Oxidation Case Studies

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Introduction

- Summary and explanation
- Simple calculations
- Show some applications

DISINFECTION KINETICS

Chick's Law

$$\frac{dN}{dt} = -kN$$

N is the number of microorganisms at time t, and k is a constant (dimension : t^{-1}).

This constant applies only for a fixed concentration of a certain disinfectant

INTEGRATION OF CHICK's LAW

Integrating for N, $N=N_o$ at $t = 0$

$$\ln N/N_0 = -kt$$

$$N/N_0 = e^{-kt}$$

Watson's Law

$$C^n t = \text{constant}$$

Simplified:

$$Ct = \text{constant}$$

Applies only for

- **a fixed rate of "kill"**
- **a certain organism**
- **a specific disinfectant**

Example

Ct value for ozone is 1.0 $mgL^{-1}min$.

We could achieve that with

1 mg/L ozone residual for 1 minute

Or: 0.4 mg/L for 2.5 minutes

CHLORINE RESIDUALS

Free – $HOCl$ and OCl^-

Combined – NH_2Cl, $NHCl_2$

Total = Free + combined

CHLORINE REACTIONS WITH AMMONIA

$$Cl_2 + H_2O \Leftrightarrow HOCl + H^+Cl^-$$

$$HOCl + NH_3 \Leftrightarrow NH_2Cl + HOH$$

$$HOCl + 2NH_2Cl \rightarrow N_2 + 3H^+Cl^- + H_2O$$

Net reaction: 2 x 2nd + 3rd :

$$3\ HOCl + 2\ NH_3 \rightarrow N_2 + 3H^+Cl^- + 3H_2O$$

CHLORINE REACTIONS WITH AMMONIA

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$$HOCl + 2NH_2Cl \rightarrow N_2 + 3H^+Cl^- + H_2O$$

Net reaction: 3 x 1st + 2 x 2nd + 3rd :

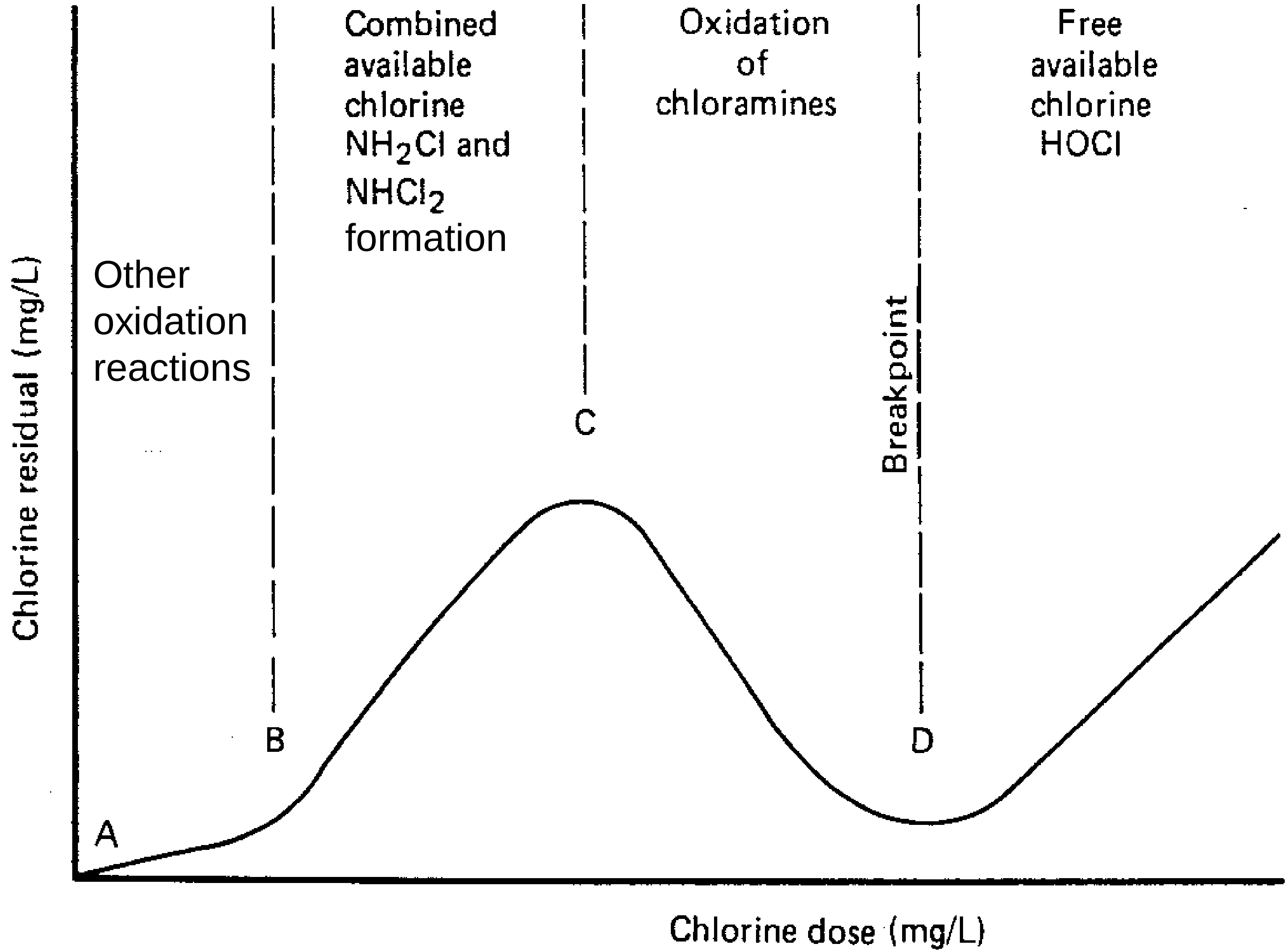
$$3\,Cl_2 + 2\,NH_3 \rightarrow N_2 + 6H^+Cl^-$$

MEASUREMENT OF CHLORINE (OR CHLORAMINES)

DPD – pink color develops

KI solution – I^{-1} oxidized to I, forms I_2

Color of DPD or I_2 can be measured, or I_2 titrated with FAS solution


Combined available chlorine NH_2Cl and $NHCl_2$ formation
Oxidation of chloramines
Free available chlorine HOCl
Other oxidation reactions
Chlorine residual (mg/L)
Breakpoint
A
B
C
D
Chlorine dose (mg/L)

DISINFECTION BYPRODUCTS

- THMs - CHX_3, e.g. $CHCl_3$
- Chlorite and chlorate,
  ClO_2^- ClO_3^-
- Bromoform - $CHBr_3$
- Bromate - BrO_3^-

ClO2 made from Sodium Chlorite

Acidification of Chlorite

$5\ ClO_{2-} + 4\ H_+ \rightarrow 4\ ClO_2 + 2\ H2O + Cl^-$

Oxidation of Chlorite by Chlorine

$2\ NaClO_2 + Cl_2 \rightarrow 2\ NaCl + 2\ ClO_2$

Oxidation of Chlorite by Persulfate

$2\ NaClO_2 + Na_2S_2O_8 \rightarrow 2\ ClO_2 + 2\ Na_2SO_4$

From Sodium Hypochlorite and Sodium Chlorite

$NaOCl + 2\ NaClO_2 + 2\ HCl \rightarrow 2\ ClO_2 + 3\ NaCl + H_2O$

Electrochemical oxidation of chlorite

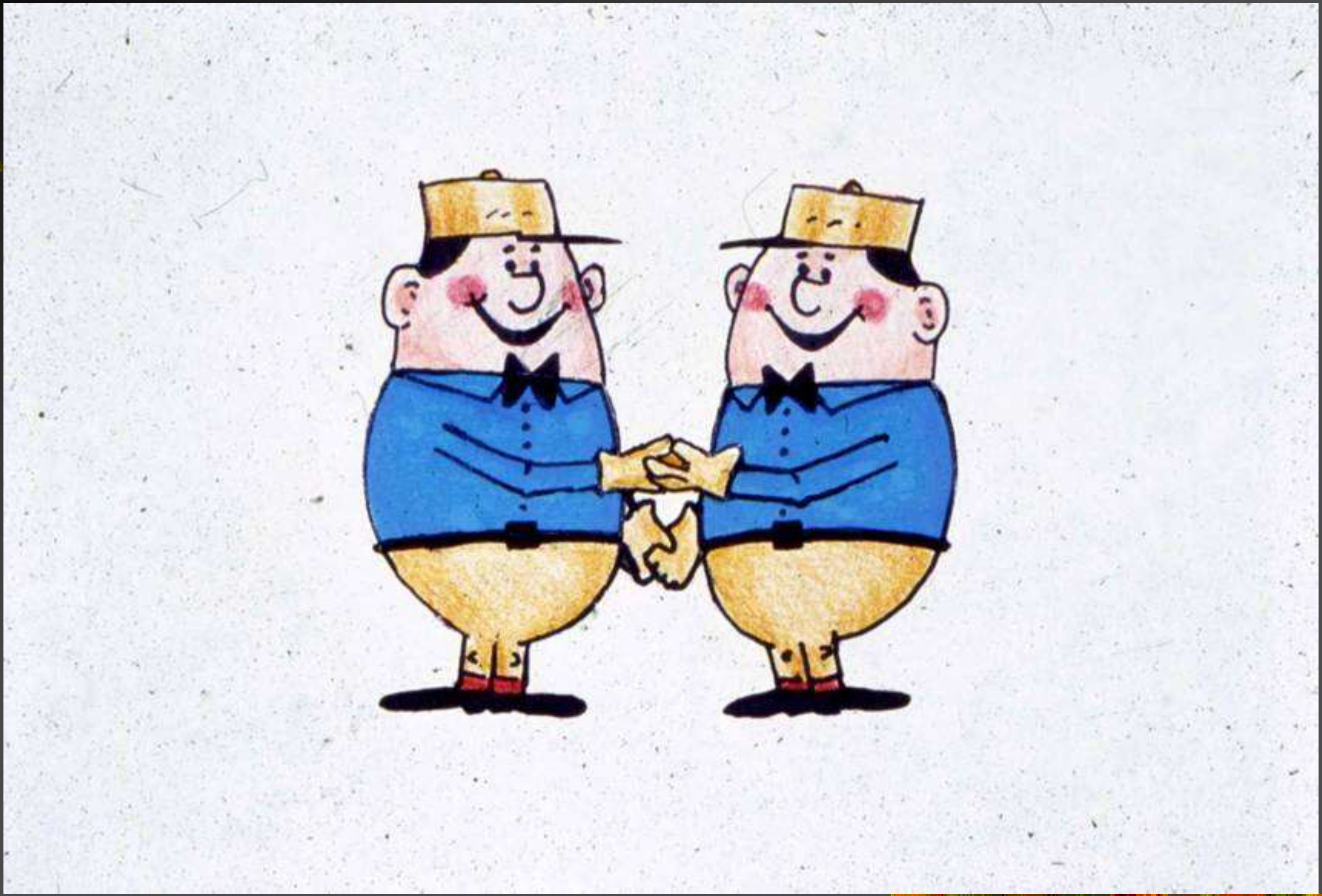
$ClO_{2-} \rightarrow ClO2 + e-$

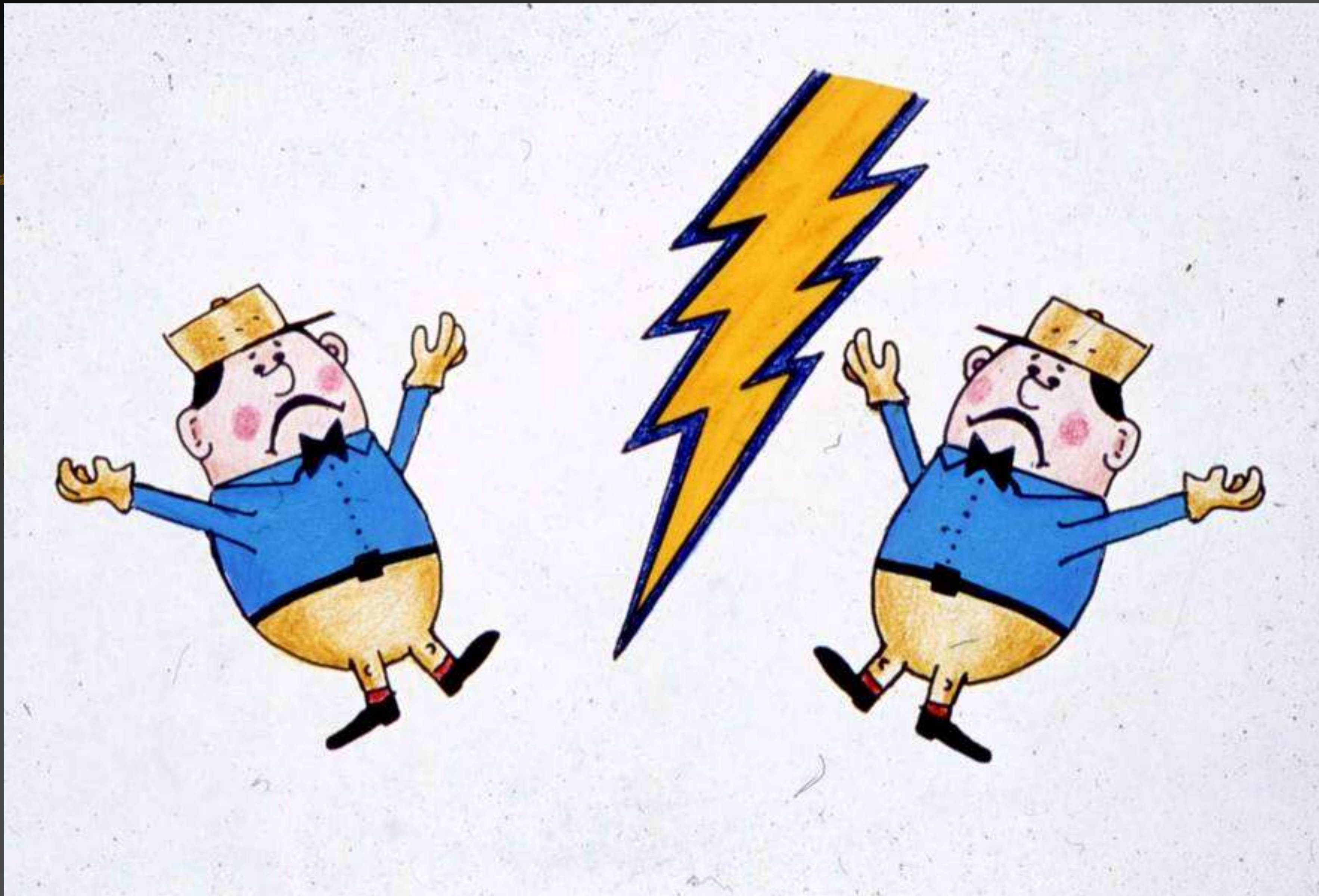
Dry chlorine/chlorite (laboratory method)

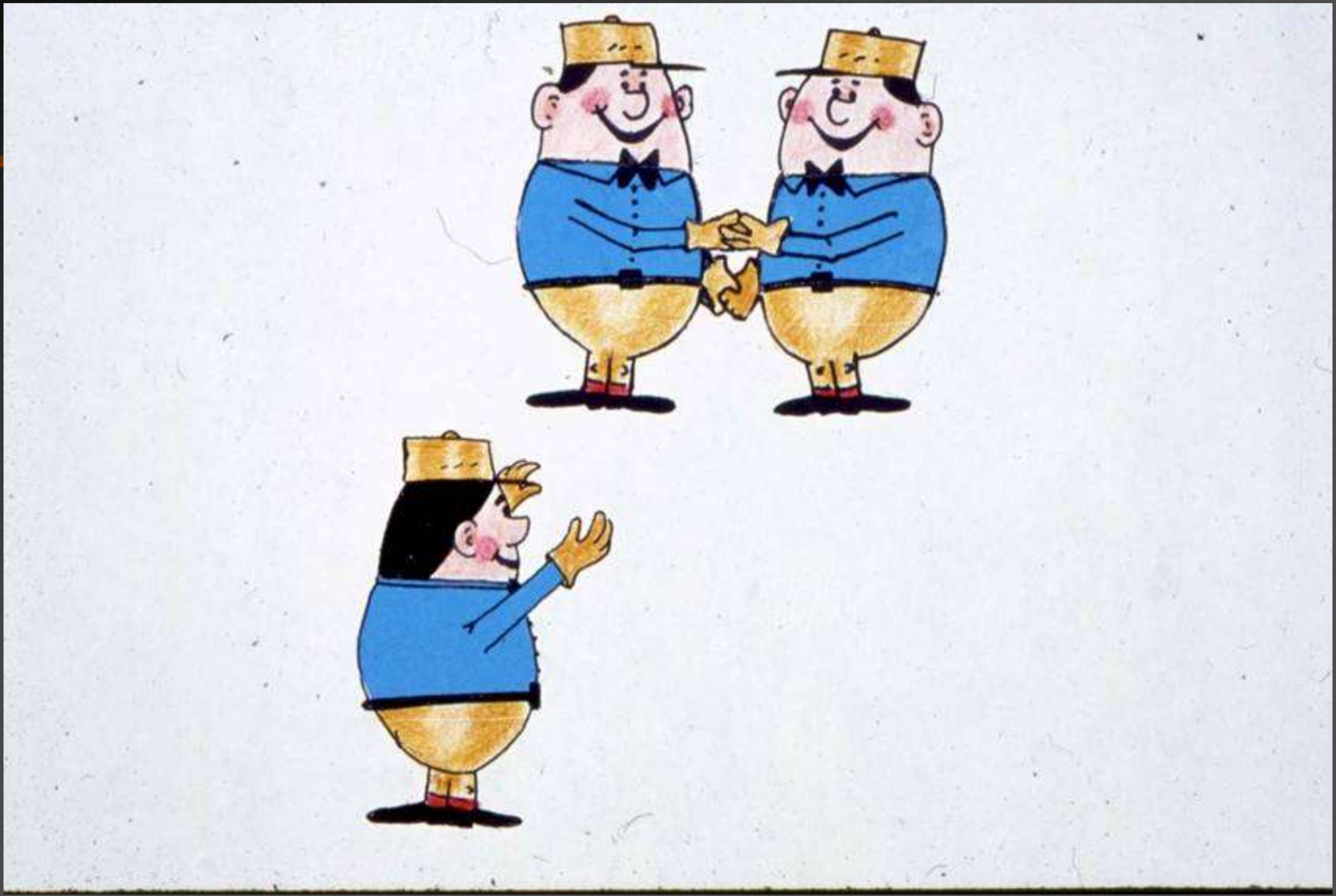
$NaClO_2 + 1/2\ Cl_2$ --> $ClO_2 + NaCl$ (solid)

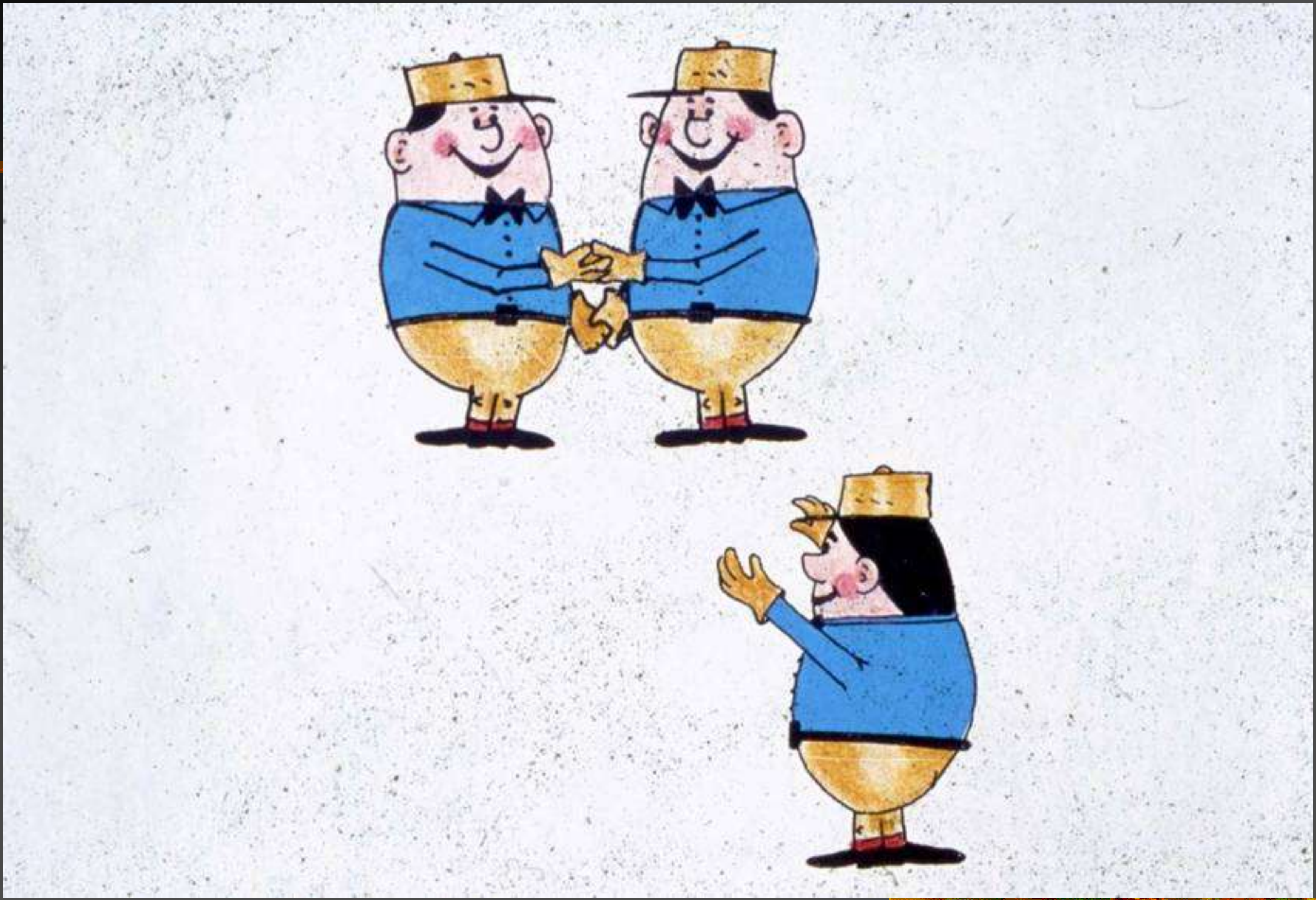
OZONE PRODUCTION

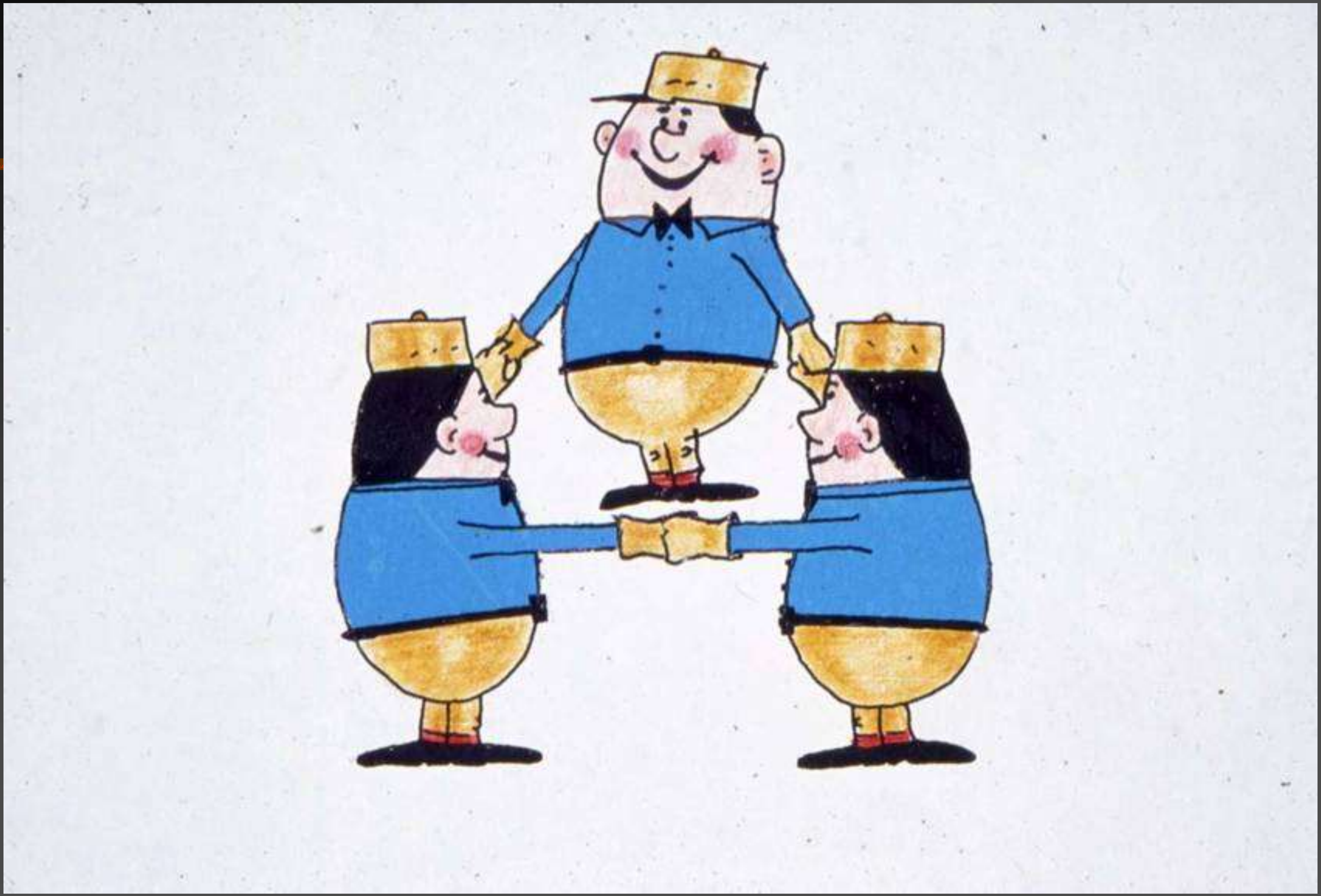
- Electron bombardment
- UV irradiation at < 200 μm
- Electrolytically

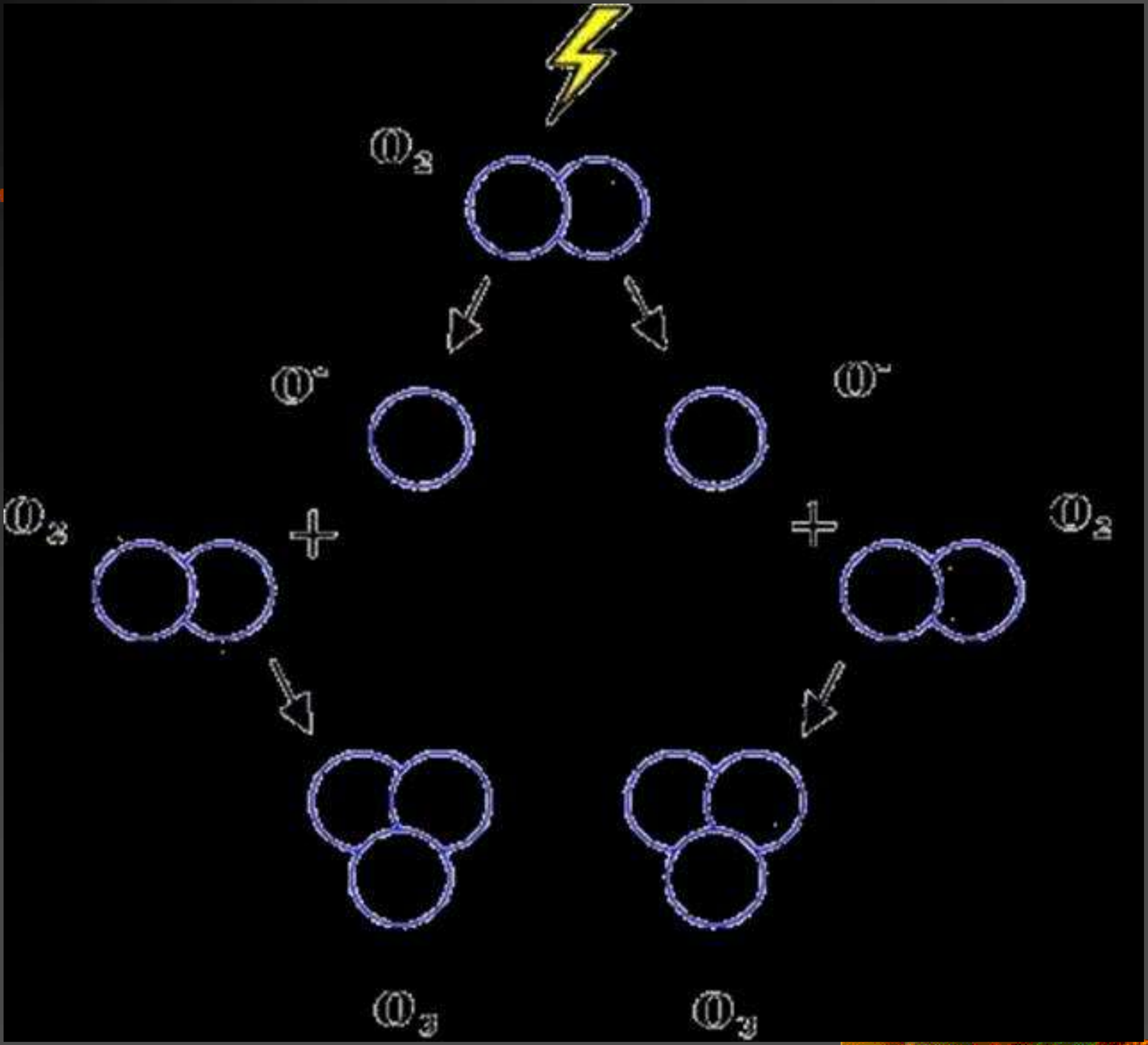


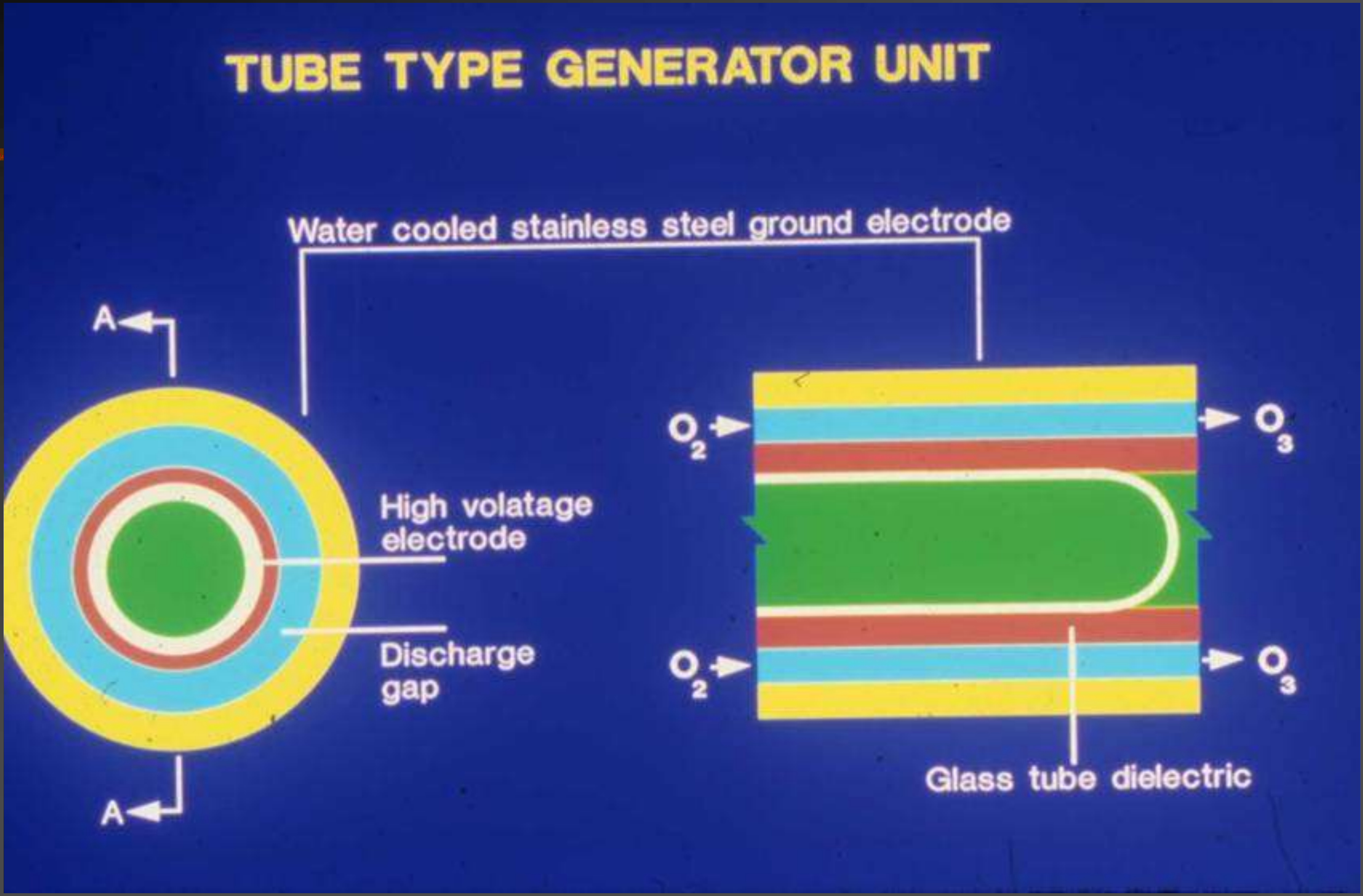




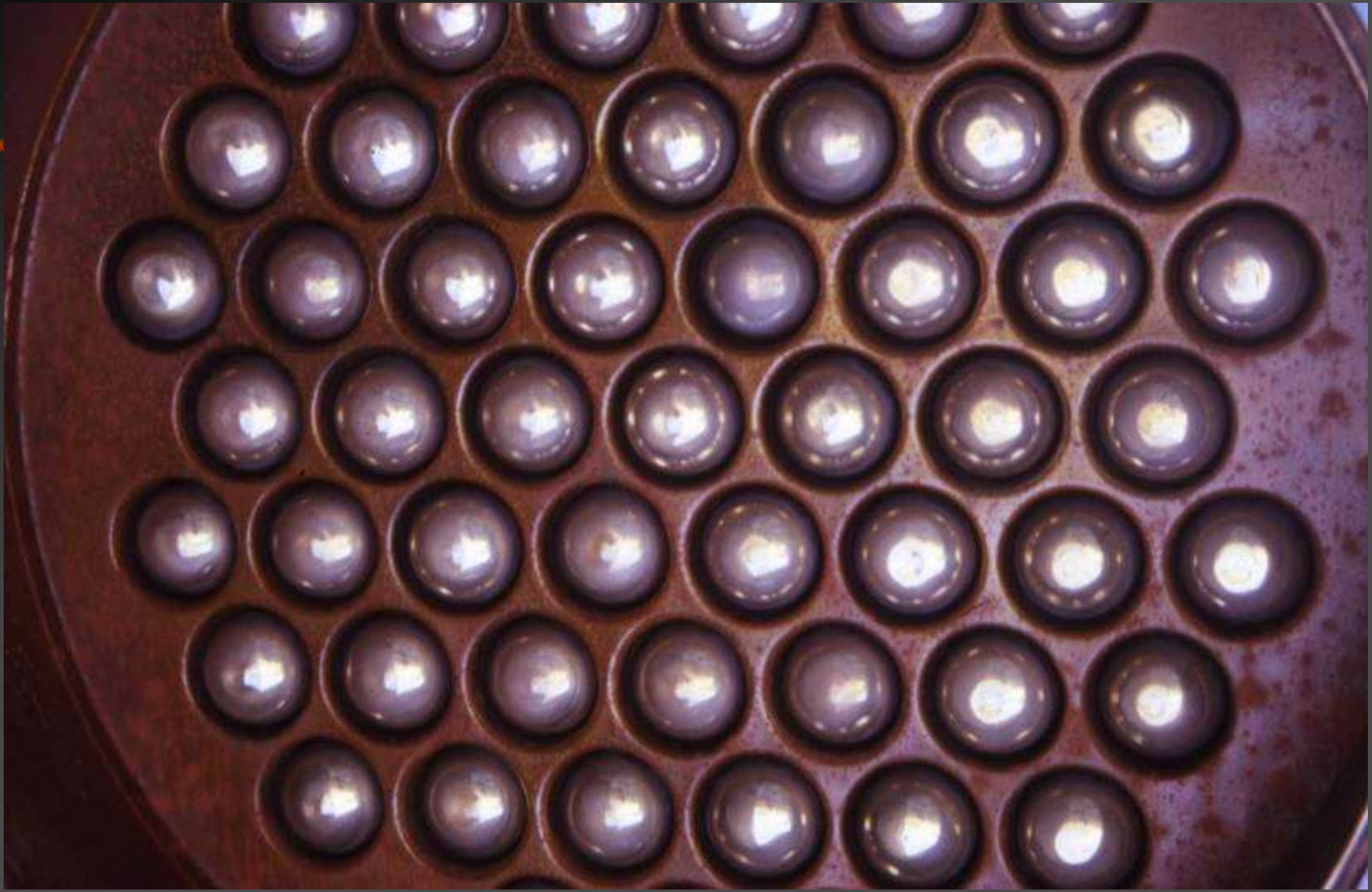





O2
O-
O-
O2
+
+
O2
O3
O3

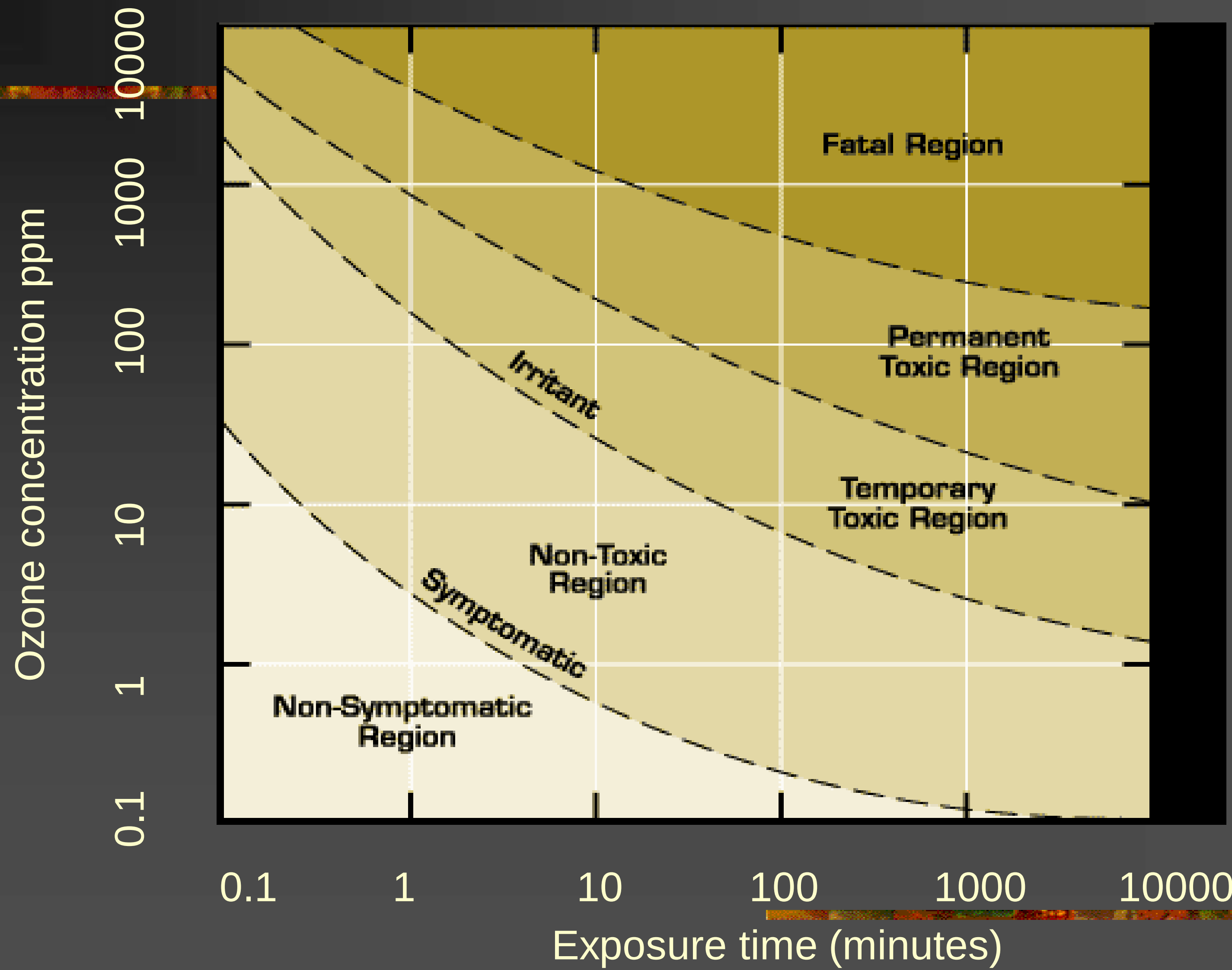

TUBE TYPE GENERATOR UNIT
Water cooled stainless steel ground electrode
A
A
High volatage electrode
Discharge gap
O_2
O_2
O_3
O_3
Glass tube dielectric

Corona Discharges in Ozone Generation

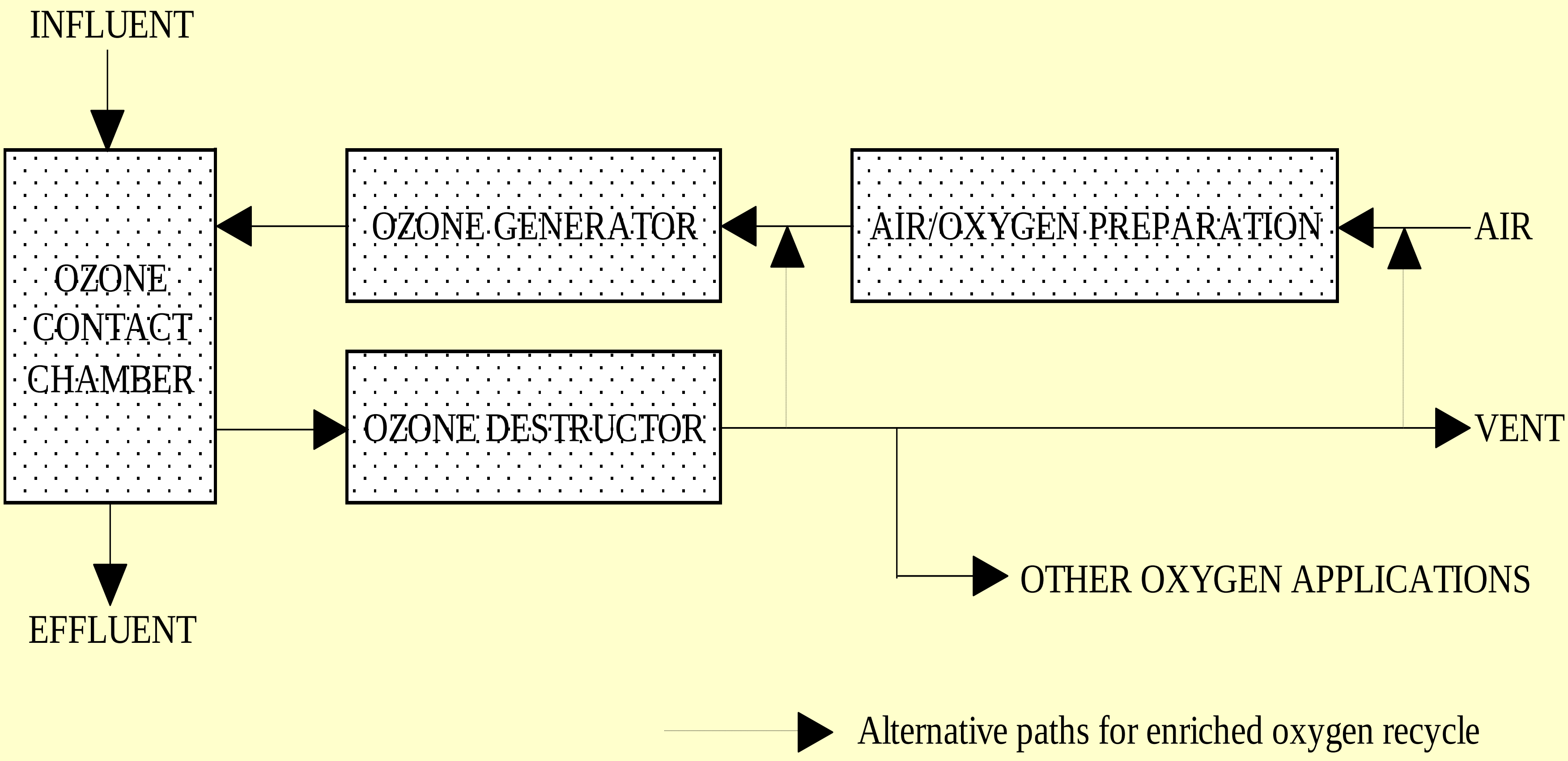


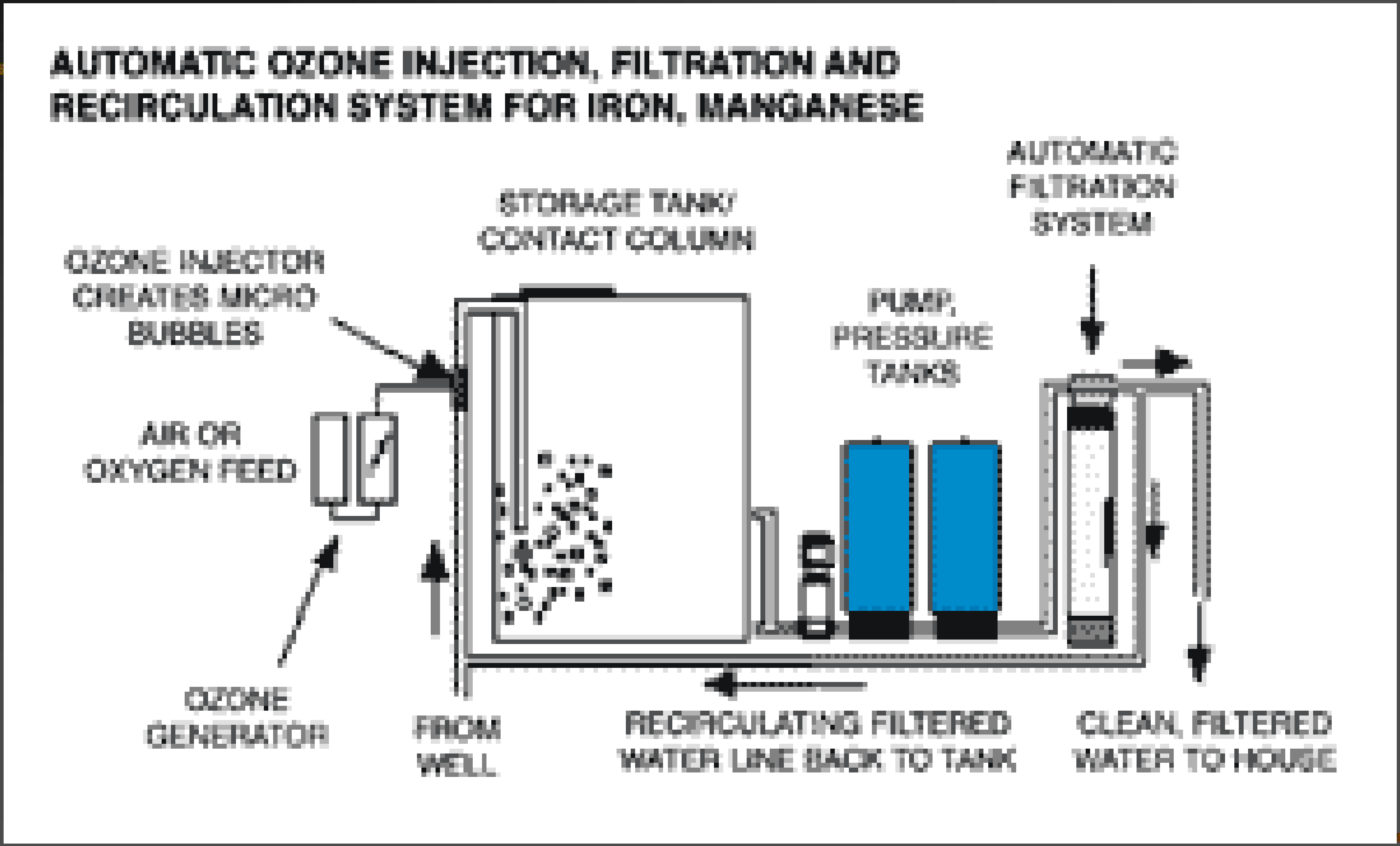
Large Ozone Generators

Toxicity of ozone to humans



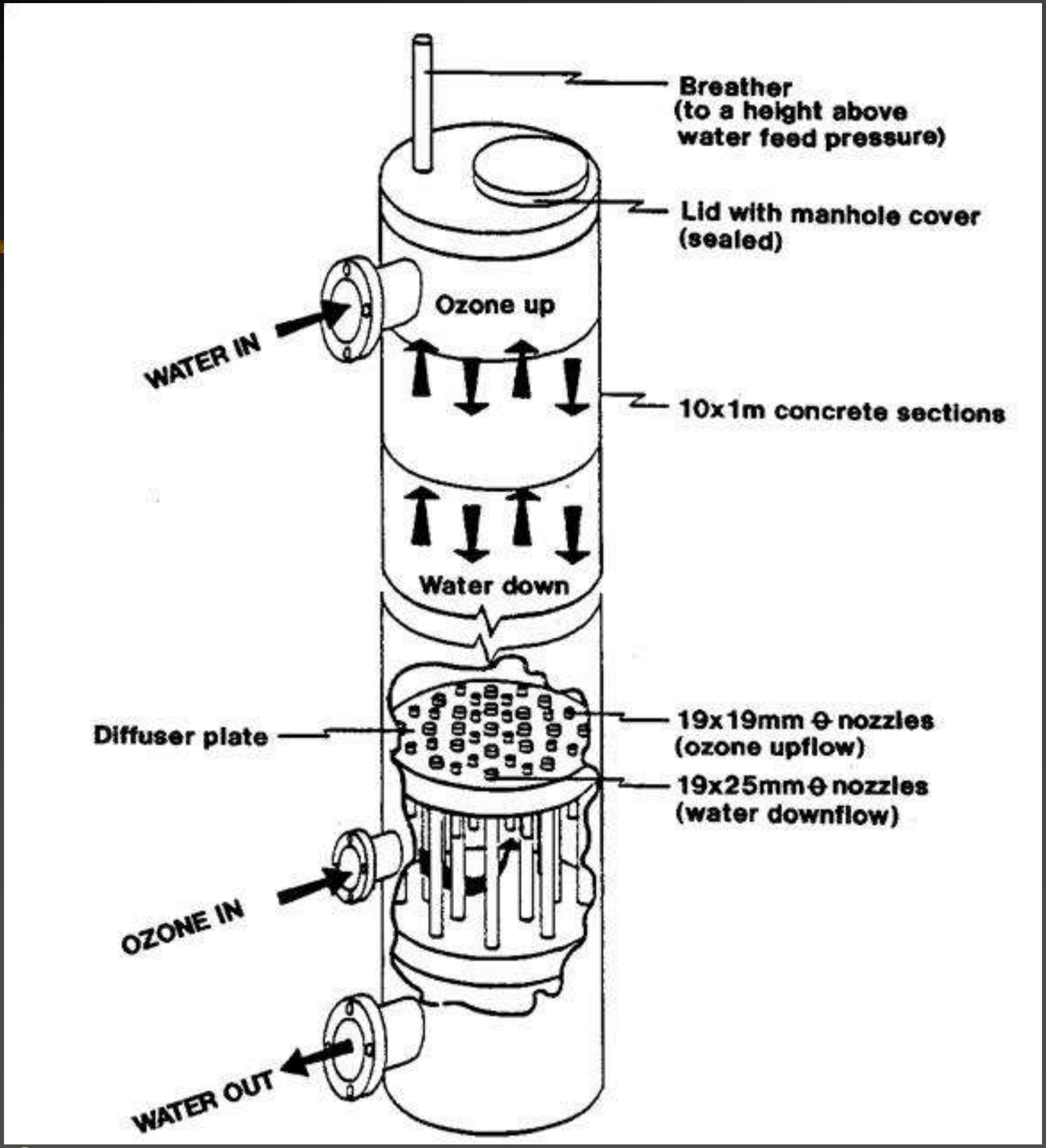
COMPONENTS OF AN OZONATION SYSTEM

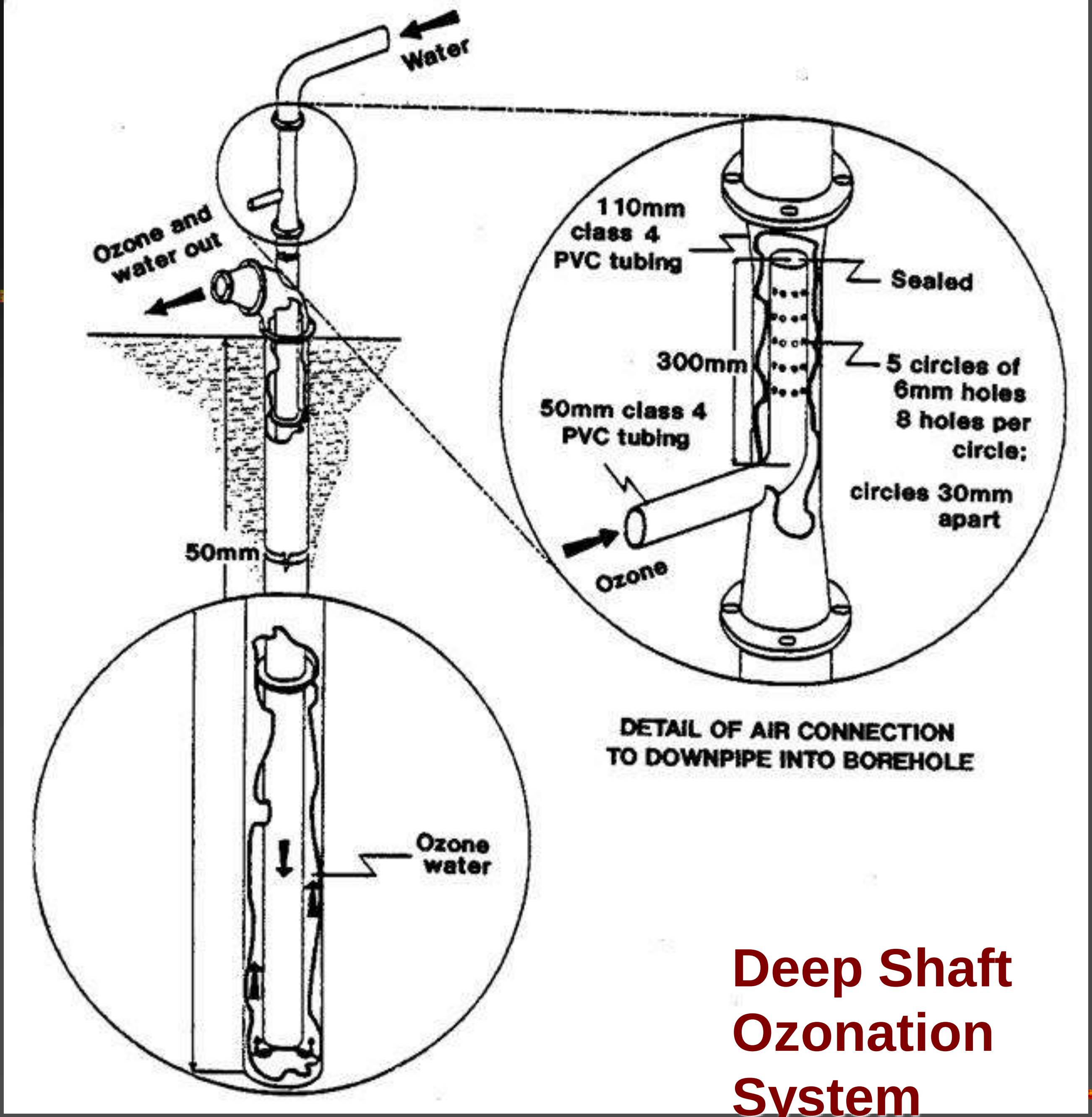




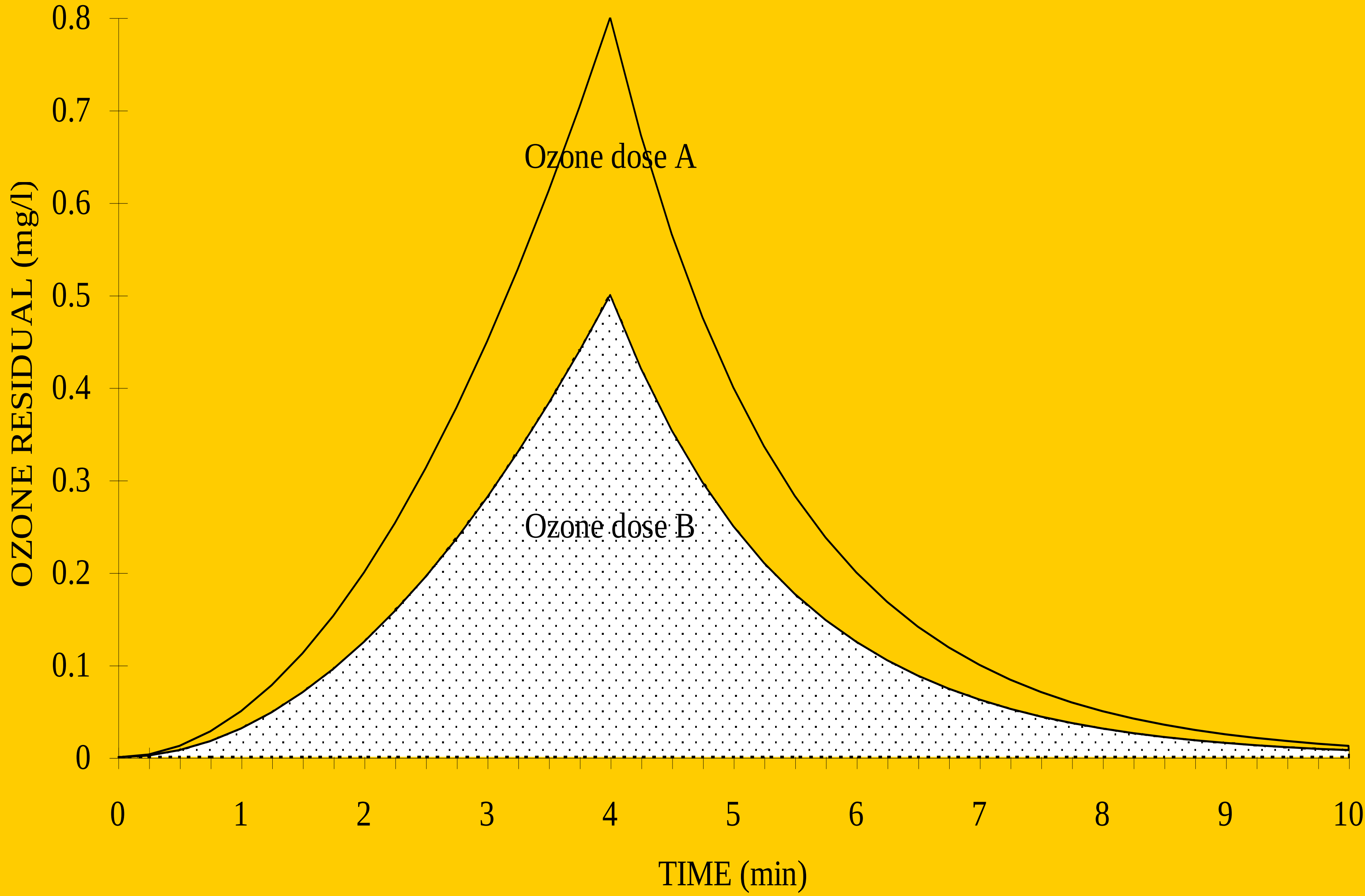
AUTOMATIC OZONE INJECTION, FILTRATION AND RECIRCULATION SYSTEM FOR IRON, MANGANESE
AUTOMATIC FILTRATION SYSTEM
STORAGE TANK/ CONTACT COLUMN
OZONE INJECTOR CREATES MICRO BUBBLES
PUMP, PRESSURE TANKS
AIR OR OXYGEN FEED
OZONE GENERATOR
FROM WELL
RECIRCULATING FILTERED WATER LINE BACK TO TANK
CLEAN, FILTERED WATER TO HOUSE

BUBBLE COLUMN CONSTRUCTION DETAILS

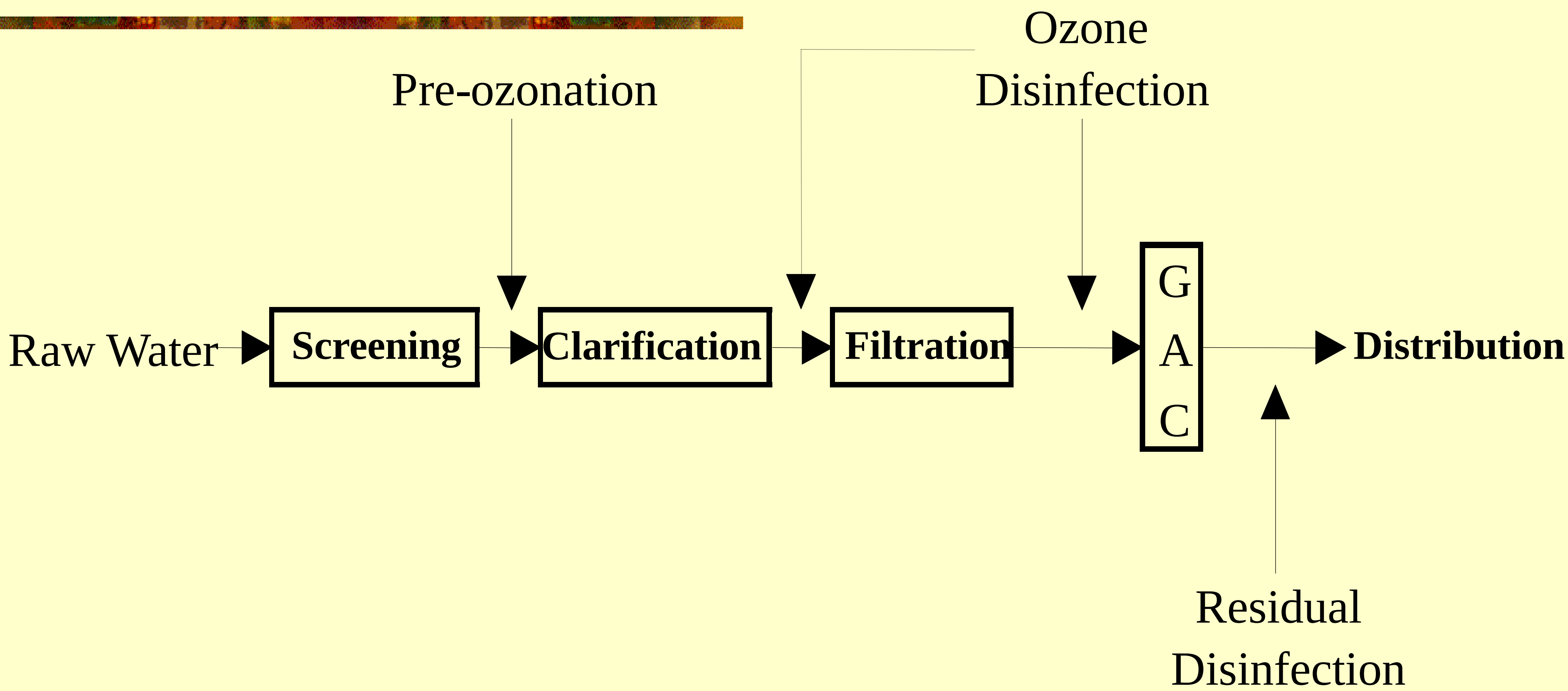




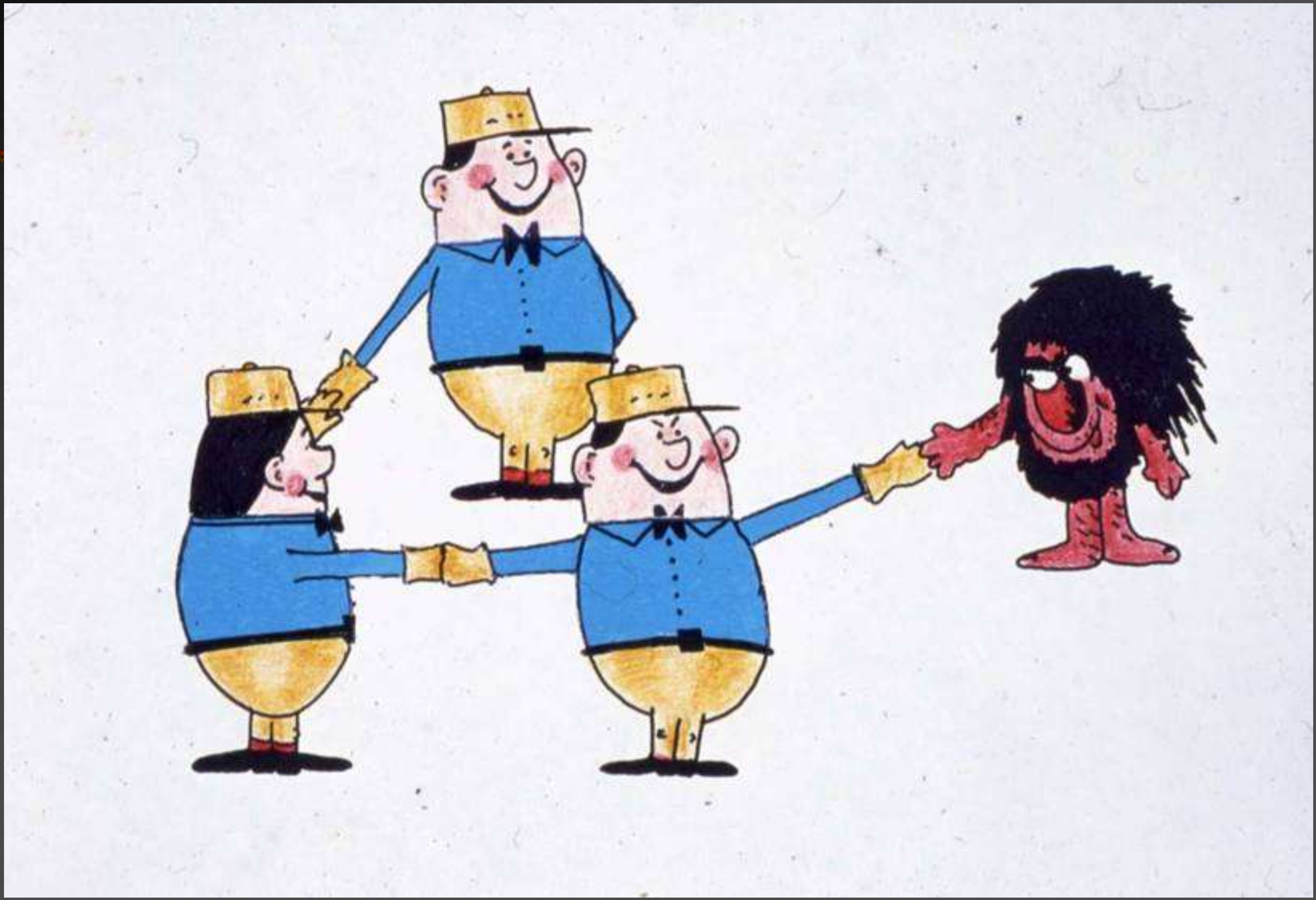
Deep Shaft Ozonation System

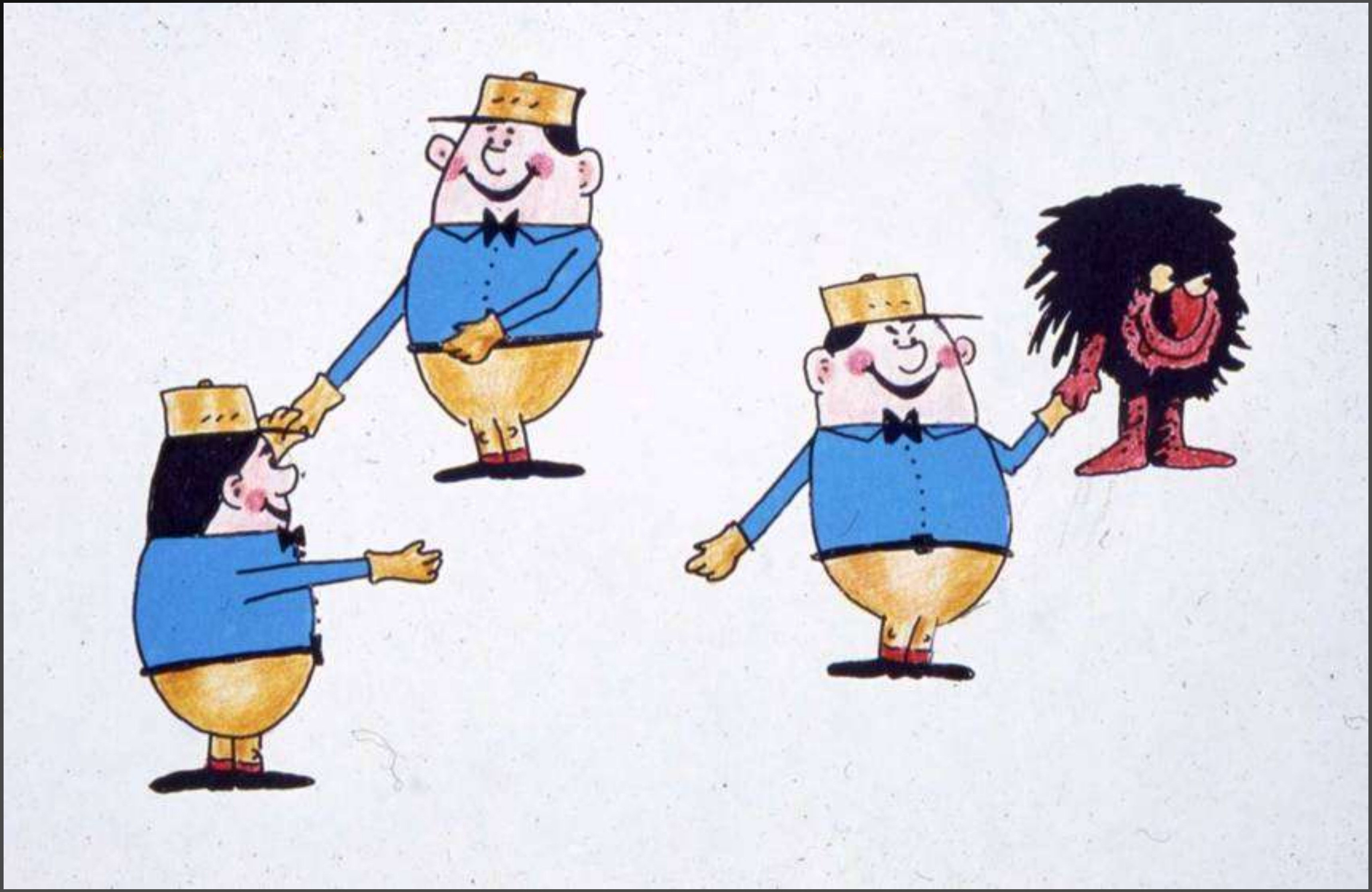


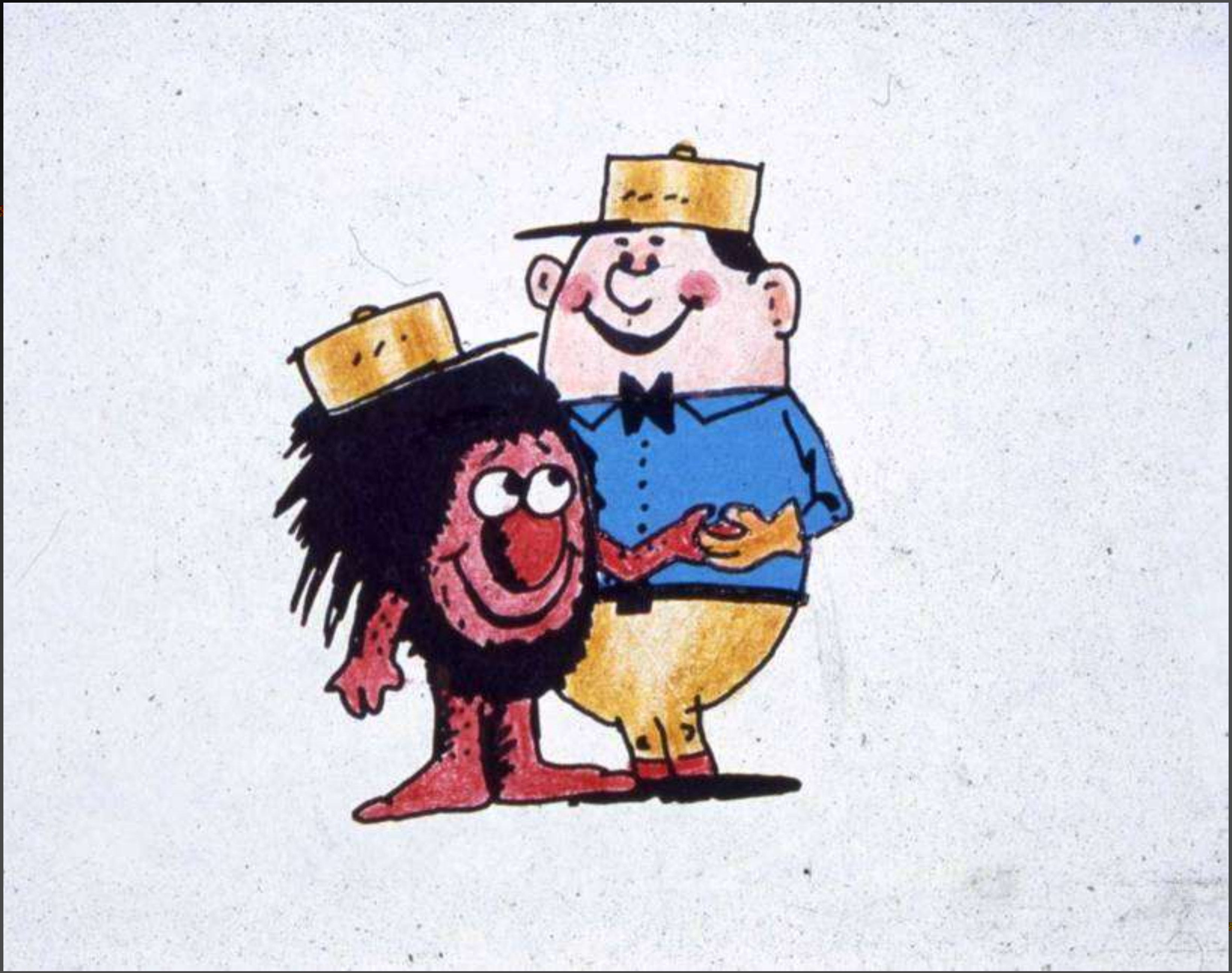
OZONE RESIDUAL (mg/l)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Ozone dose A
Ozone dose B
0
1
2
3
4
5
6
7
8
9
10
TIME (min)



Ozone
Disinfection
Pre-ozonation
Raw Water
Screening
Clarification
Filtration
G
A
C
Distribution
Residual
Disinfection

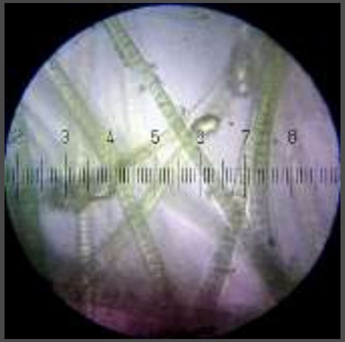






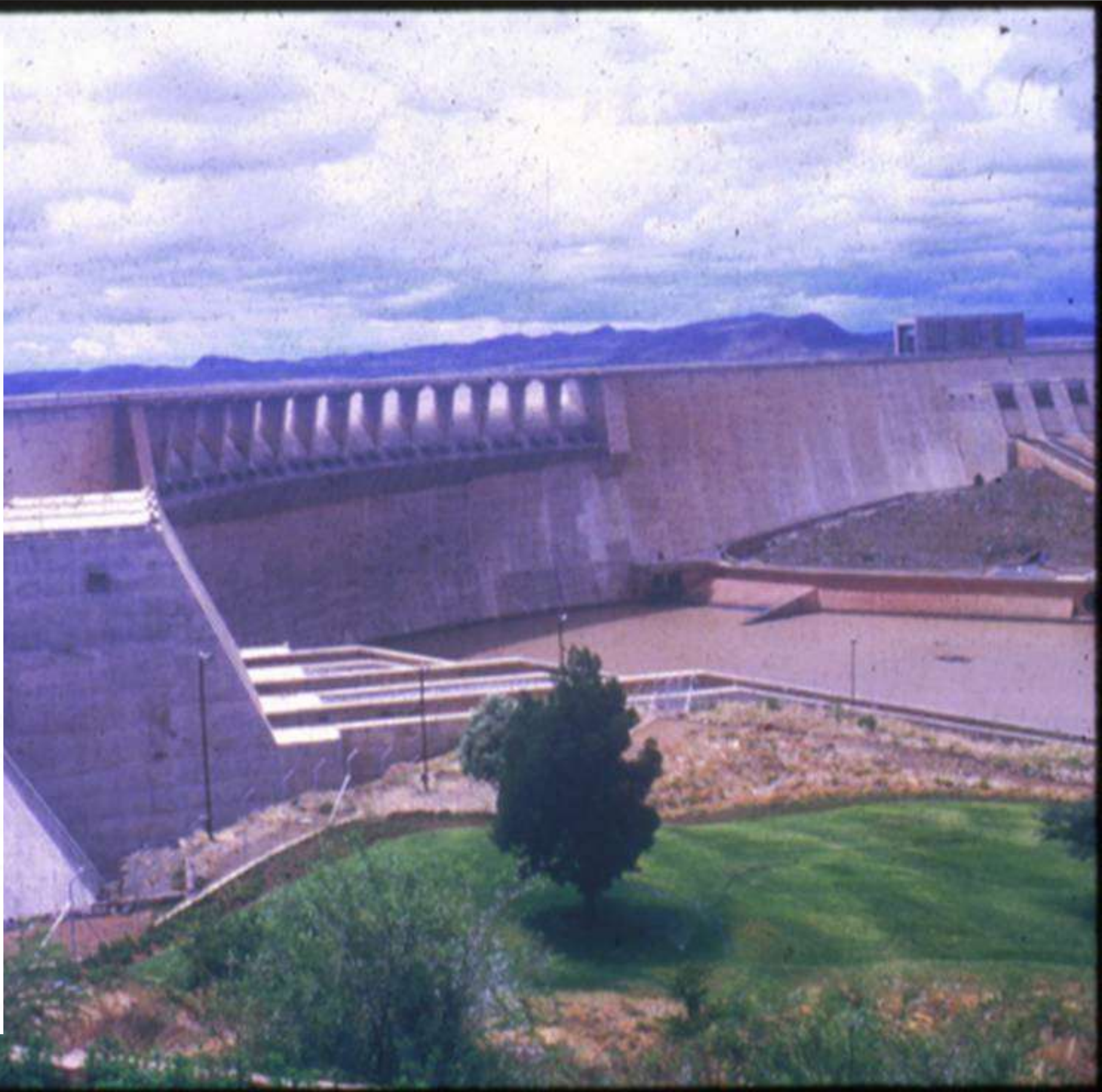
OTHER USES OF OZONE IN WATER TREATMENT

- **Iron and Mn removal**
- **Color removal**
- **Geosmin and 2-MIB**
- **Cyanotoxins – cylindrospermopsin, microcystin, anatoxin***
- **Microflocculation**
- **Biodegradability**



***Produced by** *Cylindrospermopsis, Microcystis* and *Anabena* genera

Scarce Water Resources near Mines



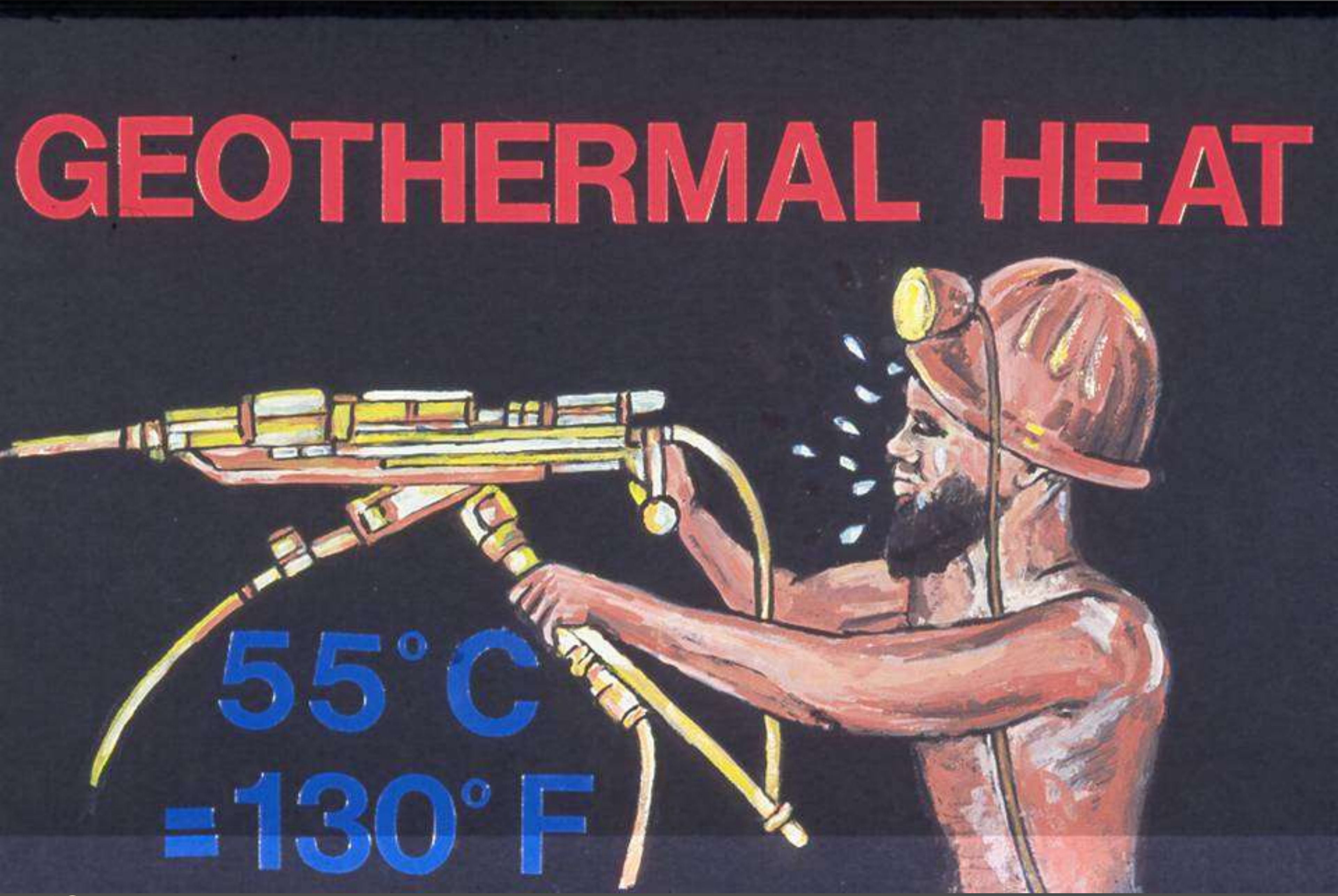
Further Applications of Ozone in The Water Technology Field

- **Wastewater treatment**
- **Effluent disinfection**
- **Cooling water treatment**
- **Swimming pools**
- **Ozonated ice**
- **Ozonated air**
- **AOP (advanced oxidation processes)**

Mine Water Cooling

Case Study: Mining Application


2 ½ miles
GOLD
REEF


GEOTHERMAL HEAT
55°C
=130°F

DUST


CHILLED
SERVICE
WATER
~~TEPID
POTABLE
WATER~~

NITRITE SOURCES IN MINE WATER

EXPLOSIVES

MICROBIAL ACTIVITY

- $NH_3 + O_2 \rightarrow NO_2^-$
  Nitrosomonas
- $NO_2^- + O_2 \rightarrow NO_3^-$
  Nitrobacter

POSSIBLE INHIBITORS

- High temperatures
- Heavy metals
- Disinfectant byproducts or residues


2
3
4
A
D

Ozonation Bubble Column

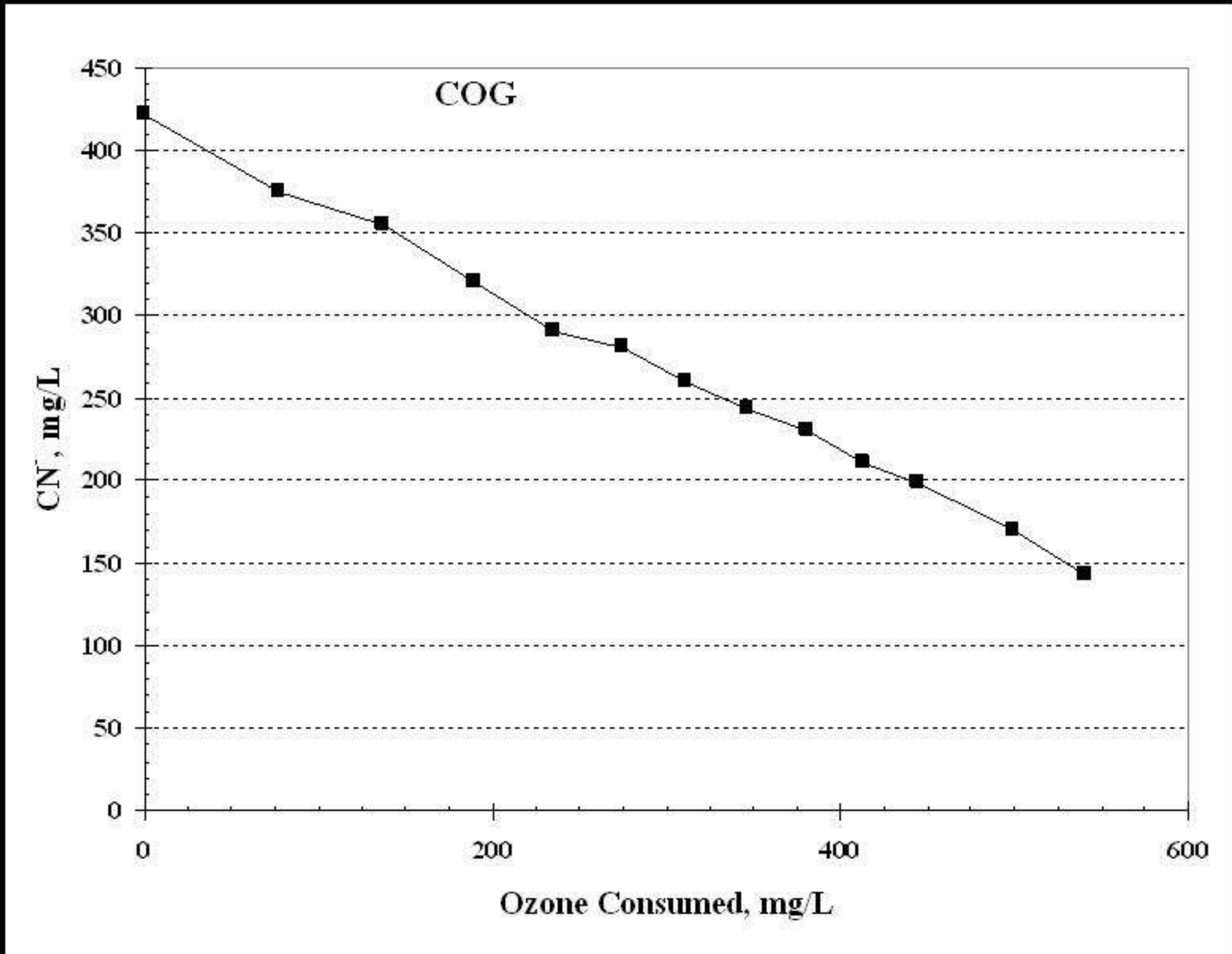
Oxidation of cyanides, thiocyanate and TOC in the Reclamation of Water in Steel Processing

- BHP near Wollongong, Australia reuses wastewater after biological and activated carbon treatment
- Cyanides interfere with biological treatment and need to be lowered to 200 mg/L before activated sludge
- Cyanates are incompletely removed if over 250 mg/L

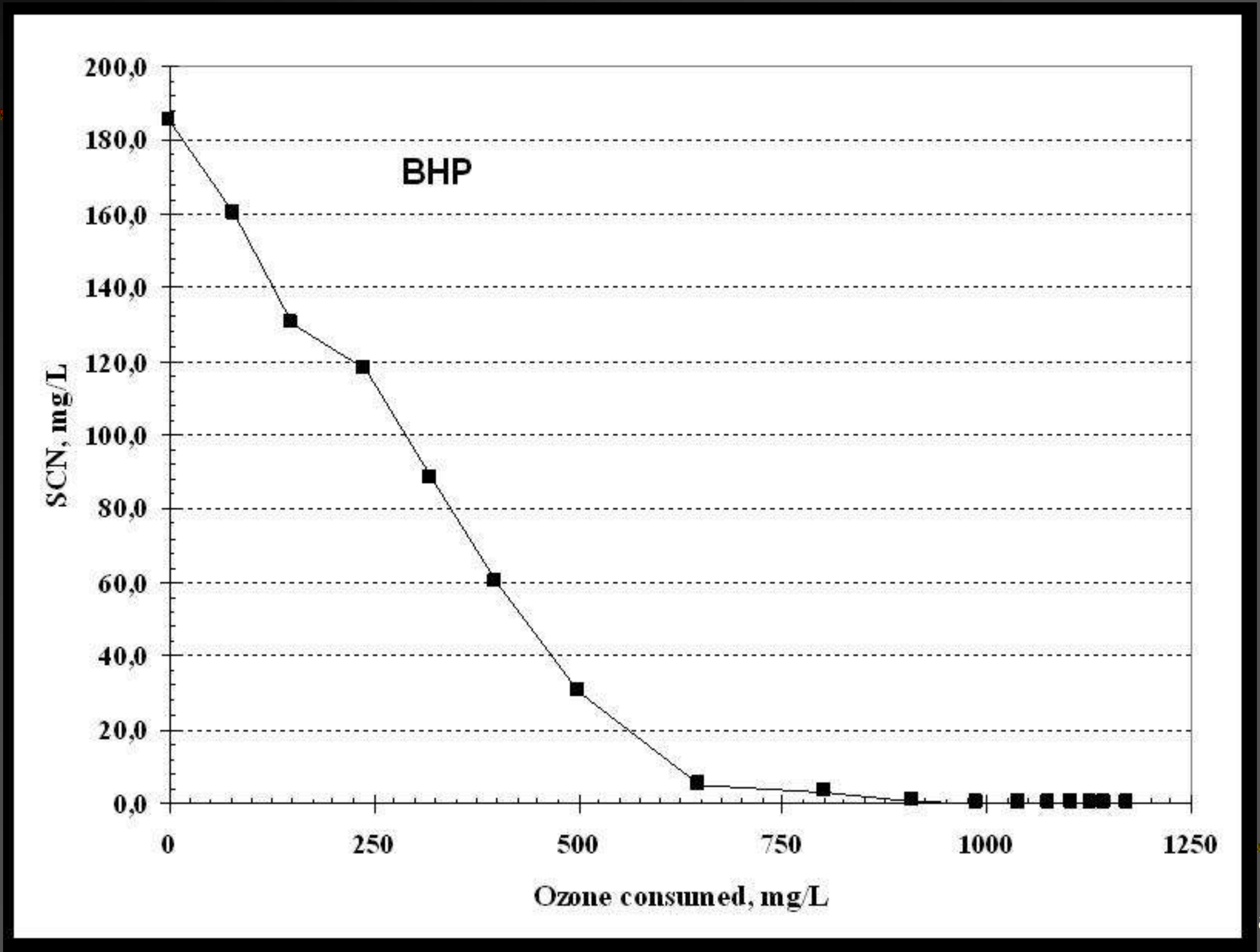
BHP Ozonation Investigations

- Ozone was tested to observe efficacy to remove CN- and SCN-
- Ozone requirements due to competitive reactions observed
- Ozone needs to replace or enhance activated carbon treatment

CYANIDE REMOVAL FROM COG

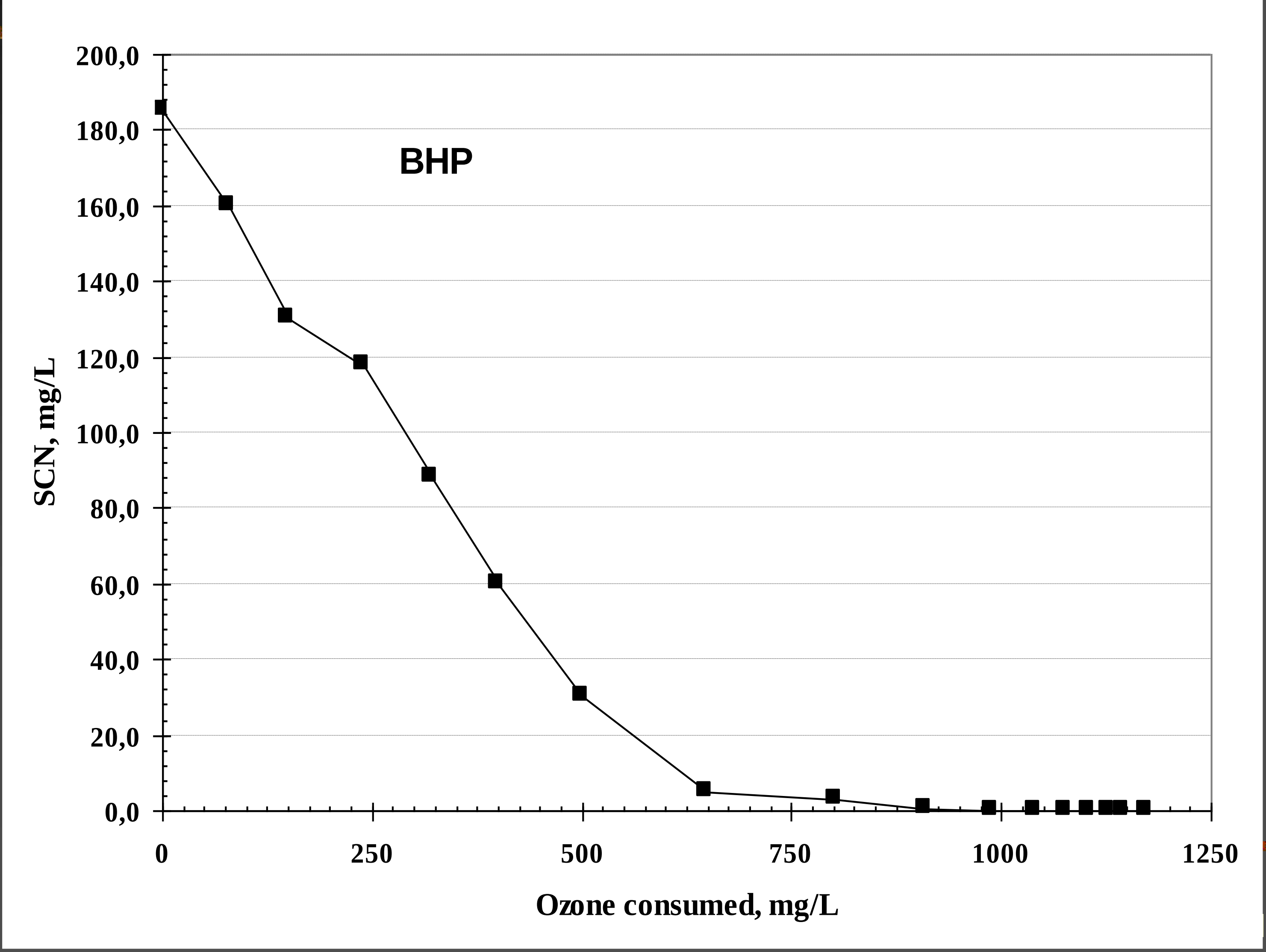


CYANIDE REMOVAL FROM BHP

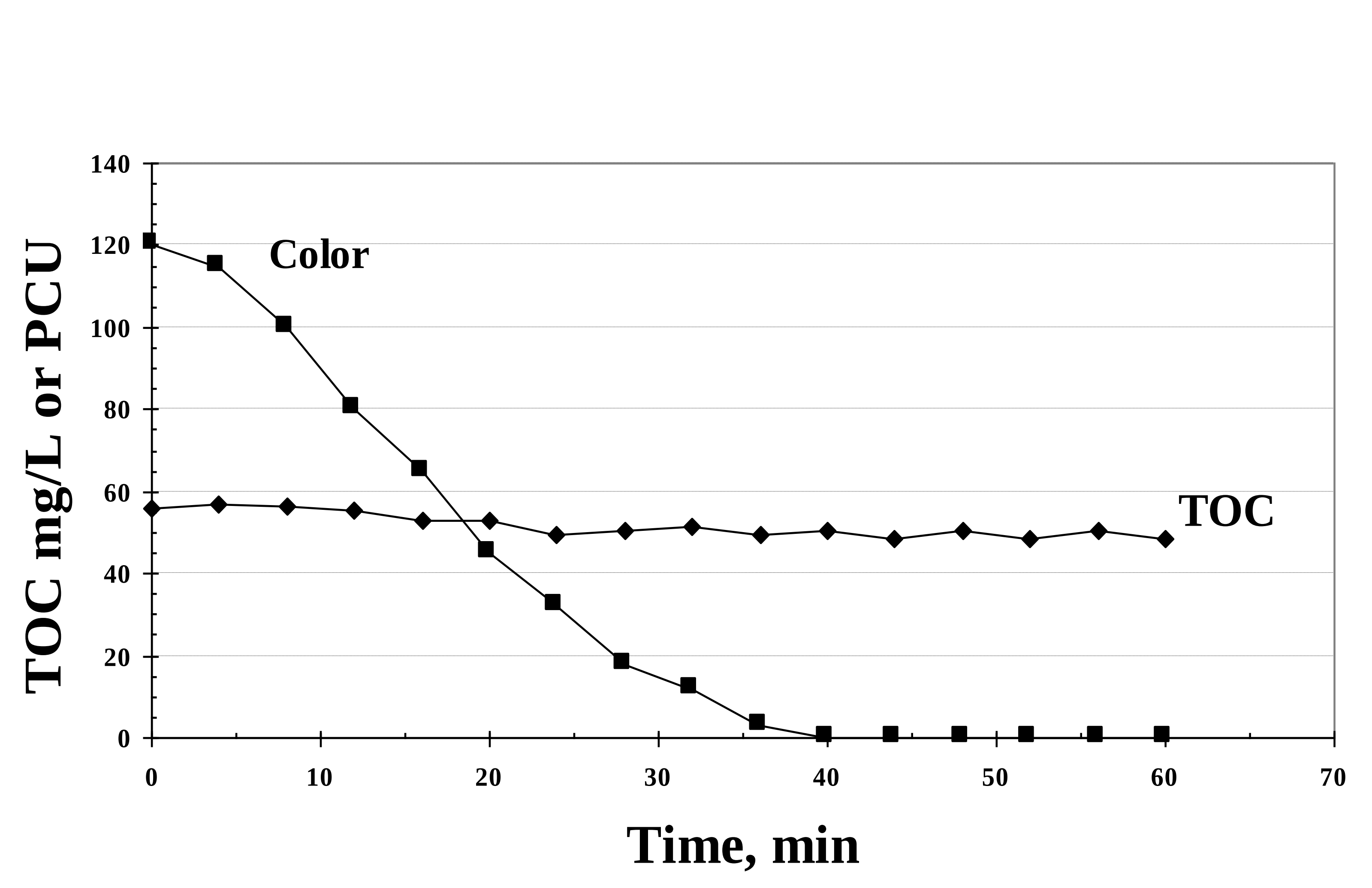


ations

CYANATE REMOVAL FROM BHP



TOC AND COLOR REMOVAL FROM ACTIVATED SLUDGE EFFLUENT



Cost Implications: CN-

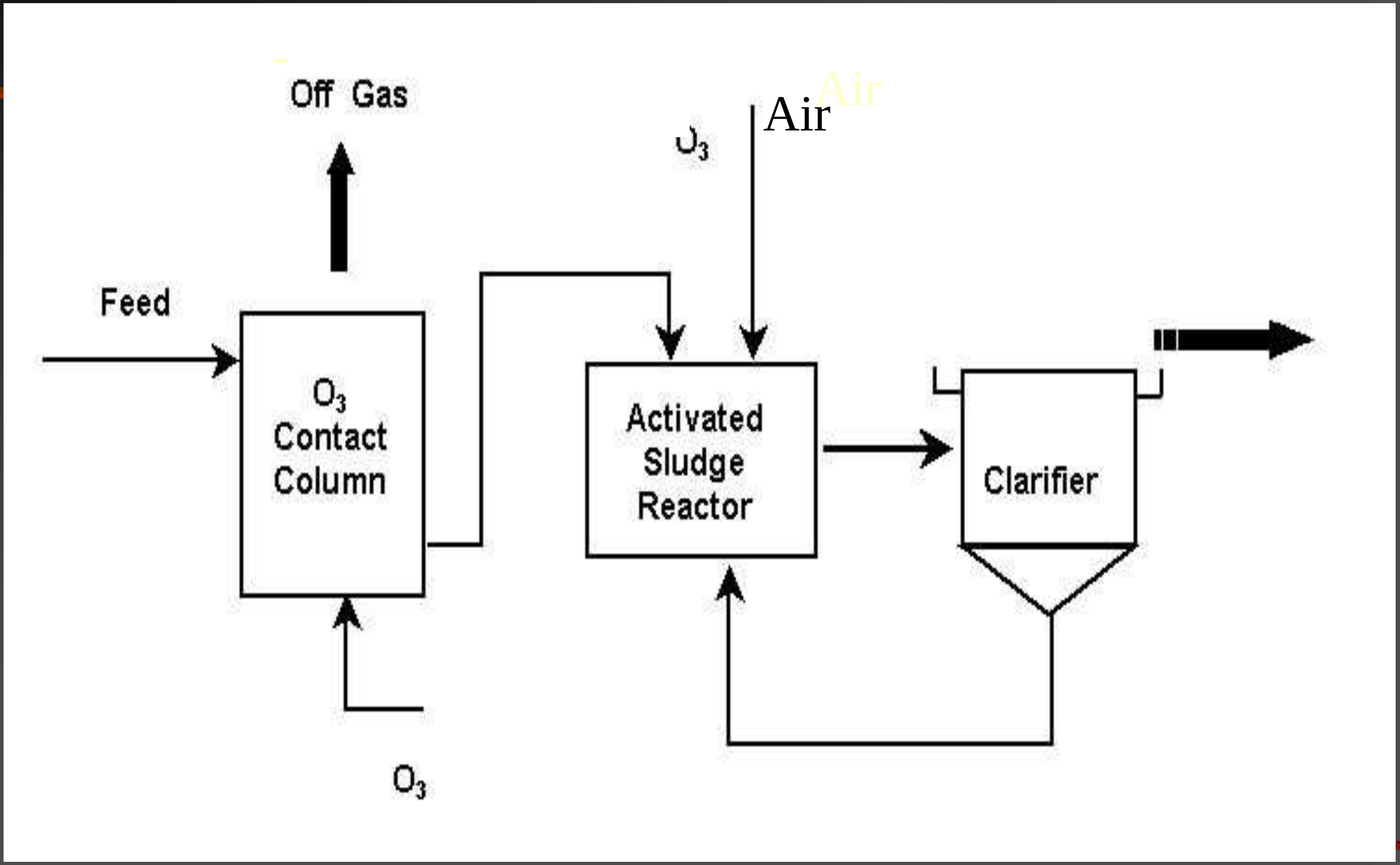
- **Capital cost of ozone installation $ 0.64 million**
- **Amortisation, maintenance operation *$16,000 per month***
- **Present alternative, formaldehyde costs $ 7000 per month, more COD**
- **Ozone not cost effective**

Cost implications: SCN-

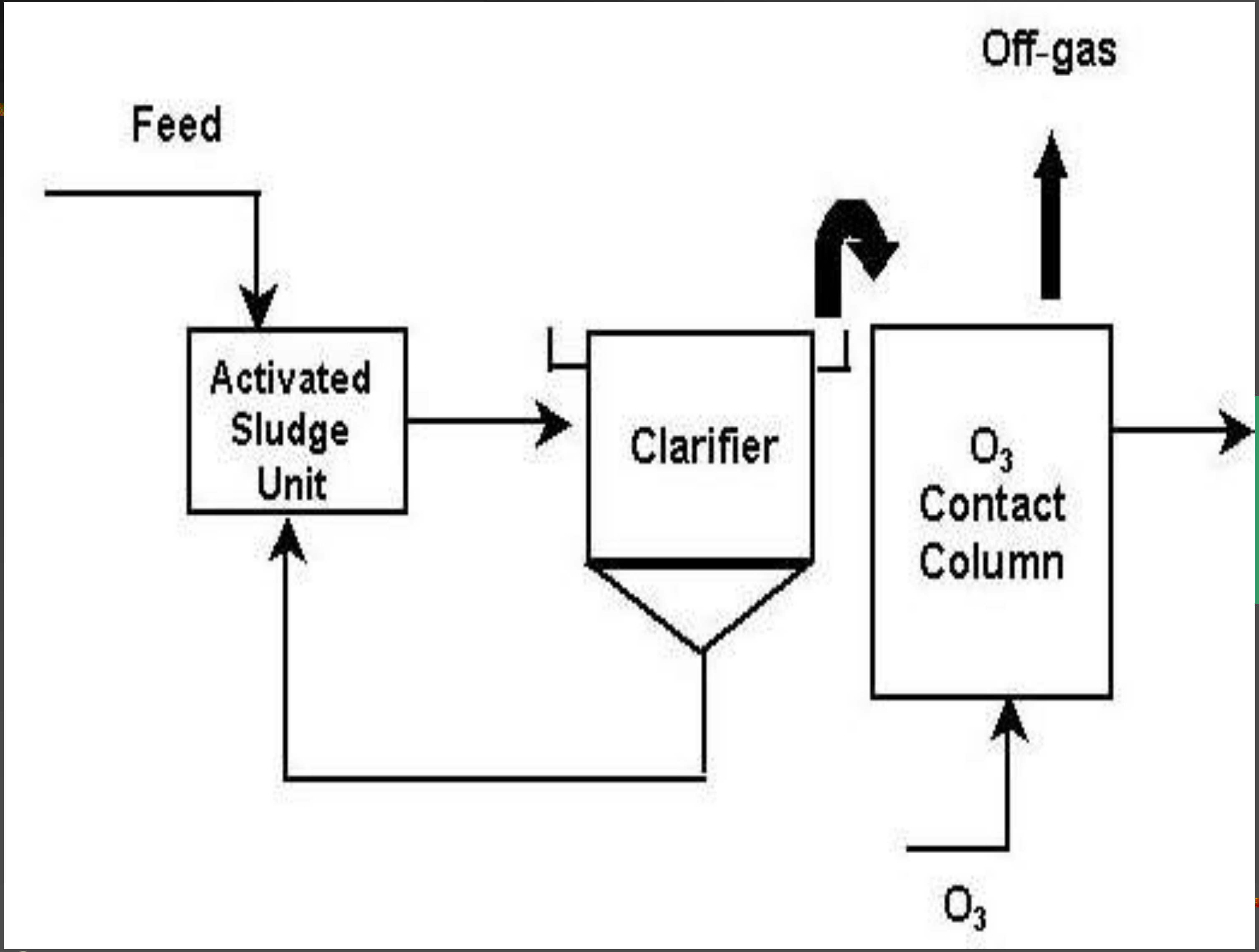
- **Capital required $ 2.0 million**
- **Monthly costs $ 76 000**
- **No other method SCN- removal** There will be a much smaller risk in achieving treatment objectives
- **Ozone not economical**

SYNTHETIC ORGANIC REMOVAL BY INTEGRATED OZONOLYSIS/ ACTIVATED SLUDGE

CONVENTIONAL PREOZONATION + ACTIVATED SLUDGE



POST-OZONATION: Remove degradables first

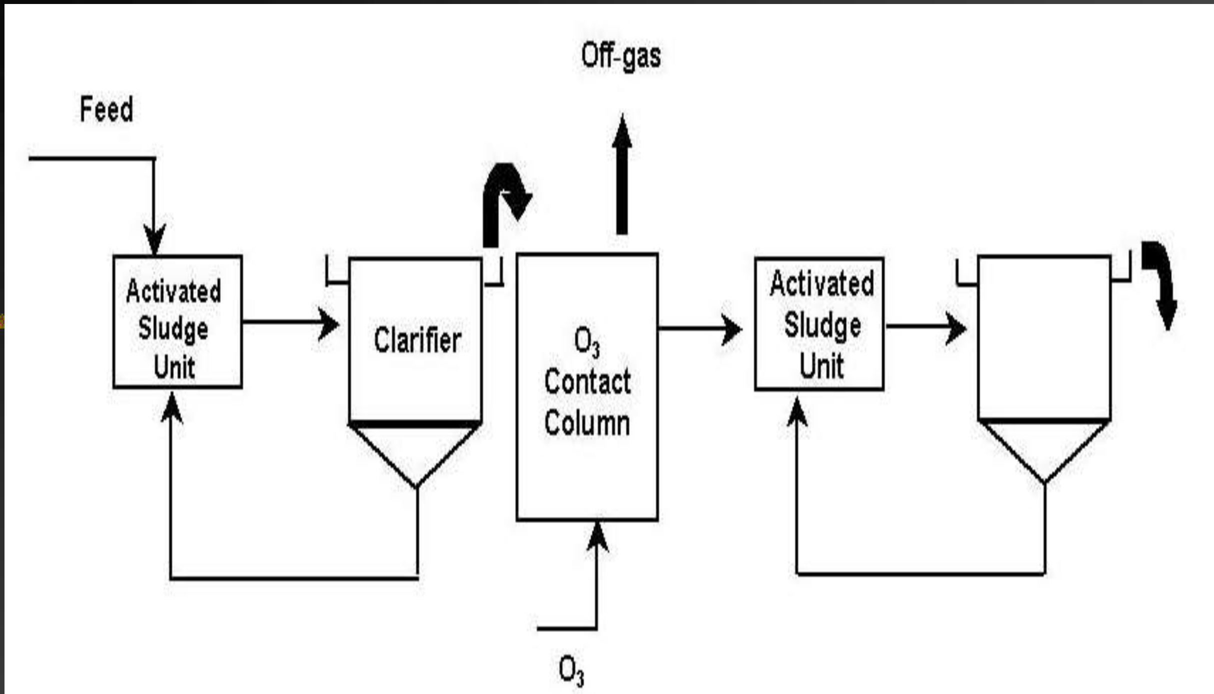


More Treatment required

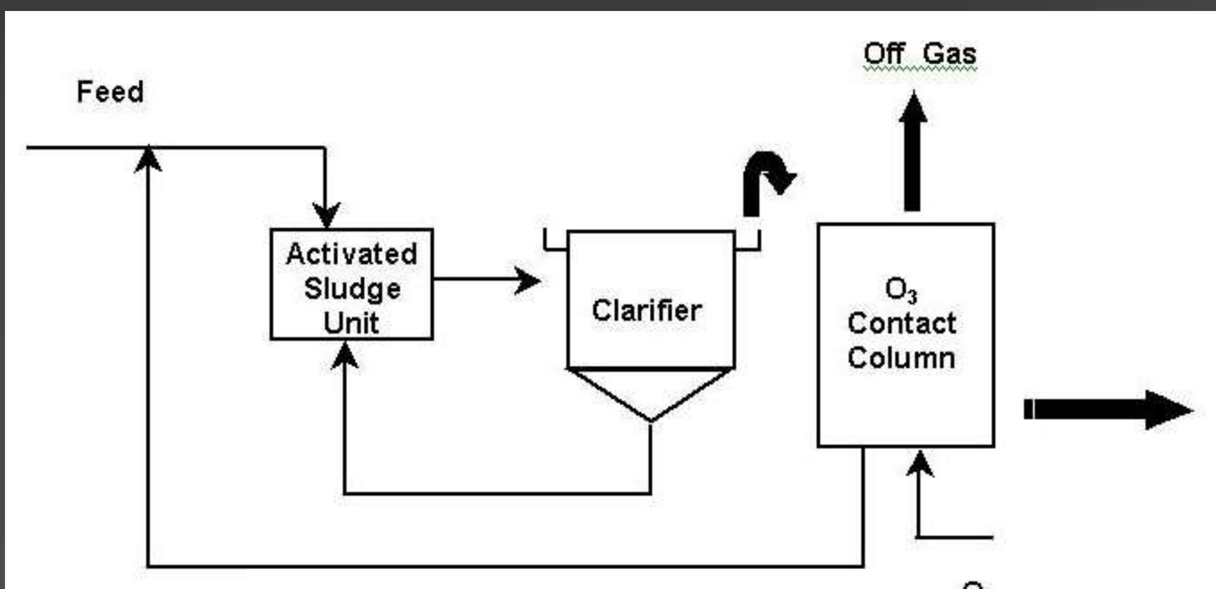
Since ozonolysis results in biodegradable byproducts, more biological treatment required after post-ozonation

This requirement can be resolved in two possible ways:

- ¶ **another biological treatment stage**
- ¶ **recirculation to biological treatment**



Biological treatment before and after ozonation

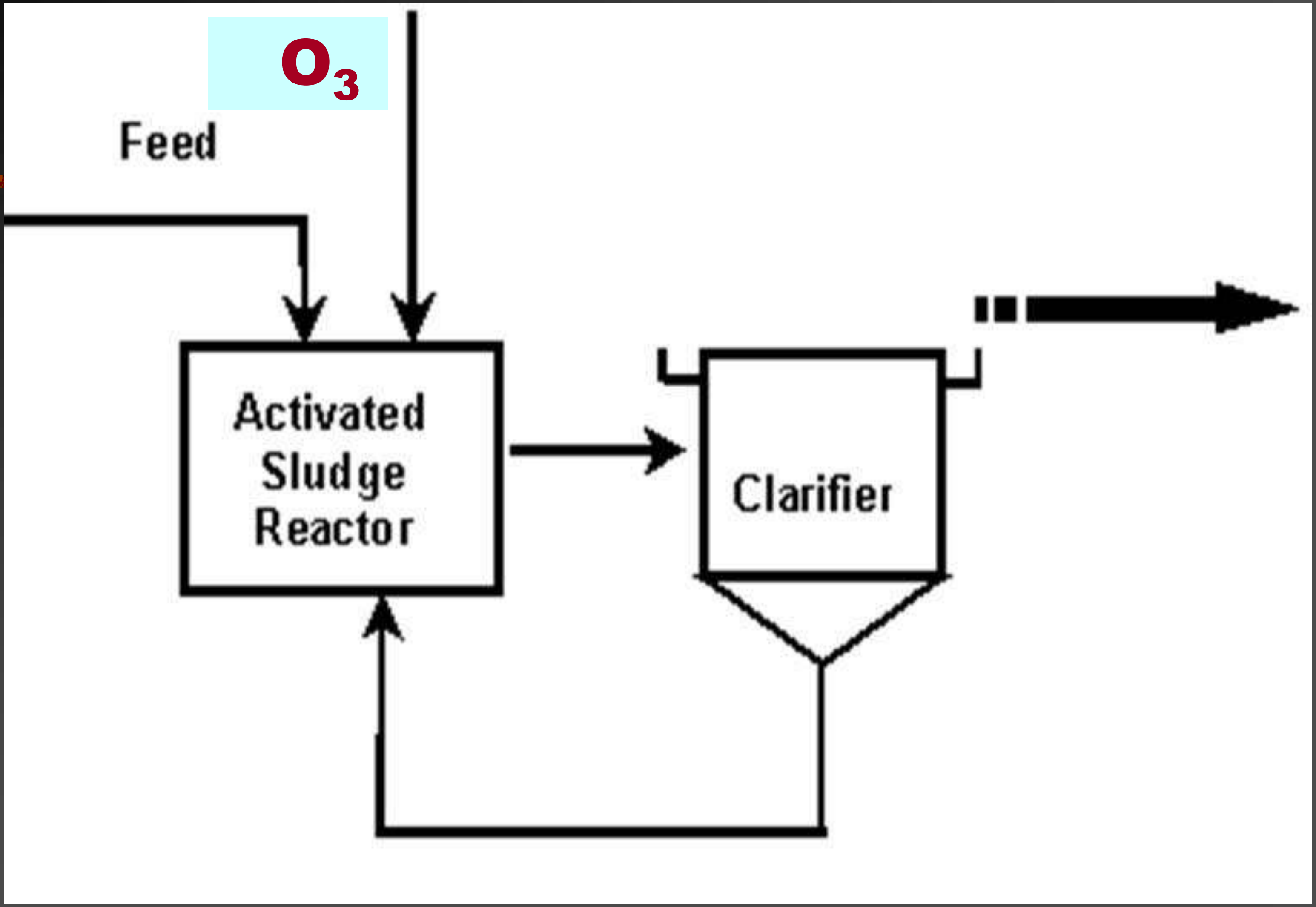


Ozonated Recycle

Using a large ozonated recycle

Neither approach is quite satisfactory:

- Another biological treatment stage would be costly and
- Recirculation never results in complete treatment and increases flow through the unit



THE SOLUTION INVESTIGATED

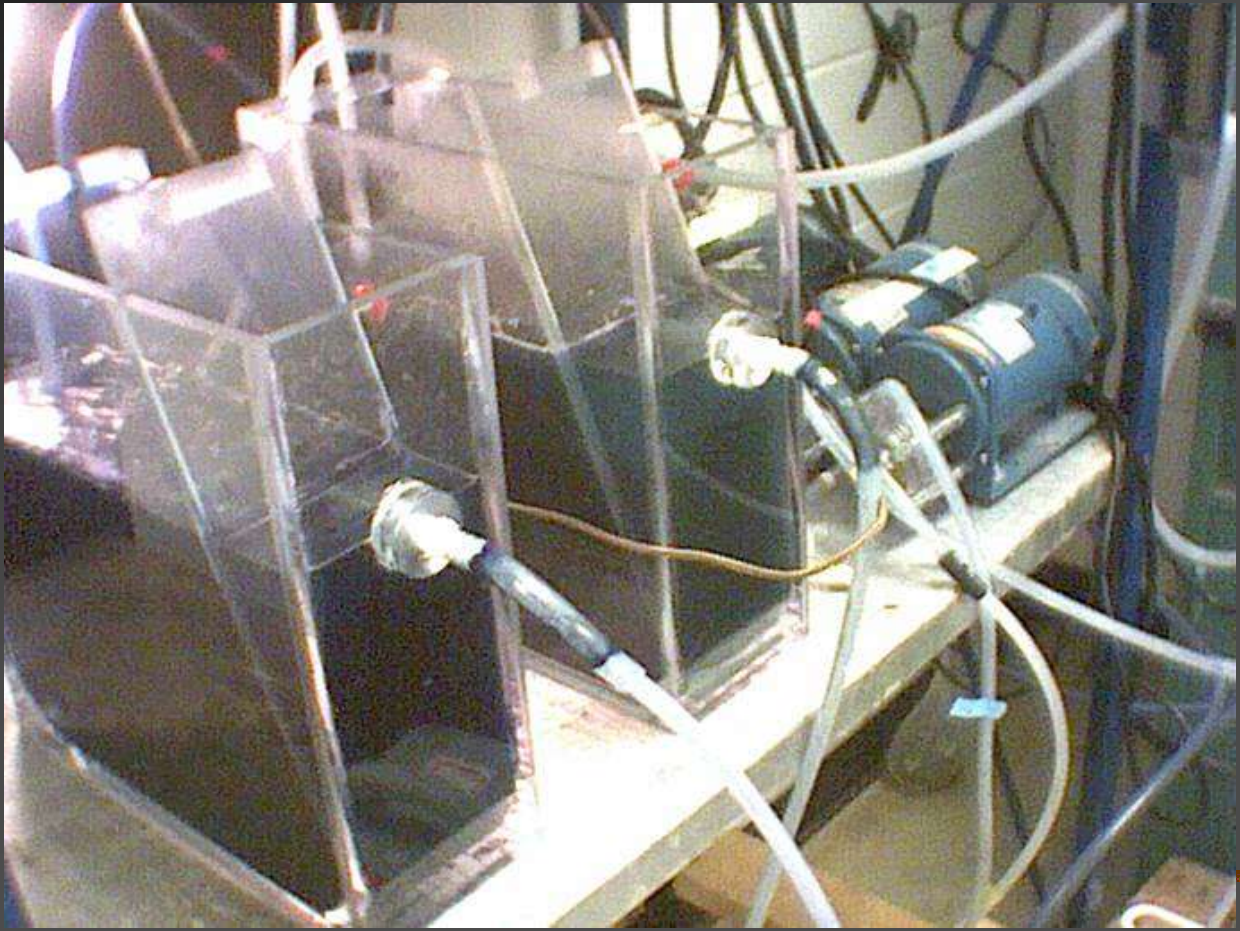
Expected benefits of ozonation within the activated sludge system:

- Ozone reacts with effluent level concentrations
- All effluent gets “recycled”, i.e. all degradable byproducts subjected to biological treatment
- At high enough organic ozonolysis reaction rates, no residual ozone for bacterial inactivation
- Simpler process configuration

Experimental Set-up

Activated sludge with wastewater containing methylene blue

ozonated

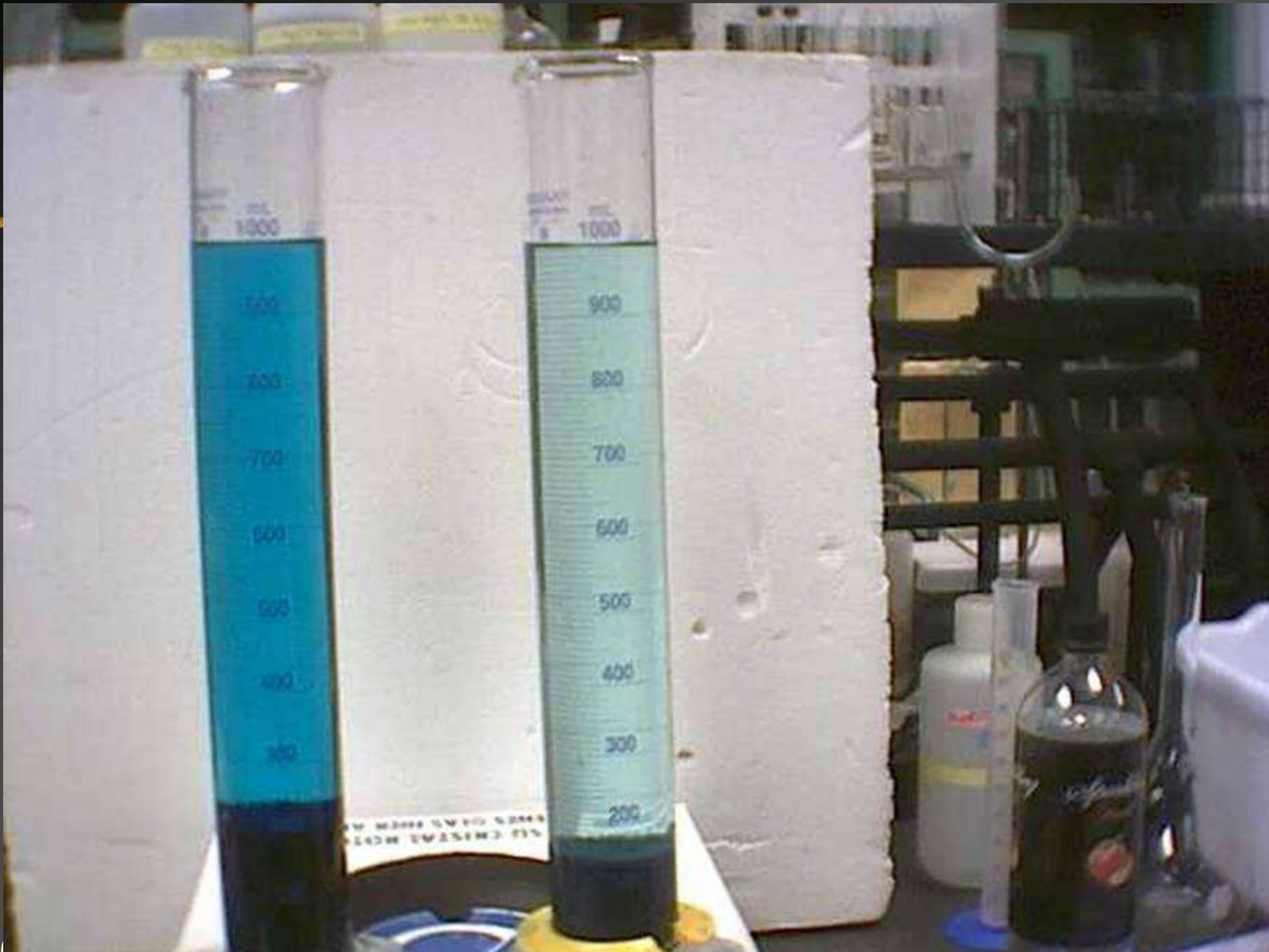


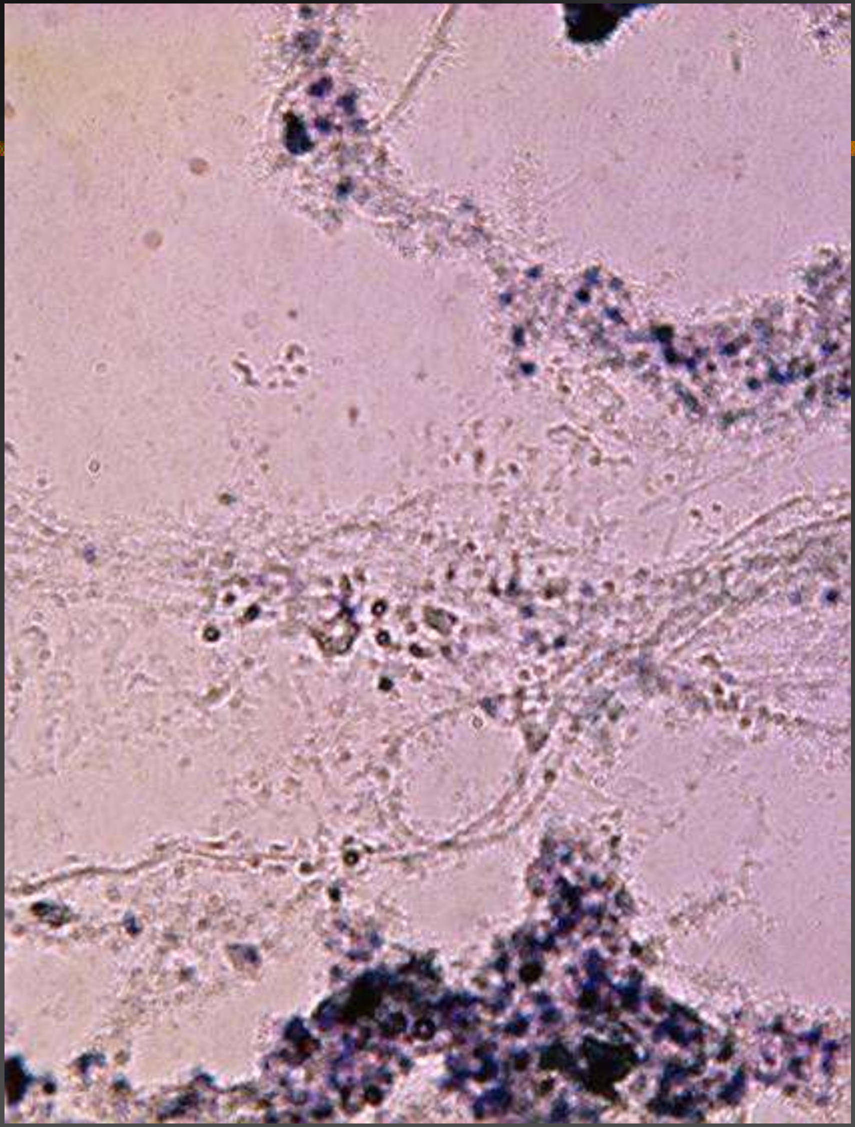
Results

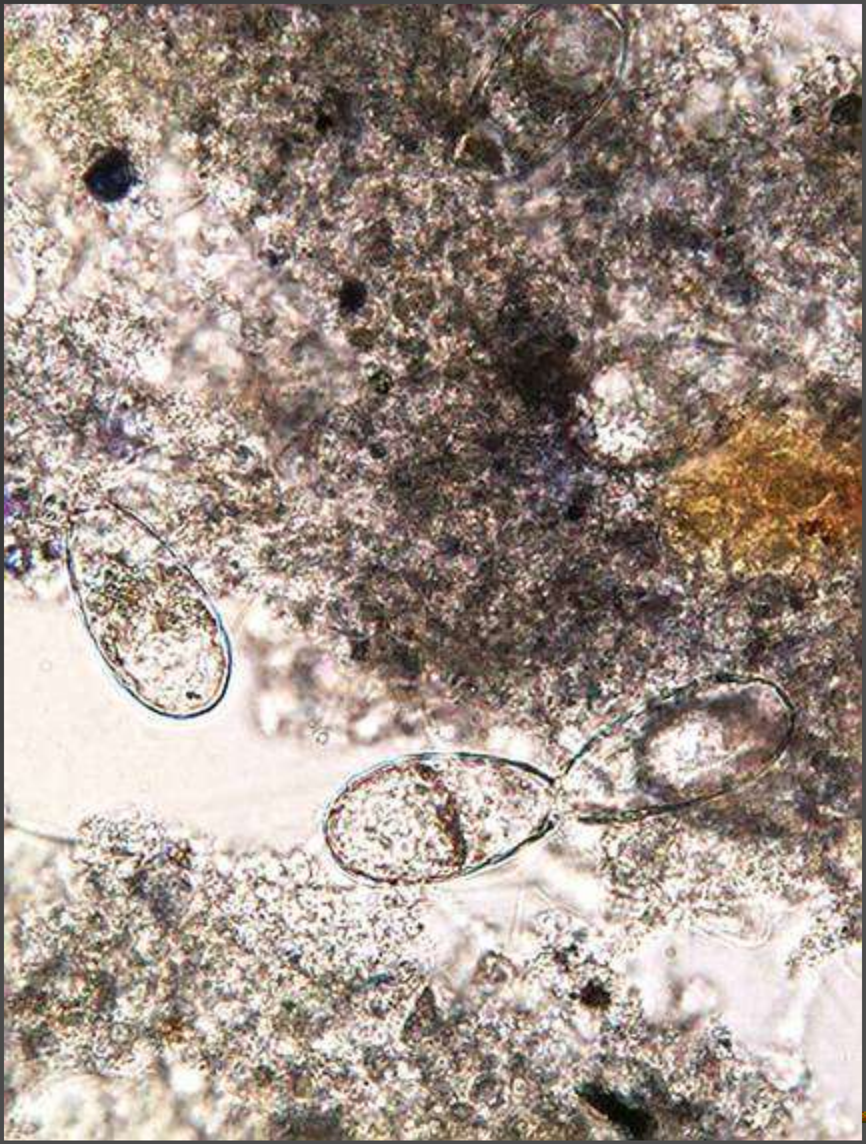
- MeBl removal in ozonated activated sludge 95%

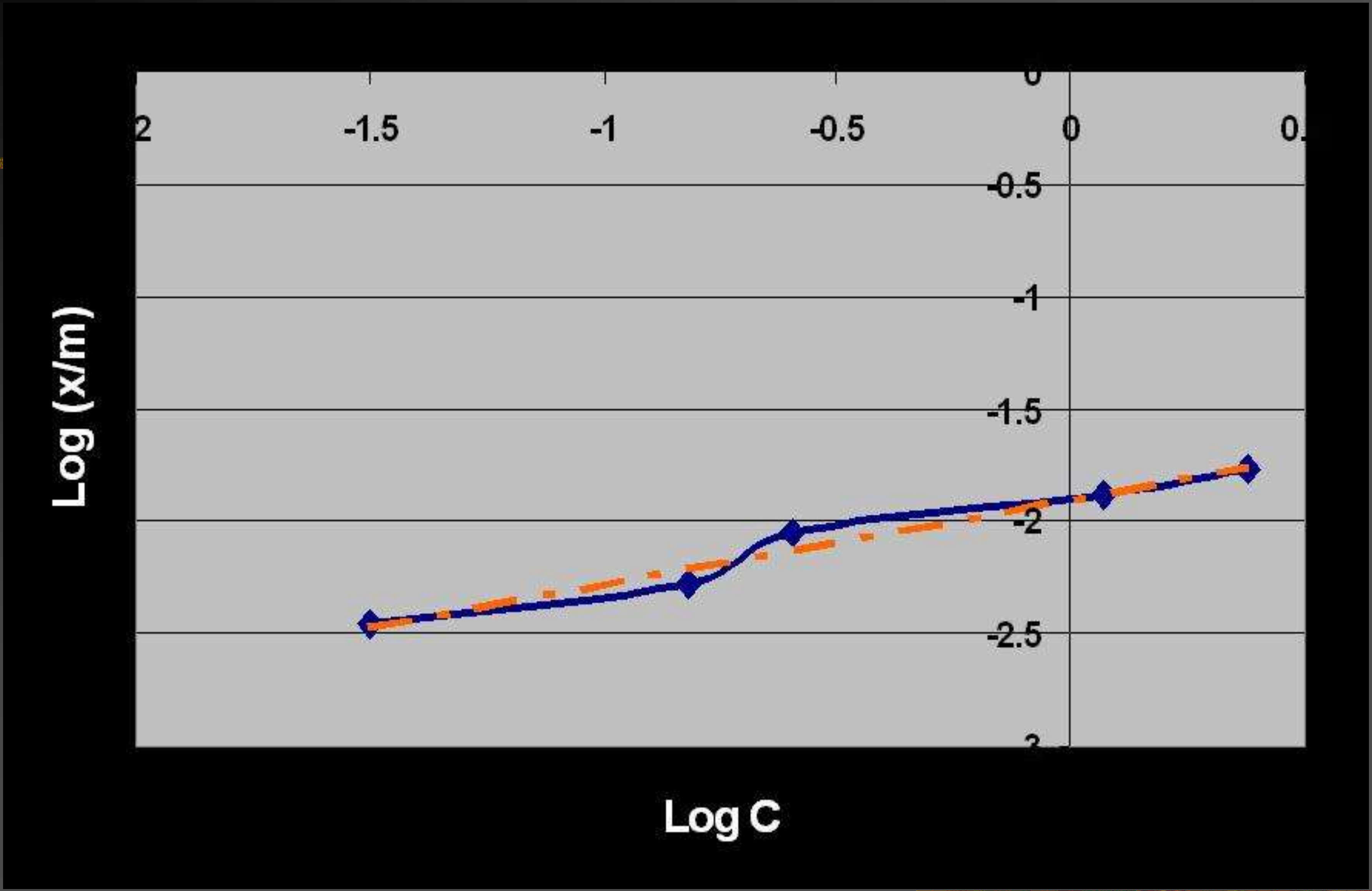
  vs. 40% in control
- COD removal in ozonated activated sludge 80.5%

  vs. 79.5% in control
- Better biomass settling


mL
1000
900
800
700
600
500
400
300
200







Log (x/m)
Log C
-1.5
-1
-0.5
0
-0.5
-1
-1.5
-2
-2.5

Conclusions

- Ozone can be dosed within an activated sludge system for the ozonolysis of non-biodegradables
- Effect on biomass beneficial, if minimal
- Byproducts mainly biodegradable
- Economical integrated procedure

Pilot Scale Implementation at Van Diest Supply Company, Iowa