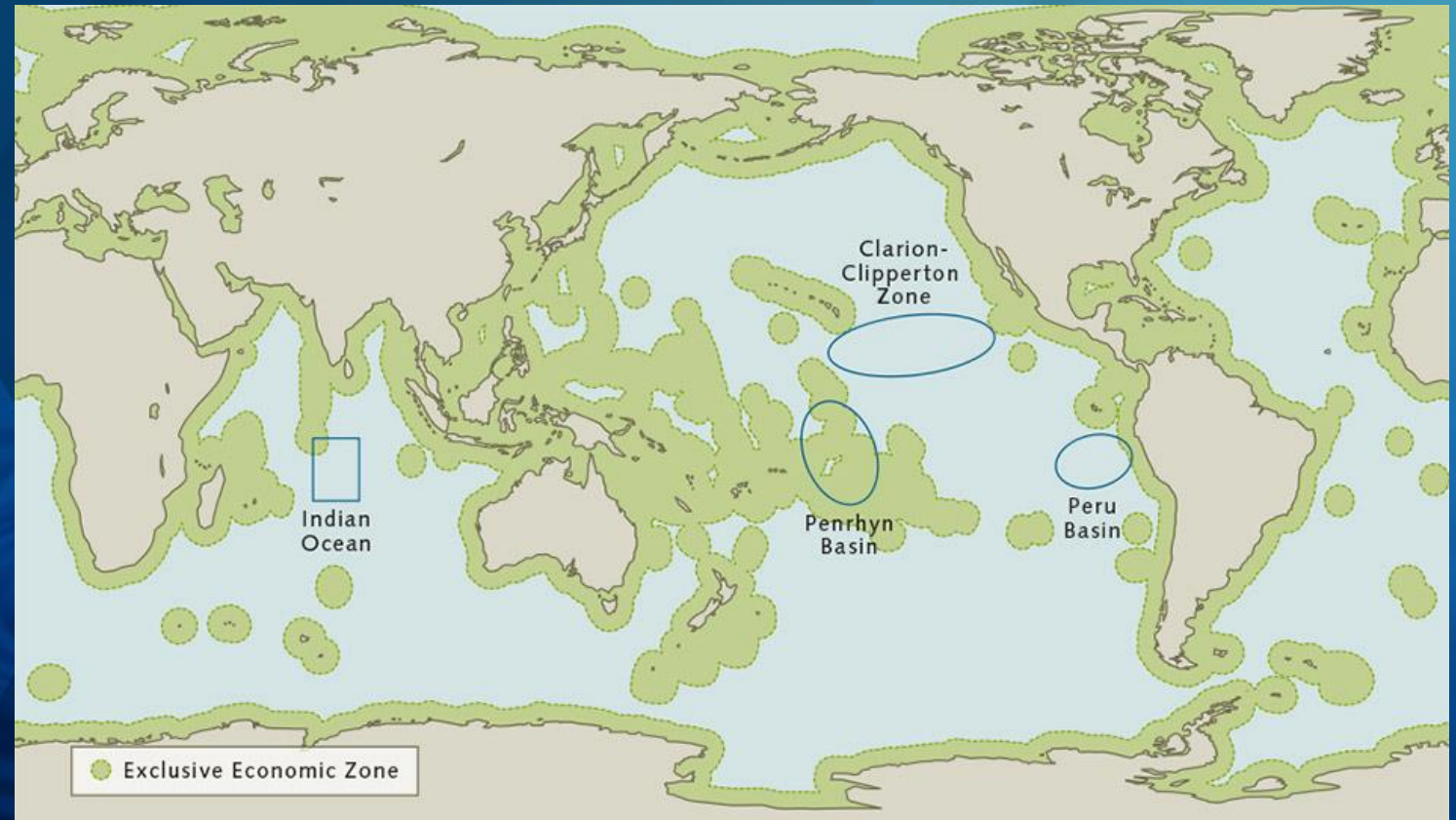
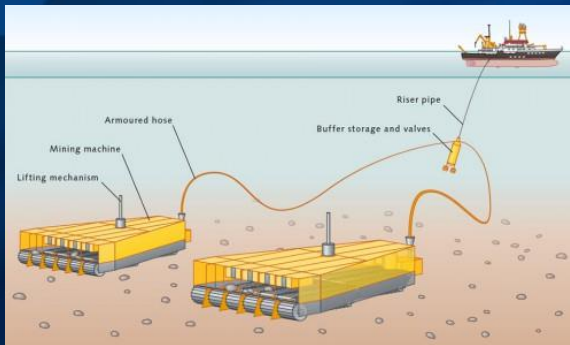
1. South Africa- 33.5%
2. Australia 15%
3. China
4. Gabon
5. Brazil
6. India
7. Malaysia
8. Ukraine
9. Kazakhstan
10. Ghana



(List from 2020 article in NS Energy)

Nodules on the sea floor can contain up to ~30% Mn

- Approx. 5,000 m deep



Almost 90% of Mn mined is used
in production of steel

- Other uses

- Batteries
- Drink cans
- Rubber additive
- Glass
- Fungicide
- Fertilizers
- Ceramics
- Fireworks
- Food supplement



Manganese (Mn) is an essential nutrient



3 oz = 5.8 mg



1 cup = 2.5 mg



1.5 mg



2 mg

Manganese (Mn) is an essential nutrient

- Recommended Adequate Intake (AI) values (mg/day)*

- Infants, <1 year: 0.003–0.06
- Children: 1.2–1.5
- Preteens/teens: 1.9–2.2 (boys), 1.6 (girls)
- Adults: 1.8–2.3

- Tolerable upper intake level = 11



3 oz = 5.8 mg



1 cup = 2.5 mg



1.5 mg

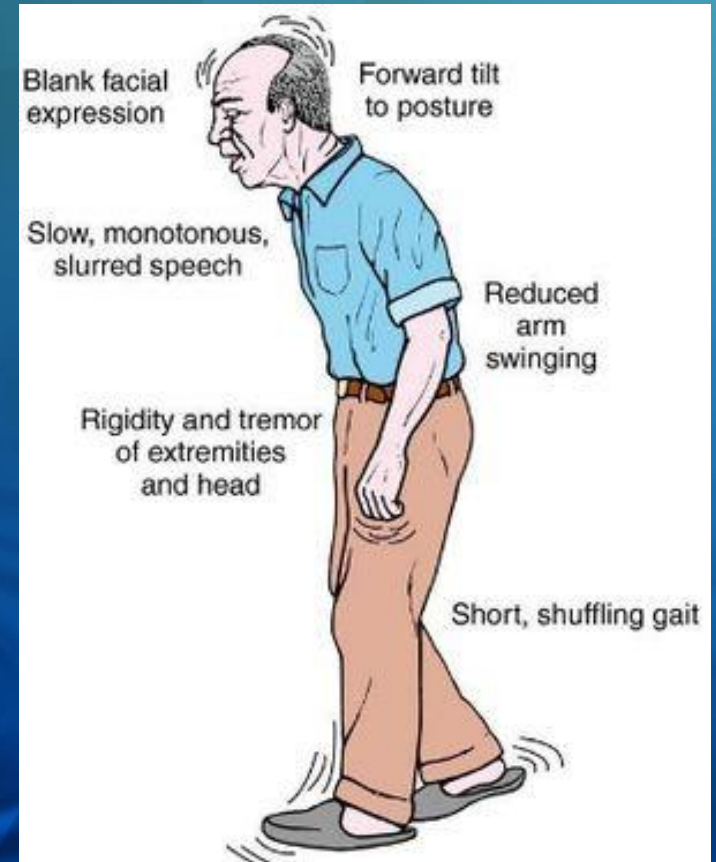


2 mg

*determined by the Food & Nutrition Board of the Institute of Medicine (IOM)

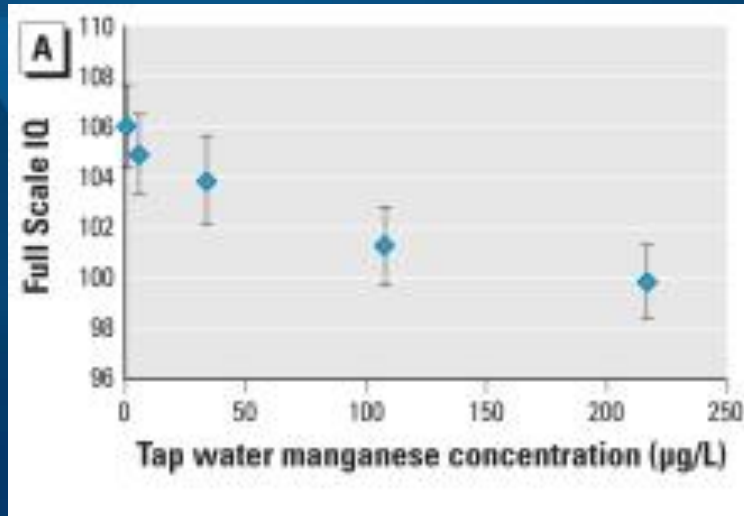
High levels of Mn can cause health issues

- Manganism
 - From inhalation
 - Similar to Parkinson's
 - Motor skill decline
 - Gait disturbances
 - Speech impairment



University of British Columbia:
https://wiki.ubc.ca/SPPH381B/TermProject/Alkaline_battery-_Samin/Granulation/Neurobehavioral_dysfunctions,_called_Chronic_manganese_poisonin

Exposure to Mn in drinking water can cause more subtle effects



Research | Children's Health

Intellectual Impairment in School-Age Children Exposed to Manganese from Drinking Water

Maryse F. Bouchard,^{1,2} Sébastien Sauvé,³ Benoit Barbeau,⁴ Melissa Legrand,⁵ Marie-Ève Brodeur,¹ Thérèse Bouffard,⁶ Elyse Limoges,⁷ David C. Bellinger,⁸ and Donna Mergler¹

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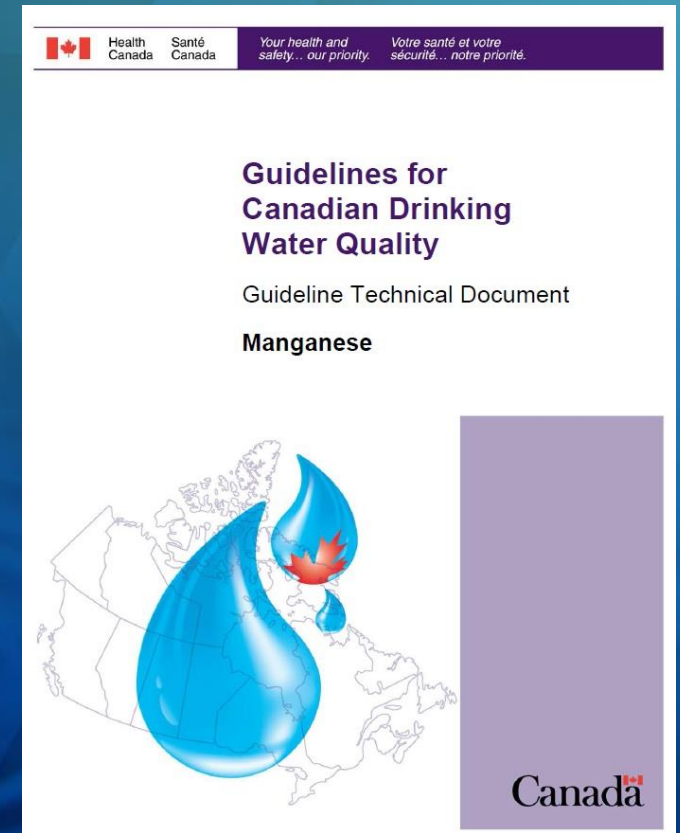
BACKGROUND: Manganese is an essential nutrient, but in excess it can be a potent neurotoxicant. Despite the common occurrence of manganese in groundwater, the risks associated with this source

manganese intoxication from water containing > 1,000 µg manganese/L, one presenting with attention and memory impairments (Woolf

- Over 6 pt difference in IQ (Bouchard et al. 2011)
- Decrease memory, attention, and motor skills (Olhote et al. 2014)
- High blood and high hair Mn conc. associated with lower IQ SCORES (Haynes et al. 2015)

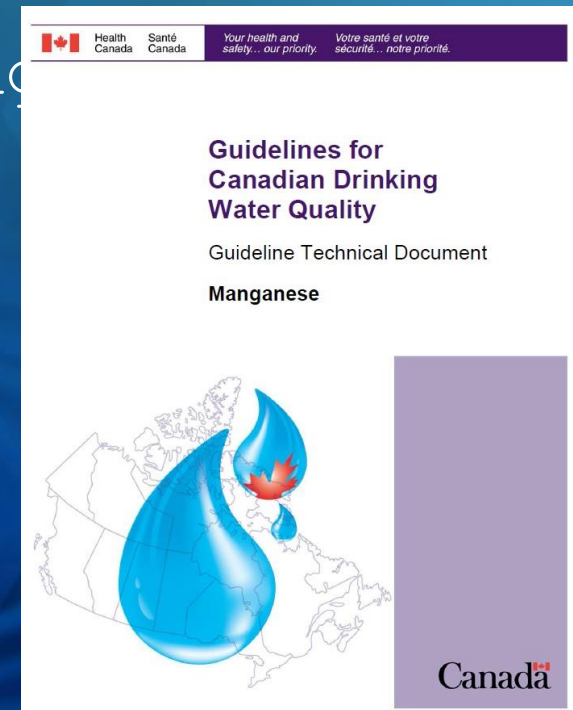
General conclusions about high Mn levels from Canada Health:

- The CNS is the primary target of Mn toxicity
- Elderly and children most susceptible
- Infants and children may experience:
 - Changes in behavior
 - lower IQ and test scores
 - Impaired reading ability
 - Speech and memory difficulties
 - Lack of coordination



In 2019, Canada set more strict limits on Mn

- Maximum Acceptable Concentration (MAC) = 0.12 mg/L
- Aesthetic Objective (AO) = 0.02 mg/L



The Secondary Maximum Contaminant Level (SMCL) for Mn is 0.05 mg/L

- Basically our “Aesthetic Objective”
 - Unpleasant taste and color
 - Costly problems to water distribution systems



<https://www.wateronline.com/doc/the-hidden-dangers-of-manganese-in-drinking-water-0001>



<https://tataandhoward.com/2017/01/importance-treating-manganese-drinking-water/>



<https://www.safewater.org/operation-water-drop-listings/2016/11/13/manganese-analysis-for-high-school-operation-water-drop>

Is regulation coming to US?

- Long, slow process
 - CCL → RD → MCL
- On list for potential regulation



IL-EPA Manganese Requirements

Drinking Water Illinois State MCL

Requires Treatment if $Mn > 0.15 \text{ mg/L}$
Because of Health Concerns

Removal Mechanisms vs Treatment Technologies



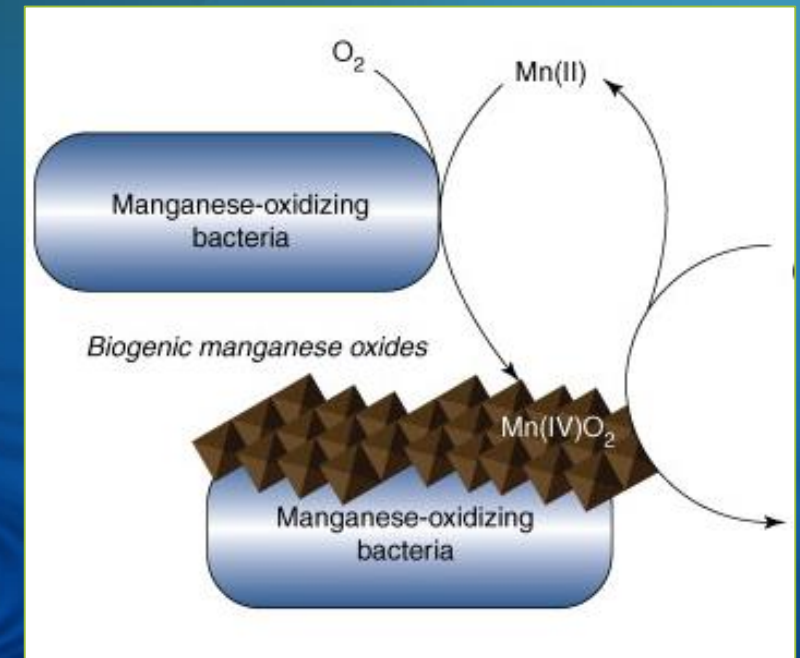
Removal Mechanisms vs Treatment Technologies

- Biological uptake
- Ion exchange
- Precipitation
- Adsorption

- Coagulation-filtration
- Membrane filtration
- Lime softening
- Biological filtration
- Ion exchange
- Oxidation/precipitation/filtration
- Adsorptive treatment
 - GAC and catalytic oxide media

Biological uptake/filtration

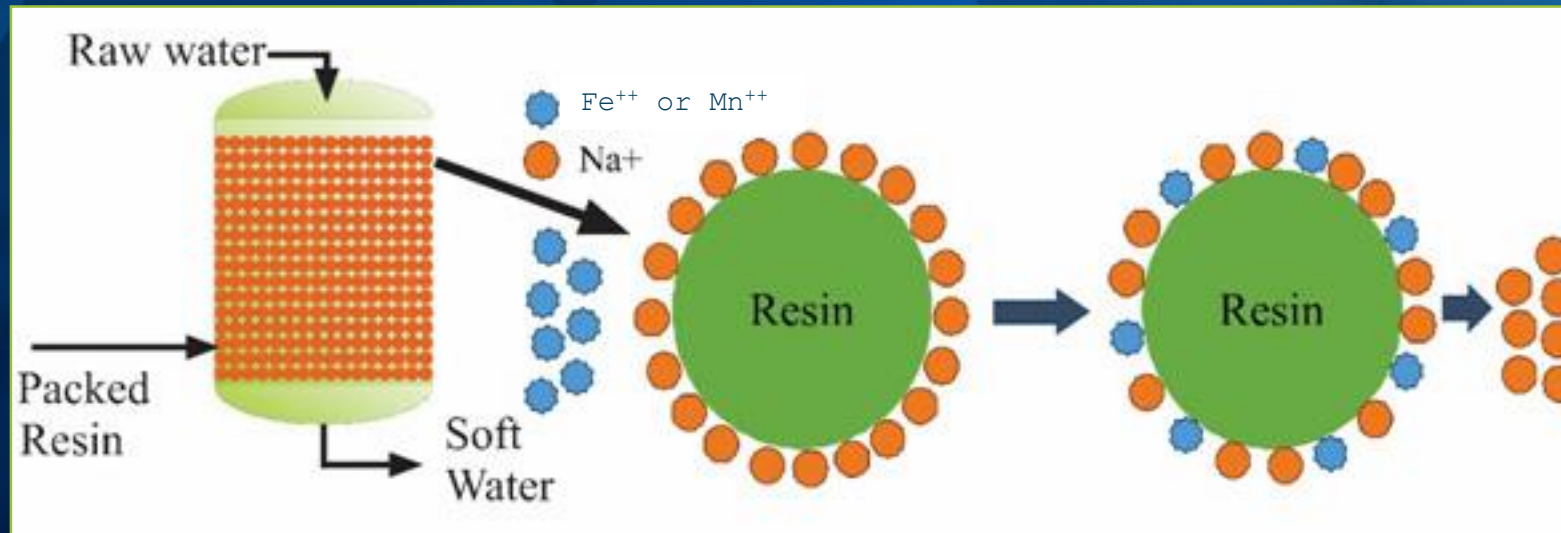
- Promote growth of certain bacteria
 - Sand, gravel, anthracite, GAC
- No or very little chemical addition required
 - Nutrient feed may be needed
- Specific conditions are required
 - Start up period
 - Living things are picky
 - Fe & Mn removed in two separate stages



[https://www.cell.com/trends/biotechnology/fulltext/S0167-7799\(08\)00286-2?code=cell-site](https://www.cell.com/trends/biotechnology/fulltext/S0167-7799(08)00286-2?code=cell-site)

Ion Exchange

- Performance based on raw water quality and target effluent concentrations
- High TDS residuals
- 7 gpm/ft² with 6-8 gpm/ft² backwash

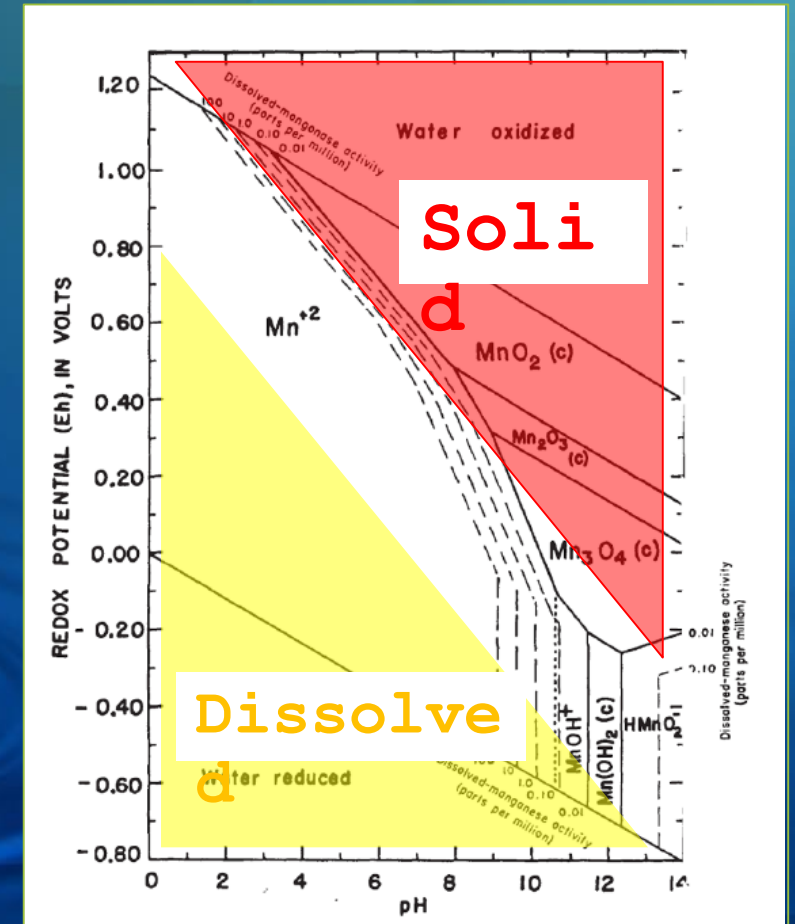


Precipitation (via supersaturation or oxidation)

High redox, high pH = water **oxidized**

Low redox, low pH = water **reduced**

This is traditional treatment!
Oxidation → precipitation →
filtration



Eh-pH diagram describing the stability of solid ("c") and aqueous phases of Mn as a function of redox potential and pH, at 25 C and 1atm

Comparing oxidants for Traditional Mn removal •

Oxygen
(aeration)

Ozone

Chlorine

Potassium
permanganate

Chlorine
dioxide

Comparing oxidants for Traditional Mn removal.

| | Oxidant Required <i>per mg/L Mn</i> | Oxidation Reaction Time <i>per mg/L Mn</i> | Benefits & Drawbacks |
|------------------------|---|--|---|
| Oxygen (aeration) | 0.29 | 80 minutes to days | No chemical use/easy to use, weak, may require detention, \$\$, low loading rates |
| Ozone | 0.67 | < 5 min | Strong, tricky to operate, \$\$\$ |
| Chlorine | 1.28 | 15 minutes to 12 hrs | Easy, safe, common disinfectant, weak, may require detention |
| Potassium permanganate | 1.92 | <7 min | Strong, messy, undesirable to work with |
| Chlorine dioxide | 2.4 | <5 min | Strong, requires additional safety considerations, \$\$ |

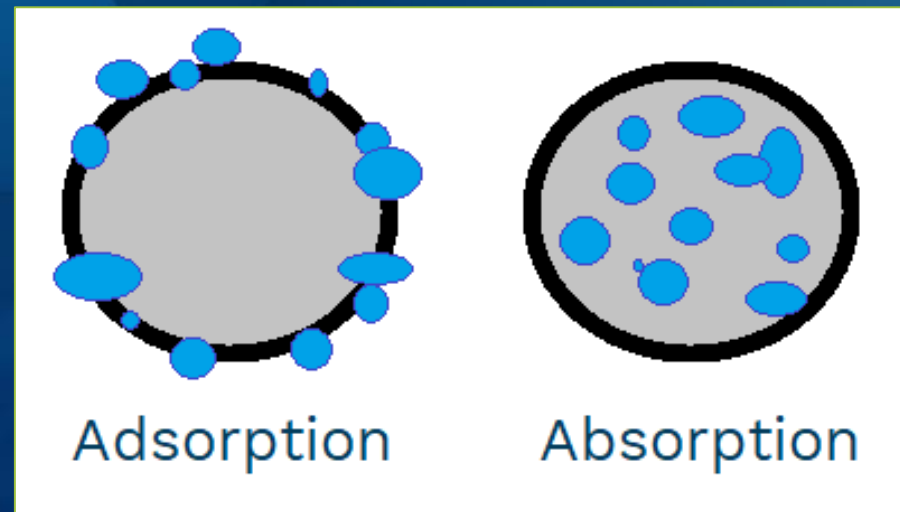
Compare Mn to Fe oxidation

| | <u>Oxidant Required</u> | | <u>Oxidation Reaction Time</u> | |
|---------------------------|-------------------------|-------------|--------------------------------|-------------------------|
| | per mg/L Fe | per mg/L Mn | per mg/L Fe | per mg/L Mn |
| Oxygen (aeration) | 0.14 | 0.29 | <10 min to 4 hr | 80 minutes to days |
| Ozone | 0.43 | 0.67 | < 1 min | < 5 min |
| Chlorine | 0.63 | 1.28 | Instantaneous to 1 hr | 15 minutes to 12 hrs |
| Potassium permanganate | 0.94 | 1.92 | <5 min | <7 min |
| Chlorine dioxide | 1.2 | 2.4 | <5 min | <5 min |

Comparing oxidants:

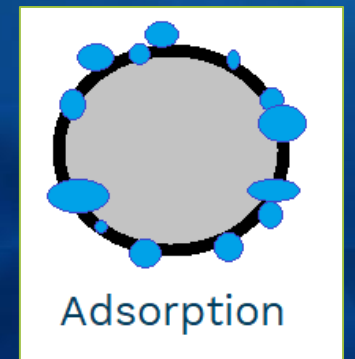
| Treatment Technology | Benefits | Drawbacks |
|---|---|---|
| Aeration, Filtration | <ul style="list-style-type: none">•No chemical use•Easy to operate | <ul style="list-style-type: none">•Entrained air can interfere with filtration if not broken•May require breaking head and repumping•Not effective for complexes with organic material•Low filter loading rates for effective removal•High capital cost |
| Chlorination, Filtration | <ul style="list-style-type: none">•Chlorine often used for disinfection and present at treatment plant, Easy to operate | <ul style="list-style-type: none">•May require pH adjustment•Low filter loading rates for effective removal•High capital cost |
| Ozone, Filtration | <ul style="list-style-type: none">•Strong oxidant, requires little reaction time | <ul style="list-style-type: none">•May oxidize manganese to permanganate•May oxidize manganese dioxide-containing media to permanganate•Difficult to operate•High capital and operations and maintenance costs |
| Chlorine Dioxide, Filtration | <ul style="list-style-type: none">•Effective for iron complexed with organic material•No trihalomethane formation | <ul style="list-style-type: none">•Generated on site with variety of chemicals•Requires careful operation and maintenance•Chlorite is a by-product•High capital cost |
| Potassium permanganate, Filtration | <ul style="list-style-type: none">•Strong oxidant, requires short reaction times•Can reform manganese dioxide coating on media | <ul style="list-style-type: none">•Causes staining if spilled•May be overfed, resulting in pink or purple water |

Adsorption: contaminants removed by sorption onto media surfaces



Adsorption: contaminants removed by sorption onto media surfaces

- **Iron oxides**- arsenic
- **GAC**- inorganic metals, organic compounds, radionuclides
- **Manganese oxides**- iron, manganese, arsenic, radium, H₂S
 - Oxides (negatively charged) adsorb ions to surface of particle
 - Evolution: Greensand → fusion-bonded coating → Pyrolusite (MnO₂)
 - Reaction is very fast! Key for Mn



Adsorptive (Catalytic) Filtration Allows for High Loading Rates

- >2x the typical 3-4 gpm/ft² (sand/anthracite)
- Smaller filters, smaller building
- Eliminate KMnO₄, detention basin, booster pump(s)
- Uses sodium hypochlorite -current common disinfectant
- Longer media life - 20+ years for pyrolusite
- Less backwash waste

Compare These 400 gpm Plants

a) Traditional media system, 3.14 gpm/ft²

- Eight (8) 54" diameter tanks
- 19,120 gallons bw waste (@ 15 gpm/ft² for 10 minutes)

b) Pyrolusite media system, 6.29 gpm/ft²

- Four (4) 54" diameter tanks
- 7,960 gallons bw waste (@ 25 gpm/ft² for 5 minutes)




Raw Water



Backwash

Rinse/filtrate to waste

Finished water -> Storage/Distribution

 Chemical feed(s)

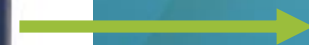


Raw Water



Chemistry
Flow Rate

Backwash



Rate
Duration
Frequency

Rinse/filt
er to
waste



Duration

Finished water →
Storage/Distribut
ion



Chemistry
Quality
target



Chemical
feed (s)

dose



Raw Water

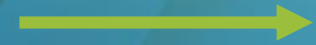


Chemistry
Rate

Rinse/filt
er to
waste



Duration



Backwash

Rate
Duration
Frequency



Finished water →
Storage/Distribut
ion

Chemistry



Chemical
feed (s)

dose



Raw Water

Chemistry
Rate

Rinse/filt
er to
waste
Duration

Monitor &
adjust!

Backwash

Rate
Duration
Frequency

Finished water →
Storage/Distribut
ion
Chemistry

Chemical
feed (s)

dose

Keep a filter log

3.3 Filter Log Sheet

FILTER MODEL NO:

NAME OF COMPANY:

SERIAL NO:

PERIOD OF THIS SHEET:

NOTE: Please record all calibrations of instruments or other occurrences related to this system.

| | | | | | | | | | |
|---|--|--|--|--|--|--|--|--|--|
| DATE | | | | | | | | | |
| TIME | | | | | | | | | |
| UNIT IN SERVICE | | | | | | | | | |
| INLET PRESSURE (<i>psi or bar</i>) | | | | | | | | | |
| OUTLET PRESSURE (<i>psi or bar</i>) | | | | | | | | | |
| DIFFERENTIAL PRESSURE (<i>psi or bar</i>) | | | | | | | | | |
| | | | | | | | | | |
| FLOW RATE (<i>gpm or lpm</i>) | | | | | | | | | |
| WATER TEMP (deg F or C) | | | | | | | | | |
| INLET CHLORINE (<i>ORP in mV</i>) | | | | | | | | | |
| OUTLET CHLORINE (<i>OPR in mV</i>) | | | | | | | | | |
| INLET IRON (<i>Fe in mg/l</i>) | | | | | | | | | |
| OUTLET IRON (<i>Fe in mg/l</i>) | | | | | | | | | |
| TOTALIZED (<i>gallons or liters</i>) | | | | | | | | | |
| *BACKWASH INITIATED | | | | | | | | | |
| | | | | | | | | | |
| OPERATOR'S INITIALS | | | | | | | | | |

Reference the Troubleshooting Guide where trends or differences are noted. This is a template; make copies as necessary.

NOTES: * BACKWASH REQUIRED- MANUAL if 10-15 psi or .7-1BAR DP increase, TIME OR VOLUME (TOTALIZED)

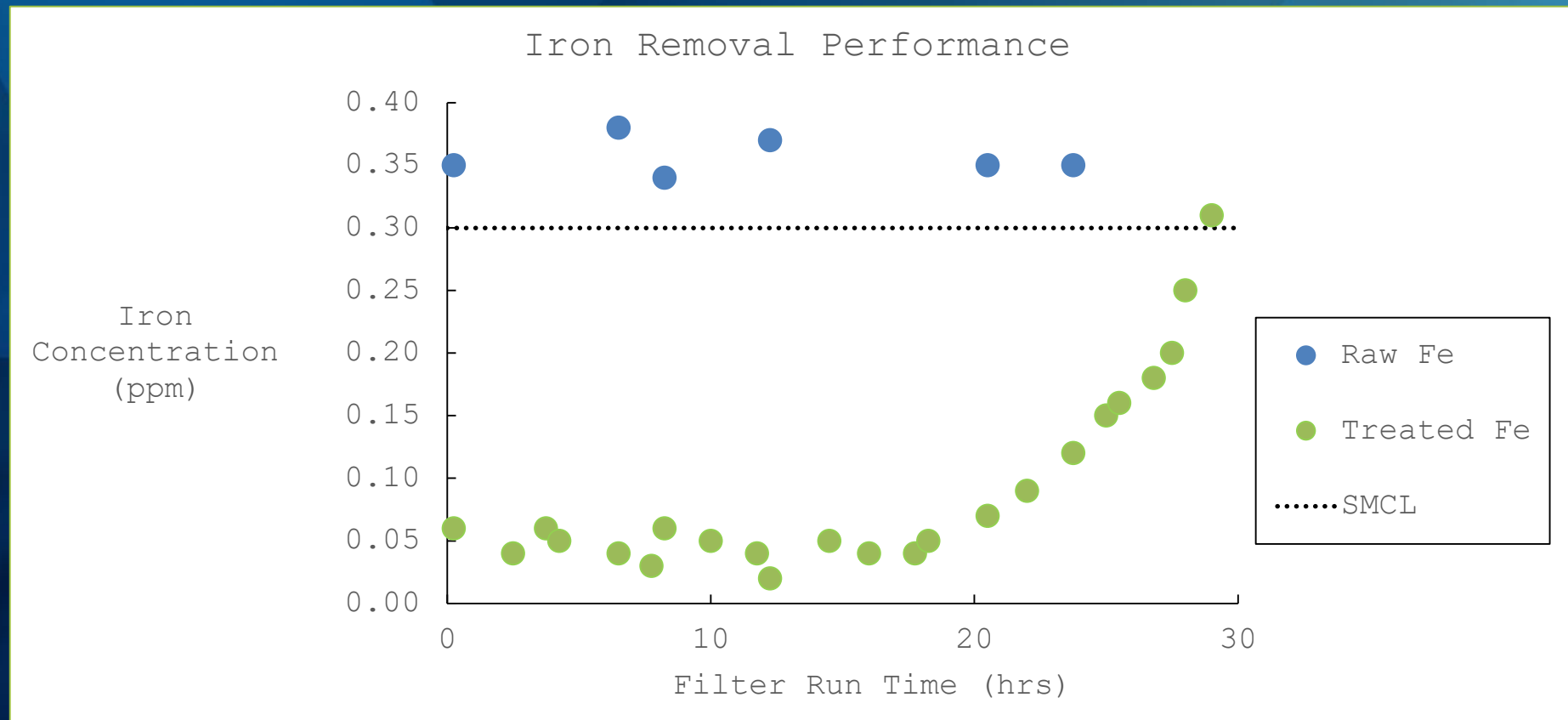
Optimize your backwash procedure

- Most backwash based on time, pressure differential, or gallons throughput
 - Consider duration, frequency, rate, bed expansion, rinse to waste
 - Air scour



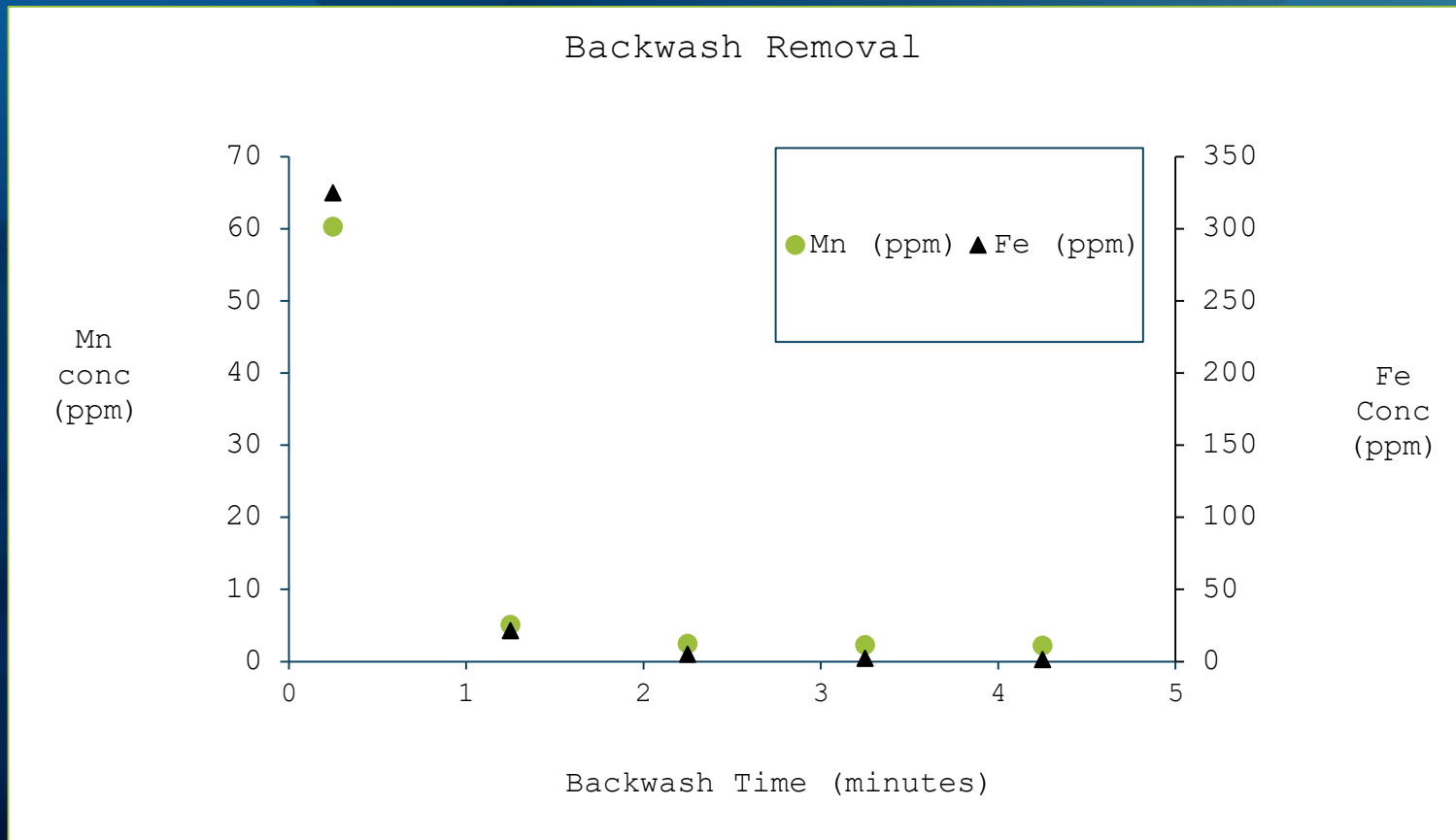
Optimize your backwash procedure

- When do you backwash?



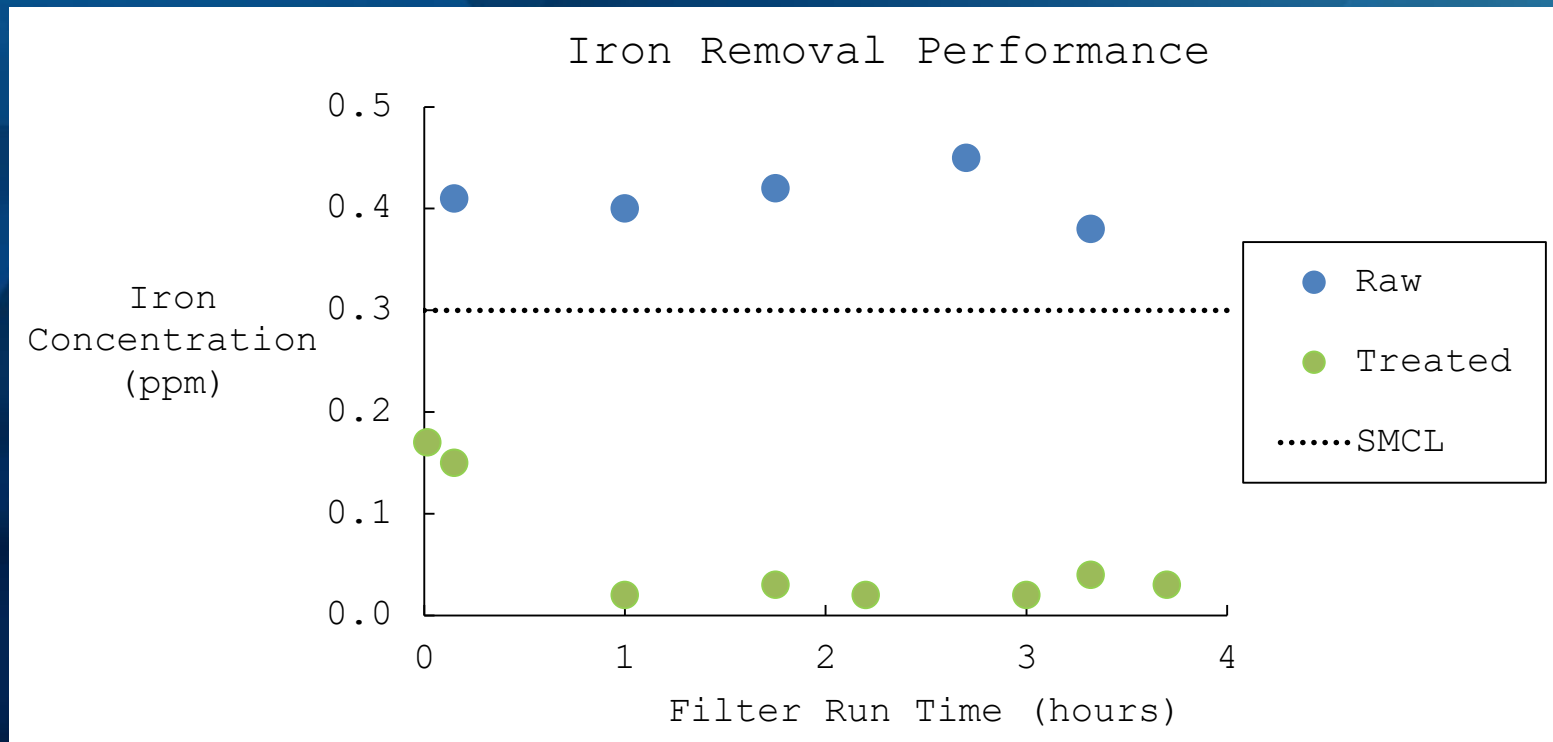
Optimize your backwash procedure

- How effective is your backwash?



Optimize your backwash procedure

- Do you include a rinse/filter-to-waste step?



Monitor Measurables:

- Raw and effluent water quality
- Chem feed systems



Inspection Focus:

- Measure freeboard, replace gaskets
- Calibrate Chem feeds, instruments, analyzers
- Photograph media surface, collect sample for lab analysis
- Review BW duration, frequency, rate set points
- Monitor complete backwash monthly, listen
- Drain and inspect tank underdrains
- Inspect filters every 3-5 years... or as needed.

In summary

- Mn is difficult to remove, catalytic media technology of choice
- Understand your system and removal mechanism(s)
- Monitor your system and make adjustments
- The more data you have the better
- Questions?



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