Cost Saving & Performance Enhancements Modifications at a Lime-Based Treatment System

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Rushton AMD Treatment System

Pennsylvania Mines, LLC

Chemistry of the Rushton AMD Discharge

Pumped Flow = 3,000 - 5,000 gpm

Rushton Mine AMD Chemistry from the Initial Evaluation conducted on March 31, 2010.							
Temp °C	**pH**	**Conduct. µS**	**“Hot” Acidity**	**Cold Acidity**	**Iron mg/L**	**Manganese mg/L**	**Aluminum mg/L**
			mg/L (as $CaCO_3$)				
10.4	3.3	1950	400	600	121.5	13.5	24.0

Rushton Mine AMD Chemistry from the Pre-aeration Study conducted on July 27, 2010.							
Temp °C	**pH**	**Conduct. µS**	**“Hot” Acidity**	**Cold Acidity**	**Iron mg/L**	**Manganese mg/L**	**Aluminum mg/L**
			mg/L (as $CaCO_3$)				
10.6	4.7	1650	196	306	105.2	8.04	9.42

Treatment Process Evaluation & Improvements at the Rushton Treatment Plant

- **Lime Neutralization Process**
- Mixing/Aeration Process
- Polymer Flocculation Process
- Settling Process
- Sludge Management

Lime Neutralization of AMD

Water Chemistry

Impacts on Treatment Approaches

Hydrated Lime System

Multi-Step Process

1. Silo Storage
2. Powder Feed System
   a) Vibrator/Auger Feed
3. Slurry Production
   a) Mixing Tank
   b) Clean Water (Process) Source
4. Slurry Dosing
   a) Liquid Feed System
   b) Scale Formation
5. Mixing System
   a) Mix & Dissolve Slurry
   b) Oxidize & Precipitate Metals

Implications of Chemistry

Impacts of Carbon Dioxide ($H_2CO_3^*$)
on Lime Dosing

Acidity & Alkalinity Definitions

Mine Drainage Waters:

Alkalinity = $[HCO_3^-] + [CO_3^{2-}] + [OH^-]$

Endpoint $pH_{4.0\text{-}4.8}$

"Hot" Acidity = $[H^+] + 3[Al^{3+}] + 3[Fe^{3+}] + 2[Fe^{2+}] + 2[Mn^{2+}]$....- *Alkalinity*

Endpoint $pH_{8.0\text{-}8.5}$

Net Acidity = $[H^+] + 3[Al^{3+}] + 3[Fe^{3+}] + 2[Fe^{2+}] + 2[Mn^{2+}]$....- *Alkalinity*

Calculated Acidity = $(50{,}000\times10^{-pH})+(5.7\times C_{al})+(2.7\times C_{Fe3+})+(1.8\times C_{Fe3+})+(1.8\times C_{Mn})$ - $C_{Alkalinity}$

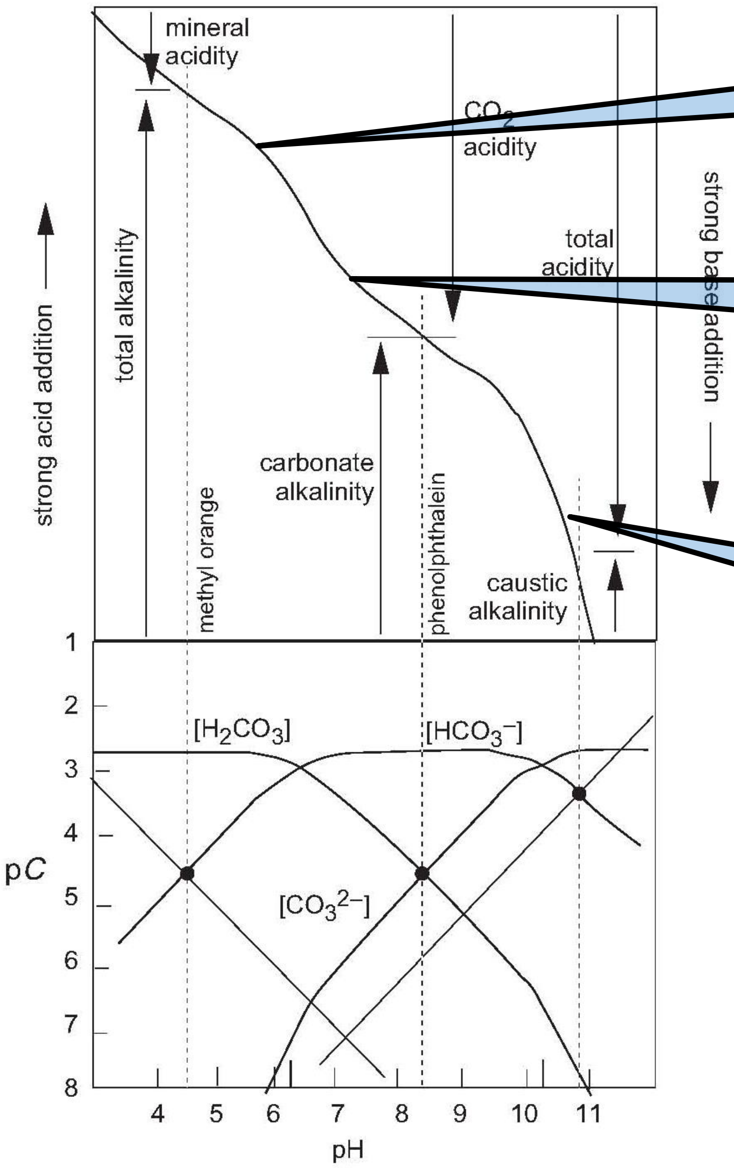
Cold Acidity = $[H^+] + [H_2CO_3^*] + 3[Al^{3+}] + 3[Fe^{3+}]$ ....

Endpoint $pH_{8.0\text{-}8.5}$

Carbon Dioxide Acidity = $[H_2CO_3^*]$ = Cold Acidity – Hot Acidity

Range: 5 to 250 mg/L (as $CaCO_3$)
For AMD pH water with pH < 5

Effects of Carbon Dioxide Acidity on Lime Dose



1st Area Shows
Fast pH Change

$2H^+ + Ca(OH)_2 \rightarrow Ca^{2+} + H_2O$

2nd Area Shows
Slow pH Change

$2H_2CO_3 + Ca(OH)_2 \rightarrow Ca^{2+} + 2HCO_3^- + 2H_2O$

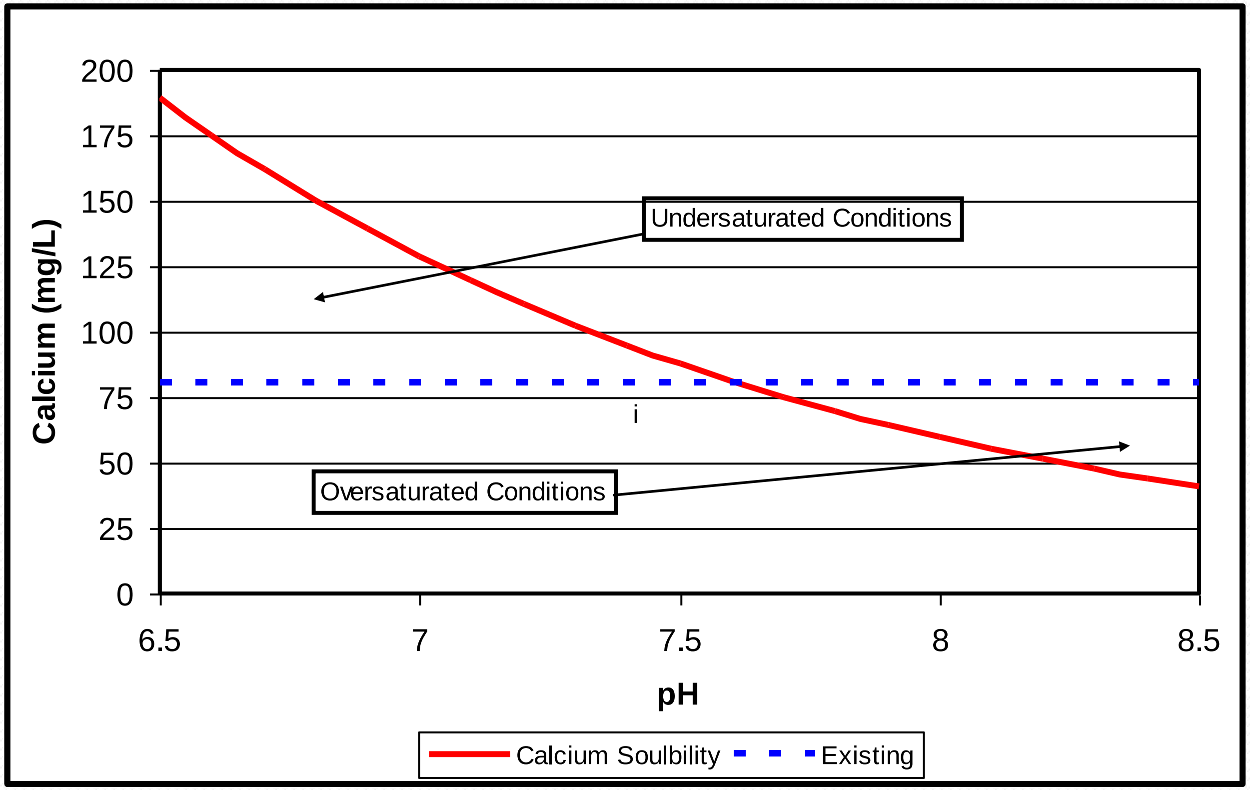
3rd Region Shows
Fast pH Change

$2HCO_2^- + Ca(OH)_2 \rightarrow H_2O + Ca^{2+} + CO_3^{2-}$

Complications of Lime Dose

2) Calcium Solubility as a function of pH

Step 1: $2CO_2 + Ca(OH)_2 \rightarrow Ca^{2+} + 2HCO_3^-$
Step 2: $2HCO_3^- + Ca(OH)_2 \rightarrow H_2O + Ca^{2+} + 2CO_3^{2-}$
Step 3: $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)}$



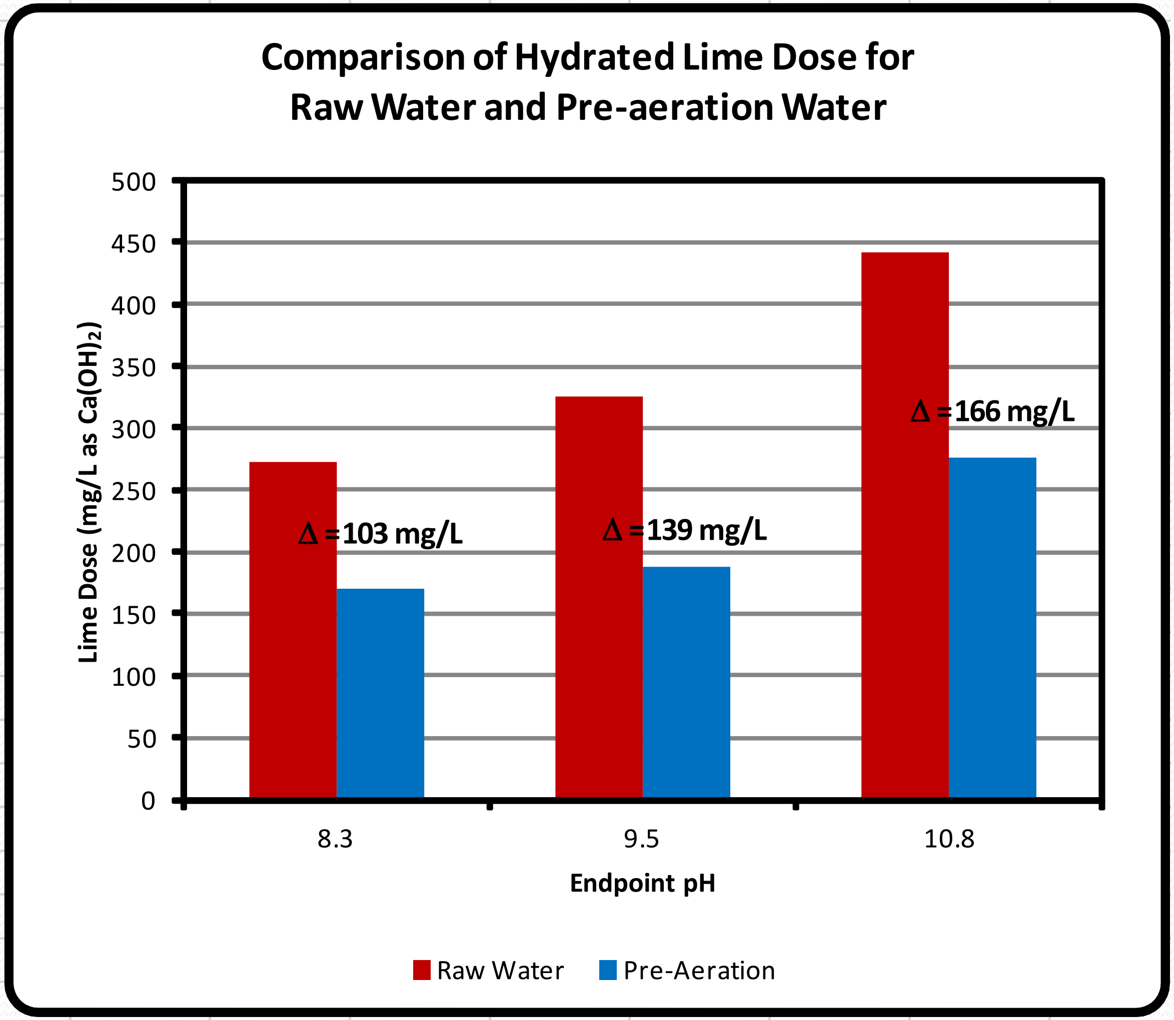
Comparison of hydrated lime dose tests

(AMD inlet on left and aerated AMD on right)

Field $Ca(OH)_2$ Titrations

Effects of Carbon Dioxide on Lime Dose

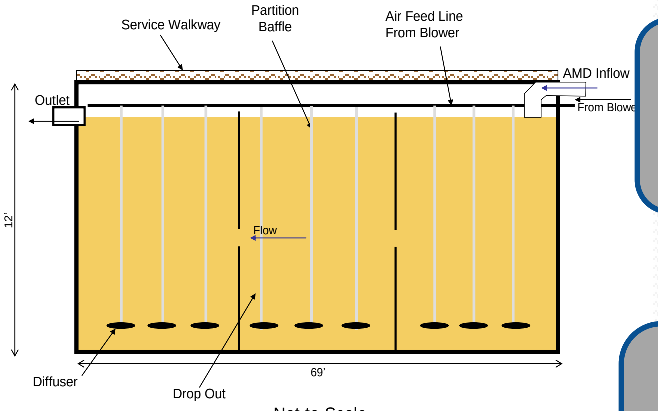
Rushton Mine Raw Water Calcium = 170 mg/L



Pre-Aeration System

at the Rushton AMD Treatment Plant

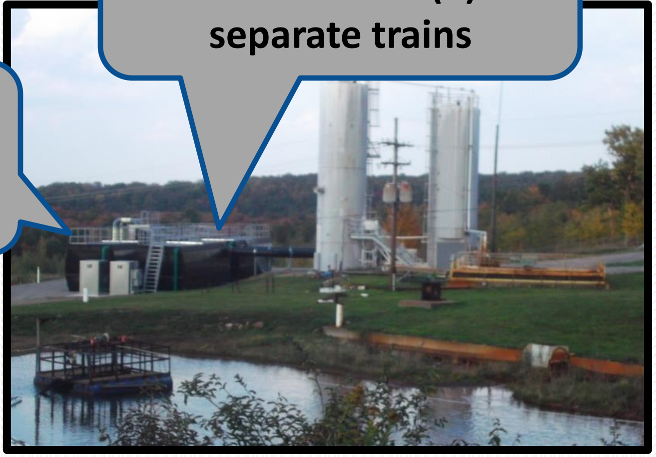
Side View



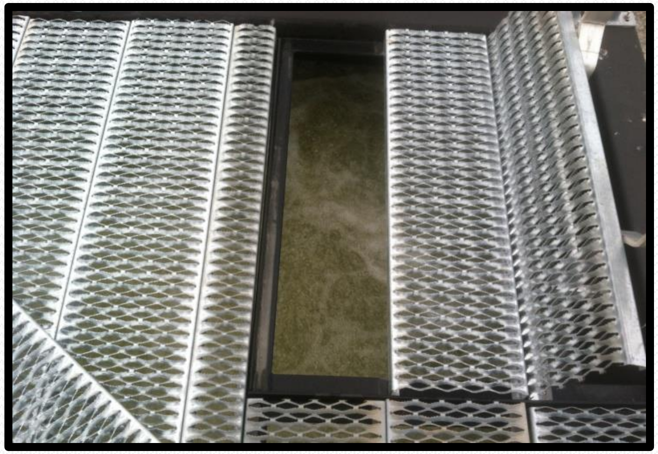
Not-to-Scale

Four (4) 35,000 gallon tanks in two (2) separate trains

Dention Time = 30 min. at Max. Flow (4,700 gpm)

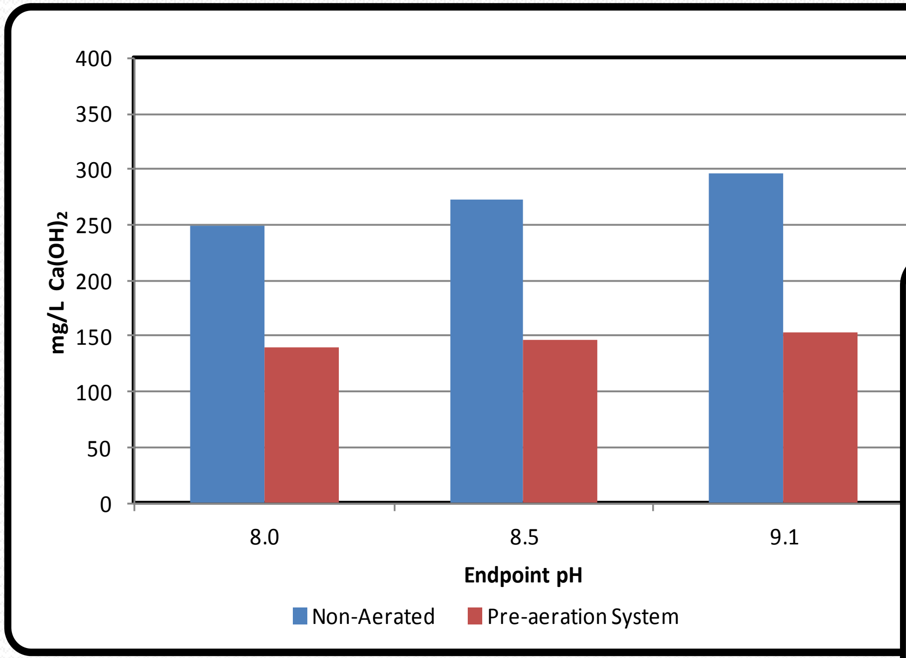


Two (2) 30 Hp Blowers delivering 1,000 SCFM ea.

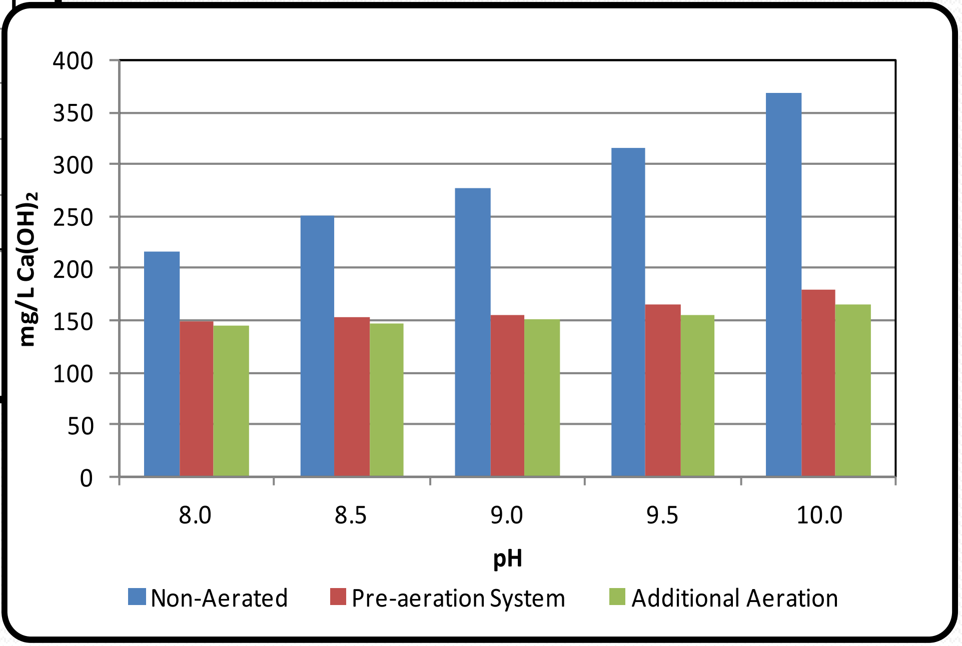


Effects of Pre-aeration System on Lime ($Ca(OH)_2$)Dose

Flow = 4,700 gpm

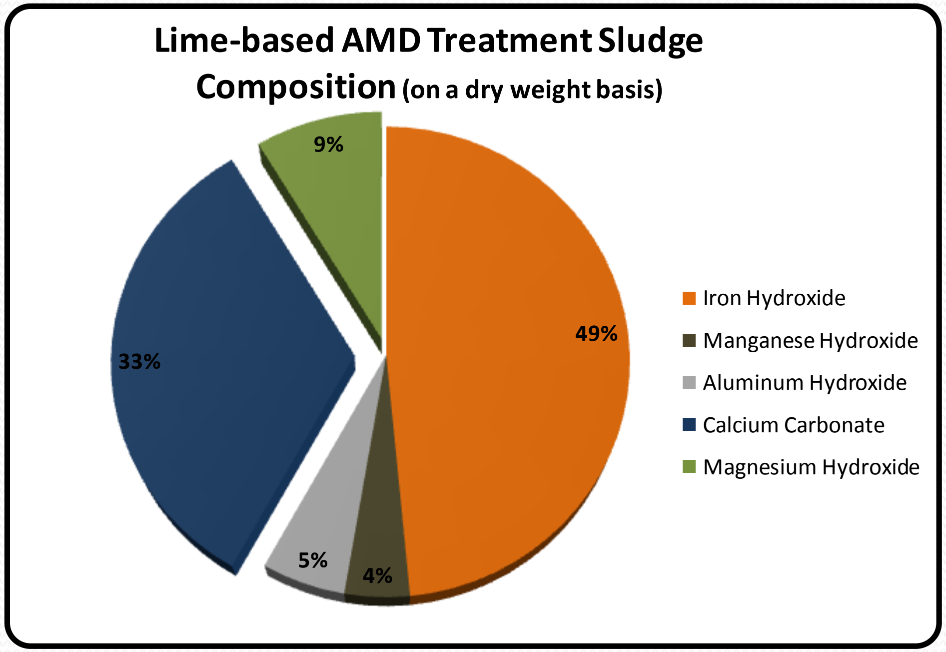


Flow = 3,000 gpm



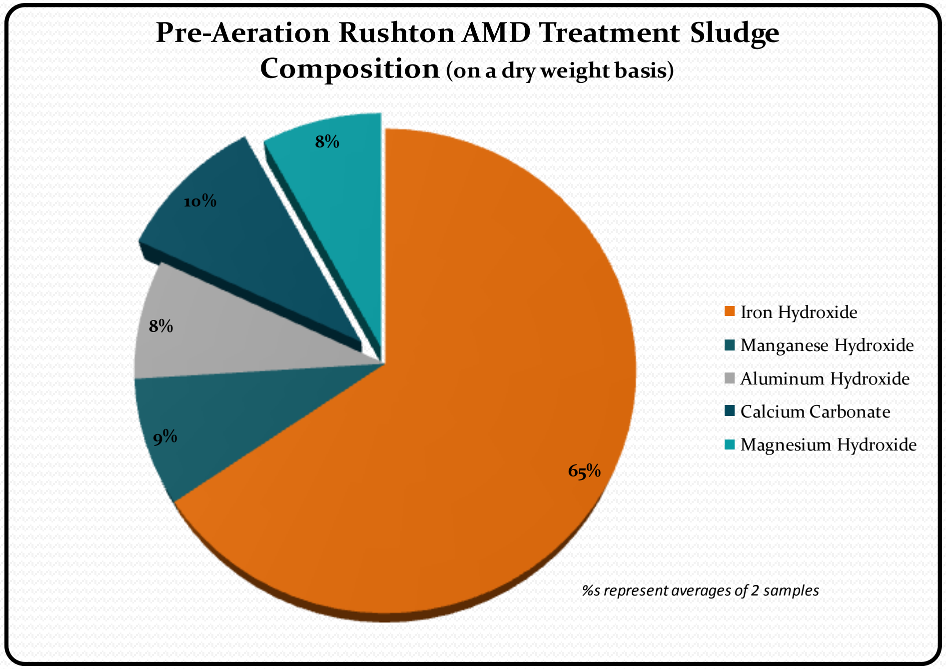
Effects of P{re-aeration on Sludge Composition

Prior To Installation of Pre-aeration



Lime-based AMD Treatment Sludge Composition (on a dry weight basis)

Post Installation of Pre-aeration



Pre-Aeration Rushton AMD Treatment Sludge Composition (on a dry weight basis)

%s represent averages of 2 samples

LIME CONSUMPTION AFTER PRE-AERATION

- Two truck loads per week reduced to one truck load per week after Pre-aeration System Installed.
  - 22 to 24 tons per truckload ~ 1,200 tons per year.
- Operational pH adjustments require minimal increase in dose.
  - ~ 1% dose increase yields 0.1 pH change between 9 and 10
- Manganese removal can be more effectively achieved with minimal increase in lime dose.
- Estimated savings per year ~ $150-200,000

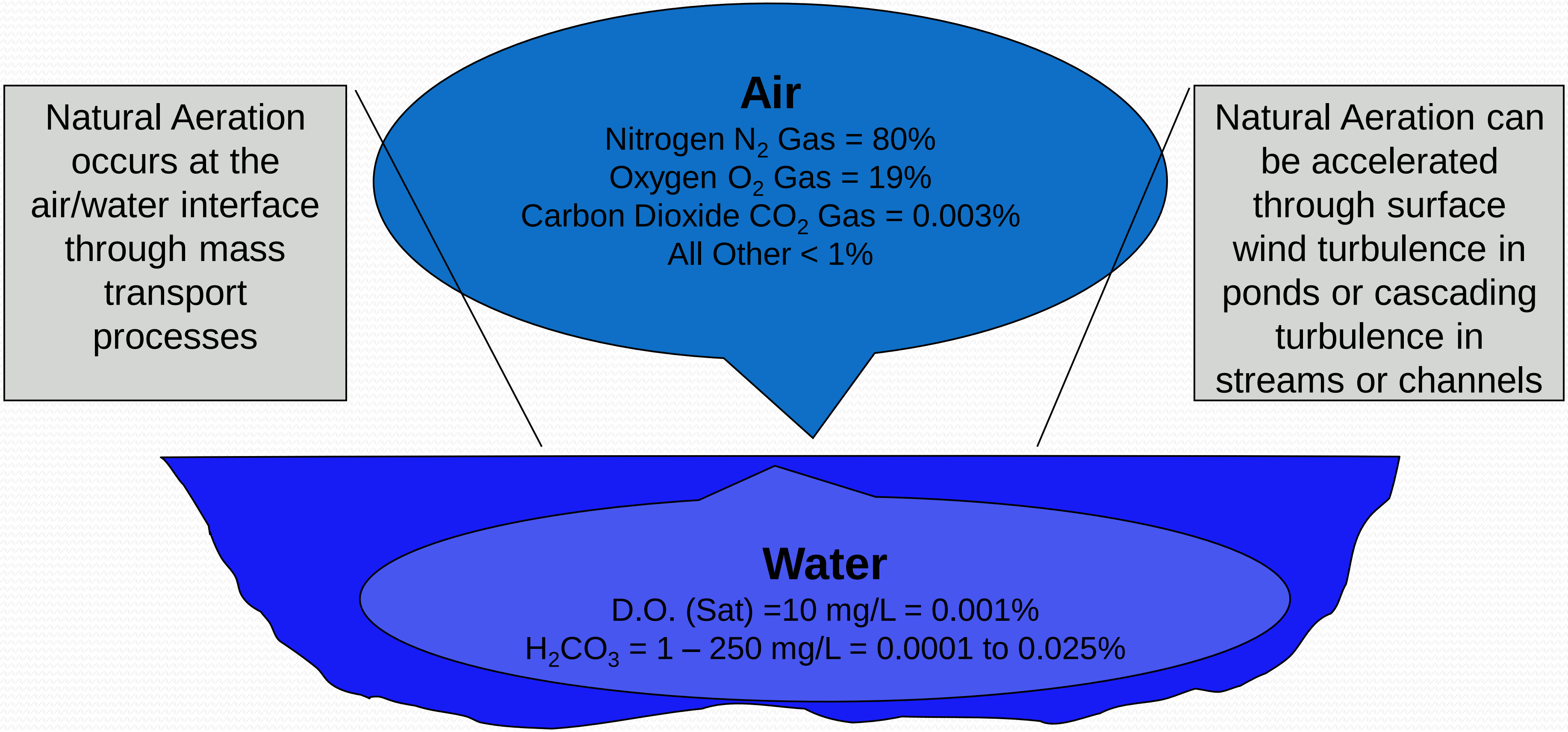
Removal of Carbon Dioxide From Water

Natural & Mechanical Process
Background

Natural Aeration

Henrys Law

$$H = K_{eq} = \frac{P_x}{\gamma_x C_x}$$



Natural Aeration occurs at the air/water interface through mass transport processes

Air

Nitrogen N_2 Gas = 80%
Oxygen O_2 Gas = 19%
Carbon Dioxide CO_2 Gas = 0.003%
All Other < 1%

Natural Aeration can be accelerated through surface wind turbulence in ponds or cascading turbulence in streams or channels

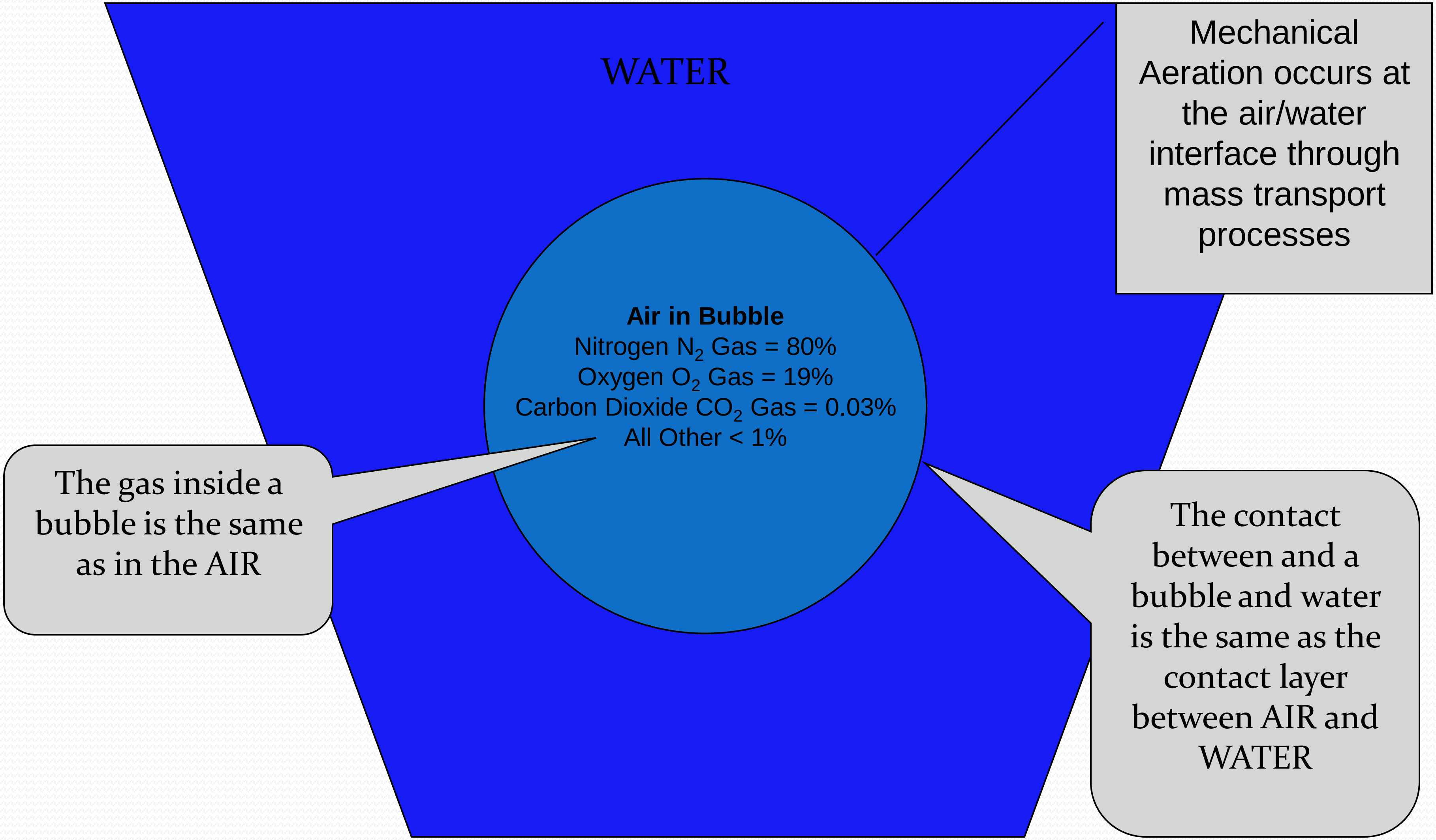
Water

D.O. (Sat) =10 mg/L = 0.001%
H_2CO_3 = 1 – 250 mg/L = 0.0001 to 0.025%

Mechanical Aeration

What is a Bubble?

→ a pocket of air suspended in water.



WATER

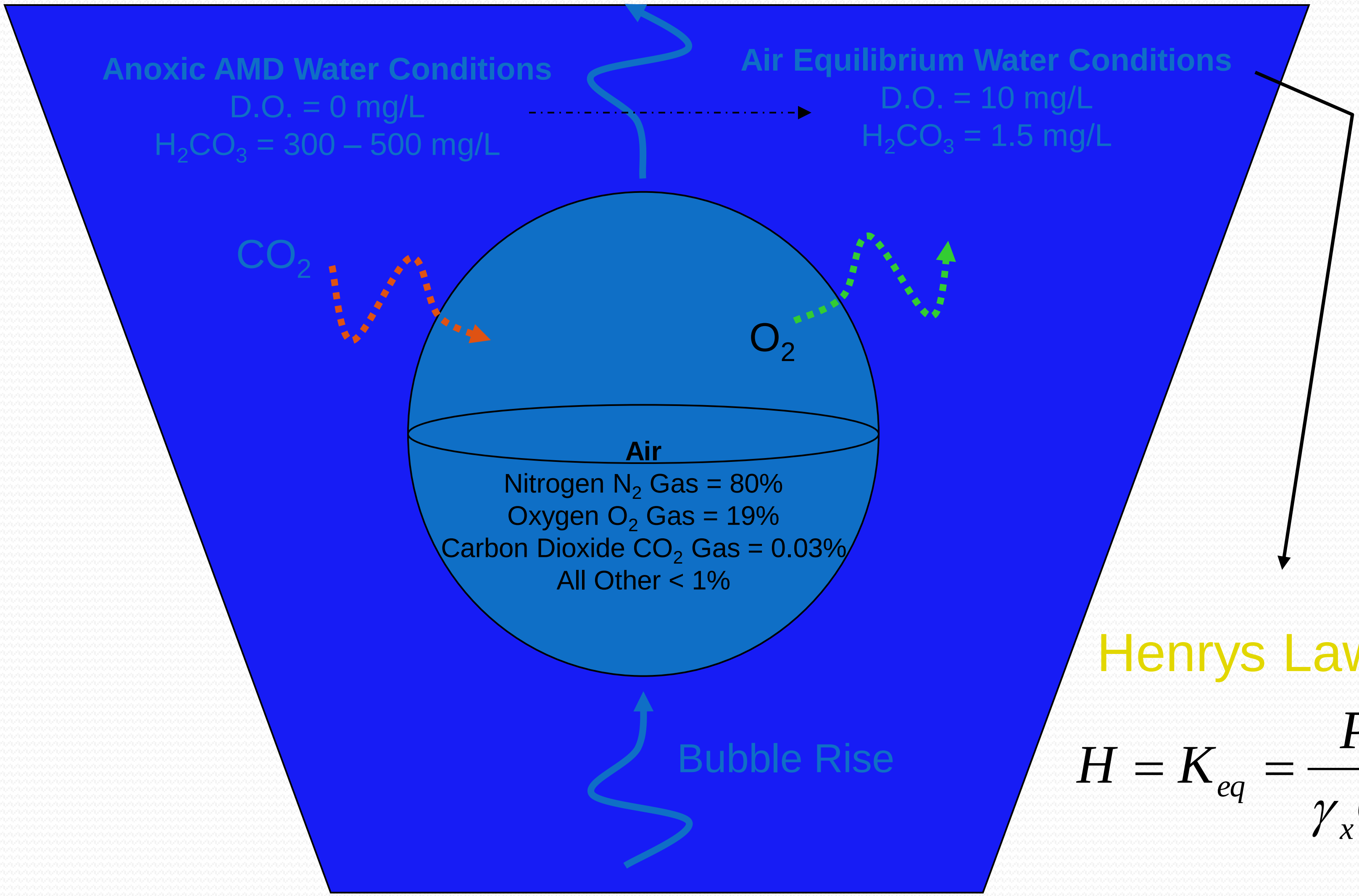
Air in Bubble
Nitrogen N_2 Gas = 80%
Oxygen O_2 Gas = 19%
Carbon Dioxide CO_2 Gas = 0.03%
All Other < 1%

Mechanical Aeration occurs at the air/water interface through mass transport processes

The gas inside a bubble is the same as in the AIR

The contact between and a bubble and water is the same as the contact layer between AIR and WATER

Gas Transport from and to Air Bubbles



Anoxic AMD Water Conditions
D.O. = 0 mg/L
H_2CO_3 = 300 – 500 mg/L

Air Equilibrium Water Conditions
D.O. = 10 mg/L
H_2CO_3 = 1.5 mg/L

CO_2

O_2

Air
Nitrogen N_2 Gas = 80%
Oxygen O_2 Gas = 19%
Carbon Dioxide CO_2 Gas = 0.03%
All Other < 1%

Bubble Rise

Henrys Law

$$H = K_{eq} = \frac{P_x}{\gamma_x C_x}$$

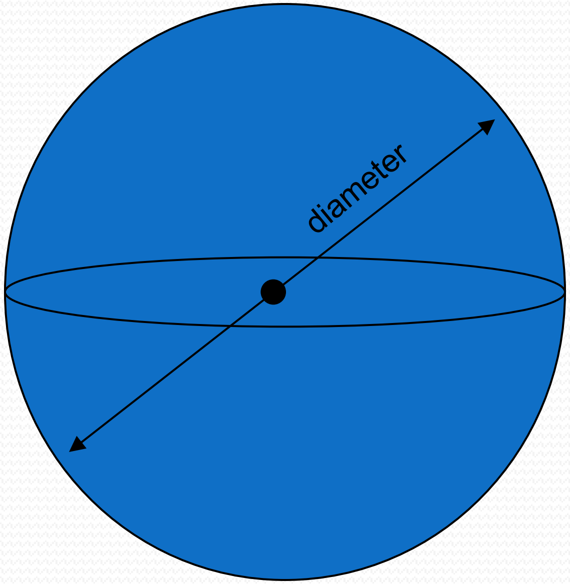
Bubble Geometry

Sphere

Not-to-scale

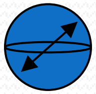
Coarse Bubble

Diameter ~ 1 cm



Fine Bubble

Diameter ~ 0.1 cm



Surface Area = $4\pi r^2$	3.14 cm^2	0.0314 cm^2
Volume = $^4/_3\pi r^3$	0.523 cm^3	0.000523 cm^3
Surface Area: Volume Ratio	6	**60**

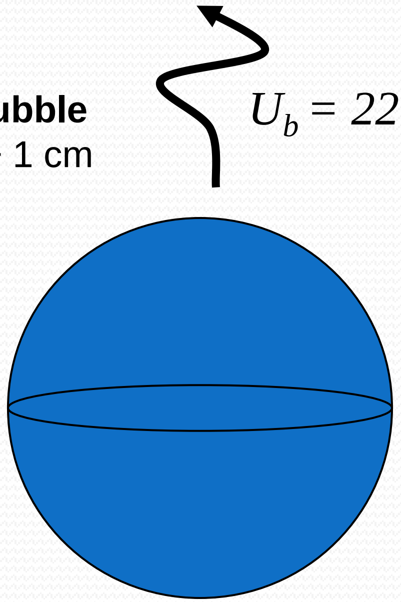
An EQUAL volume of fine bubbles has 10 times the surface area as coarse bubbles

$\therefore$ 10 times the gas transport

Bubble Rise Through Water

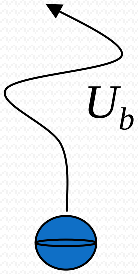
Not-to-scale

Coarse Bubble
Diameter ~ 1 cm



$U_b = 22.3$ cm/sec

Fine Bubble
Diameter ~ 0.1 cm



$U_b = 7.0$ cm/sec

Small single bubble

Large bubble swarm

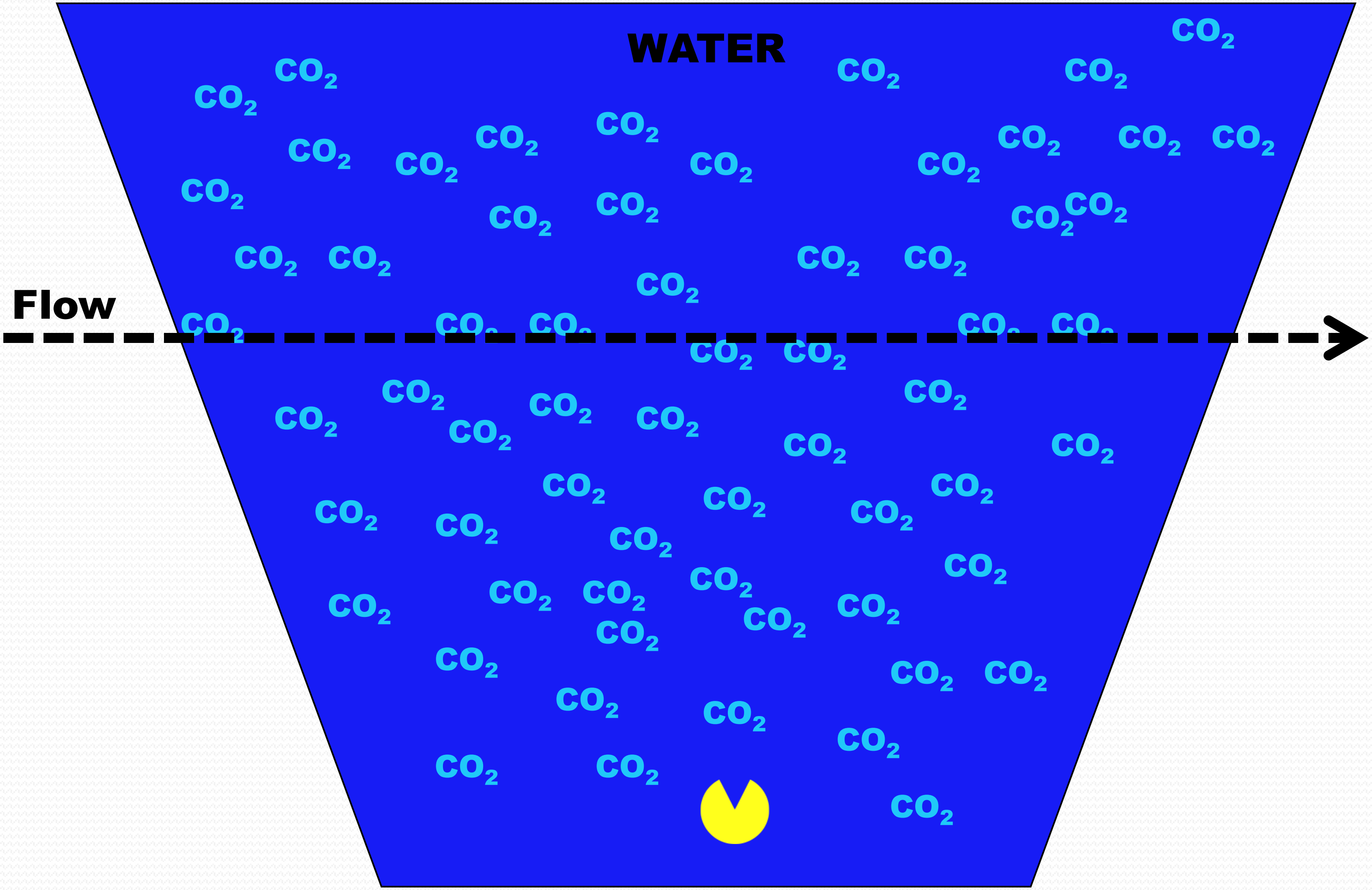
Bubble Rise Velocity (Stokes Law) = $U_b = \frac{2g(p_w - p_a)}{9 v_w p_w} \times R_b^2 = 31.5 \times R_b^2$

Reactor Depth (ft)	Average Travel Time (sec)	
	Coarse	Fine
2	2.7	13.7
10	8.6	43.3

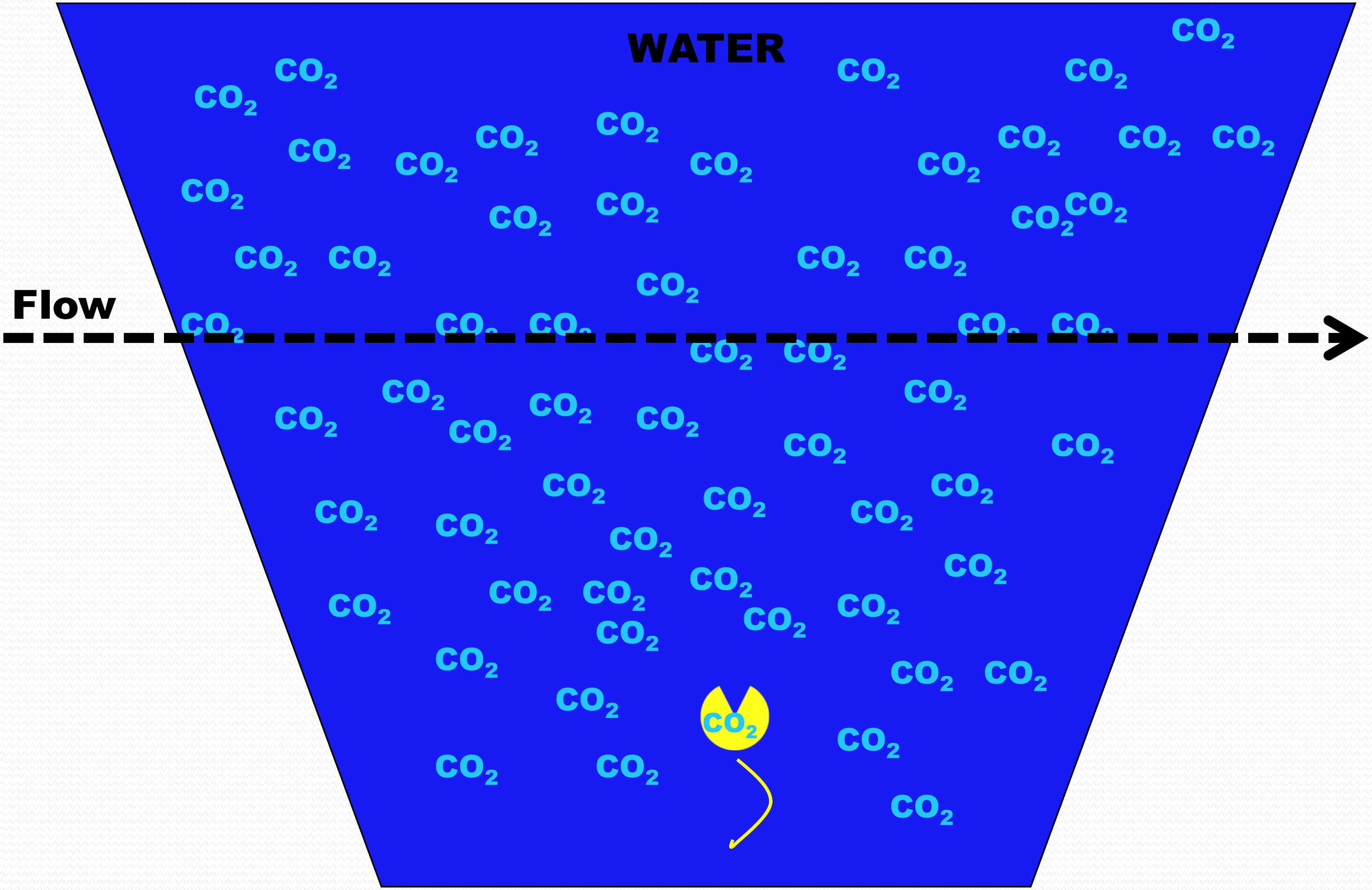
Fine Bubbles rise at less than one-third the rise of coarse bubbles

∴ Greater than 3 times the gas transport

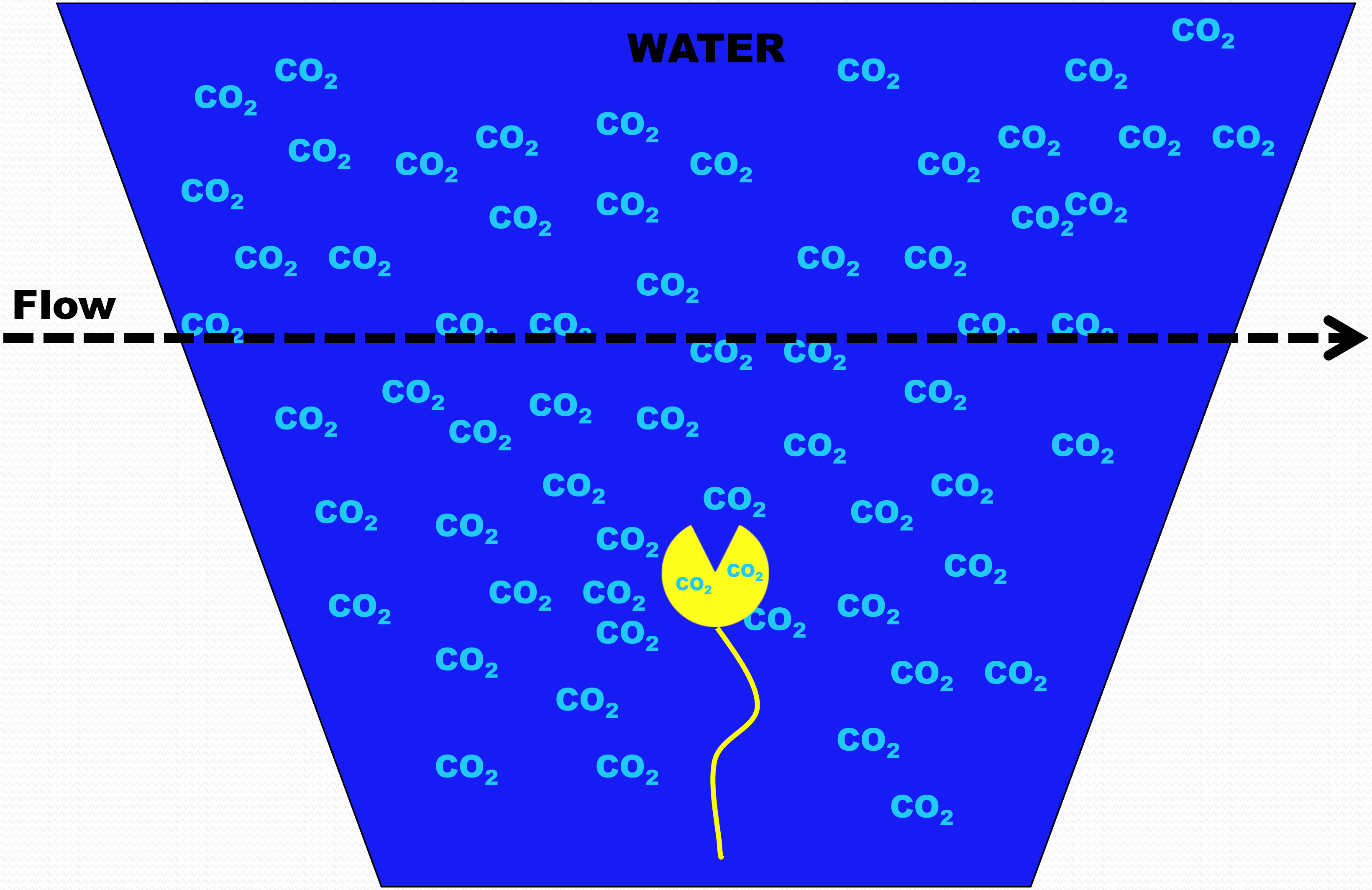
Single Bubbles



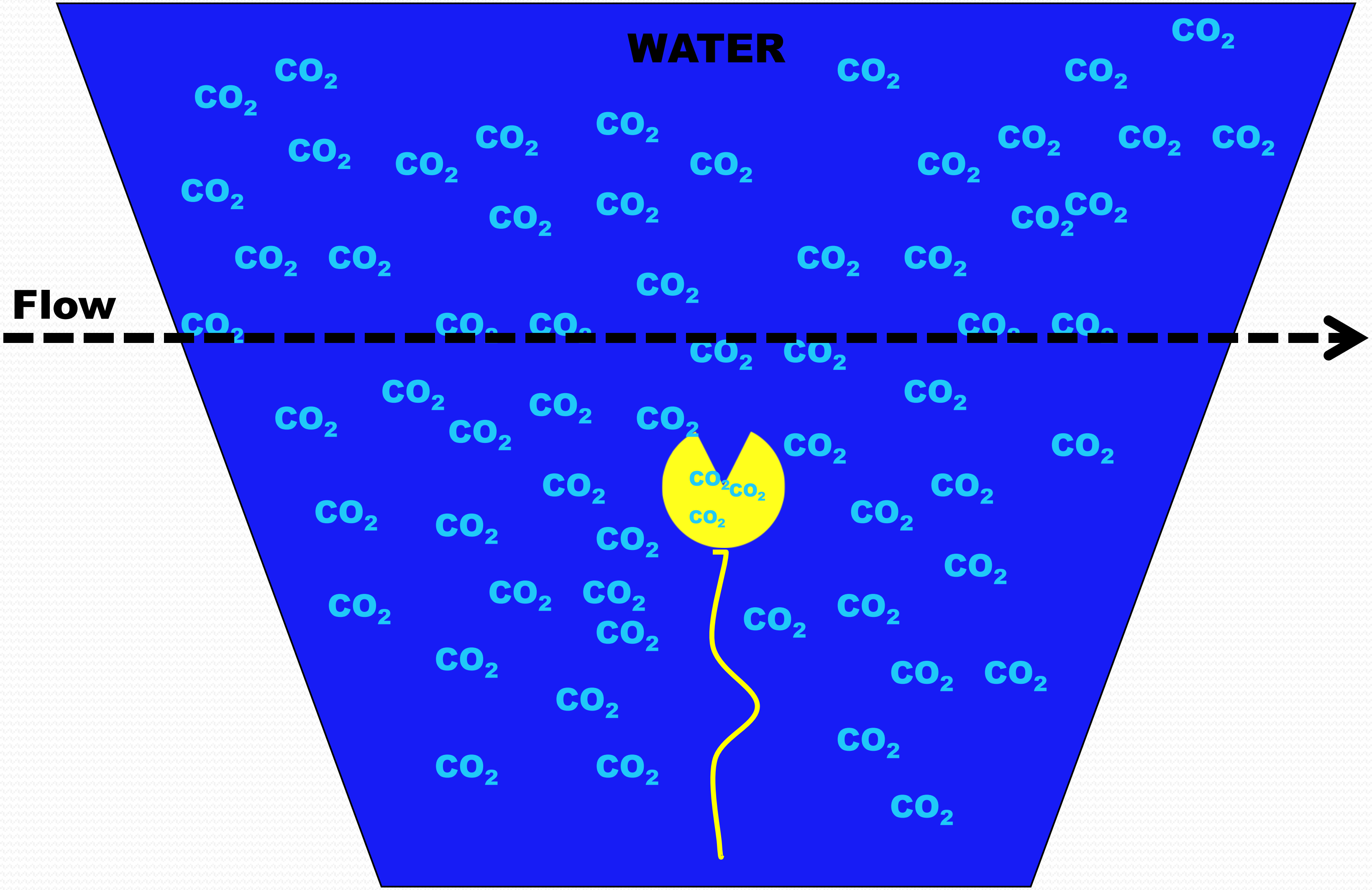
Single Bubbles



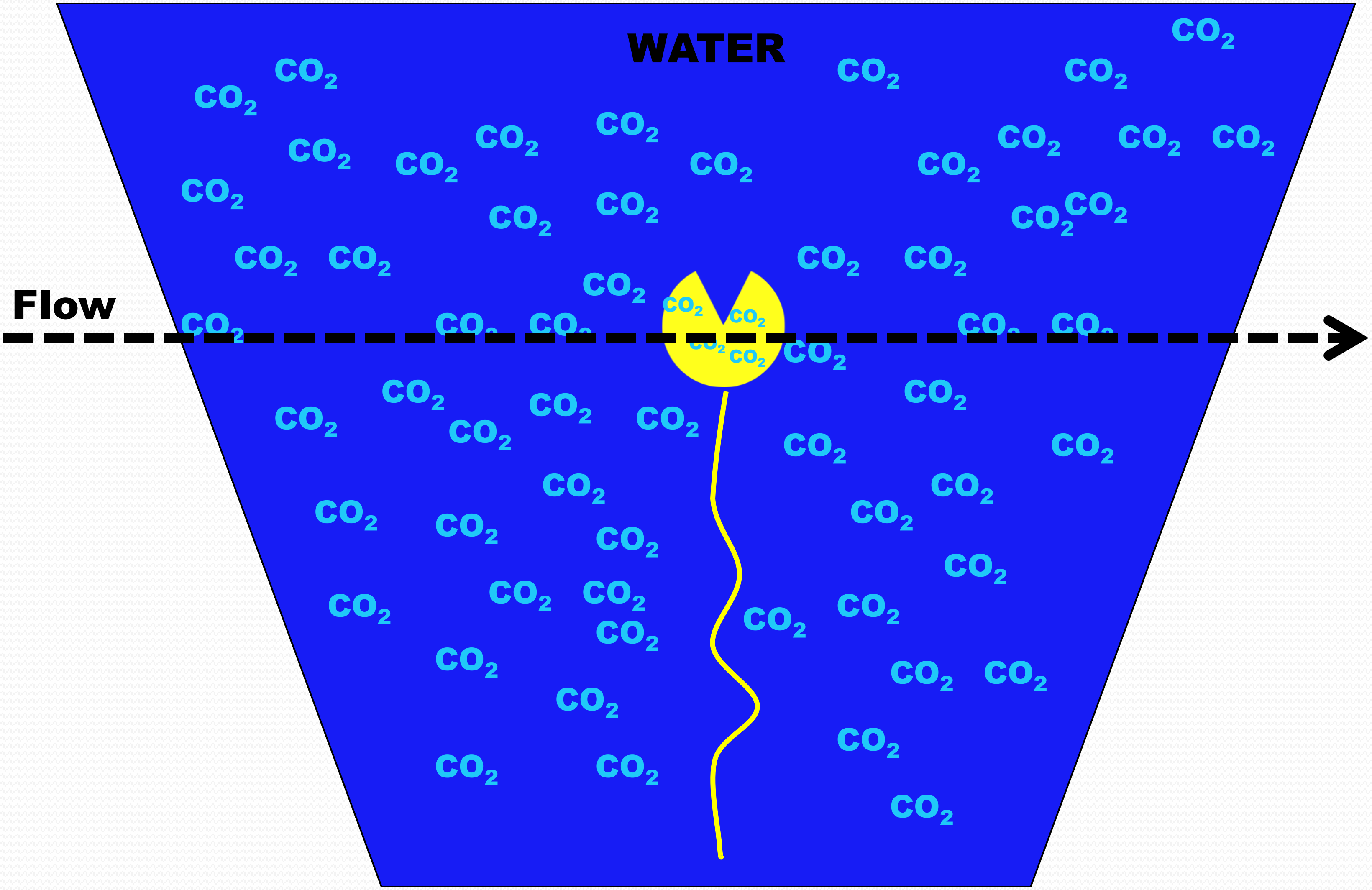
Single Bubbles



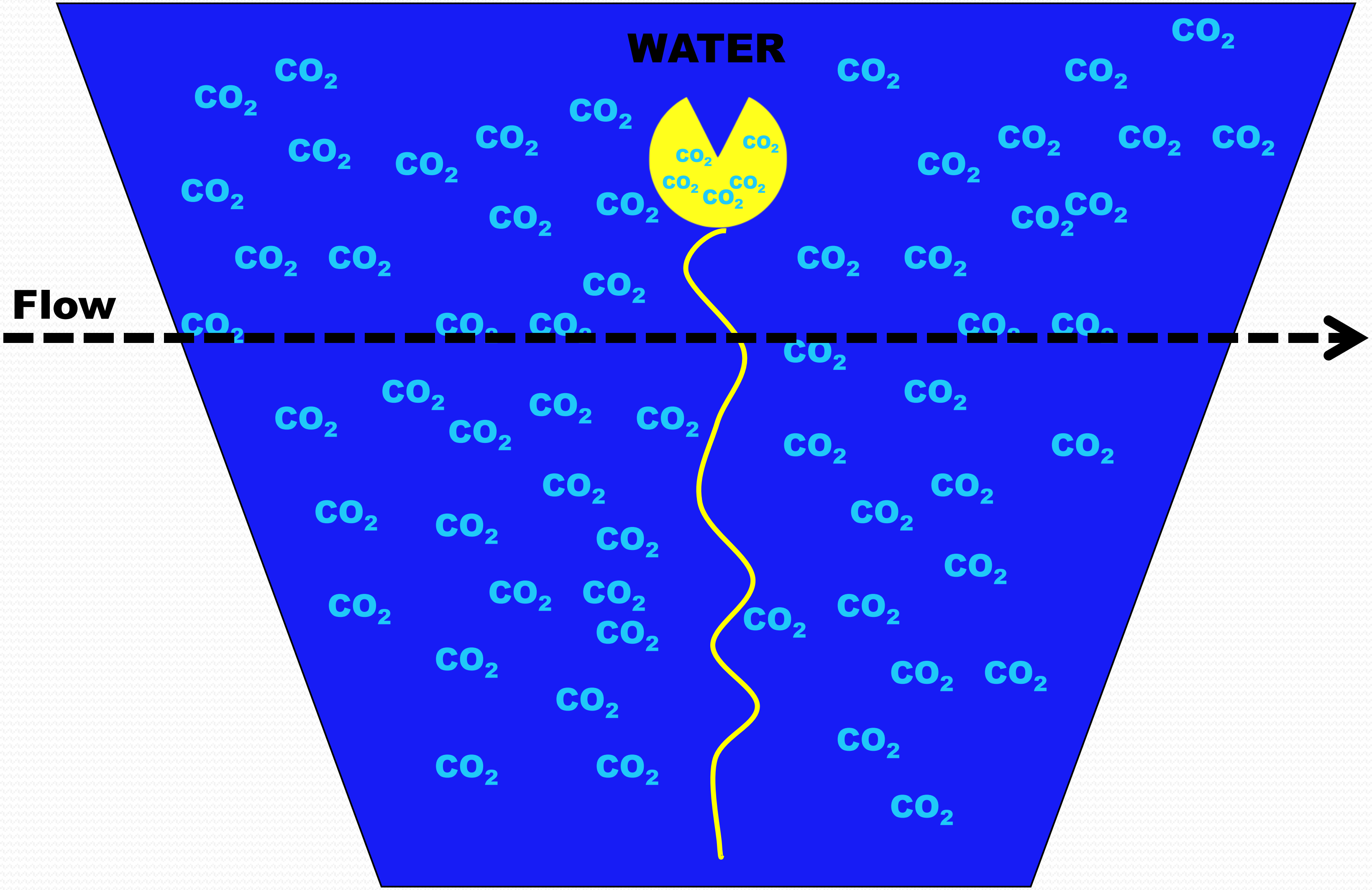
Single Bubbles



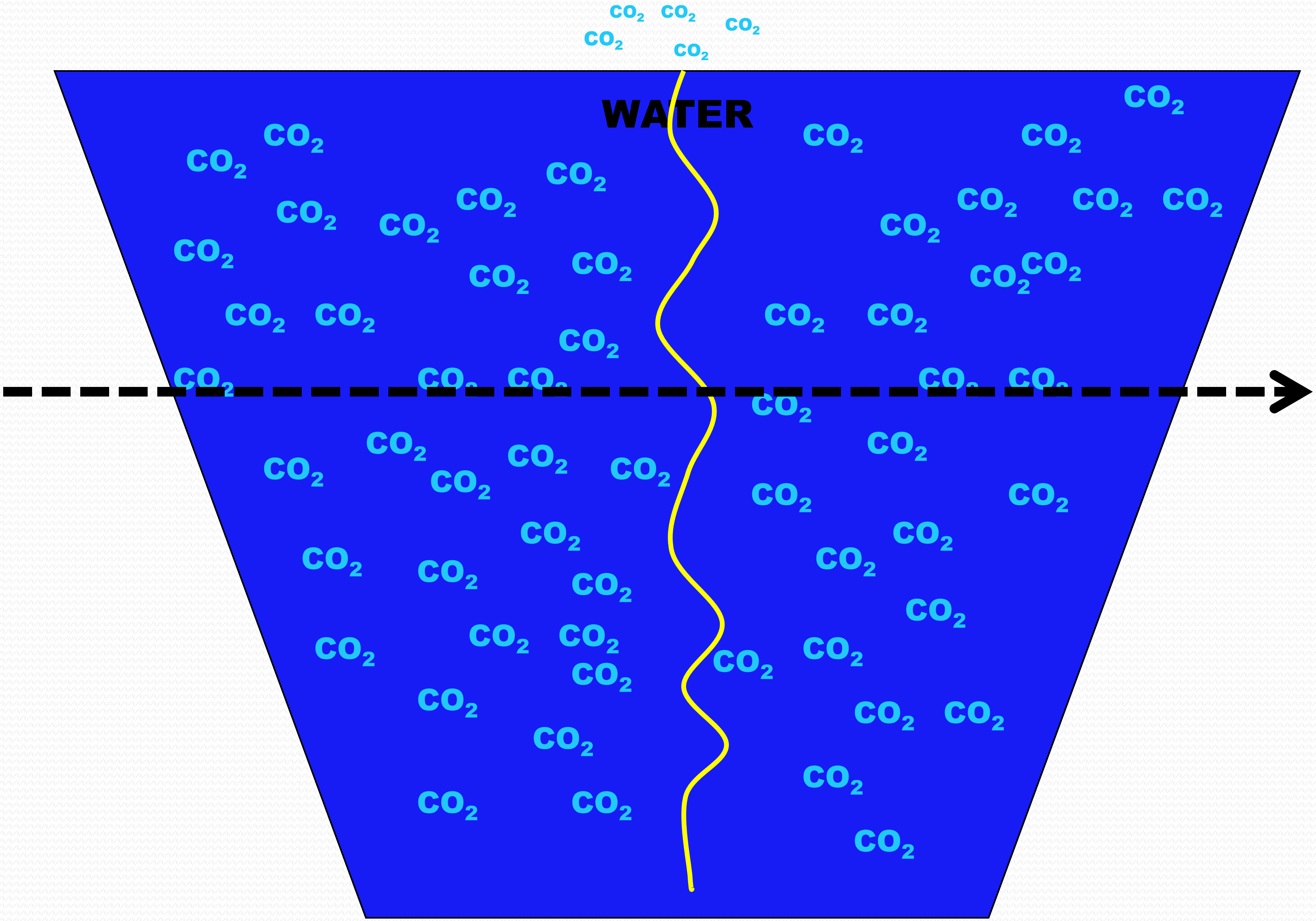
Single Bubbles



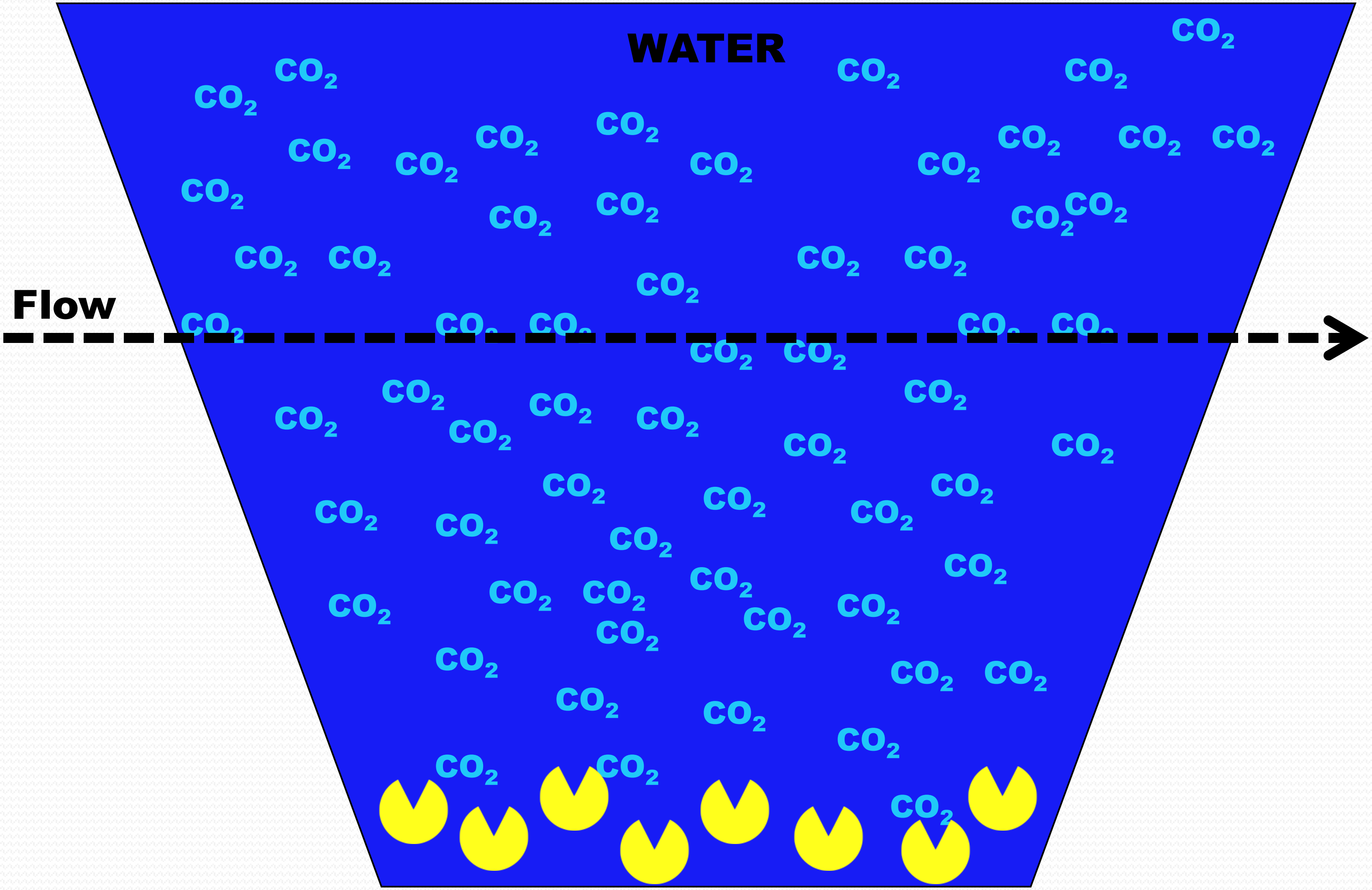
Single Bubbles



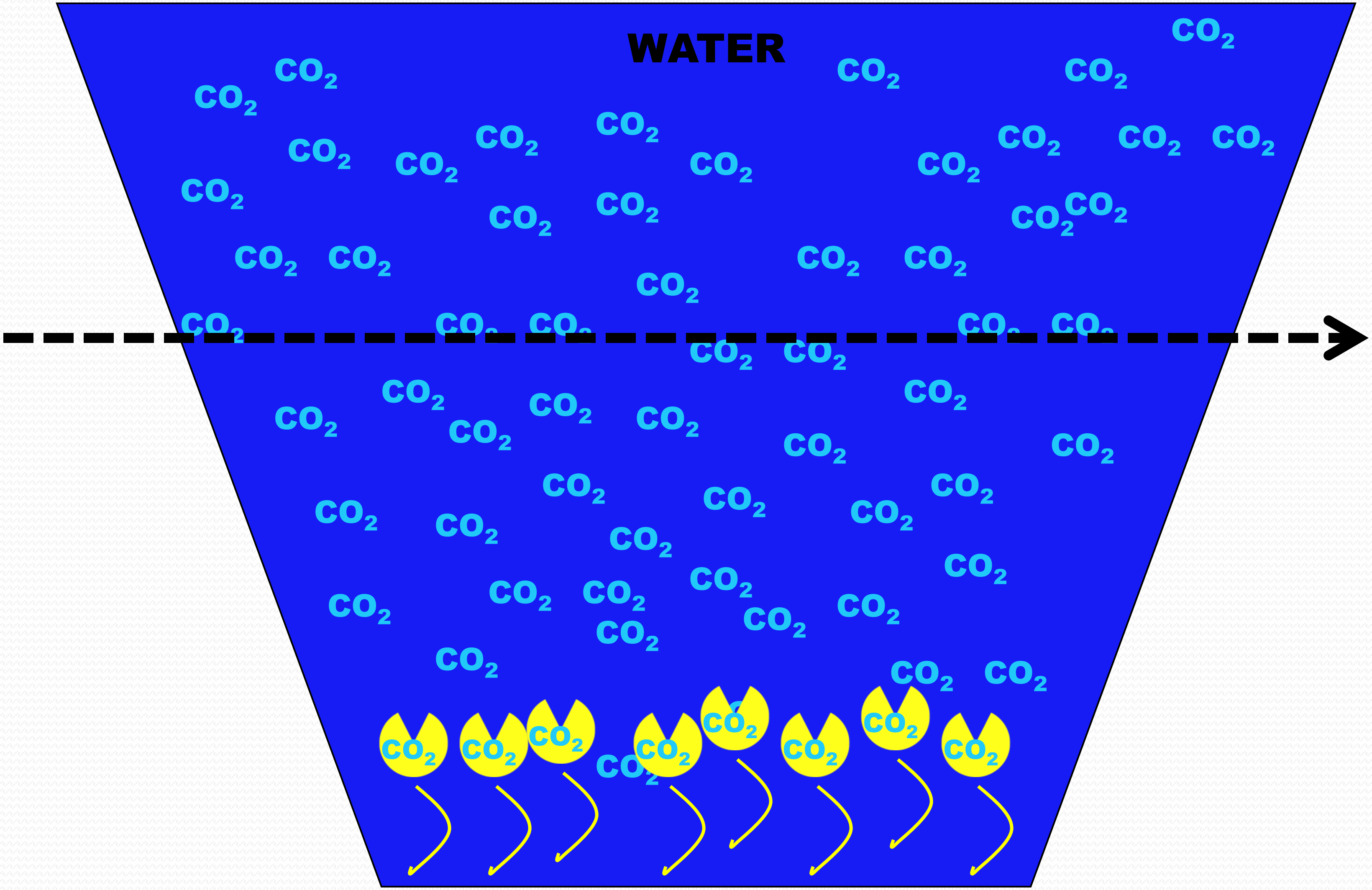
Single Bubbles



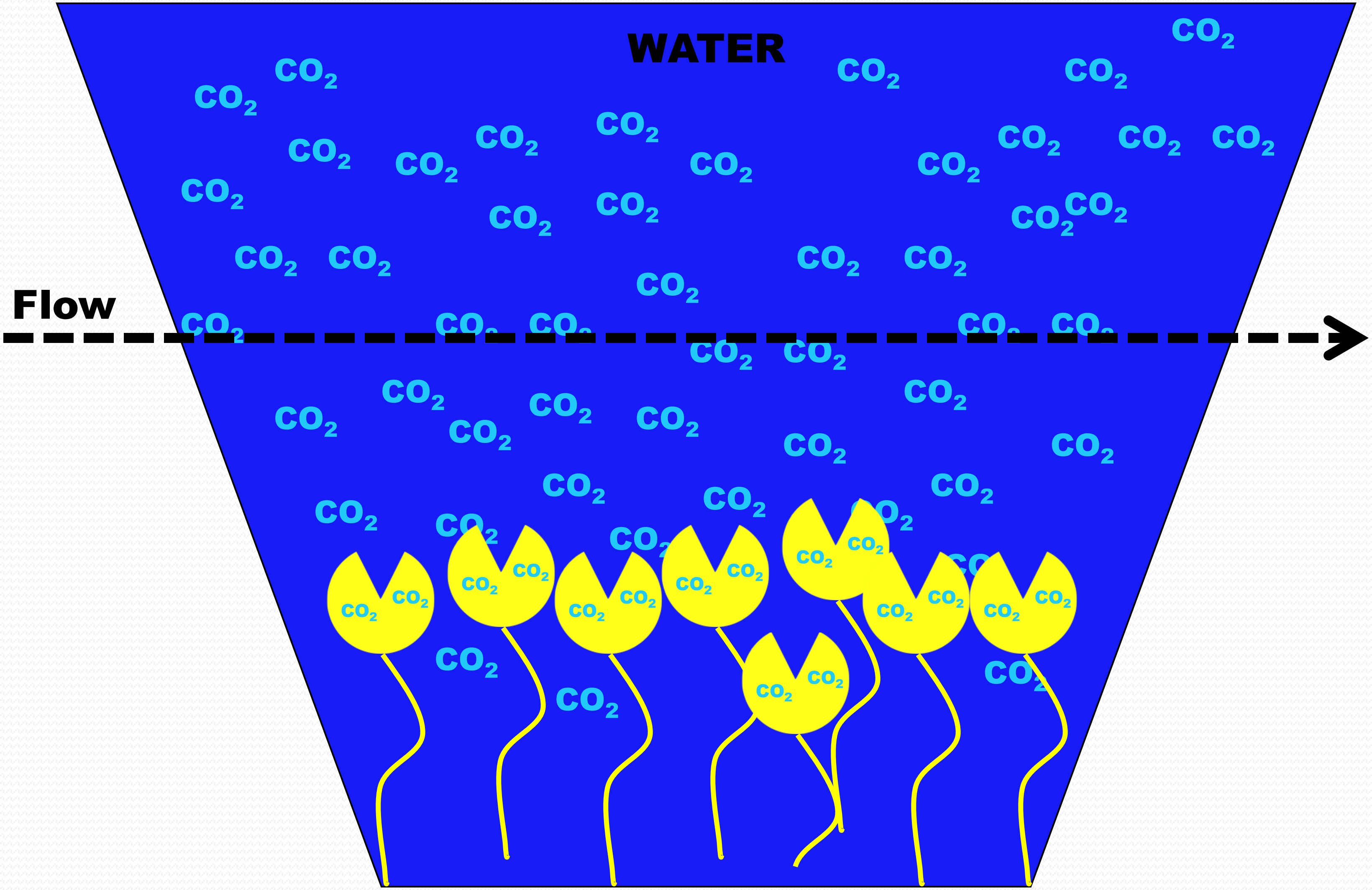
Swarm of Bubbles



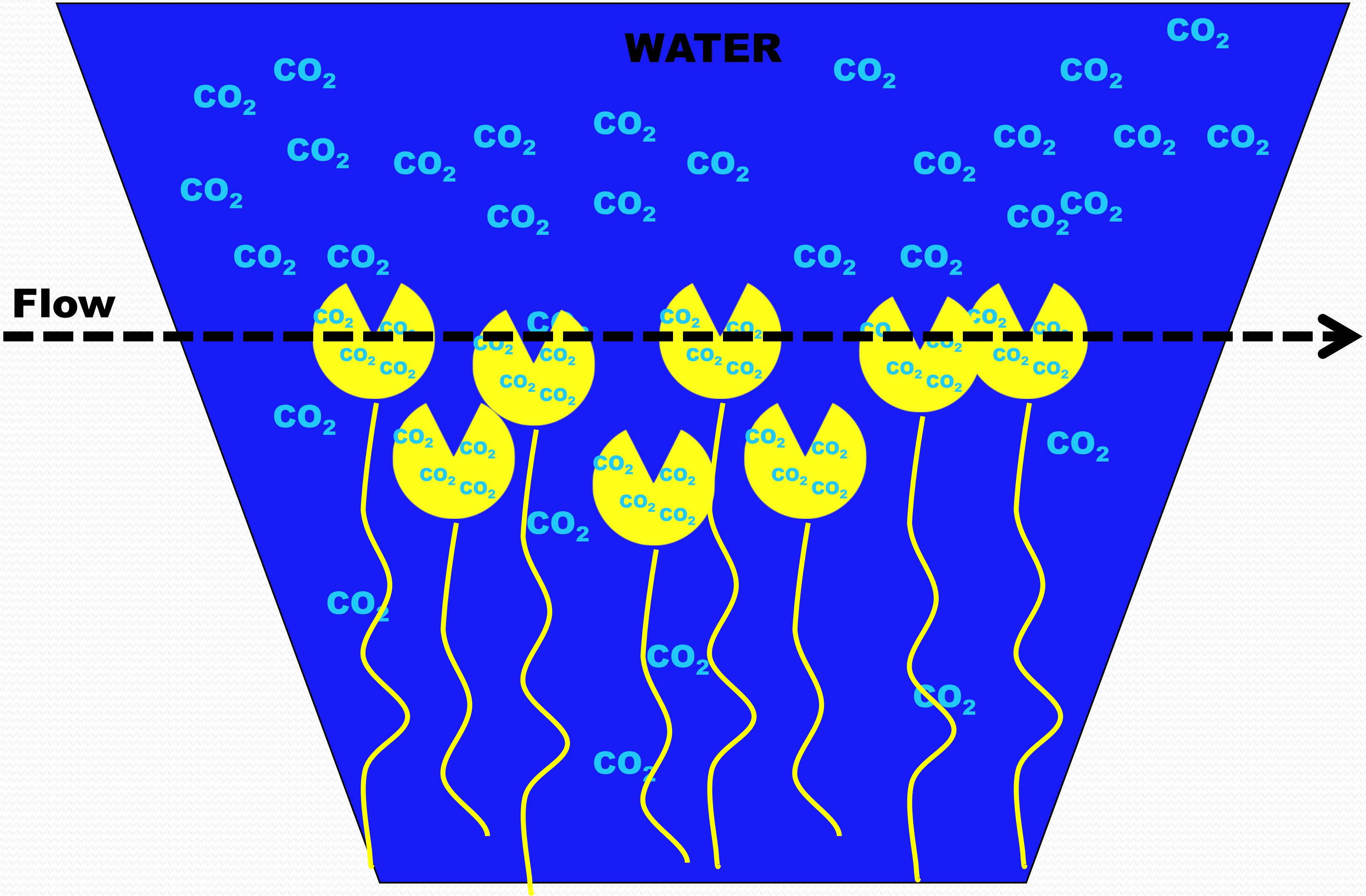
Swarm of Bubbles



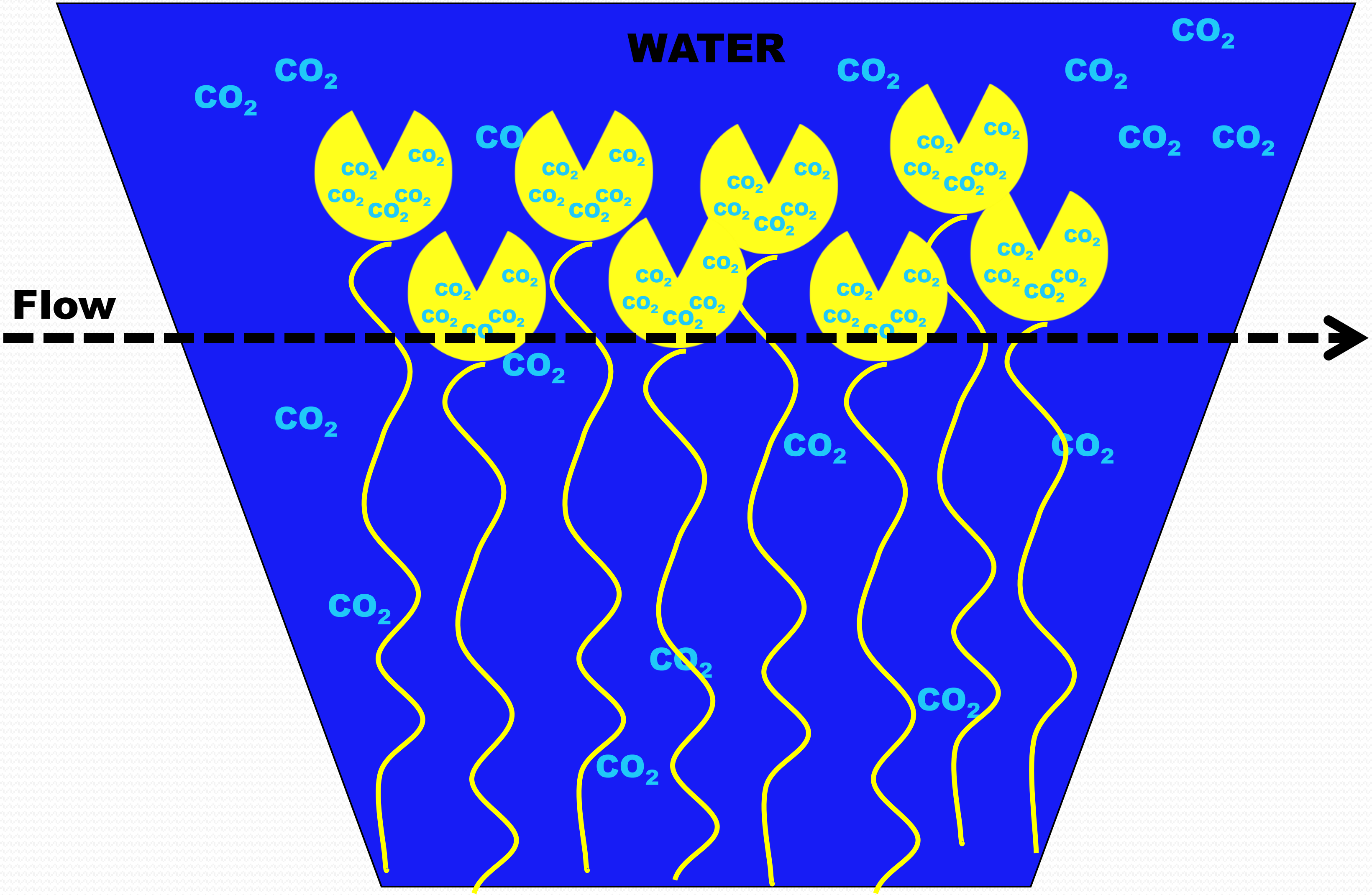
Swarms of Bubbles



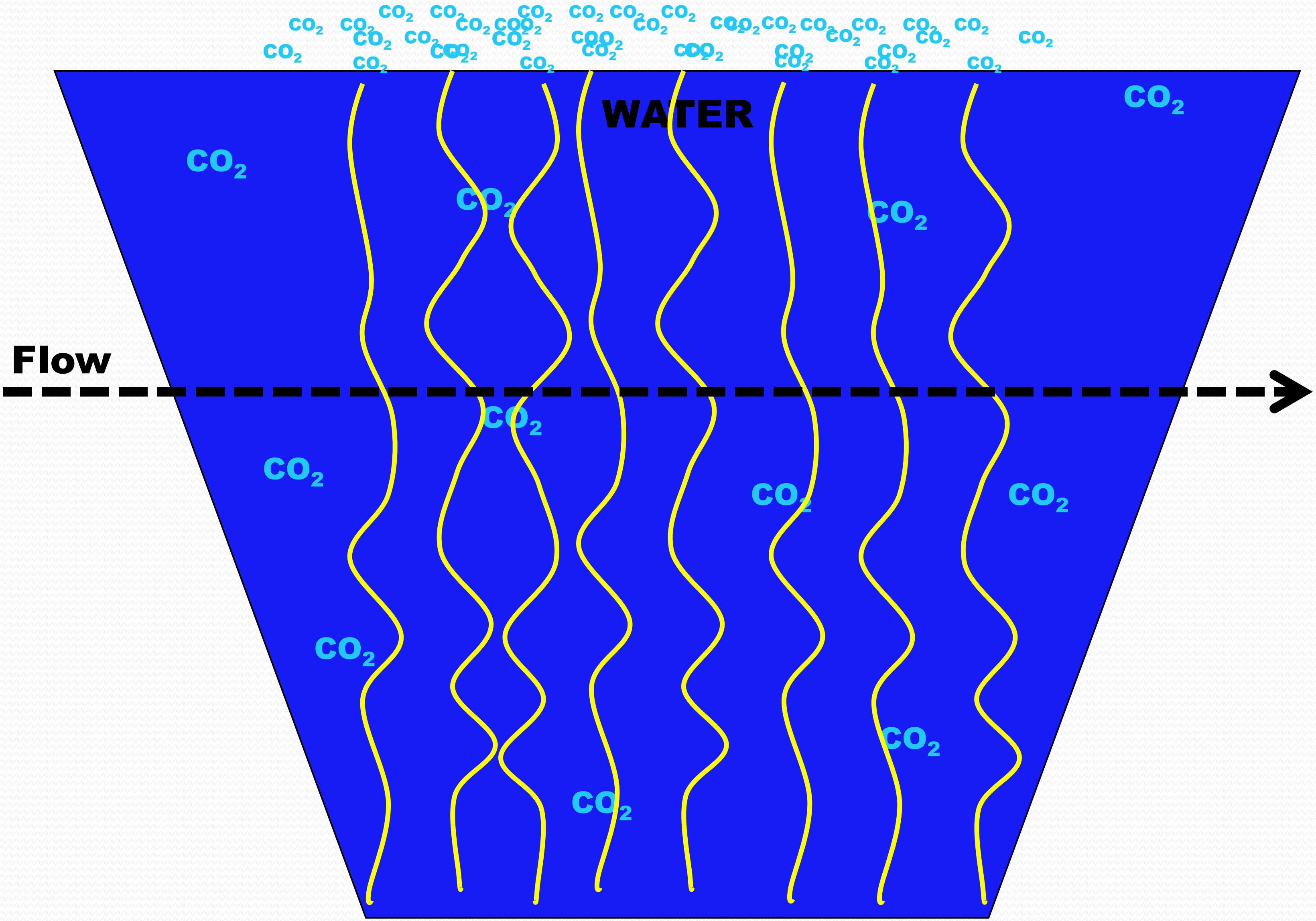
Swarms of Bubbles



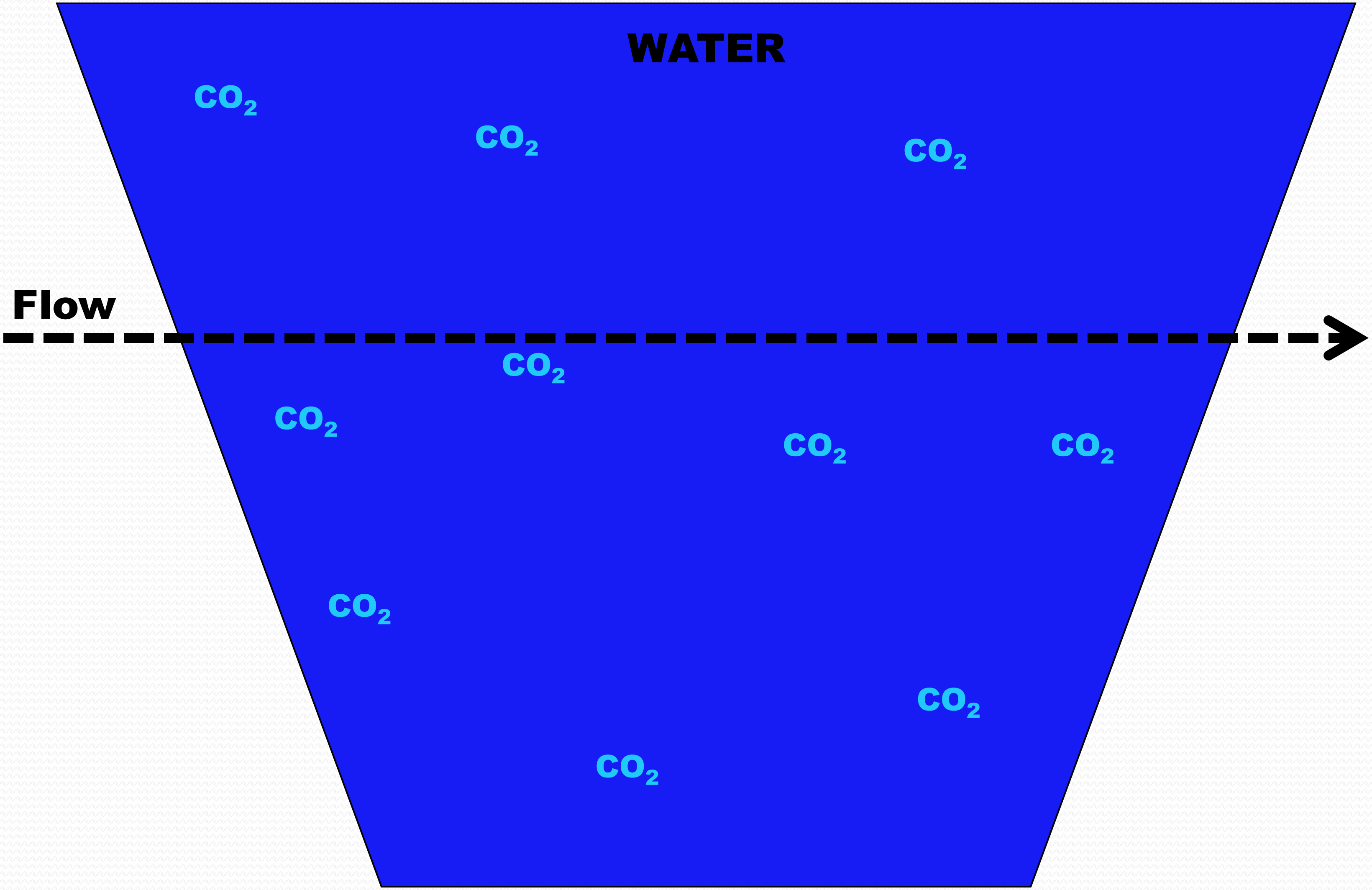
Swarms of Bubbles



Swarms of Bubbles



Swarms of Bubbles



Mass (Environmental) Transport Processes?

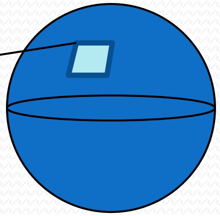
What is a Mass Transport Process?

1. It is the transport of a mass from one phase (solid, liquid, or gas) to another phase (solid, liquid, or gas) with and without reaction.
2. In the case of carbon dioxide removal from water, it is the transport of a soluble gas (in water) to the gaseous phase across the liquid:gas interface, and in this case with no reaction.

Reference: B. E. Logan. 1999 . Environmental Transport Processes . John Wiley & Sons, Inc. NY.

Mass (Environmental) Transport Coefficients

K_{wa} versus $K_{L,a}$



K_{wa} in units of m^2/sec

1. Mass Transport Coefficient that is independent of Reactor Design (i.e., CSTR vs. PFR, coarse or fine bubbles, reactor depth).
2. Translatable across reactor types and bubble aeration types.
3. Can be varied with temperature if $E_{a,app}$ is known.

$K_{L,a}$ in units of sec^{-1}

1. Combines K_{wa} and a_v into a Reactor Specific Value.
2. Specific to a single reactor and aeration type.
3. BLACK BOX Coefficient.

Mass (Environmental) Transport Equations (for water:air interface)

Continuously Stirred Reactor (CSTR):

Reaction Rate

$$-dc/dt = K_{wa} \times a_v \times (C_{eq} - C) - kX$$

K_{wa} = Mass Transport Coefficient ;a_v = interfacial area (e.g., bubble surface area)
C_{eq}= Equilibrium Concentration; C = Reactor Out Concentration

Plug Flow Reactor (PFR):

Determined by Henry's Law

$$-dc/dt = 1/(K_{wa} \times a_v) \times \ln (Co/(C_{eq} - C)) - kX$$

K_{wa} = Mass Transport Coefficient; a_v = interfacial area (e.g., bubble surface area)
Co = Initial Concentration; C_{eq}= Equilibrium Concentration;
C = Reactor Out Concentration

Note: Both K_{wa} and C_{eq} are affected by temperature of the water.

Determining Mass Transport Coefficent (K_{wa}) for Carbon Dioxide

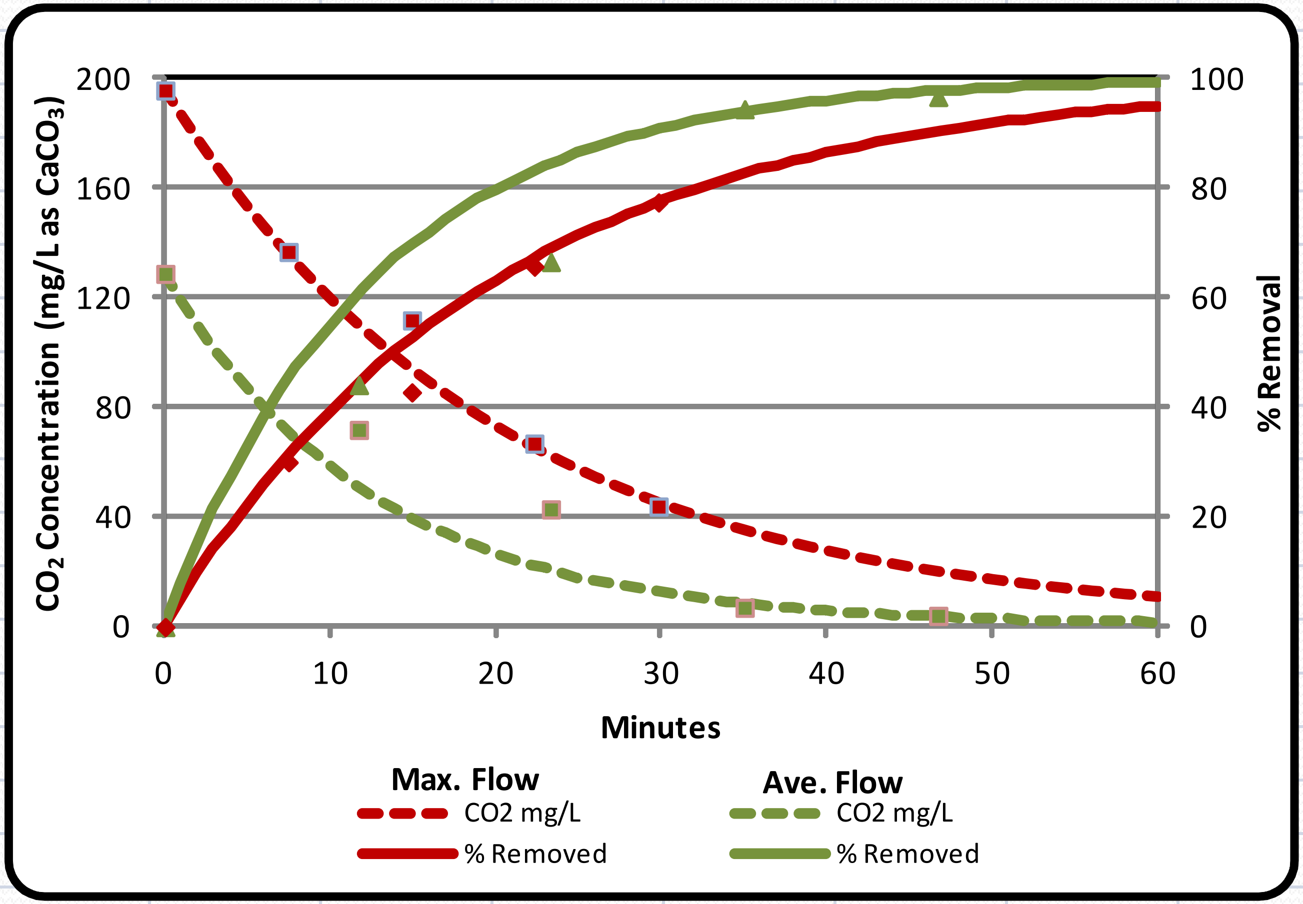
Field Testing

Pre-aeration Pilot Studies

Aeration Studies Conducted at Different Detention Times, Air Flows, Bubble Type, & Water Temperature (i.e., different AMD source waters).

Yield K_{wa} & $E_{a,app}$ for CO_2

Full-scale Pre-aeration System Performance



Pre-Aeration System Design

Design Model Determines

Detention Time & Air Flow for
CSTR/PFR & Bubble Types

Pre-aeration System Design Model

K_{wa} in units of m^2/sec
$E_{a,app}$ in units of KJ/mole

- **Adjusts for Reactor Depth.**
- **Adjusts for Air Volume (or Bubble Size).**
- **Adjusts for Air Volume to Reactor Volume.**
- **Adjusts for Temperature of Water.**
- **Computes Detention Time for PFR.**
- **Computes Detention Time and # of CSTRs.**
- **Computes Efficiency of Carbon Dioxide Removal.**

Comparison of Two Distinctly Different Bubble Pre-aeration Systems

Pre-aeration System	Maelstrom Oxidizer©
PA Mines - Rushton Site	Rosebud Mines – St. Michael Site
Q = 4,800 gpm	Q = 3,600 gpm
CSTR/PFR – 2 in series	CSTR/PFR – 4 units
Design DT ~ 28 min	Design DT ~ 3.1 min
Reactor Depth = 9 ft	Reactor Depth = 2 feet
Coarse Bubble Air Diffusers	Fine Bubble Air Diffusers
Air Flow = 1,000 cfm (60 Hp)	Air Flow = 13,000 cfm (120 Hp)
AMD Temp. = 10°C	AMD Temp. = 12°C
CO2 Acidity = 150-200 mg/L	CO2 Acidity = 180 mg/L
AMD pH = 4.0 to 5.0	AMD pH = 5.5 to 6.0
Iron Oxide Technologies, LLC	***Environmental Solutions, LLC***

Model Results for the Two Bubble Pre-aeration Systems

Pre-aeration System

- PA Mines - Rushton Site
- Q = 4,800 gpm
- Predicted DT = 28 min

Maelstrom Oxidizer©

- Rosebud Mines – St. Michael Site
- Q = 3,600 gpm
- Predicted DT ~ 3.6 min

Iron Oxide Technologies, LLC *Environmental Solutions, LLC*

Direct Comparison of Two Distinctly Different Bubble Pre-aeration Systems (based on Model)

Pre-aeration System	Maelstrom Oxidizer©
PA Mines - Rushton Site	Rosebud Mines – St. Michael Site
Q = 4,800 gpm	Q = 4,800 gpm
Design DT ~ 28 min	Design DT ~ 3.6 min
AMD Temp. = 10°C	AMD Temp. = 10°C
CO2 Acidity = 180 mg/L	CO2 Acidity = 180 mg/L
Removal = 90%	Removal = 90%
CSTR/PFR – 2 units in series	CSTR/PFR – 6 units in series
Air Flow = 1,000 cfm (60 Hp)	Air Flow = 19,500 cfm (180 Hp)
Iron Oxide Technologies, LLC	***Environmental Solutions, LLC***

Direct Comparison of Costs for Bubble Pre-aeration Systems

Pre-aeration System

- PA Mines - Rushton Site
- Q = 4,800 gpm

- Eq. Capital Costs ~ $550,000
- Electricity Costs ~ $28,500/yr
- Maintenance – Low
- Lime Savings ~ $200,000/yr

Iron Oxide Technologies, LLC

Maelstrom Oxidizer©

- Rosebud Mines – St. Michael Site
- Q = 4,800 gpm

- Eq. Capital Costs ~ $400,000
- Electricity Costs ~ $94,500/yr
- Maintenance – High
- Lime Savings ~ $200,000/yr

Environmental Solutions, LLC

Conclusion of Pre-aeration Systems Design Modeling & Comparison

- **Model Adequately Predicts A Range of Bubble Pre-aeration Designs**
  - Bubble Type, Reactor Type, Reactor Depth, Temperature, Air Flow, etc.
- **Can Be Used as a Design Tool to Determine DT for Pre-aeration Systems**
  - Various designs, equipment, configurations, etc.
- **Selection of Pre-aeration System is Owner Decision**
  - Capital Costs
  - Operating Costs
  - Maintenance Requirements
  - Site/Existing Conditions