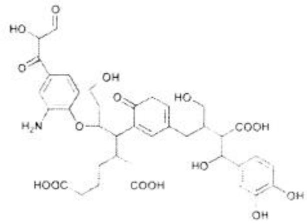
Drinking Water Treatment

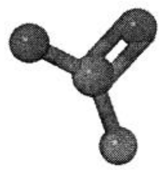
Cranfield



Organics & Inorganics Removal

Peter Jarvis

Centre for Water Science



Aim of lecture

Cranfield UNIVERSITY

- Understand the regulatory framework for control of contaminants in drinking water in UK
- Understand what the main organic and inorganic pollutants in water are and where they come from
- Look at main ways of controlling organic and inorganic contaminants in drinking water treatment

Cranfield UNIVERSITY

Water pollution

Water quality regulations

Drinking Water Directive 98/83/EC, 1998

World Health Organisation

Water Supply (Water Quality) Regulations, 2000

44 Regulatory parameters in drinking water: *chemical & microbial*

Monitored by the Drinking Water Inspectorate (DWI)

www.cranfield.ac.uk

Cranfield UNIVERSITY

Water Quality Standards

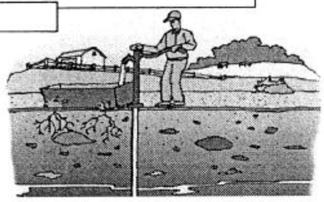
Parameter	Standard (PCV)
1,2 dichloroethane	3.0 µg/l
aluminium	200 µg/l
ammonium	0.5 mg/l (guide value)
antimony	5 µg/l
arsenic	10 µg/l
benzene	1.0 µg/l
benzo(a)pyrene	0.010 µg/l
boron	1 mg/l
bromate	10 µg/l
cadmium	5 µg/l
Chloride	250 mg/l (guide value)
Chromium	50 µg/l
Clostridium perfringens	0 per 100 ml
coliform bacteria	0 per 100 ml
colony counts - 2 day at 37°C - 3 day at 22°C	No abnormal change
colour	20 mg/l Pt/Co scale
conductivity	2500 µS/cm at 20°C (guide value)
copper	2.0 mg/l
Cryptosporidium	<1 oocyst per 10 litres
cyanide	50 µg/l
E. coli and Enterococci	0 per 100 ml
fluoride	1.5 mg/l
gross alpha activity gross beta activity	0.1 Bq/l 1 Bq/l
iron	200 µg/l
lead	25 µg/l to 2013 Then 10 µg/l on and after 25/12/2013
manganese	50 µg/l
mercury	1 µg/l
nickel	20 µg/l
nitrate	50 mg/l
nitrite	0.50 mg/l (at customer taps), 0.1 mg/l (at WTW)
odour / taste	Dilution no. 3 at 25°C
PAH (sum of 4)	0.1 µg/l (total of 4 named PAHs)
pesticides	0.1 µg/l All pesticides apart from Aldrin, dieldrin, heptachlor, heptachlor epoxide which are 0.03 µg/l where measured 0.5 µg/l
pH (hydrogen ion)	6.5 (min)–10 pH units
selenium	10 µg/l
sodium	200 mg/l
solvents (sum of 2)	10 µg/l for the sum of both
sulphate	250 mg/l (guide value)
tetrachloromethane	3 µg/l
total indicative dose (TID)	Guide value 0.10 mSv/year
total organic carbon	no abnormal change (guide value)
trihalomethanes (THMs)	total trihalomethanes 100 µg/l
tritium	Guide value 100 Bq/l
turbidity	4 NTU units at customer taps 1 NTU unit at treatment works

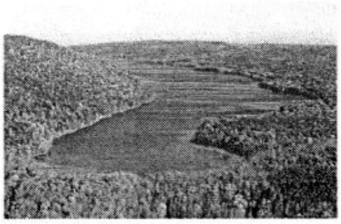
www.cranfield.ac.uk

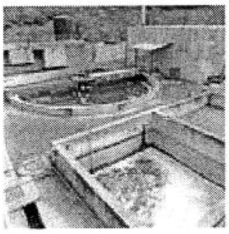
Water Quality problems

Cranfield UNIVERSITY

- Water source dependent







Ground or Surface water

Soil/rock type

Anthropogenic inputs

Concentrate on:

Cranfield UNIVERSITY

Organic & Inorganic contaminants in drinking water

www.cranfield.ac.uk

What makes an organic compound organic?

~~Carbonates~~ ~~Carbon oxides~~ ~~Elemental carbon~~

Chemical structure based around the carbon atom.

- Lipids
- Solvents
- Proteins
- Hydrocarbons
- Carbohydrates

Occurrence in surface and ground water from:

- Naturally occurring NOM
- Industrial, Agricultural & Domestic
- Formation during treatment & in distribution

Water Source

- Moorland and upland source waters have high concentrations of natural organic matter (NOM)
- Lowland waters are likely to have inputs from both agricultural and anthropogenic sources and naturally derived NOM.

- Focus here on
  - Disinfection by-product precursors:

  Residual NOM + Chlorine = DBPs
  - Pesticides

Regulatory framework

Cranfield UNIVERSITY

- Natural organic matter

UK/EU legislation

No significant change in DOC of treated water

Disinfection by-products

Trihalomethanes (THMs)

Total of 100 μg/L (ppb) *at tap*

Haloacetic acids (HAAs)

not yet regulated

- Pesticides

UK/EU legislation

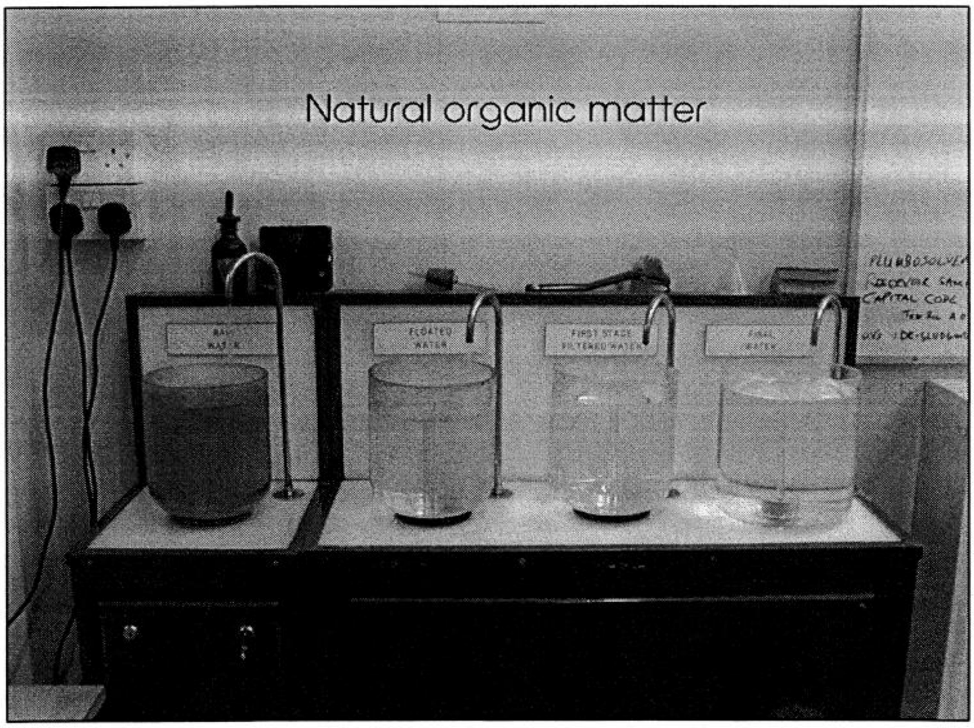
Individual pesticides very low [ ]

100 ng/L (ppt)

Total pesticides

500 ng/L (ppt)

www.cranfield.ac.uk

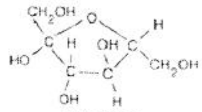


What is NOM?

Any substance of natural organic origin

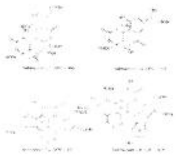
Humic acid

Proteins

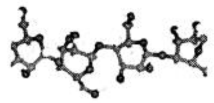


Sugars

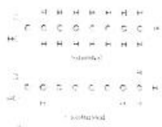
Hydrocarbons



Fulvic acids



Polysaccharides

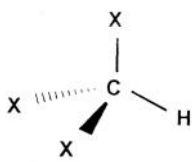


Fatty acids

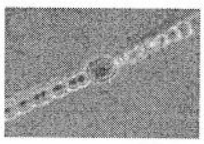
Biological degradation of these compounds

Why remove NOM?

- Disinfection by-products (DBPs)



- Taste and odour problems



- Bacterial re-growth in distribution

- Interference with downstream processes
  - Membrane fouling
  - Oxidation of metals

NOM laden waters

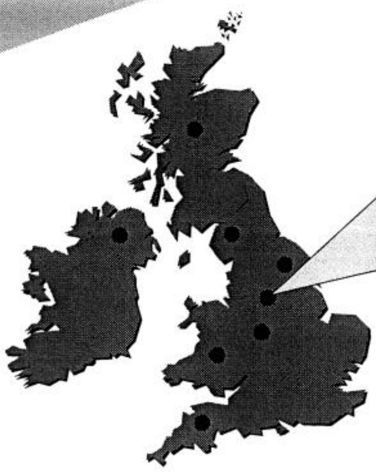
Cranfield UNIVERSITY

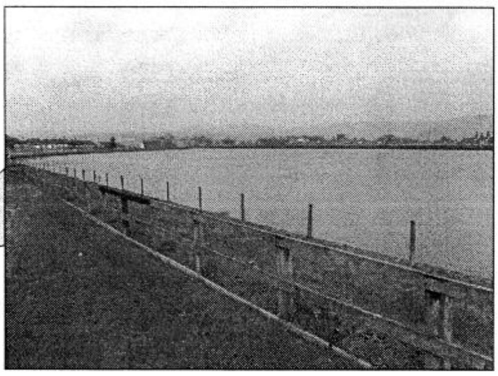
- NOM laden water:
  - High DOC – dissolved organic carbon
  - High water colour
  - High absorbance of UV light at 254 nm (UV_{254})
    - High MW (molecular weight)
    - Presence of double bonds
    - Aromatic structure

www.cranfield.ac.uk

NOM – extent

Cranfield UNIVERSITY



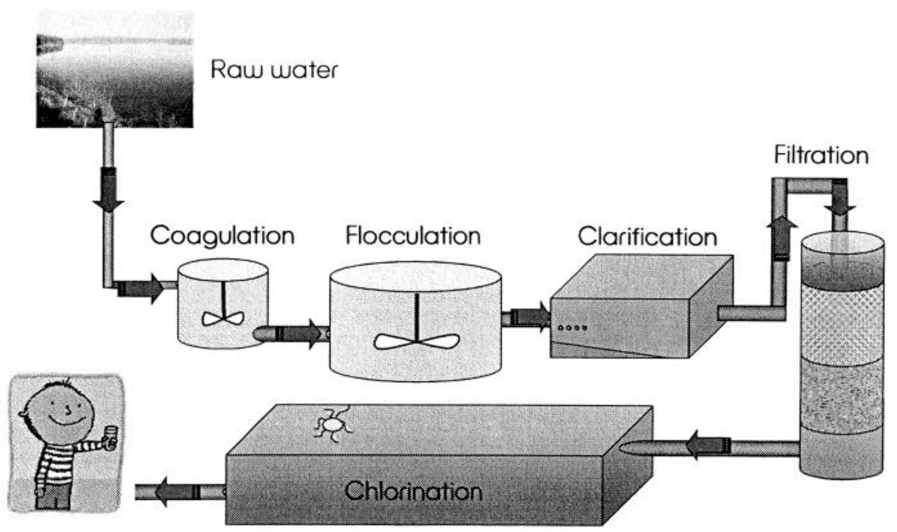


www.cranfield.ac.uk

Process options for NOM removal

Process	Typical DOC Removal, (%)	Disadvantages
Coagulation Main way	10 - 80	High coagulant doses and sludge production. Removal efficiencies related to water source.
Ion Exchange/ Adsorption	60 - 80	Higher costs. Generation of waste streams.
Membranes	80 - 100	High costs. Still requires pre-treatment to prevent membrane fouling.
Ozonation /Biodegradation	27 - 75	Variable removal efficiencies.
Advanced Oxidation Processes	60-90	Not proven at full scale.

NOM removal - Coagulation

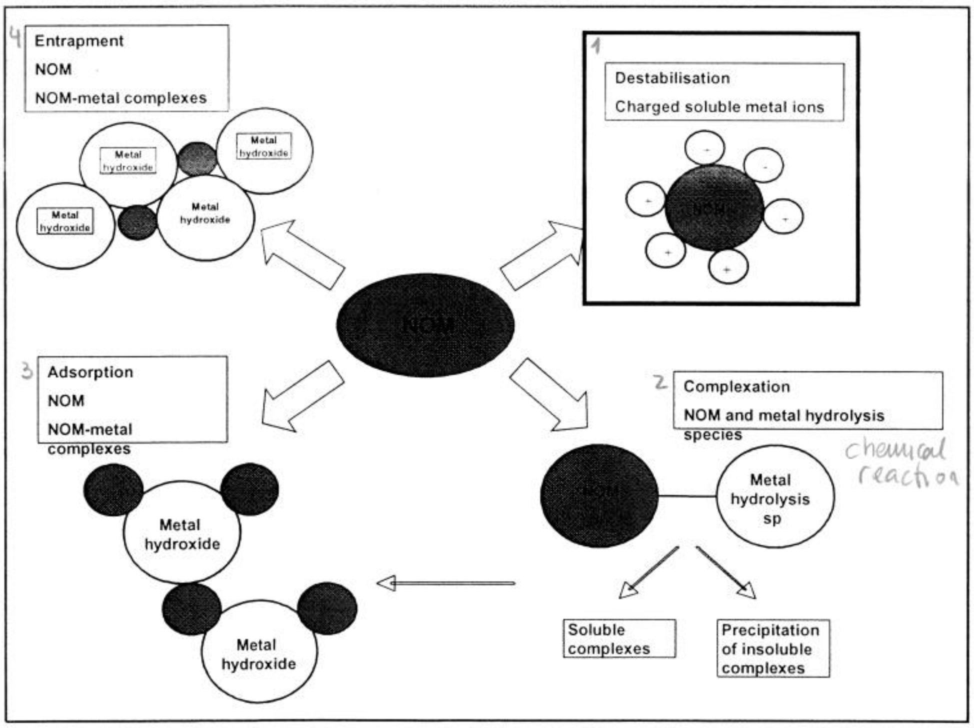


NOM removal - coagulation

Cranfield UNIVERSITY

Chemical	Common name	Formula	Molecular weight	%metal ion
Iron sulphate	Ferric sulphate	$Fe_2(SO_4)_3$	400	14
Iron chloride	Ferric chloride	$FeCl_3$	162	14
Aluminium sulphate	Alum	$Al_2(SO_4)_3 \cdot 14 H_2O$	594	17-18
Aluminium chloride	PACL	$Al_2(OH)_5Cl$	Polymeric form	12

www.cranfield.ac.uk



Coagulation – efficiency is dependent on organic compounds present

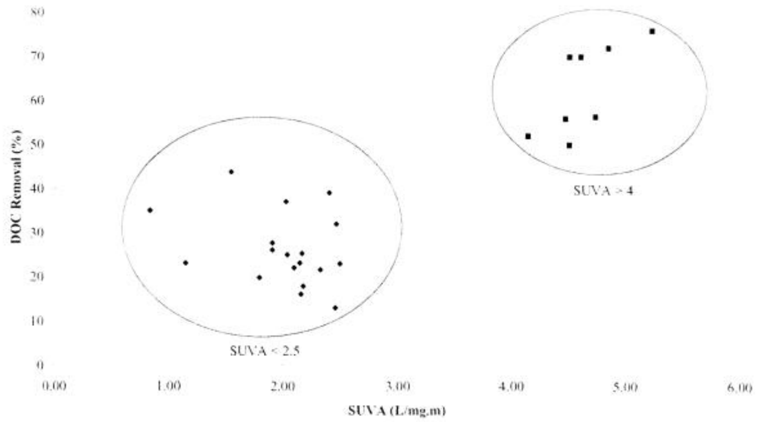
Cranfield UNIVERSITY

SUVA = Specific UV Absorbance

SUVA	*Ratio of UV_{254} abs to DOC (dissolved organic carbon)*
>4	High hydrophobicity, high MW aquatic humics
2-4	Mixture of hydrophobics and hydrophilics
<2	Low hydrophobicity, low MW non-humics

Coagulation – efficiency is dependent on organic compounds present

Cranfield UNIVERSITY

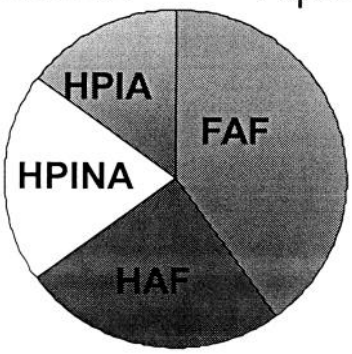


Coagulation – efficiency is dependent on organic compounds present

Cranfield UNIVERSITY

Hydrophobic NOM

- Larger (HMW)
- Colour
- Higher charge
- Easier to remove



Hydrophilic NOM

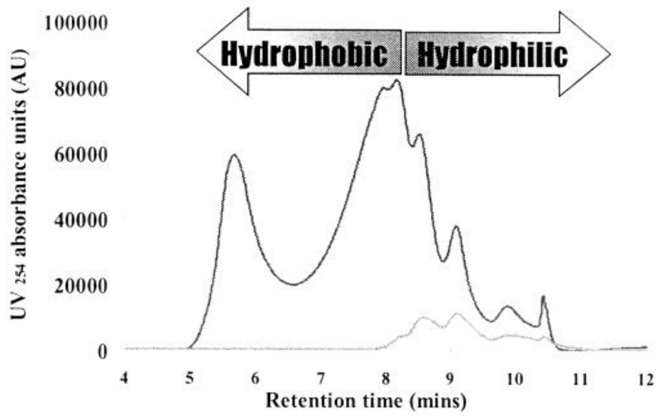
- Small (LMW) Lower Molecular Weight
- Non coloured
- Low charge
- Difficult to remove

www.cranfield.ac.uk

Coagulation – efficiency is dependent on organic compounds present

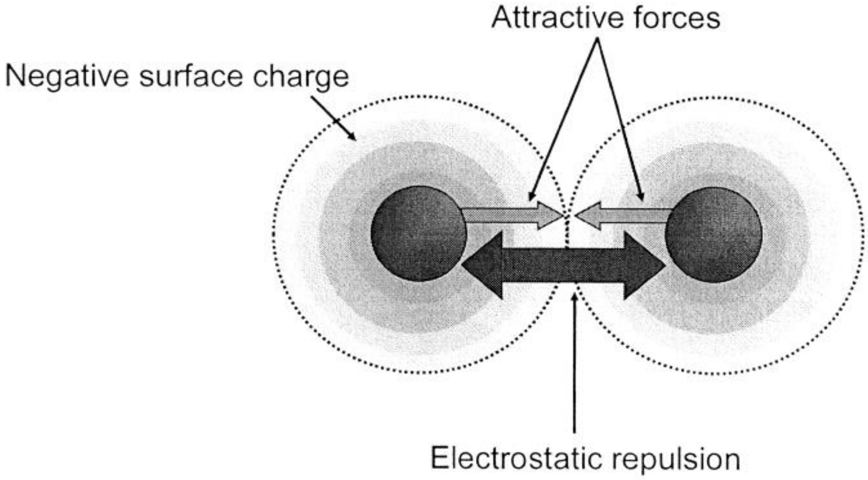
Cranfield UNIVERSITY

High Performance Size Exclusion Chromatography



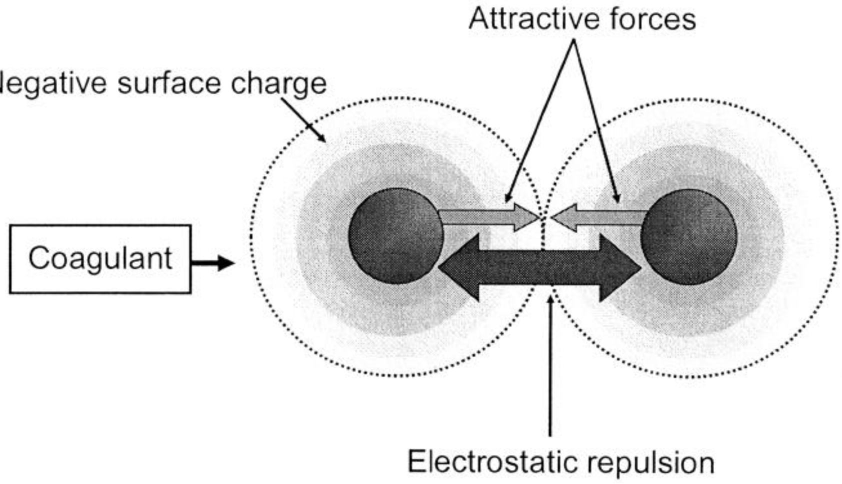
Increasing retention time → decreasing molecular size

Coagulation – optimised with zeta potential



www.cranfield.ac.uk

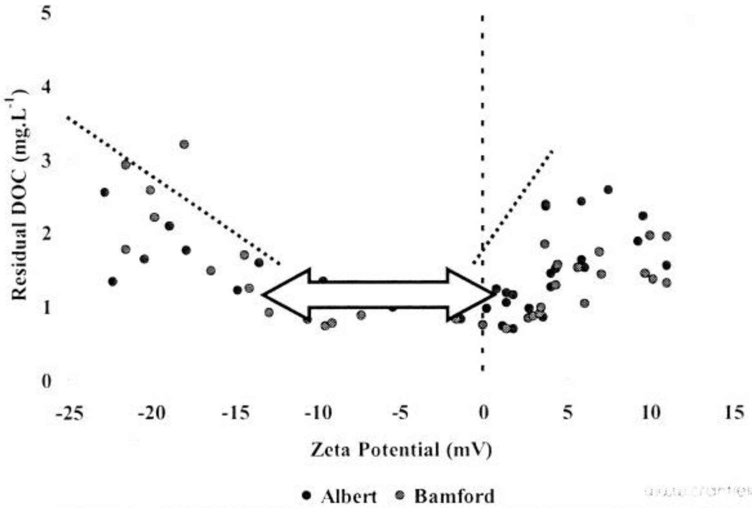
Coagulation – optimised with zeta potential



www.cranfield.ac.uk

Cranfield UNIVERSITY

Coagulation – optimised with zeta potential

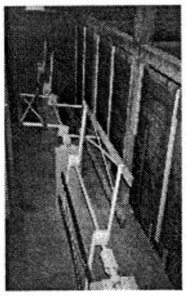


www.cranfield.ac.uk

Cranfield UNIVERSITY

Problems – specific times of year, NOM load is very high

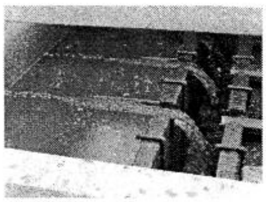
Flocculation



Sed tank/DAF

- Floc breakage

Filters



-Floc breakage

-High particle load

-Early breakthrough

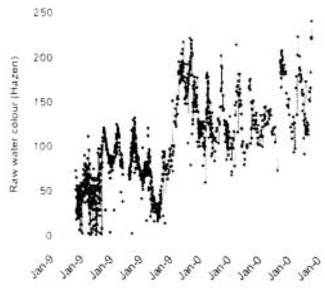
-Failed THM consents

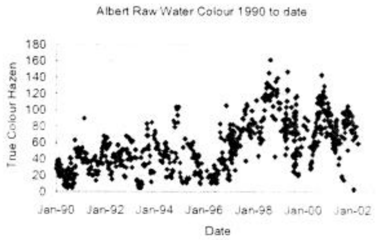
www.cranfield.ac.uk

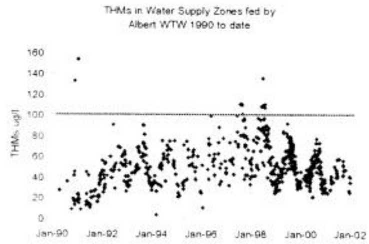
NOM

Cranfield UNIVERSITY

- Continuing problem
- Climate change
- Land management practice
- THMs

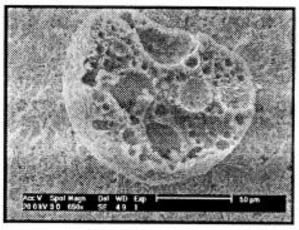






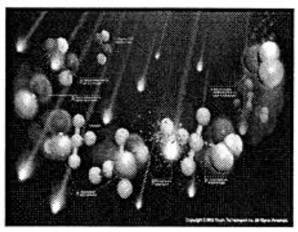
www.cranfield.ac.uk

Processes for improved NOM removal



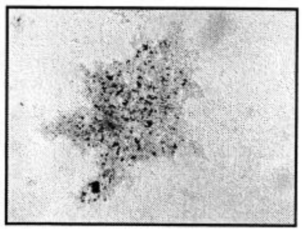
IEX & coagulation

Alternative processes?



AOPs

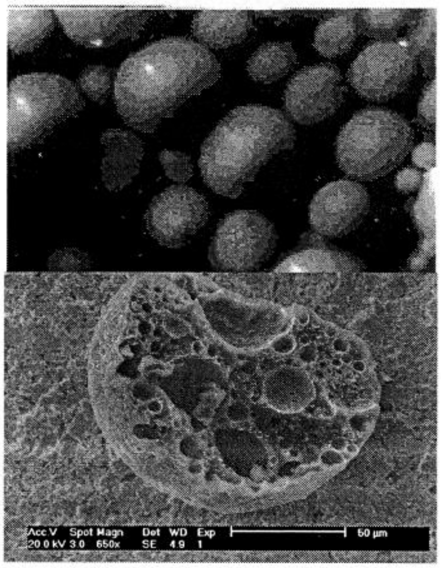
PAC & coagulation



www.cranfield.ac.uk

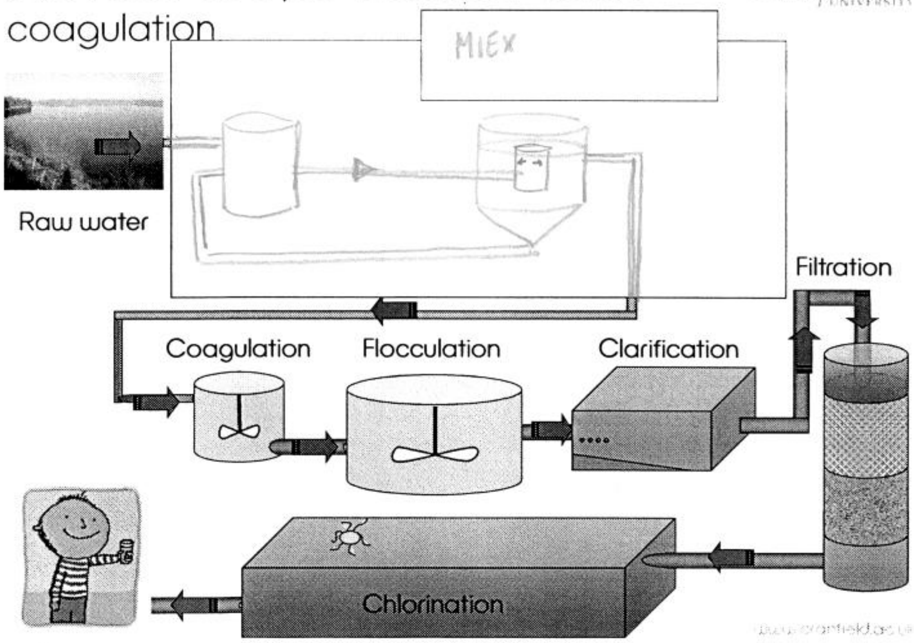
Magnetic Ion Exchange (MIEX) Orica

- Continuous ion exchange process
- MIEX is a strong base anion exchange resin
- Effective over the whole pH range
- Highly selective for humic substances
- No pre-treatment required for solids removal because process takes place in CSTR
- 110 MLD plant in Perth



MIEX used as a pre-treatment before coagulation

Cranfield UNIVERSITY

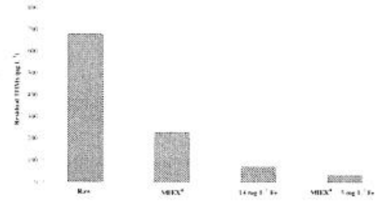


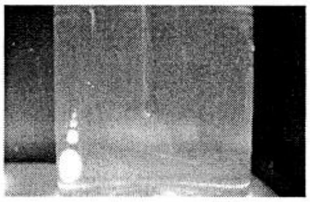
www.cranfield.ac.uk

MIEX - Performance

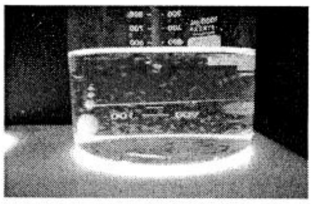
Cranfield UNIVERSITY

- Excellent colour, UV_{254} and DOC removal.
- Significantly better than coagulants for THMFP.





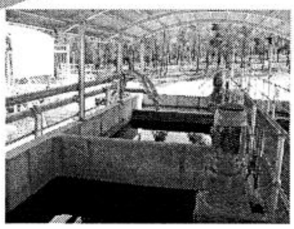
Ferric sulphate

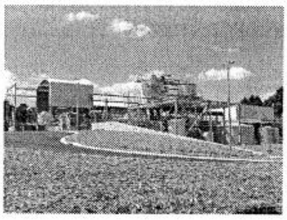


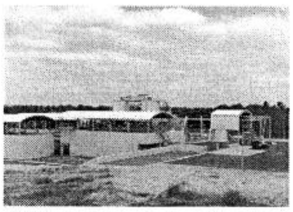
MIEX + Ferric sulphate

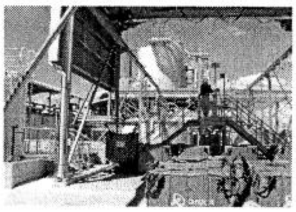
Wanneroo MIEX

Cranfield UNIVERSITY

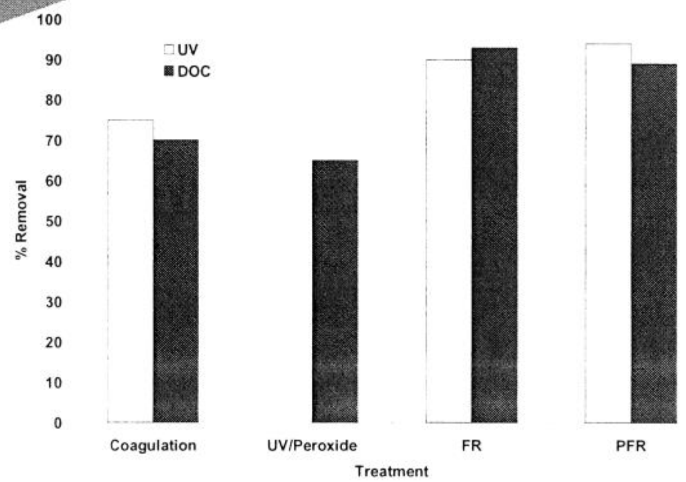








Advanced Oxidation Processes - AOPs



www.cranfield.ac.uk

Micropollutants

www.cranfield.ac.uk

Micropollutants – removal with conventional coagulation

Cranfield UNIVERSITY

Classification	Coag
Steroids	<20
Industrial chemicals	<20-40
Antibiotics	<20-40
Antidepressants	<20-40
Anti-inflams.	<20
Lipid regulators	<20
X-ray contrast media	<20-40
Synth. musks	<20-40
Antimicrobials	<20-40
Surfactants	<20-40

www.cranfield.ac.uk

Micropollutants – alternative processes

Cranfield UNIVERSITY

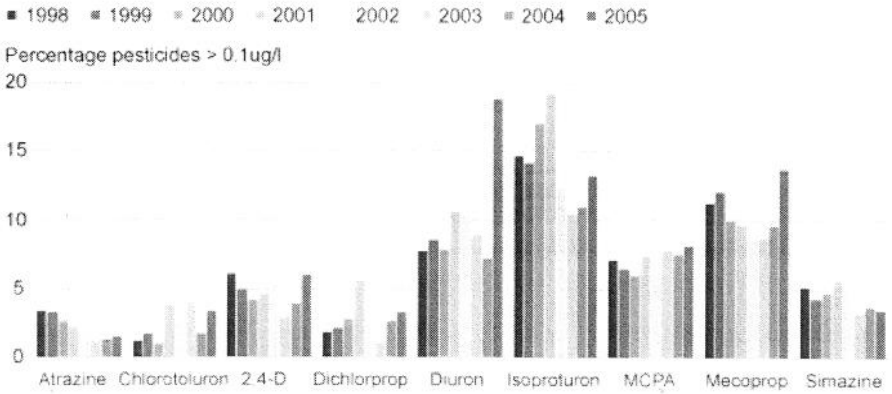
Classification	GAC	AOP	UV	Cl_2/ClO_2	Coag
Steroids	>90	>90	>90	<20	<20
Industrial chemicals	>90	>90	>90	>90	<20-40
Antibiotics	40-90	20-90	40-90	20-90	<20-40
Antidepressants	70-90	20-90	40-90	20-70	<20-40
Anti-inflams.	>90	20-90	70-90	20-70	<20
Lipid regulators	>90		>90	20-70	<20
X-ray contrast media	70-90	70-90	20-90	20-70	<20-40
Synth. musks	70-90	70-90	>90	20-70	<20-40
Antimicrobials	70-90	70-90	40-90	20-70	<20-40
Surfactants	>90	>90	40-90	<20	<20-40

www.cranfield.ac.uk

Pesticides

- About 300 chemical compounds are approved for use as pesticides in the UK.
- In terms of weight of substances applied to arable land in the UK in 2002
  - 71% herbicides and desiccants
  - 12% fungicides
  - 11% growth regulators
  - insecticides and nematicides (2%), molluscicides (1%) and seed treatments (1%).
- The most extensively used herbicides were glyphosate, isoproturon, fluroxypyr, mecoprop-P and diflufenicam.

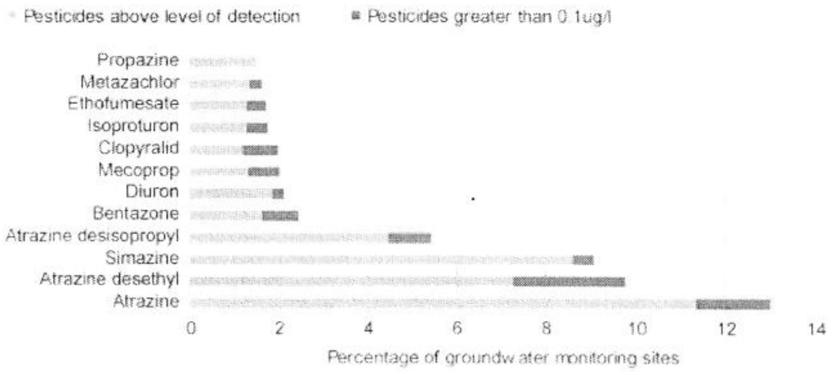
Pesticide prevalence
Surface Water



Source: Environment Agency

Pesticide prevalence
Ground water

Cranfield UNIVERSITY

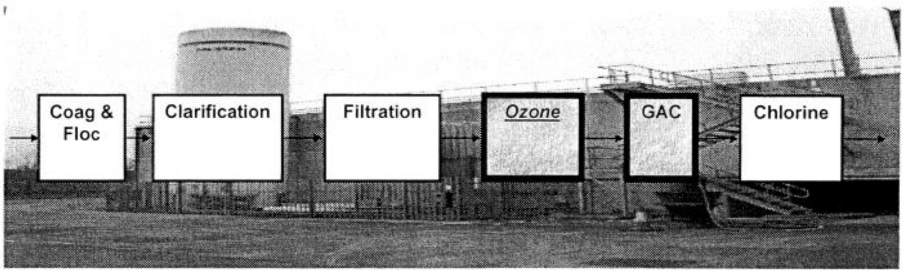


Source: Environment Agency

www.cranfield.ac.uk

Cranfield UNIVERSITY

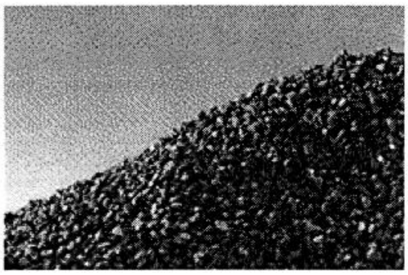
Removal of micropollutants



www.cranfield.ac.uk

Cranfield UNIVERSITY

Activated Carbon



Granular

Powdered

www.cranfield.ac.uk

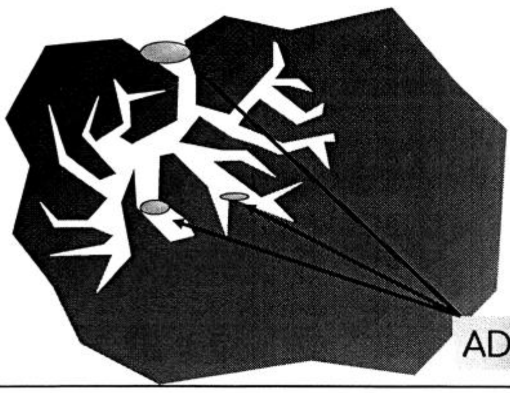
Cranfield UNIVERSITY

GAC is most widely used adsorbent in water and wastewater treatment

Macropore > 50 nm
Mesopore (2-50 nm)
Micropore (< 2nm)

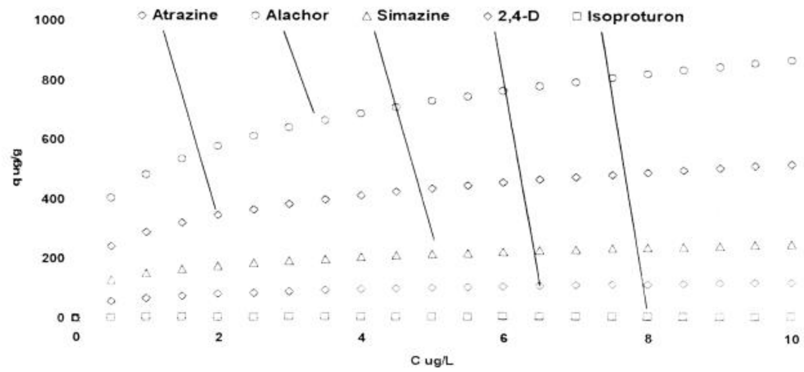
1 gram = Surface area of Football Pitch (approx 1000 m^2)

Coal
Wood
Coconut



Pesticides - GAC

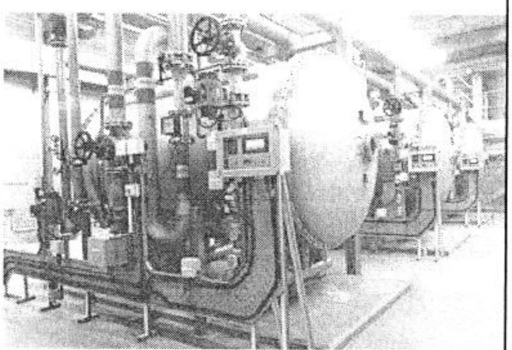
Cranfield UNIVERSITY



Ozone

Cranfield UNIVERSITY

- Used on surface water sites in the UK
- Control of pesticides and organic matter
- Works in conjunction with downstream GAC
  - partially degraded organics adsorbed onto GAC
  - degraded further by ozone
  - GAC removes residual ozone



Ozonation - ozone production

Cranfield UNIVERSITY

- Produced by electrical discharge of dried air
- High voltage & frequency (eg 10kV, 700Hz) used with dry air feed
- Produces 5-7% O_3 in air
- High toxicity (TLV 0.1 ppm), hence vent gas ozone destructors essential
- Effective but high CAPEX

www.cranfield.ac.uk

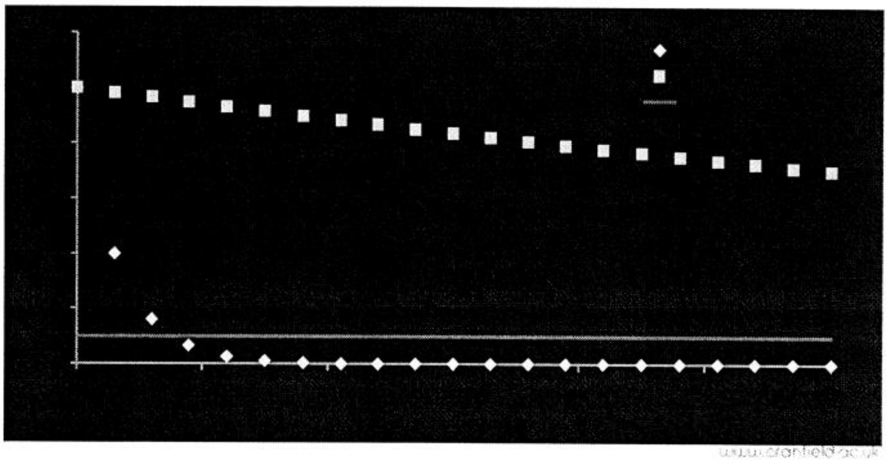
Example - Ozonation

Cranfield UNIVERSITY

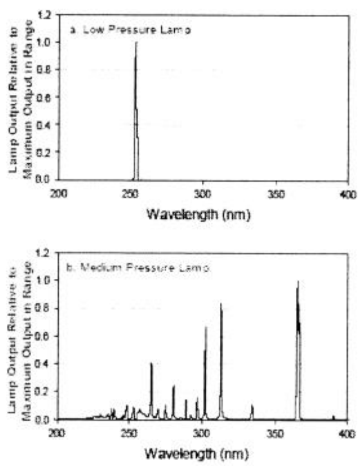
Molecule	k_{O3} ($M^{-1}s^{-1}$)	Half life ($t_{1/2}$)[a]
Microcystin	3.4×10^4	1 s
Isoproturon	305	30s
Endrin	<0.02	20 d
Atrazine	6	96 min
MIB	10	> 1h
Geosmin	10	> 1h
Estradiol	7×10^9	5 ms
MTBE	0.14	2.8d

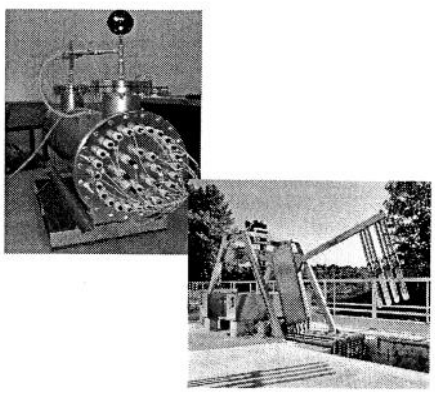
www.cranfield.ac.uk

Example - Ozonation



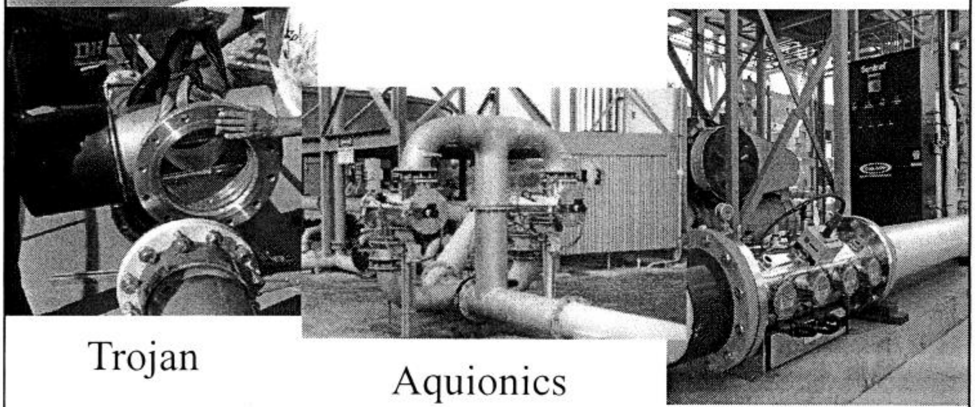
Ultra violet light





UV Reactors

Cranfield UNIVERSITY



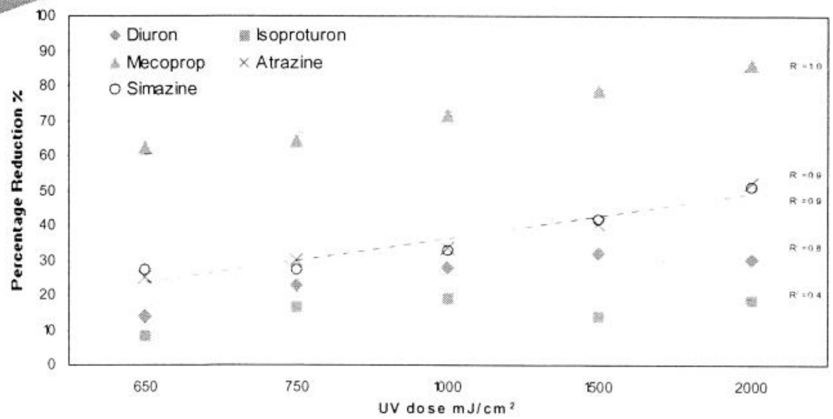
Trojan

Aquionics

Calgon

Pesticides - UV

Cranfield UNIVERSITY



Cranfield UNIVERSITY

Summary

- Natural organic matter
  - Significant problem especially at elevated levels
  - Coagulation good at removing hydrophobic material
  - Treatment processes required for hydrophilics
- Pesticides
  - GAC & Ozone best solution depending on pesticides
  - UV potential new process for removing specific pesticides

www.cranfield.ac.uk

Cranfield UNIVERSITY

Drinking Water Treatment

Inorganic Removal

Peter Jarvis

Centre for Water Science

What makes an inorganic compound inorganic?

Carbonates | Carbon oxides | Elemental carbon

Chemical structure that does not contain carbon

anions | elemental

cations | uncharged | minerals

Occurrence in surface and ground water from:

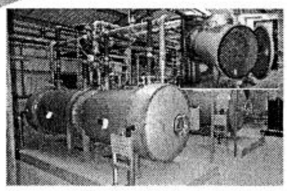
- Naturally occurring from rocks & minerals
- Industrial, Agricultural & Domestic
- From treatment & in distribution system

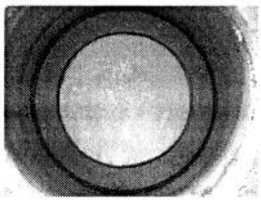
Main Problems

- The main regulated inorganic contaminants include:
  - Nitrate (NO_3^-) 50 mg/L (ppm)
  - Fluoride (F) 1.5 mg/L
  - Iron (Fe) 200 μg/L (ppb)
  - Manganese (Mn) 50 μg/L (ppb)
  - Arsenic (As) 50 μg/L (ppb)
  - Bromate (BrO_3^-) 10 μg/L (ppb)
  - Lead (Pb) 50 > 10 μg/L (ppb)

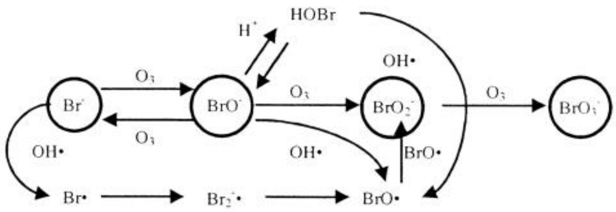
Bromate formation

Cranfield UNIVERSITY





Strong oxidation of bromide:
Ozonation

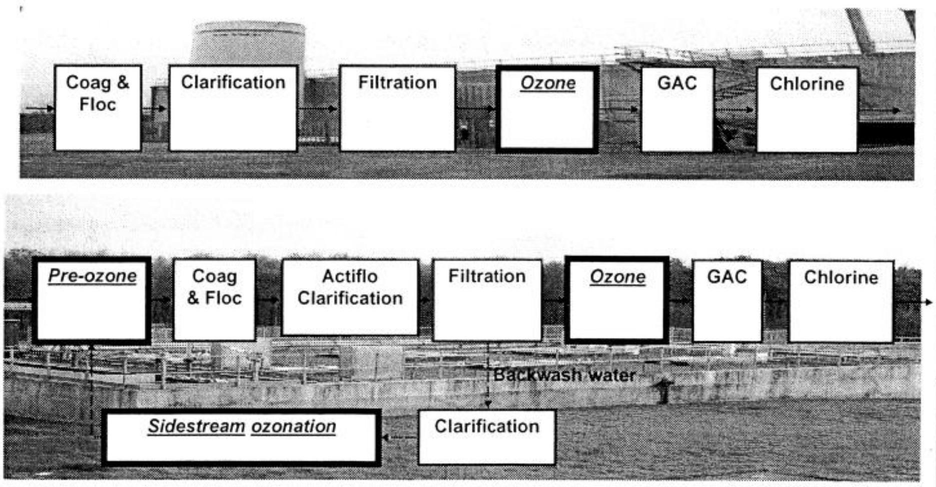


- 10 μg/L regulatory limit – since 2003

www.cranfield.ac.uk

Bromate Formation

Cranfield UNIVERSITY



www.cranfield.ac.uk

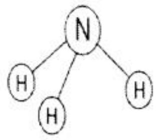
Cranfield UNIVERSITY

Bromate formation

- Factors influencing bromate formation
  - Bromide concentration
  - Ozone dose and contact time
  - pH

$$HBrO \Leftrightarrow BrO^{-} + H^{+}$$
$$OH\bullet$$

  - Natural organic matter
  - Temperature
  - Alkalinity/ammonia



Cranfield UNIVERSITY

Bromate formation models

$$\log\,[BrO_3^-] = b_1 + b_2 \log[Br^-] + b_3 \log[DOC] + b_4 \log[pH] + b_5 \log[O_3]$$

$$+ b_6 \log[time] + b_7 \log[NH_3\text{-}N] + b_8 \log[Alk]$$

- Empirical models
- Developed for specific waters
  - Accuracy high (R^2 between 0.91- 0.98)
- A useful tool for industrial application without investment in analysis for specific water
  - Predict bromate formation
  - Change operational parameters

An example

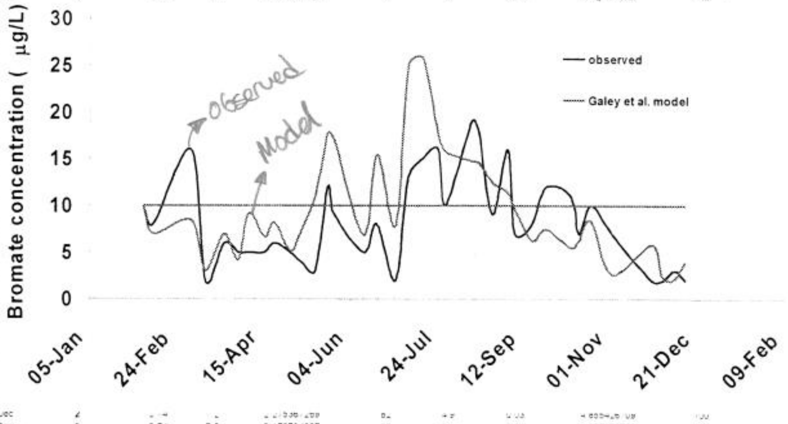
Cranfield UNIVERSITY

Date	Final bromate (ug/L)	TOC (mg/L)	pH	Applied ozone (mg/L)	Bromide (ug/L)	Temp (C)	Ammonia (mg/L)	Contact time (mins)	Alkalinity (mg/L)
05-Feb	**10**	1.72	8.2	2.56834046	83	5	0.03	8.696463721	100
11-Feb	**8**	1.52	8.1	1.877857545	81	5	0.03	6.542553191	100
05-Mar	**16**	1.65	7.9	1.770184988	101	9	0.03	9.609375	100
13-Mar	**2**	3.01	7.2	2.399341318	68	6.1	0.03	8.669982406	100
24-Mar	**6**	1.68	8	1.744624045	84	8	0.03	6.115168003	100
01-Apr	**5**	1.98	7.5	1.710203657	85	9	0.03	4.62406015	100
07-Apr	**5**	4.34	8.2	4.888155131	54	9	0.03	5.662733139	100
16-Apr	**5**	3.41	7.8	3.52271695	64	9	0.03	5.747663551	100
22-Apr	**6**	3.12	8	3.432796581	79	10	0.03	4.967240444	100
01-May	**5**	2.47	7.8	2.046497918	74	10	0.03	4.806249531	100
07-May	**4**	1.92	8	1.787868118	78	11.6	0.04	4.946529226	100
15-May	**3**	1.97	7.8	2.601674173	76	15.1	0.03	5.009187583	100
22-May	**12**	1.3	8.4	1.910772947	82	16.1	0.03	4.689101156	100
26-May	**9**	1.42	8.4	2.109467451	91	13.9	0.04	4.949969093	100
12-Jun	**5**	3.62	7.8	3.059006388	75	15	0.03	4.872043501	100
19-Jun	**8**	2.63	8.7	2.850770548	73	16.2	0.03	4.875380518	100
30-Jun	**2**	4.4	7.6	3.98481784	71	15.4	0.04	8.305782445	100
07-Jul	**13**	1.85	8.3	3.1640625	82	15.6	0.03	10.11087437	100
15-Jul	**15**	1.53	8.1	2.999875706	86	15.9	0.03	9.651600753	100
24-Jul	**16**	1.79	8.3	2.751209323	76	15.9	0.03	4.695287306	100
29-Jul	**10**	1.63	8.3	2.165593083	88	16.7	0.03	4.9568632	100
13-Aug	**19**	1.87	8	2.658109148	83	17.2	0.03	5.131979492	100
17-Aug	**18**	1.66	8.2	2.154164557	83	17.4	0.03	4.701489799	100
25-Aug	**9**	1.51	7.9	2.084094225	85	15.1	0.03	5.207063318	100
03-Sep	**16**	1.58	7.7	2.235910763	88	14.3	0.03	5.796462179	100
07-Sep	**7**	1.64	7.7	2.156206083	79	13	0.03	5.195660989	100
17-Sep	**8**	2.5	7.8	2.218416273	68	12.3	0.03	4.806249531	100
25-Sep	**12**	1.9	7.5	2.172095504	77	13.6	0.03	5.120903277	100
09-Oct	**11**	2.09	7	2.698670241	71	11.5	0.03	4.872043501	100
14-Oct	**7**	2.88	7.7	2.935207688	76	10.4	0.03	4.655366616	100
21-Oct	**10**	3.98	7.8	4.242237177	62	9.6	0.03	9.580155526	100
02-Nov	**7**	2.87	7.6	1.89064233	43	6.3	0.03	4.545373918	100
25-Nov	**2**	3.04	7.4	3.516845955	43	7	0.03	9.554436987	100
01-Dec	**2**	2.74	7.2	2.275367269	82	4.9	0.03	4.855426709	100
08-Dec	**3**	2.74	7.5	2.172784637	90	3.1	0.04	4.855426709	100
14-Dec	**2**	3.07	7.5	2.860788923	82	6.4	0.03	5.471218721	100

www.cranfield.ac.uk

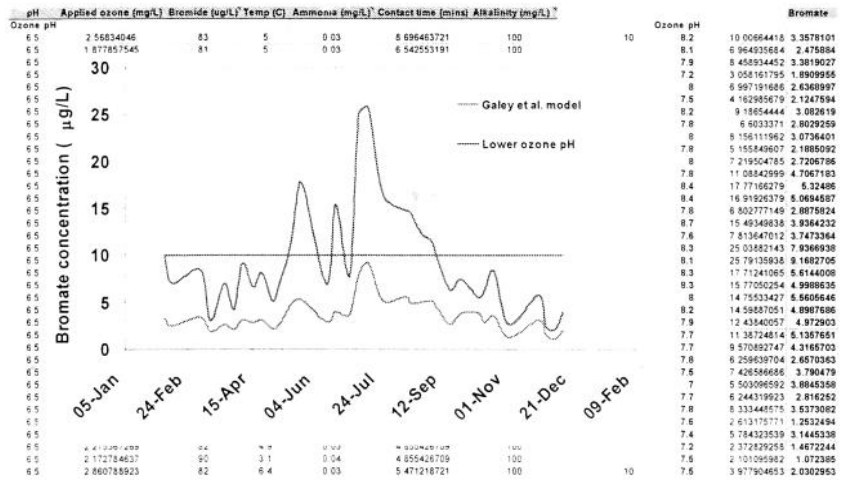
An example

Cranfield UNIVERSITY

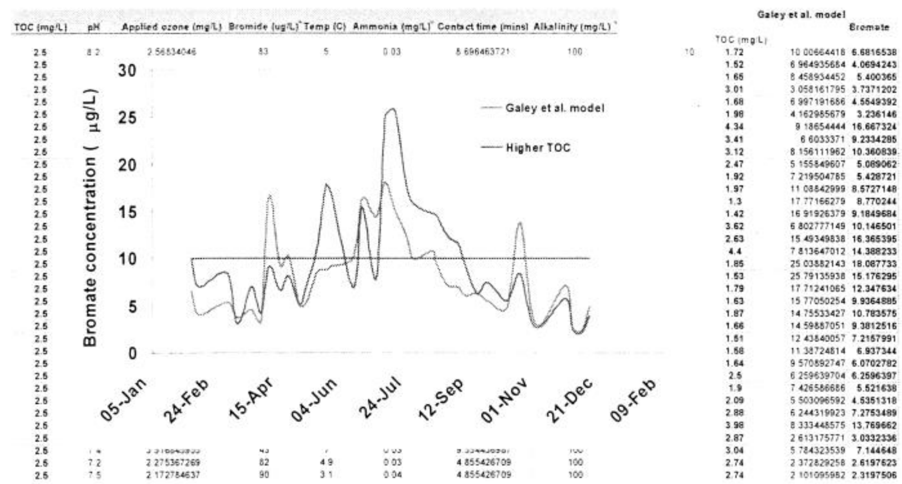


www.cranfield.ac.uk

An example – Ozonation pH

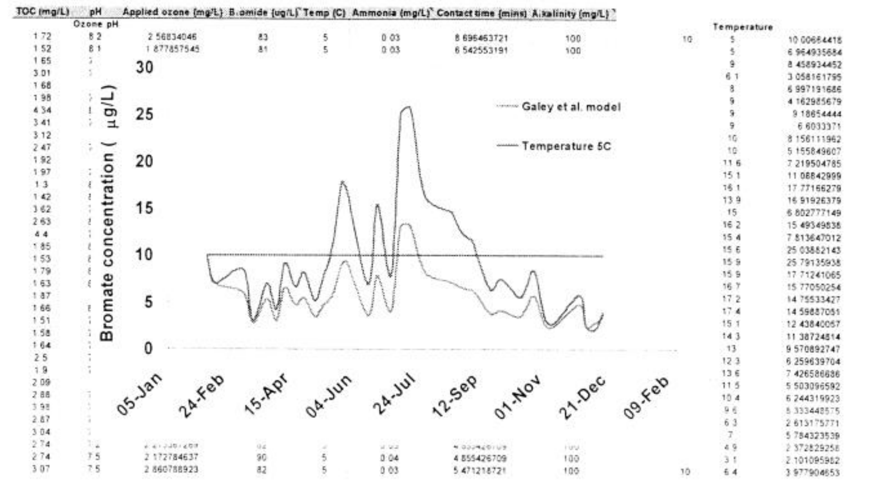


An example – Organic content of water



An example – Temperature

Cranfield UNIVERSITY



Bromate

Cranfield UNIVERSITY

- Ozonation pH, ozone dose key and contact time key control variables
- Other variables, can't do much!

- On-line tool for monitoring bromate formation based on raw water quality and ozonation parameters
  - Direct input:
    - water temperature, ozonation pH and contact time
  - DOC estimated from UV_{254} correlation
  - Winter/summer average bromide used

Nitrate Problem

Cranfield UNIVERSITY

- Mostly from excess nitrate fertilizers
  - intrusion into groundwater over 5 - 20 years
  - surface run-off into surface waters - may be seasonal
  - sewage works final effluent
- Health risks
  - methaemaglobinaemia
  - carcinogenic nitrosamines
- EU Directive 50mg/L NO_3 = 11.3 mg/L as N
- 55% of England has been designated as being in Nitrate Vulnerable Zone (NVZ).

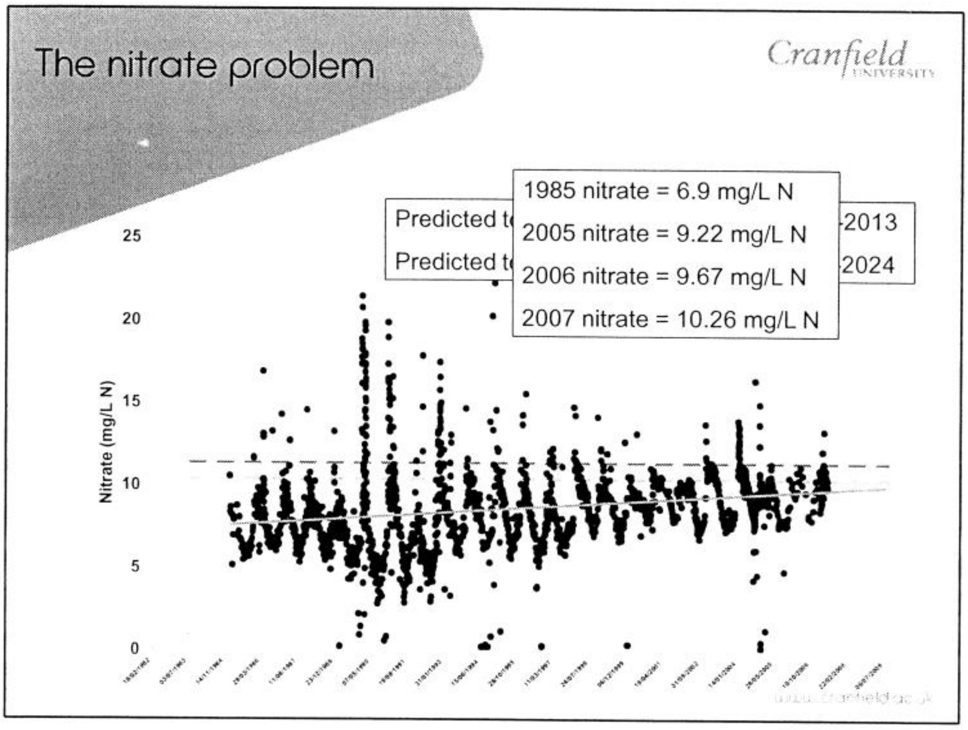
www.cranfield.ac.uk

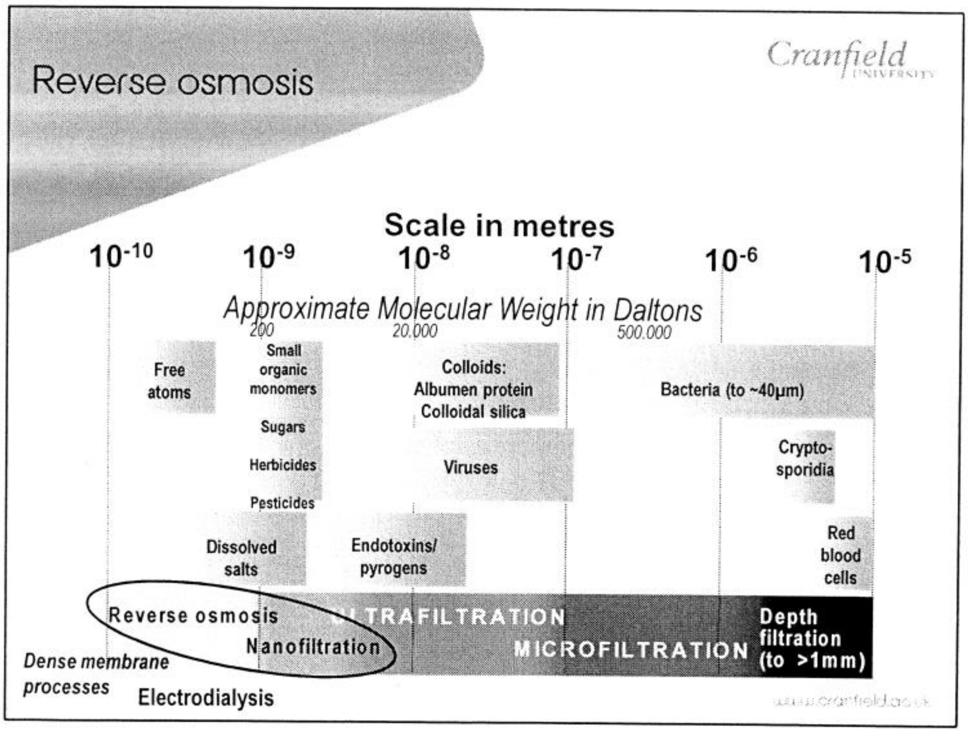
Nitrate removal

Cranfield UNIVERSITY

- Reverse osmosis
- Ion-exchange
- Biological

www.cranfield.ac.uk

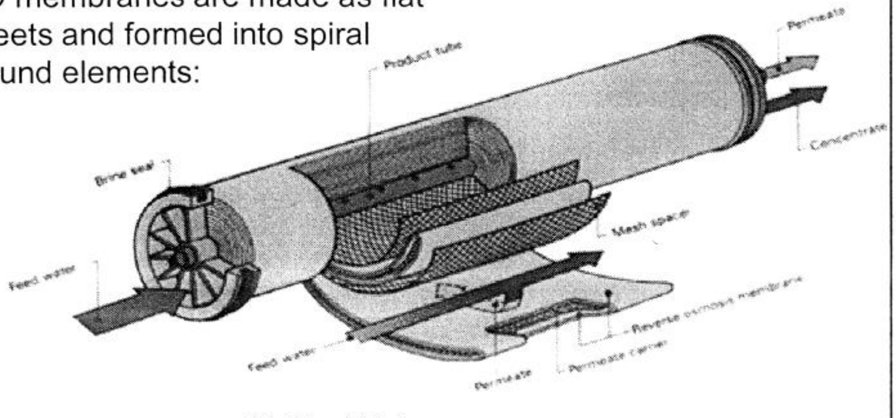

The nitrate problem
Cranfield UNIVERSITY
1985 nitrate = 6.9 mg/L N
2005 nitrate = 9.22 mg/L N
2006 nitrate = 9.67 mg/L N
2007 nitrate = 10.26 mg/L N
Predicted t
2013
Predicted t
2024
Nitrate (mg/L N)
25
20
15
10
5
0


Reverse osmosis
Cranfield UNIVERSITY
Scale in metres
10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5}
Approximate Molecular Weight in Daltons
200
20,000
500,000
Free atoms
Small organic monomers
Sugars
Herbicides
Pesticides
Colloids: Albumen protein Colloidal silica
Viruses
Bacteria (to ~40µm)
Crypto-sporidia
Red blood cells
Dissolved salts
Endotoxins/ pyrogens
Reverse osmosis
Nanofiltration
ULTRAFILTRATION
MICROFILTRATION
Depth filtration (to >1mm)
Dense membrane processes
Electrodialysis
www.cranfield.ac.uk

RO element

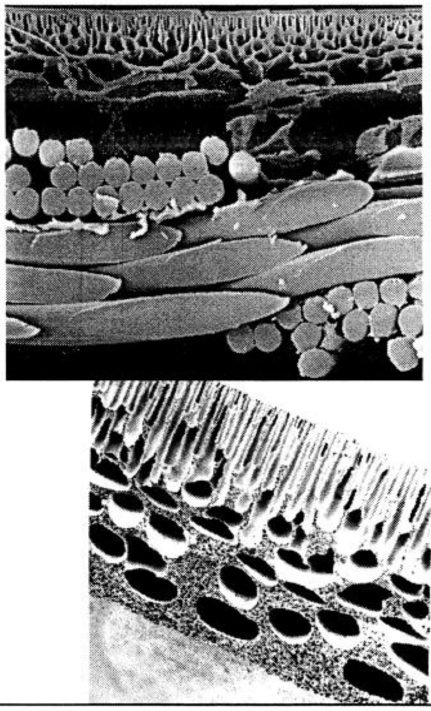
Cranfield UNIVERSITY

RO membranes are made as flat sheets and formed into spiral wound elements:



Spiral Wound R.O element

RO membrane structure



- Generally *anisotropic*: symmetry in one direction
- RO membranes have additional ultrathin "active" layer for added permselectivity to form a *composite* material

Reverse Osmosis

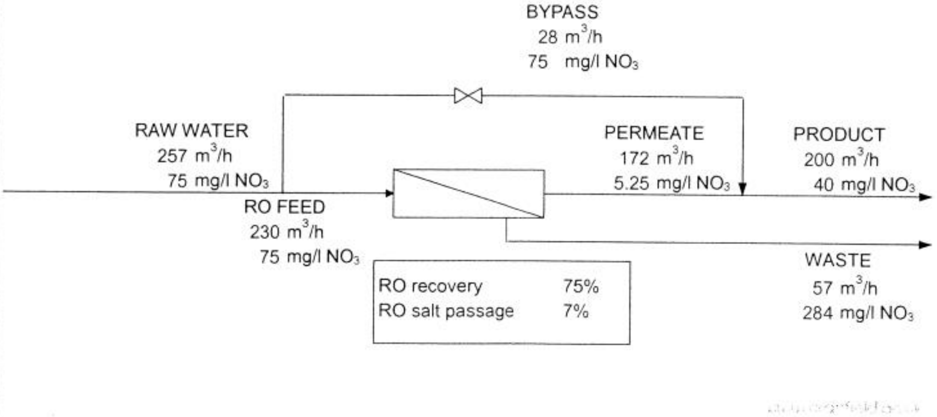
Cranfield University

- Reverse osmosis is not nitrate specific
- Nitrate rejection in low pressure membranes typically about 90%
- Recovery typically 75%
- Operated with raw water bypass
- Permeate may need re-mineralisation

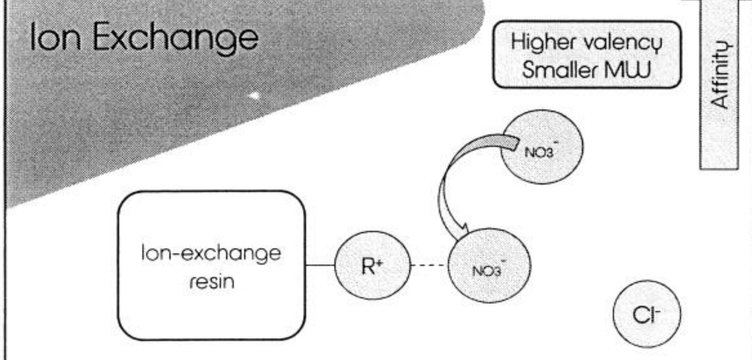
Reverse Osmosis

Cranfield University

Example 200m^3/h product at 40mg/l from 75mg/l supply



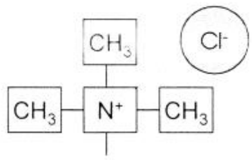
Ion Exchange

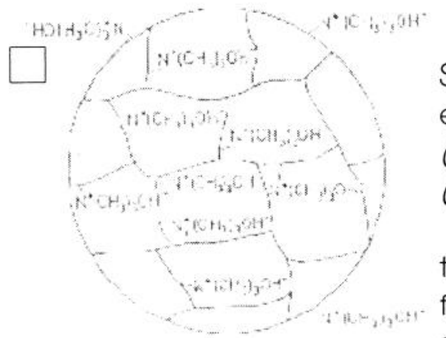


Cation	Anion
Fe^{3+}	CrO_2^-
Al^{3+}	SO_4^{2-}
Pb^{2+}	SO_3^-
Ba^{2+}	HPO_4^{3-}
Sr^{2+}	CNS^-
Cd^{2+}	CNO^-
Zn^{2+}	$\boxed{NO_3^-}$
Cu^{2+}	NO_2^-
Fe^{2+}	Br^-
Mn^{2+}	Cl^-
Ca^{2+}	CN^-
Mg^{2+}	HCO_3^-
K^+	$HSiO_3^-$
NH^{4+}	OH^-
Na^{2+}	F^-
H^+	
Li^+	

- Reduces nitrate levels in groundwater for potable/food uses
- Uses resins with functional groups that have selectivity for NO_3 and SO_4
- Regeneration with salt - low hazard
- Waste regenerant high in salt and sodium nitrate
- Poor chemical efficiency

Ion Exchange





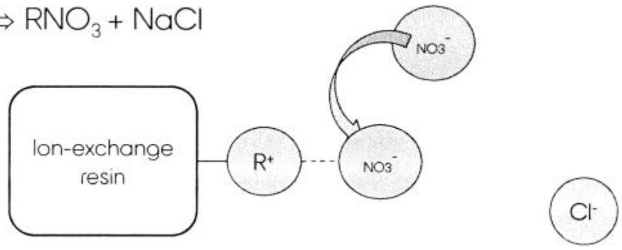
Strongly basic anion exchange resin
(Low affinity for OH^-)
(Remains ionised even at high pH)

tri-methyl ammonium functional group on a styrene - divinyl benzene polymer matrix

Ion Exchange

Functional group: Strong base quaternary ammonium

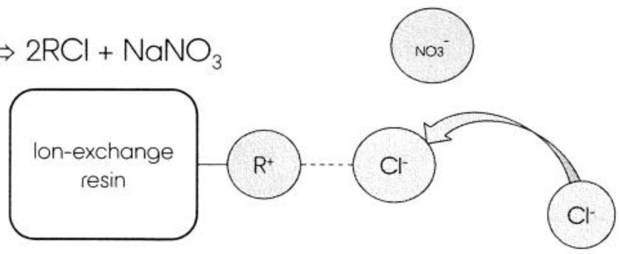
Exhaustion:
$RCl + NaNO_3 \Rightarrow RNO_3 + NaCl$



Ion Exchange

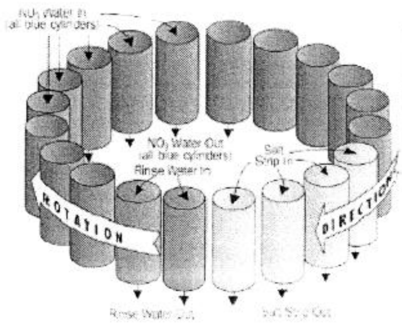
Functional group: Strong base quaternary ammonium

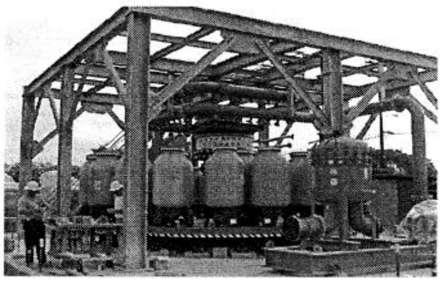
Regeneration:
$RNO_3 + NaCl \Rightarrow 2RCl + NaNO_3$



Regeneration ratio: 10 - 15 on nitrate

Calgon ISEP Process





Ion Exchange

- Spent regenerant
  - sewer discharge if possible
  - biological denitrification - salinity may be a problem

Biological Processes

Cranfield UNIVERSITY

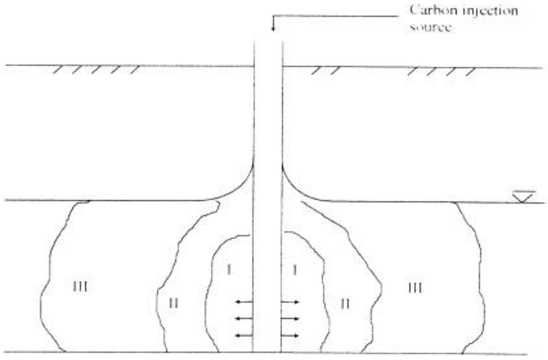
- Aerobic heterotrophic bacteria, under anaerobic conditions, use nitrate as an electron acceptor for electrons and hydrogen and allows the nitrate to be reduced to the gaseous forms of nitrogen (N).

- Denitrification can be summarised by:
  - $2NO_3 + C_2H_5OH \rightarrow N_2 + 3H_2O + 2CO_2$

www.cranfield.ac.uk

Groundwater Treatment

Cranfield UNIVERSITY



Zone I - Biochemical reactor
Zone II - Filter
Zone III - Storage of low NO_3^- water

www.cranfield.ac.uk

Iron and Manganese

Occurrence

Pipe corrosion

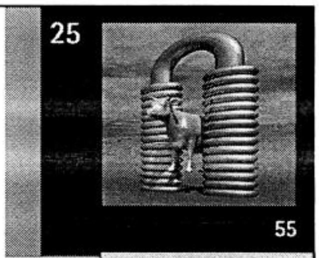
Coagulant chemicals

Naturally occurring

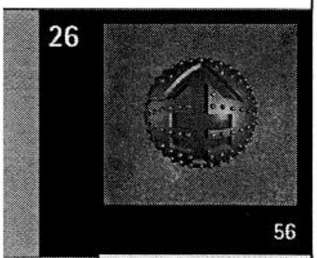
Mn^{++}
typically up to 1mg/l but occasionally higher

Fe^{++}
typically up to 5mg/l Fe but may be higher

Present in:
Acidic/reducing/anaerobic water
Can organically complex usually less than 0.5mg/l



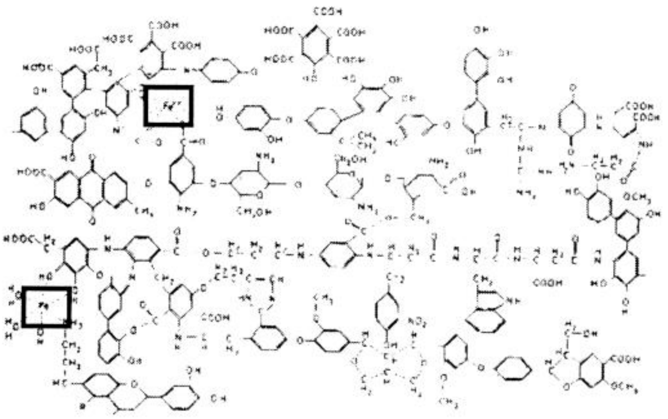
Manganese



Iron

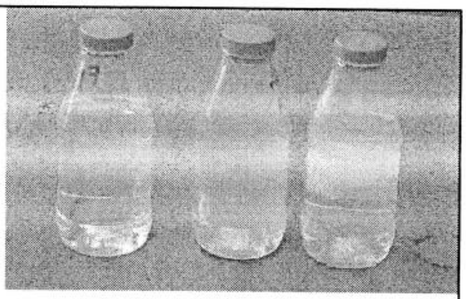
Occurrence

Cranfield UNIVERSITY



www.cranfield.ac.uk

Problems

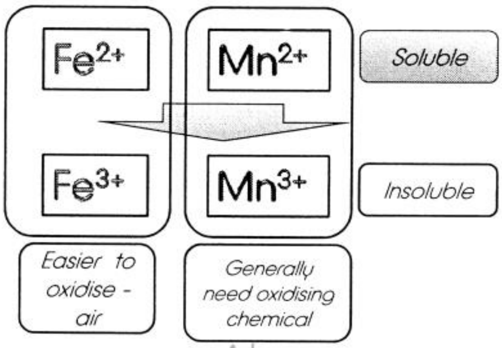


- Effects
  - turbidity
  - metallic taste and odour
  - spotting of laundry
  - discoloration of vegetables in cooking
  - industrial processes
- EU Directive
  - iron 200 μg/l Fe
  - manganese 50 μg/l Mn

www.cranfield.ac.uk

Physico-Chemical Processes

Cranfield UNIVERSITY



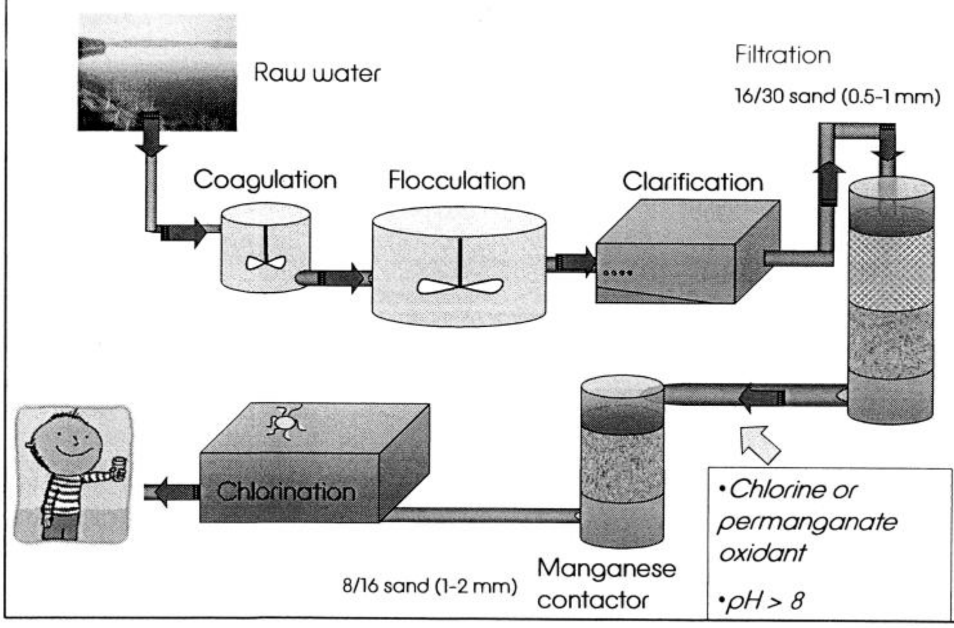
$Cl/KMnO_4$

- Precipitation
  - Aeration
  - Oxidising chemical
  - pH adjustment
- Filtration
  - Sand
  - Polarite (manganese dioxide)
  - BIRM (sand coated with manganese dioxide)
  - Manganese greensand (zeolite)

www.cranfield.ac.uk

Fe, Mn removal

Cranfield UNIVERSITY



Physico-Chemical Processes

Cranfield UNIVERSITY

Oxidation of iron in alkaline solution by aeration

$$4Fe(HCO_3)_2 + O_2 + 2H_2O \Rightarrow 4Fe(OH)_3 + 8CO_2$$

Aeration by forced draught packed tower
compressed air injection

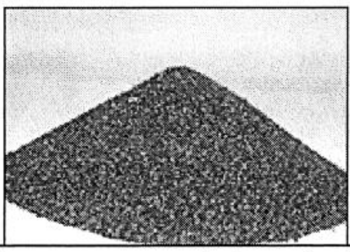
Oxidation by strong oxidant (chlorine or permanganate)

$$3Fe^{2+} + MnO_4^- + 2H_2O + 5OH^- \longrightarrow MnO_2 + 3Fe(OH)_3$$

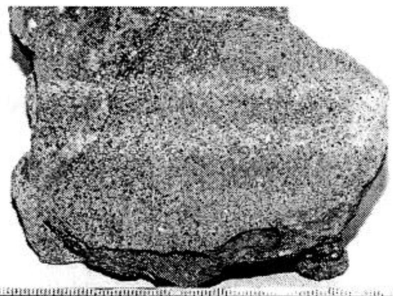
$$3Mn^{2+} + 2MnO_4^- + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

www.cranfield.ac.uk

Physico-Chemical Processes



Manganse greensand = Iron potassium silicate with MnO_2 coat



Greensand = Iron potassium silicate

Removal of iron & manganese using manganese greensand:

Chemistry is not well documented
natural ion exchange
catalytic oxidation of Mn and Fe by $2MnO_2 \Rightarrow Mn_2O_3 + ½O_2$
regeneration with $KMnO_4$

www.cranfield.ac.uk

Biological Processes

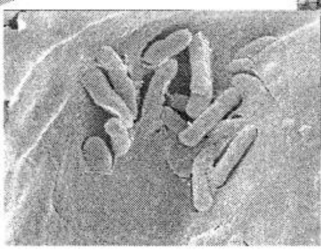
Cranfield University

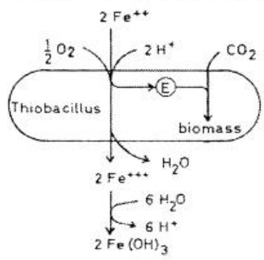
- Fixed film of bacteria on coarse sand
- High rate
  - iron removal at 20 - 50m/h
  - manganese removal at 10 - 25m/h
- Usually three stage
  - stage 1 - biological iron removal
  - stage 2 - re-aeration
  - stage 3 - biological manganese removal

Degremont Ferazur®/Mangazur® Process

www.cranfield.ac.uk

Biological Processes



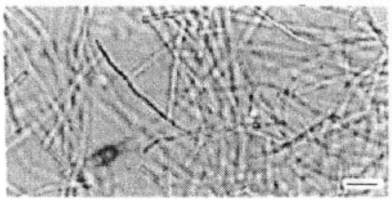


Gallionella sp
Thiobacillus ferro-oxidans
Lepothrix ochracea
Crenothrix polyspora

$4Fe^{++} + O_2 + 10H_2O \Rightarrow 4Fe(OH)_3 + 8H^+ + \text{Energy}$

www.cranfield.ac.uk

Biological Processes

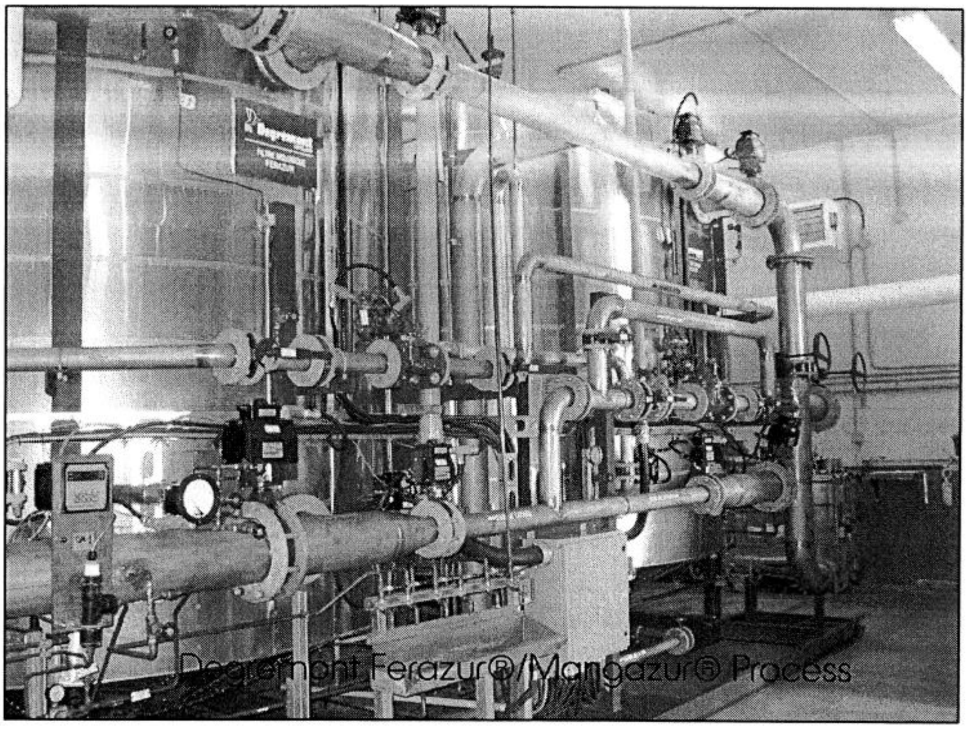


Thiobacillus ferro-oxidans
Pseudomonas manganoxidans
Leptothrix ochracea
Crenothrix polyspora

$Mn^{++} + O_2 \Rightarrow MnO_2 + 2H^+ + Energy$

Sphaerotilus sp
Siderocapsa sp

Inhibition of process by H_2S, Cl_2 and NH_4^+



Degremont Ferazur®/Mangazur® Process

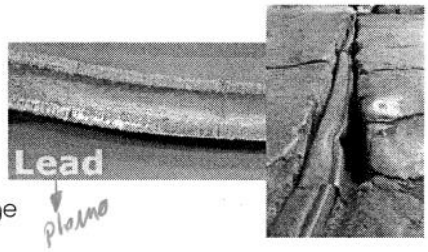
Cranfield UNIVERSITY

Lead

Cranfield UNIVERSITY

Occurrence

- Very low background concentrations in source waters (ng/L concentrations)
- Pipe corrosion
- Chronic exposure to lead:
    - Kidney disfunction
    - Mental retardation
    - Reproductive system damage
- Regulation EU:
    - 50 μg/L pre 2003
    - 25 μg/L post 2003
    - 10 μg/L 2013

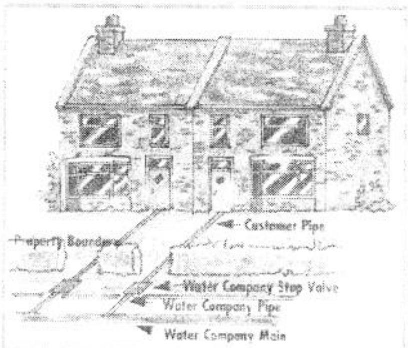


plasma

Lead pipes

Cranfield University

- Lead pipes used up until 1970's
- ~50% of properties have some lead plumbing
  North/North West/Scotland (soft waters)
- Responsibility
  - Home owner & water utility
- Problems particularly in soft water
  - Particulate lead
  - Soluble lead

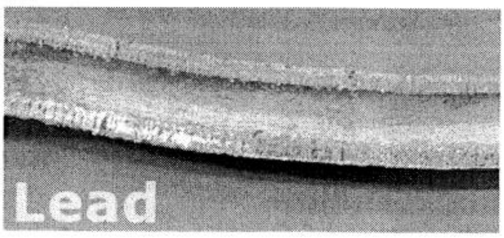


Lead pipes

Cranfield University

Plumbosolvency

- Lead is a sparingly soluble element
- Lead is quickly oxidised in water to scales of lead carbonates
  - $PbCO_3$ & $Pb_3(CO_3)_2(OH)_2$



- Lead enters distribution from the dissolution of pipe scale products
  - More soluble at lower pH >> soft waters are were problems are seen

Lead control

Cranfield UNIVERSITY

- Raise water pH
  - Reduce solubility of lead scales
  - pH >8.0 using lime
- Orthophosphate dosing (PO_4^{3-})
  - Dosed as orthophosphoric acid (H_3PO_4)
  - Produces highly insoluble scale products
    - Lead hydroxyapatite
      - $Pb_5(PO_4)_3OH$
  - Typically dosed 0.5-2.0 mg/L as P

www.cranfield.ac.uk

Lead control

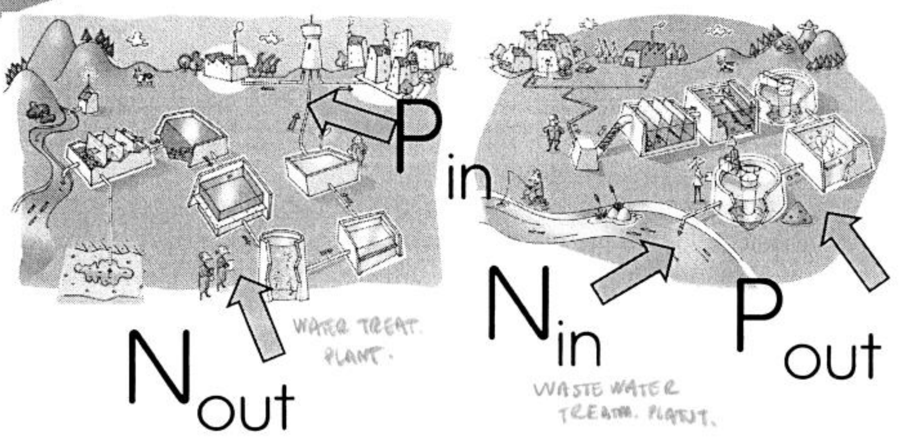
Cranfield UNIVERSITY

- Issues
  - Phosphate onto sewage works
  - Cost of phosphate up by 30-50%
  - Overdosing – build-up of the scale layer, leads to increase in particulate lead & instability
    - Pipe disturbance
- Stannous chloride ($SnCl_2$) an alternative

www.cranfield.ac.uk

Lead and nitrate control

Cranfield UNIVERSITY



www.cranfield.ac.uk

Arsenic

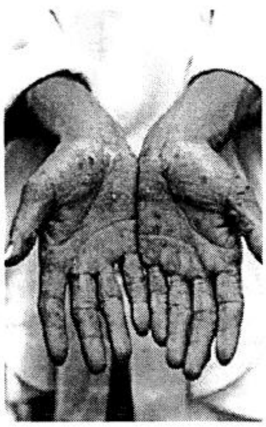
Cranfield UNIVERSITY

www.cranfield.ac.uk

Arsenic

Cranfield UNIVERSITY

- As(III) and As(V) in ground water MAJOR problem.
- 90% of the Bangladesh population of 130 million drink well water
  - alternative to polluted surface water and thereby reducing the incidence of water-borne diseases.
- Long term exposure causes wide range of health problems
  - Cancer
  - Nervous system damage



www.cranfield.ac.uk

Arsenic in Water

Cranfield UNIVERSITY

- Arsenic is common (20th in abundance)
  - Originates from arsenic containing rocks
  - Organic and <u>inorganic</u> forms in natural waters
  - Food a major source (53 µg/day)
  - Bangladesh ground waters ~1000µg/L
- Chronic exposure = cancers
- Acute exposure = sickness
- General rules
  - Arsenic (III) found in ground waters (Arsenites e.g - H_3AsO_3)
    - organoarsenic compounds
  - Arsenic (V) found in surface waters (Arsenates - $HAsO_4^{2-}$)
    - inorganic arsenic oxycompounds

www.cranfield.ac.uk

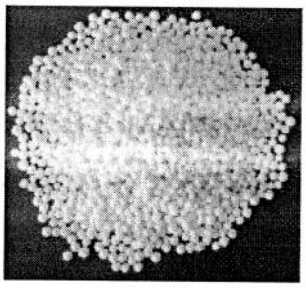
Treatment

Cranfield University

Process	% removal
Coagulation & filtration	95
Coagulation assisted microfiltration	90
Lime softening (pH > 10.5)	90
✓ Ion exchange (sulphate < 50 mg/L)	95
✓ Activated alumina (Adsorption process)	95
✓ Granular ferric hydroxide (")	98
Reverse osmosis	>95

www.cranfield.ac.uk

Activated Alumina (AA)



- Adsorption process – very effective for As(V).
- Factors such as pH, arsenic oxidation state, competing ions, empty bed contact time (EBCT).
- Regeneration (strong base/strong acid) has significant effects on the removals achieved with AA.
- Waste regenerant stream needs to be disposed of

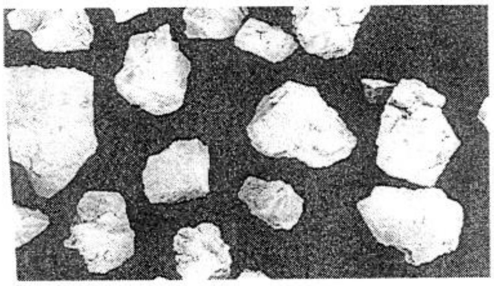
www.cranfield.ac.uk

Granular Ferric Hydroxide (GFH)

Cranfield UNIVERSITY

- AdsorpAs
  - HARBAUER GmbH & Co
  - Poorly crystallised FeOOH

  (some $Fe(OH)_3$)
  - Surface Area
    - 300 m^2/g
    - 0.2 – 2.0 mm
    - 45 g As/Kg
    - 60,000 BV



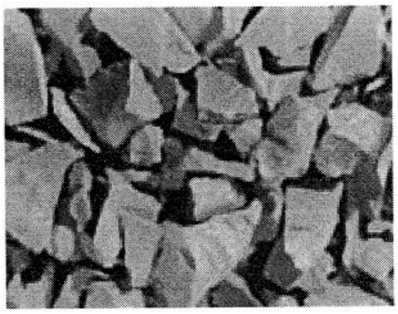
No regeneration – solid waste to dispose of

www.cranfield.ac.uk

SORB33™

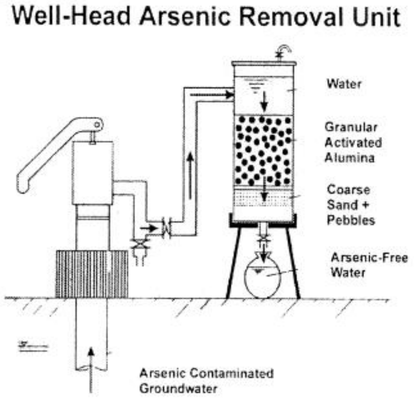
Cranfield UNIVERSITY

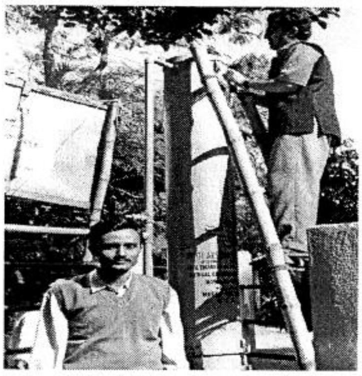
- Severn Trent & Bayer Fe_2O_3 Adsorbent
- Significantly better than FeOOH & Alumina
- As(V) and (III) <4 μg/L
- Bed Volumes > 60,000
- Not regenerated



www.cranfield.ac.uk

Well Head Process





Performance - 175 μg/L to 0

Process Costs – 17 sites

Option	Costs (£M)
Activated alumina with pH control to 6.0	45.5
Activated alumina with no pH control and regeneration on site	36.3
Activated alumina with no pH control and central regeneration facility	32.8
Membrane technology	35-62
Granular ferric media	27

Inorganics

Cranfield UNIVERSITY

- Range of inorganic problems
  - Coming in to the works NO_3, F, As, Fe, Mn
  - Formed in the works BrO_3
  - From distribution systems Pb
- Charged ions can be removed by adsorption or IEX

www.cranfield.ac.uk

Aim of lecture

Cranfield UNIVERSITY

- Understand the regulatory framework for control of contaminants in drinking water in UK
- Understand what the main organic and inorganic pollutants in water are and where they come from
- Look at main ways of controlling organic and inorganic contaminants in drinking water treatment

www.cranfield.ac.uk