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LIQUID PROCESSING FILTRATION ION EXCHANGE

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presented at
the ASME Short Course
**RADIOACTIVE WASTE MANAGEMENT FOR
NUCLEAR POWER REACTORS
AND OTHER FACILITIES**

**University of Maryland at Baltimore
Baltimore, Maryland
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What's In Waste Water (Besides H₂O)

suspended Solids

1. Course particulate >1μ
e.g. car rust, bic pens, sand
2. Colloids <1μ
e.g. clay, silica, Co-58/60, Ag110m
3. Bacteria
Grow great on ion exchange resin

B. Ionic

1. Dissociated Ions
 - a. Cations
e.g. Na⁺, Co²⁺, Cs⁺, Ca²⁺
 - b. Anions
e.g. Cl⁻, SO₄²⁻, F⁻, H₂BO₃⁻
2. Undissociated molecules
e.g. H₂BO₃ BORIC ACID
3. Complexes
e.g. EDTA(-4), EDTA-Co(-2)
DECOM WORK

C. Non Ionic

1. Dissolved
 - a. Soaps
 - b. Ethylene glycol, dry cleaning fluid
2. Non Dissolved
 - a. Oil
 - b. Grease

* TECHNICALLY, BURIAL PROBLEM.

How to Remove the Bad Guys

1. Solids

Filtration
Precipitation
Settling
Coagulation

2. Ions

Ion exchange
Reverse Osmosis
Precipitation

3. Oils, Soaps, Organics, Complexing Agents

Stop at the Source
Absorption
Segregation of Streams

Filtration - The last Frontier

(10% of the activity = 90% of the headaches)

1. Typical Isotopes

Isotopes	% Particulate
Co - 58	0 - 95%
Co - 60	0 - 95
Cr - 51	50 - 95
Mn - 54	5 - 90
Nb - 95	30 - 90
Ag - 110m	90 - 100
Cs - 137/134	0 - 2
I - 131	0 - 2

Sources of Particulates (1)

1. Corrosion



- high grade rust
- primarily Fe₂O₃ or some other iron oxide containing Co - 58/60, Cr - 51 & Mn - 54

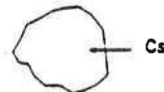
2. Resin



- Bead fracture or powder
- any isotope
- not radioactive unless isotopes attach

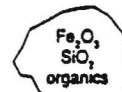
Sources Of Particulates (2)

3. Dust, Clay, Concrete



- any isotope
- not radioactive unless isotopes attach

4. Feed Water Colloids



- any isotope
- not radioactive unless isotopes attach

5. Bacteria

- Usually not radioactive

Note

- isotopes yield activity release
- all particles add to filter burden & clogging

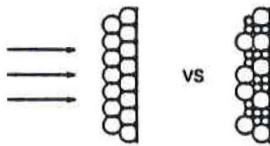
Particulate Properties (1)

1. Size

- determine filter sizing
- usual unit is the micron (μ)
 $1(\mu) = 0.00004 \text{ in}$
 $= 0.0001 \text{ cm}$
- see chart for sizing
- filtration to 5μ is easy
 0.1μ difficult
 $<0.1\mu$ extremely difficult

2. Uniformity

- the more uniform the higher the loading



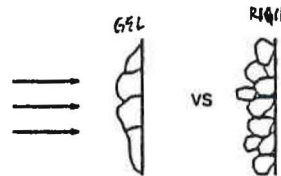
Particulate Properties (2)

3. Quantity

- the more you have the quicker the filter plugs
- measure as Total Suspended Solids (TSS)
- activity not important to plugging
- generally TSS is 0-10 ppm
- can go $> 10,000 \text{ ppm}$ during crud burst, sludge treatment or resin sluicing

4. Rigidity

- non rigid particles plug faster
- backwash/cleaning easier for rigid particles
- Fe_2O_3 and bacteria are not rigid



Particulate Properties (3)

5. Radioactivity

- exposure
- release
- need not be related to plugging time
- airborn problems on drying

6. Charge

- agglomeration rate
- removal efficiency
- varies with filter

Note

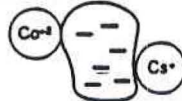
- Many of the above properties change with time. This can be used to improve processing. It also means real time testing on real streams is a must.

Colloids

- Small particles $1.0 - 0.01\mu$
- Usually charged
- Charges keep the particles from agglomerating



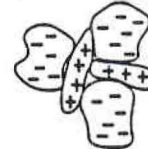
- Charges attract other ions



- Frequently composed of iron oxide (Fe_2O_3) and silica (SiO_2)
- Often from corrosion of stainless steel. These colloids in a reactor will contain Fe-59, Co-58, Co-60, Cr-51 and Mn-54
- Ag 110m is usually 80-95% colloidal

How To Get Colloids

- Filter them out.
Problem: They are very fine and require ultra filtration or reverse osmosis.
- Let them settle out.
Problem: May take years.
- Ignore them.
Problem: They are a major source of radioactivity.
- Coagulate them using a coagulant (alum, ferrous sulfate, polymer)



- Problem:
- Too much of a good thing can disperse the colloids
 - Too little does not do the job
 - Each solution must be tested

Filtration Goals

1. Maximize removal
2. Minimize waste
3. Minimize cost
4. Minimize exposure
5. Maximize run time (filter life)
6. Minimize manpower

TERMINOLOGY Filters

1. Cycle time - how long can it go without plugging
2. Sizing - what size particles will it remove
3. Sharpness of rejection - what percentage of a given size particle will it reject
4. ΔP (delta P) - pressure buildup across the filter
usual cause for removal from service
5. Backwash - reversal of flow direction to clean filter
6. Flow - how much water can be pushed through for a given ΔP

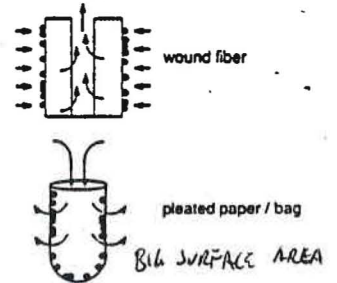
Filters

Murphy's Law of Filtration: If a filter will remove the particles that need removing, it will plug in 2 minutes or less.

Corollary: If it doesn't plug it won't remove anything either.

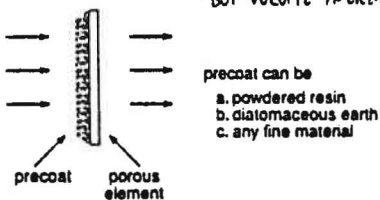
Filter Types

1. Cartridge - Disposable - 1-20 μ

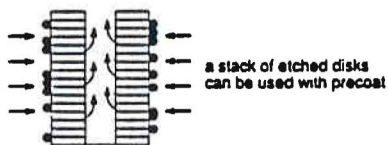


Filter Types (continued)

2. Precoat FINE PARTICULATES
- BUT VOLUME INCREASE

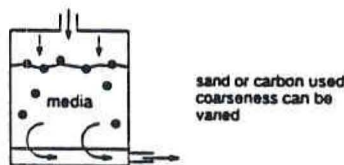


3. Etched Disk

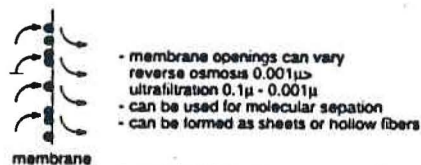


Filter Types (continued)

4. Depth CAN TRAP ~ 0.1 μ



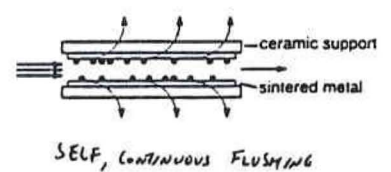
5. Membrane



SHORT LIFE TIME FOR HIGH LOADING

Filter Types (continued)

6. Cross Flow



Filter Strengths (and Weaknesses)

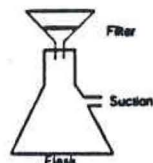
Filter	Strength	Weakness
1. Cartridge	Disposable Variable size Good removal	Expensive Moderate waste volume Exposure on changeout > 1µ only
2. Precoat	High flow Backwashable Good filtration to 1µ	High waste volume Ubiquitous precoat > 1µ only
3. Etched Disk	High flow Low waste volume Backwashable	Hard to clean Low cycle times
4. Depth	Good removal Backwashable Can go to 0.1µ	Not absolute Moderate waste volume
5. Membrane	excellent removal removes colloids	Plugging/fouling Expensive Membranes subject to attack Reject waste stream
6. Cross Flow	excellent removal variable size	Reject waste stream Fouling

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How To Know What's In Your Water

Particulates

1. Graded Filters



- Use several filters over desired range
e.g. 10µ, 5µ, 2µ, 1µ, 0.45µ, 0.22µ
- Inexpensive
- count filter papers (geometry)
- count influent and effluent
- use the effluent from one test as the influent for the next finer filter
- definitely worthwhile

2. Particle Sizing Instrumentation

- expensive
- distribution problem

* ASSUMES DISTRIBUTION

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Typical Wastewater Analysis (1)

1. Non-Radioactive Species

Species	ppm	meq / l
Na ⁺	60	2.61
Ca ²⁺	5.4	0.27
Mg ²⁺	6.7	0.56
Cl ⁻	82	2.31
SO ₄ ²⁻	20	0.42
B	240	22.2
SiO ₂	5	0.08
TOC	4	

Conductivity 415µmho (µS)

pH 6.7

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Typical Wastewater Analysis (2)

1. Radioactive Species

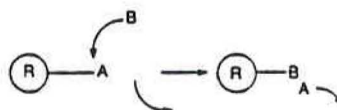
Species	µCi/cm ³	meq / l
Cr-51	1.4 E-4	9 E-11
Mn-54	1.8 E-5	8 E-11
Co-58	8.0 E-4	9 E-10
Co-60	2.5 E-4	1 E-8
I-131	1.8 E-4	1 E-11
Cs-134	1.0 E-3	6 E-9
Cs-137	1.5 E-3	1 E-7

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Ion Exchange Basics

A. Reactions

1. General



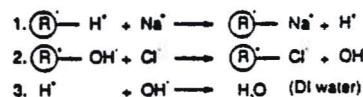
2. Cation exchange

A is usually H⁺, Na⁺, NH₄⁺ (Li⁺)

3. Anion

A is usually OH⁻, Cl⁻ (H₂BO₃⁻)

B. Neutralization



DI - (IONIZED) WATER

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Ion Exchange Basics (continued)

C. Regeneration

Force the media into its' original form by using high concentrations of the proper ion.

e.g. H₂SO₄ can reverse reaction B.1.

NaOH can reverse reaction B.2.

D. Selectivity

The preference for one ion over another

e.g. clays prefer Cs⁺ over Na⁺

It arises from:

- charge to size ratio (e.g. organics)
- size (e.g. zeolites)
- chemistry (e.g. chelating resins)
- solubility (e.g. Cl⁻ on Ag)

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Types of Materials

1. Organics - bead, macroreticular



2. Zeolites - crystalline clays, artificial



3. Glass based - high surface area



4. Carbon based - high surface area
5. Inorganic oxide - high surface area

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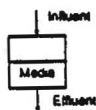
Properties of Exchangers

1. Size (bead vs powder)
2. Selectivity
3. Temperature Resistance (structural, functional)
4. Capacity
5. Mechanical strength
6. Purity (standard vs nuclear grade)

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Ion Exchanger Performance

Capacity - amount of ion that can be removed



- usually quoted in equivalents/liter or meq/ml
- typically in the range
 - 2 meq/ml for organic cation
 - 1.3 meq/ml for organic anion
 - * Not For SELECTIVE MEDIA
- not very meaningful for selective media

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Ion Exchanger Performance

Calculations Involving Capacity

- a. capacity for Na^+

$$\text{eq wt} = \text{at wt}/\text{charge} = 23/1 = 23\text{g}$$

$$\text{cation resin capacity} = (2\text{eq/l})(23\text{g/eq}) = 46\text{ g/l}$$

- b. capacity for Ca^{2+}

$$\text{eq wt} = \text{at wt}/\text{charge} = 40/2 = 20\text{g}$$

$$\text{cation resin capacity} = (2\text{eq/l})(20\text{g/eq}) = 40\text{ g/l}$$

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Ion Exchanger Performance

Throughput

- volume of water that can be treated by a given volume of media
- typically in gal/ft³
- often measured in column or bed volumes

$$\text{gal/ft}^3 = 7.5 \cdot \text{bed volumes}$$

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Ion Exchanger Performance

Throughput Calculations

What is the throughput expected for wastewater that contains 40 ppm Na. Assume the capacity of the cation exchanger is 1.9 meq/ml (eq/l).

The water contains 40 ppm Na = 40mg Na/l water

$$40\text{mg Na/l water} = \frac{40\text{mg/l}}{23\text{mg/meq}} = 1.7\text{ meq Na/l water}$$

the throughput for the cation resin is :

$$\frac{1.9\text{ eq/l resin}}{1.7\text{ meq/l water}} = \frac{1.9\text{ eq/l resin}}{1.7 \times 10^{-3}\text{ eq/l water}}$$

$$= 1100\text{ l water/l resin}$$

$$= 1100\text{ column volumes}$$

$$= (1100)(7.5)\text{ gal/ft}^3$$

$$= 8250\text{ gal/ft}^3$$

Ion Exchanger Performance

Some Notes On Throughput Calculations

- if more than one cation exists you must sum the meq/l of all the cations and use the sum to calculate the capacity

- in any solution the total meq/l of cation must equal the meq/l of anion ** MIXED BEDS*

- if the solution is neutral pH then *↑*

$$\frac{\text{throughput cation}}{\text{throughput anion}} = \frac{\text{capacity cation}}{\text{capacity anion}}$$

- calculations for selective media are next to impossible

- (AN ONLY TEST RUNS)

Ion Exchanger Performance

Decontamination Factor (DF)

$$DF = \frac{\text{influent concentration}}{\text{effluent concentration}}$$

e.g.

$$C_s = 3.0 \times 10^{-3}\text{ } \mu\text{Ci/ml} \quad \text{influent}$$

$$1.0 \times 10^{-4}\text{ } \mu\text{Ci/ml} \quad \text{effluent}$$

$$DF = \frac{3.0 \times 10^{-3}}{1.0 \times 10^{-4}} = 30$$

This says 1/30 of the C_s is getting through.

- LARGER DF, THE BETTER

Ion Exchanger Performance

Residence Time

$$\text{residence time} = \frac{\text{volume of bed}}{\text{rate of flow}}$$

- length of time for exchange
- the longer the better
- watch your units during calculation

e.g.

for a 50 cu/ft bed at 30 gpm

$$\text{residence time} = \frac{(50\text{ ft}^3)(7.5\text{ gal/ft}^3)}{30\text{ gal/min}}$$

$$= 12.5\text{ min}$$

Ion Exchanger Performance

New Bed



Mid Life



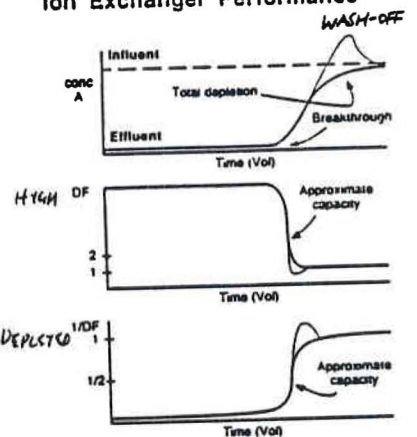
Leaking



Depleted



Ion Exchanger Performance



* SLOW FLOW WILL ACCOUNT FOR RESIN RESPONSE BETTER.

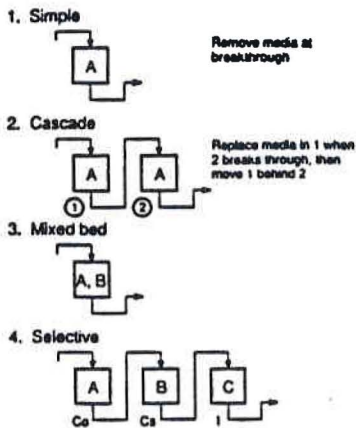
TRACKING OF ION EXCHANGERS

* SET TOLERANCE LEVEL

$\frac{1}{1000}$, etc.

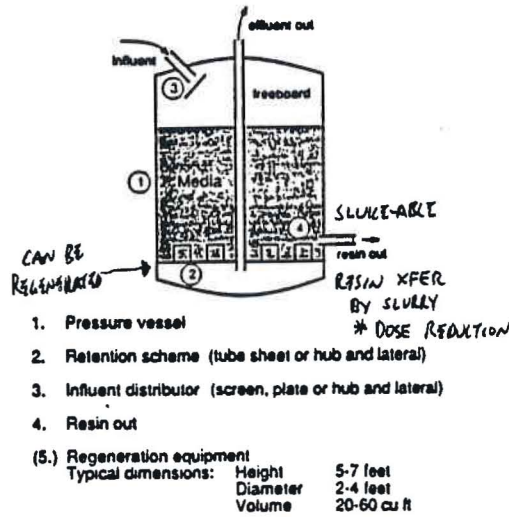
pH & CONDUCTIVITY: BY WATCHING pH IN CATION BEDS
 ↓ MIXED BEDS → DEPLETED WHEN BOTTOM REACH NEUTRAL (7)
 EFFLUENT CONDUCTIVITY SAME AS INFLUENT.

Bed Use



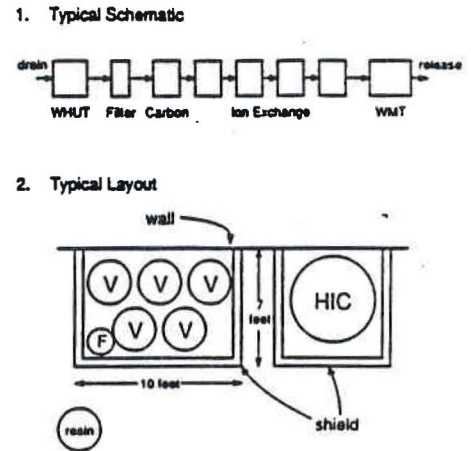
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Hardware



* PRESSURIZED SYSTEMS ARE MORE EFFICIENT

Filtration - Ion Exchange System



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Ion Exchange - Filtration

- What's in the water — ALWAYS ANALYSE FIRST
Solids - size, nature, amount
Ions - what kinds, how many
Non ionics - oils, etc.

Use filter tests, conductivity, pH, 7 spectroscopy, atomic absorption (AA), inductivity coupled plasma (ICP), ion chromatography, total organic carbon (TOC), oil and grease
- What must be removed
Where is the water going
Selective vs non selective
DF needed
- Flow rate
Peak / normal
- Vessels / Filters
Size, number, in plant, mobil, sluicable
- Will it work — ALWAYS TEST THE REAL WATER

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Trouble Shooting Your Ion Exchange / Filtration System

Problem	Possible Cause(s)
1. Poor Co/Cr/Ag removal	a. Colloids b. Oil c. Complexes (decon fluid)
2. Short bed life	a. Oil b. Organics (soaps/detergents) c. High conductivity
3. Short filter life	a. Too much sludge (Time to clean up the tanks) b. Wrong type of filter c. Crud build
4. Constant Co leakage	a. Colloids b. Soaps/detergents
5. High Co levels in the WHUT	a. Complexes (decon fluids)
6. Constant leakage of all isotopes	a. Poor sludging b. Poor regeneration

KNOW WHAT IS GOING ON IN THE PLANT

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Start a Test Program

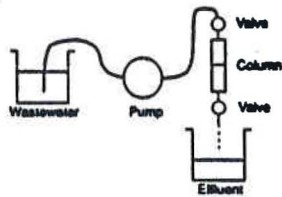
You need:

- Knowledge
 - Other courses
 - Read books / literature
 - Attend meetings - EPRI/WM
 - Talk to vendors (technical section)
 - Talk to other utilities
- Ion Exchange Set Up
 - Burets
 - Pumps
 - Valves
 - Buy one / make one
- Filter Set Up
 - Graded filters
 - Vacuum pump
- Friends
 - In the count room
 - In the chemistry lab
- Evangelize
 - There is money to be saved
 - There is volume to be reduced
 - There is offsite dose to be reduced

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Ion Exchange Test System (1)

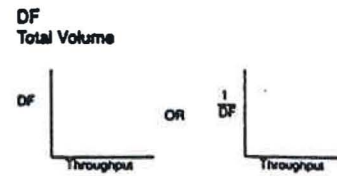
1. Equipment



- need timer
- analysis required at regular intervals for effluent
- analyze influent
- scale flow to match residence time in real system
- column diameter > 10 media diameters
- test real water, real time

Ion Exchange Test System (2)

2. Calculations



3. Results

- DF will probably be better in full system
- capacity to 1-2% of full system
- useful for media selection

Ion Exchange - Where to Learn More

1. Books

Kunin "Ion Exchange Resins"
Krieger Publishing Company

2. Courses

Am. Inst. Chem. Engr.

3. Vendors

a. Organic Resins
Dow, Rohm & Haas, Mobay, Sybron/Ionac,
Purcell

b. Selective
Mobay, Union Carbide, Steelhead, Duratek

4. Me

Dr. Herbert G. Suter
Scientific Applications
International Corporation
12360 Middlebrook Road
Suite 308
Germantown, Maryland 20874
(301) 661-1231

Useful Information

Measurement

1000 microns (μ) = 1 millimeter (mm) = 0.039 inch

100 μ is the width of a pen stroke

1 m³ = 35.3 ft³ = 1000 l

1 ft³ = 28.3 l = 7.48 gal

1 gal = 3.79 l

20 mesh	840 μ
42 mesh	350 μ
60 mesh	250 μ
100 mesh	149 μ

Ion	Atomic Weight	Equivalent Weight	Power Plant Source
Na ⁺	23	23g	salt, soap
Ca ²⁺	40	20g	concrete
Cl ⁻	35.5	35.5	salt
SO ₄ ²⁻	98	48	concrete