Enhancement of Oily Sludge Biodegradation in Historic Refinery Wastewater Lagoons

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Introduction

Historic petroleum wastes at operating or closed refineries:

- Sludge disposal pits
- Historic wastewater ponds where heavy petroleum residues have settled and resist treatment

Long-term liability at older petroleum refineries.

Potential listed hazardous classification if removed.

At some point in time, this sludge must be addressed.

Introduction

Can these sludges be treated without removal of the waste?

Introduction

Oily sludge difficult to biodegrade because of long-chain or polyaromatic hydrocarbons.

Typical remediation approaches:

- Removal—dewatering, solidification / stabilization, off-site disposal
- In-place treatment—dewatering, solidification / stabilization in place

These approaches are effective, but costly and typically disturb normal site operations

In situ biodegradation treatment typically slow

For an operating refinery operation with no immediate time constraint, in situ treatment by biodegradation can be an economical solution.

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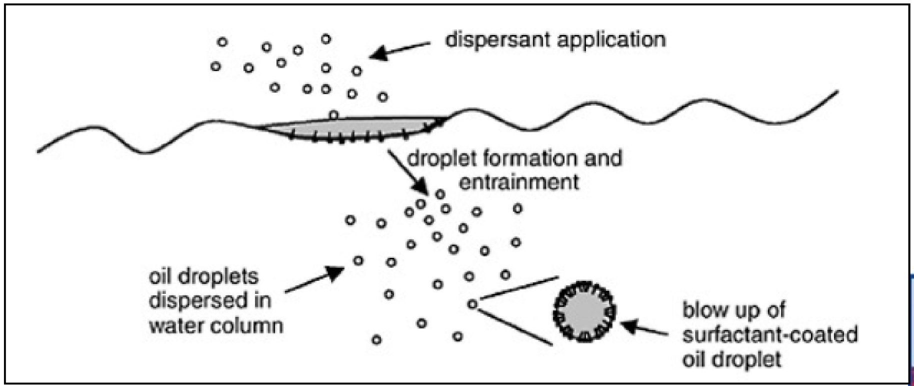
Objective

Objective: evaluate different approaches to biologically treat sludge-containing wastewaters impounded in lagoons from historic refinery wastewater treatment operations.

- Improve dispersion of the oily material to increase oil / water interfacial area and mass transfer into water phase
- Utilize microbial consortia known for heavy hydrocarbon biodegradation.



Source: Coolbaugh, "Dispersant Efficacy and Effectiveness"

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Objective

Investigate:

- Laboratory experiments of dispersion and biodegradation
- Modeling of the dispersion and biodegradation process is also conducted for comparison with the laboratory results
- Utilize dispersants and microbial consortia developed for oil spill applications for enhanced performance in this environment

LONG-TERM GOAL: attain nearly complete oily sludge biodegradation in an aqueous environment within a period of a couple of years.

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Investigative Approach

<u>Oil dispersant effectiveness test</u>:

- Oil / dispersant mixture added to water surface in flask;
- Mixing performed to disperse oil droplets into bulk water;
- Portion of bulk water retrieved through side spout;
- Oil dispersed in bulk water phase removed by dichloromethane (DCM) extraction;
- Oil concentration determined by UV absorbance in DCM;
- Calculate amount of DCM dispersed into water from original amount added to surface.

Reference: 40 CFR Part 300, Appendix C

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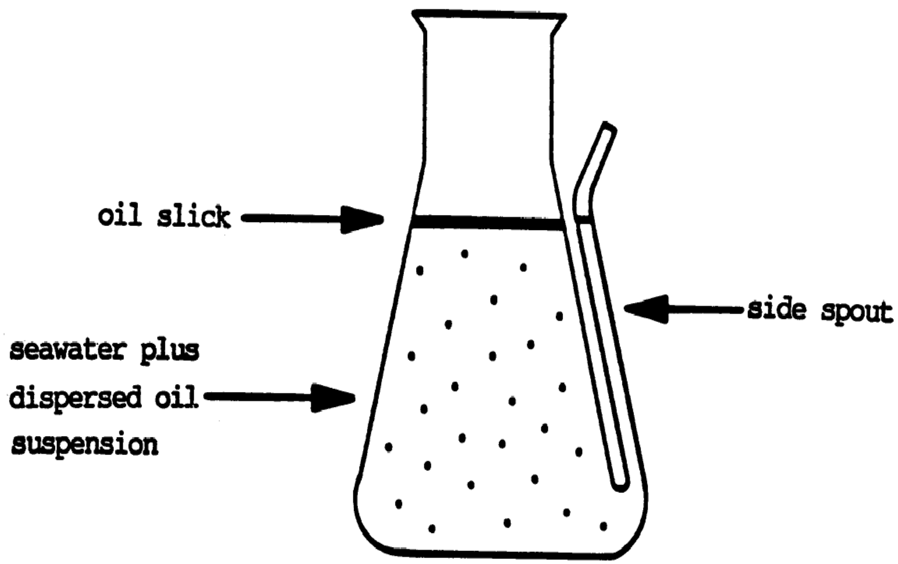
Investigative Approach

Commercially available materials used:

- Dispersants:
  - Petroclean
  - FFT formulations
  - Confidential commercially-available oil spill dispersant
- Oil degrading consortia
  - Oppenheimer formula

Investigative Approach

<u>Oil dispersant effectiveness test mixing regimes</u>



Source: Protection of Environment in Code of Federal Regulations (U.S.)

Orbital shaking at 150 rpm (similar to ocean / wave mixing

Baffle flask impeller mixing at 200-800 rpm

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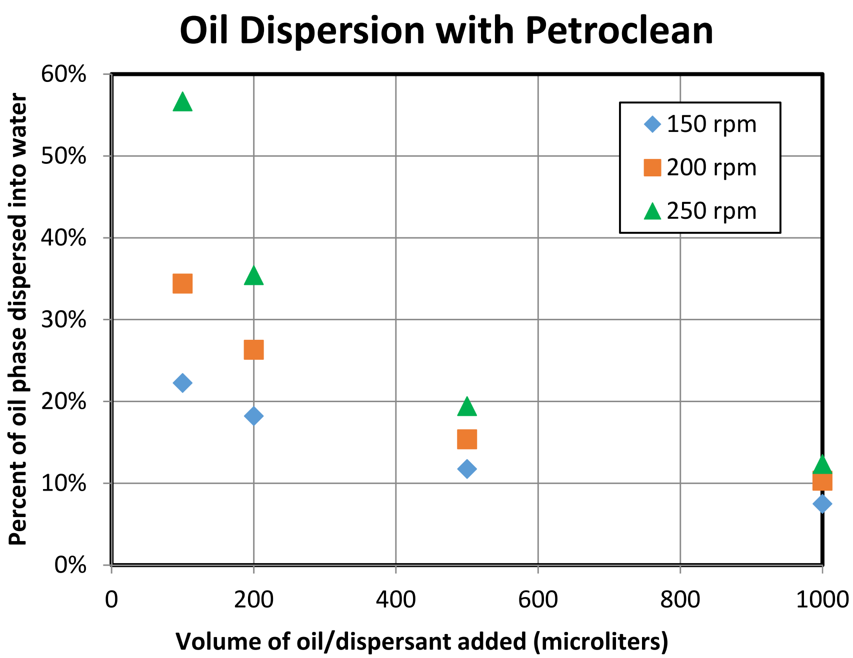
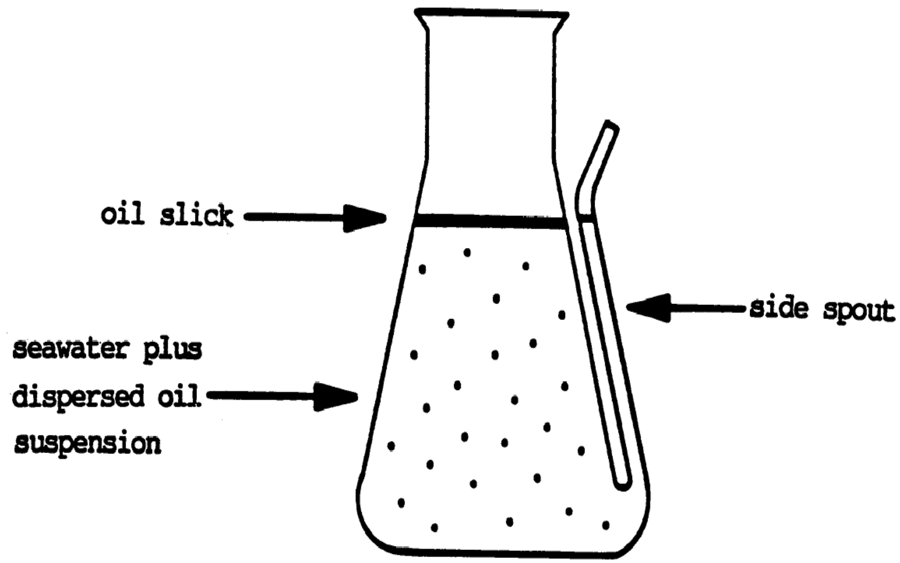
Investigative Approach

Oil dispersant effectiveness test preliminary results:



High percent oil dispersion
at lowest oil level
Suggests dispersant / water
interaction may be limiting



Orbital shaking
at 150 rpm

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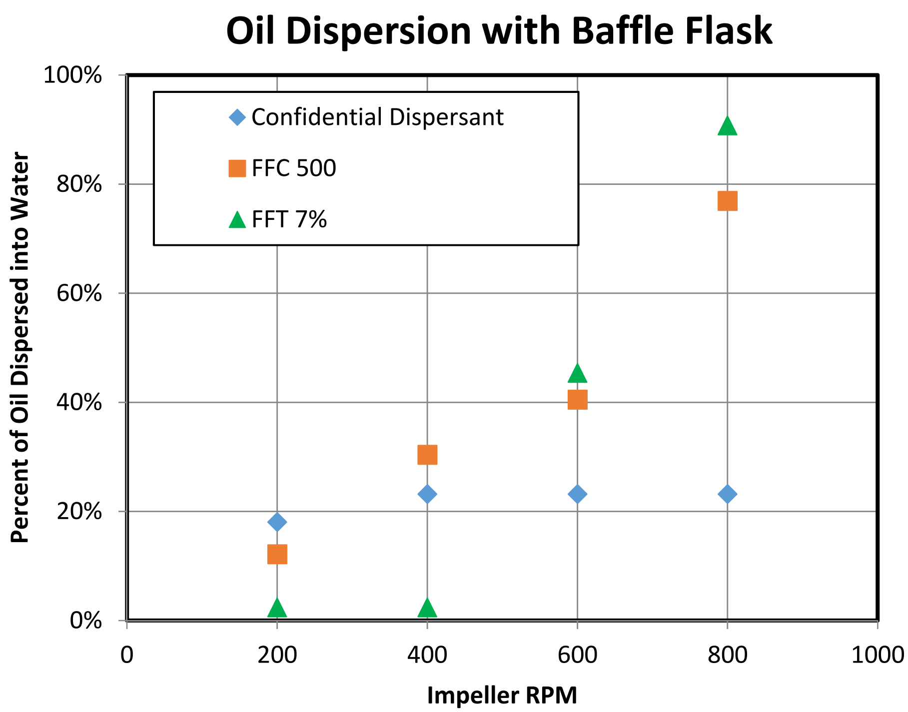
Investigative Approach

<u>Oil dispersant effectiveness test preliminary results</u>:



Increase in oil dispersed
with higher mixing rpm
for two of three dispersants

Baffle flask impeller
mixing at 200-800 rpm

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Investigative Approach

Oil / dispersant biodegradation test:

- Minimal growth media for oil-degrading microbes prepared;
- Oil / dispersant mixture added to water surface in flask;
- Mixing performed to disperse oil droplets into bulk water;
- Add oil-degrading microbial consortia to oil-dispersed-in- water solution;
- Incubate with gentle mixing for 2 to 6 weeks;
- Residual dispersed oil determined by DCM extraction and UV absorbance, after biomass removal by centrifugation.

Methodology for biodegradation testing is still under lab development.

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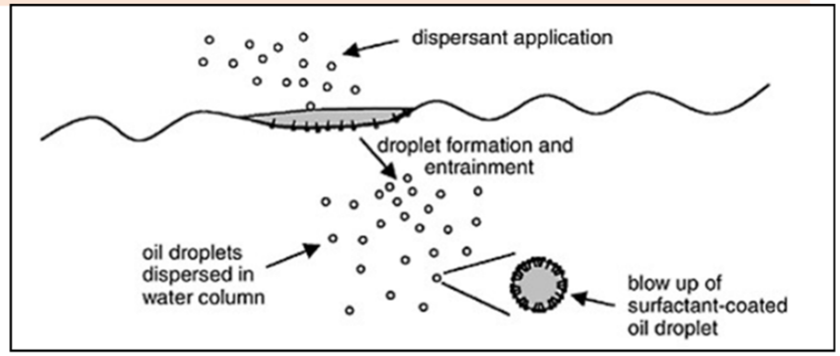
Modeling of Batch NAPL System

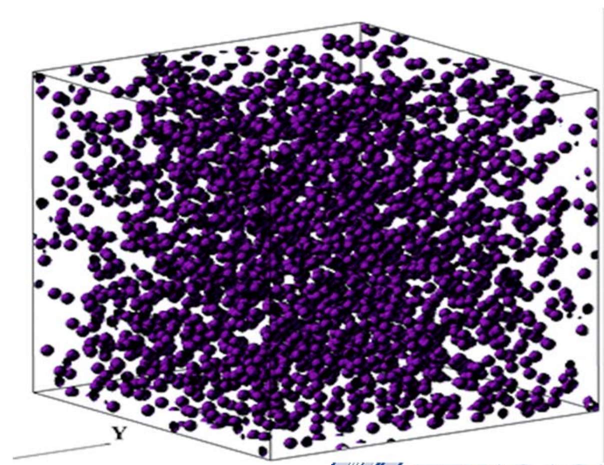
Batch system model of dispersion, dissolution, biodegradation:



Source: Coolbaugh, "Dispersant Efficacy and Effectiveness"

<u>Model assumptions:</u>

- Aerobic biodegradation (Oxygen is present in excess)
- Particles of NAPL are made of 100% of the selected compound (xylene)
- Xylene initial mass, M_x = 354 ppm
- Model on basis of (H_2O + NAPL) = 1 m^3
- M_x = 354 ppm   354 g per 1 m^3
- Diameter of particles, D_p = 100 um



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Modeling of Batch NAPL System

- Rate of mass transfer from interface into solution:
- (rate of mass transfer) = k * (Interfacial area) * (Δ Conc)
- $N_1 = k * A * (C_{1i} – C_1)$
  - N_1 = Flux at interface
  - k = Mass transfer coefficient
  - C_{1i} = Concentration at the interface
  - C_1 = Concentration in the bulk solution

Modeling of Batch NAPL System

$$\frac{dMx}{dt} = -k_c * (C^* - Cx) * (SA) * (No.P)$$

$$\frac{dCx}{dt} = k_c * (C^* - Cx) * (SA) * (No.P) - k_r Cx$$

Initial conditions	
Mx,Mass of Particles of Xylene	M_0 = 354 g
Cx,Concentration of Xylene in the Solution	C_o = 0 g/m3

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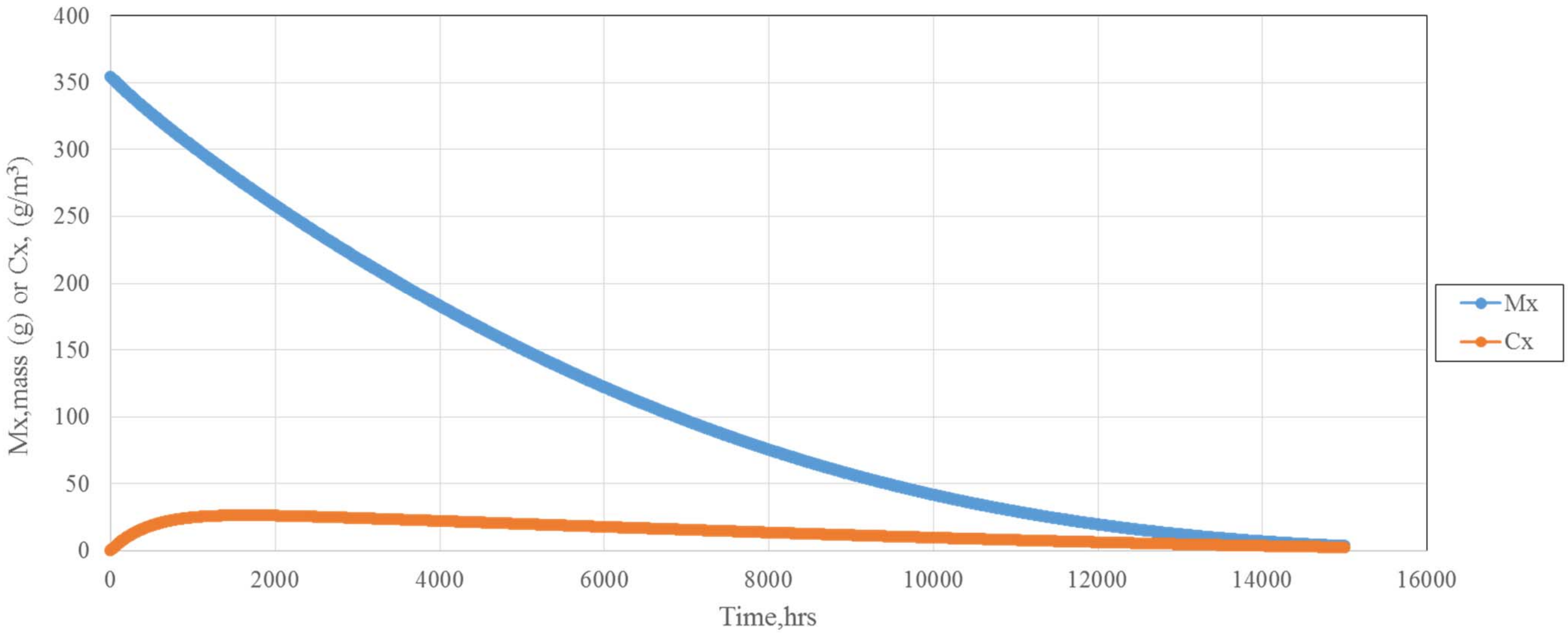
Modeling of Batch NAPL System

Definition of Variables in Model Equations

Model Parameters	Denotation	Values/Units
Mx	Mass of droplets of xylene	g
Cx	Concentration of xylene in water	g/m^3 (mg/L)
C*	Solubility limit of xylene	160 g/m^3
M_o	Initial mass of droplets of xylene (1 m^3)	354 g
C_o	Initial concentration of xylene in water	0 g/m^3
K_c	Mass transfer coefficient for xylene into water	0.0561 m/hr
K_r	Biodegradation rate constant for xylene (aerobic)	0.00165 hr^{-1}
D_{xyl}	Diffusion coefficient of xylene in water	7.808E-10 m^2/hr
D_p	Diameter of particle of xylene	100 µm
SA	Surface area	m^2
No.P	Number of particles	dimensionless
ρ_{xyl}	Density of xylene	870,000 g/m^3

Modeling of Batch NAPL System

Mass and Concentration of Particles of Xylene with D_p=100 μm



Somewhat steady decline in dispersed phase concentration.

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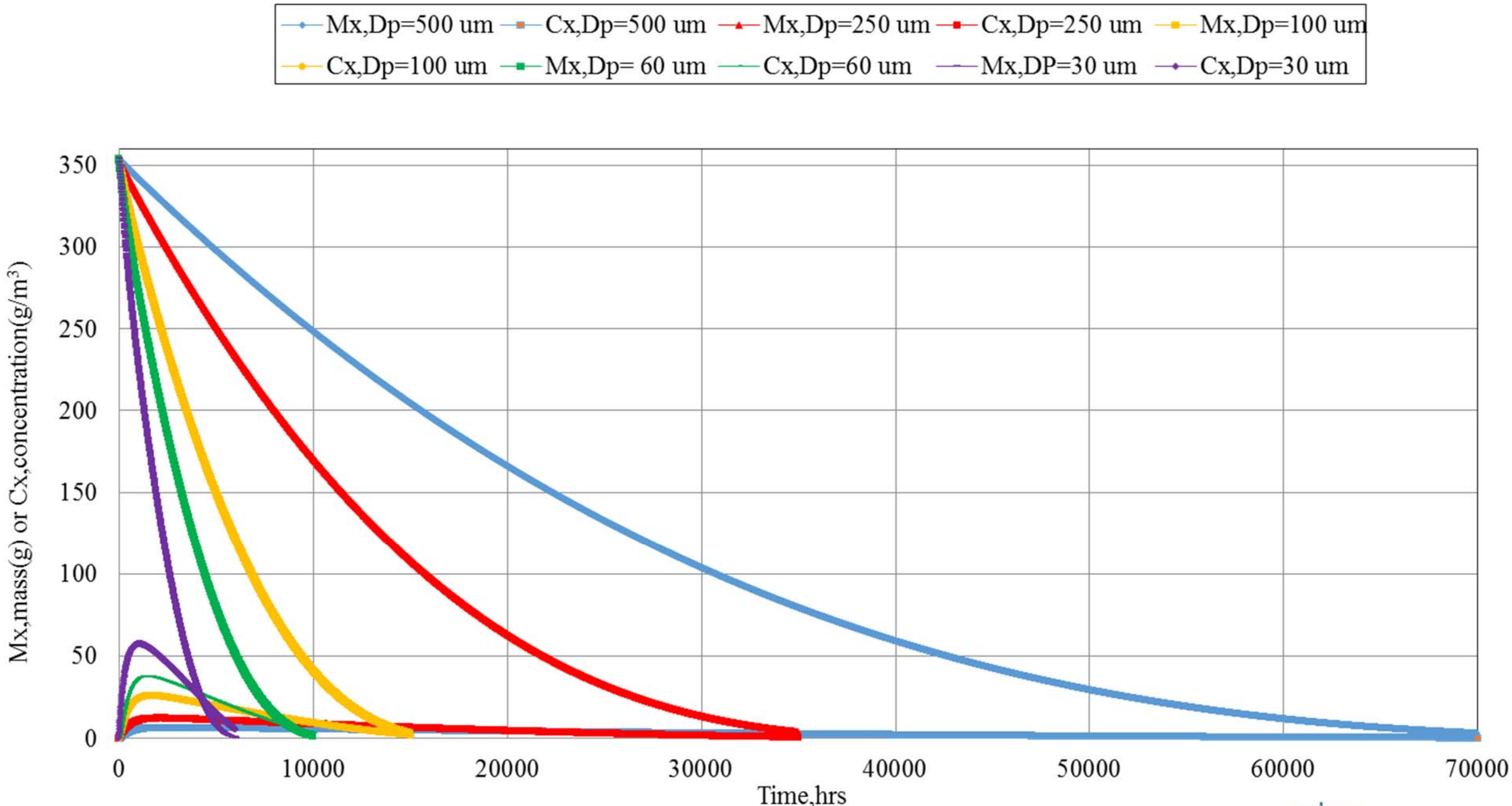
Modeling of Batch NAPL System

Mass and Concentration of Particles with Different Diameters



Smallest size particles indicate fastest total degradation time, due to greatest surface area.

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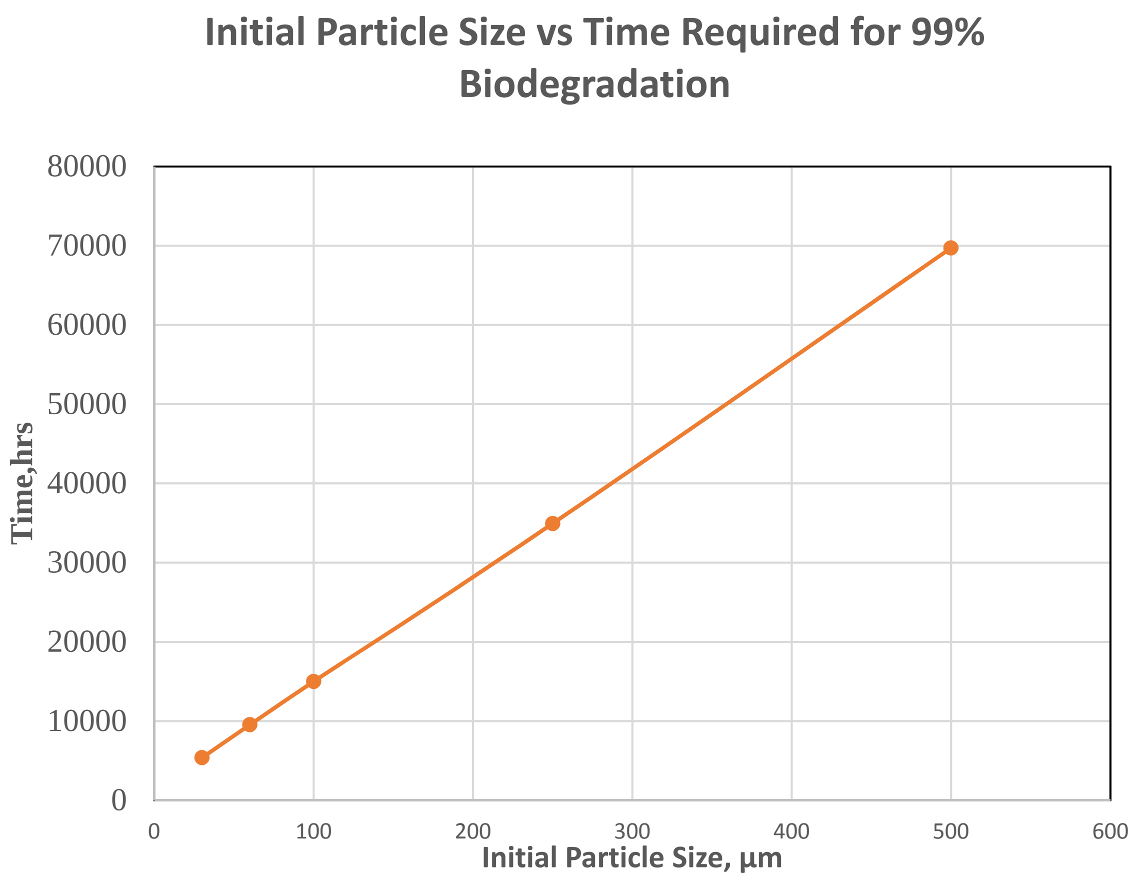
Modeling of Batch NAPL System



Smallest size particles indicate fastest total degradation time, due to greatest surface area.

Modeling of Batch NAPL System

Further model developments underway:

- Better prediction of particle size based on empirical equations using energy input, NAPL viscosity, and interfacial tension
- Mass transfer coefficient based on empirical convection equation
- Multicomponent system

Conclusion and Future Work

- Experimental work indicates dissolution of oily material into bulk phase, with increases as mixing speed / energy is increased.
- Initial modeling of process provides insight into times for mass removal by biodegradation
- FUTURE WORK:
  - Biodegradation effectiveness tests, with measurement of residual material remaining
  - Dispersant effectiveness with other oily sludge mixtures
  - Further model development for comparisons

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