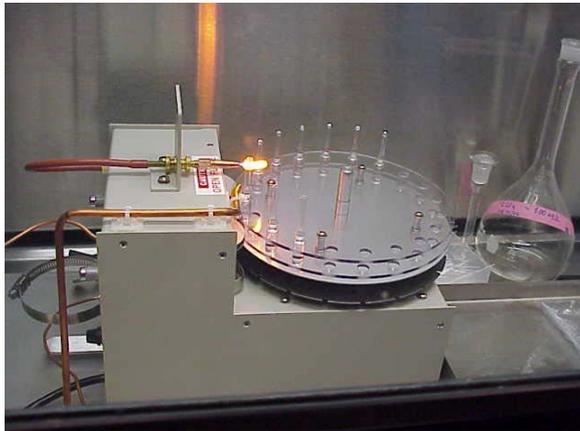
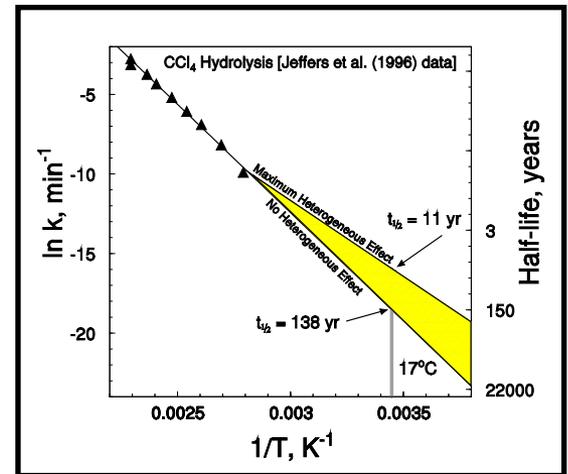


Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions



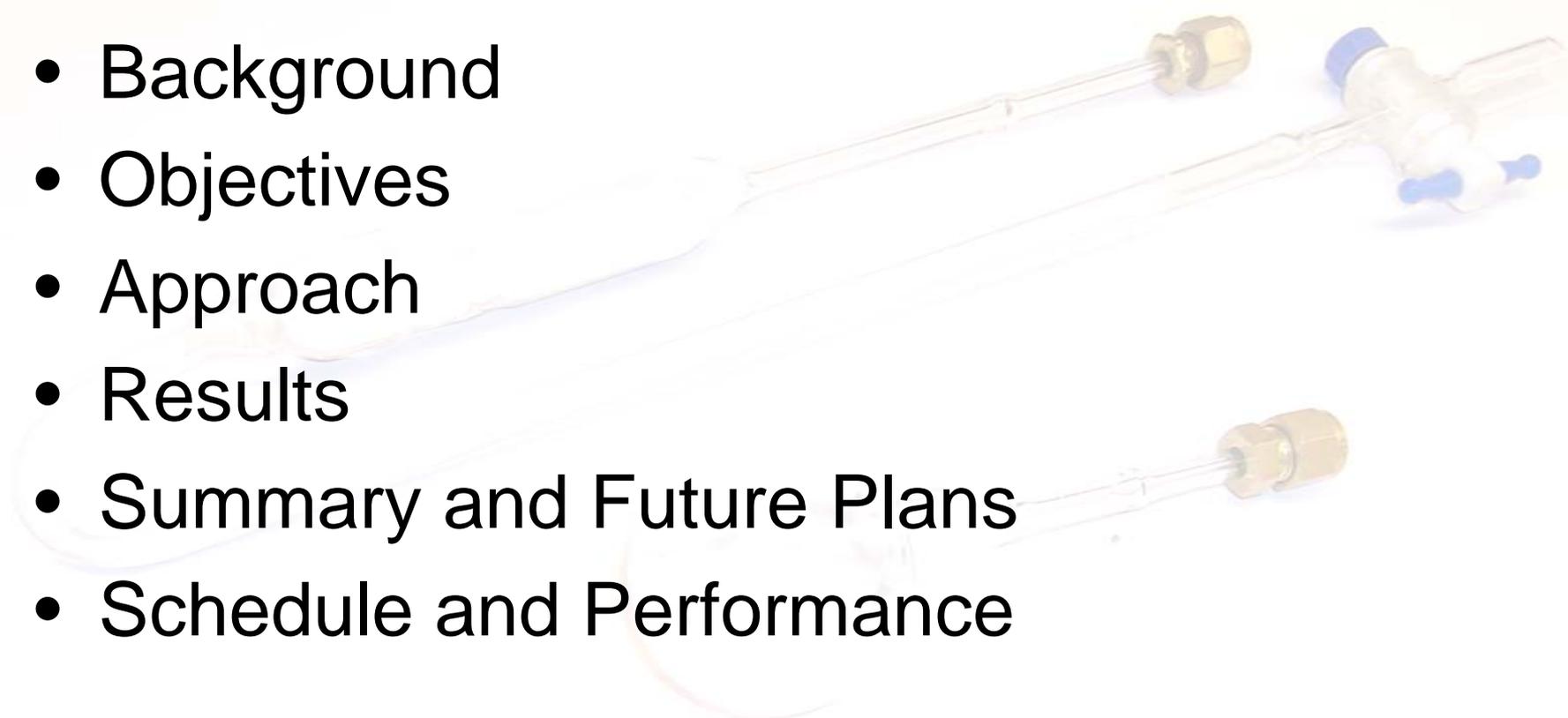
EM-22 Technical Review

30 July 2008
PNNL-SA-61815
J. E. Amonette*
P. M. Jeffers
M. J. Truex
J. S. Fruchter



Outline

- Background
- Objectives
- Approach
- Results
- Summary and Future Plans
- Schedule and Performance



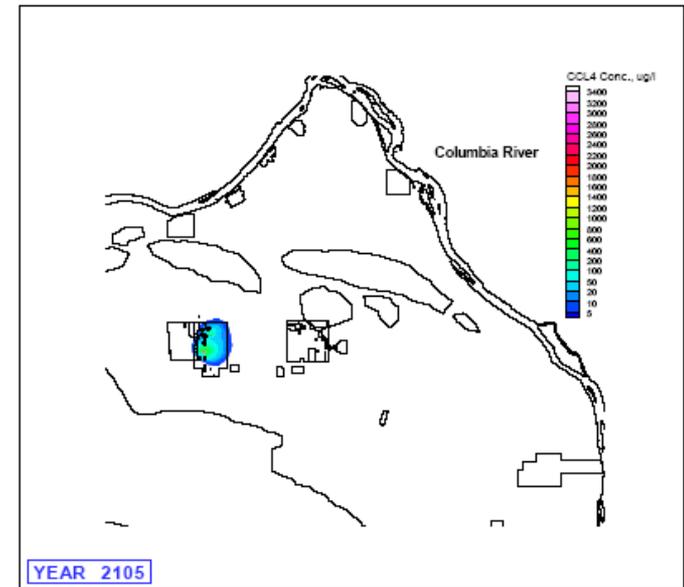
A Problem

- Large quantities of CCl_4 (CT) were disposed into trenches in the 200W Area during plutonium production activities
- Some of the CT has leaked into the groundwater and created a plume of concern at significant depth
- Some of the CT in the plume has degraded to form CHCl_3 (CF), also of concern
- To what degree will natural attenuation be of use in remediation?

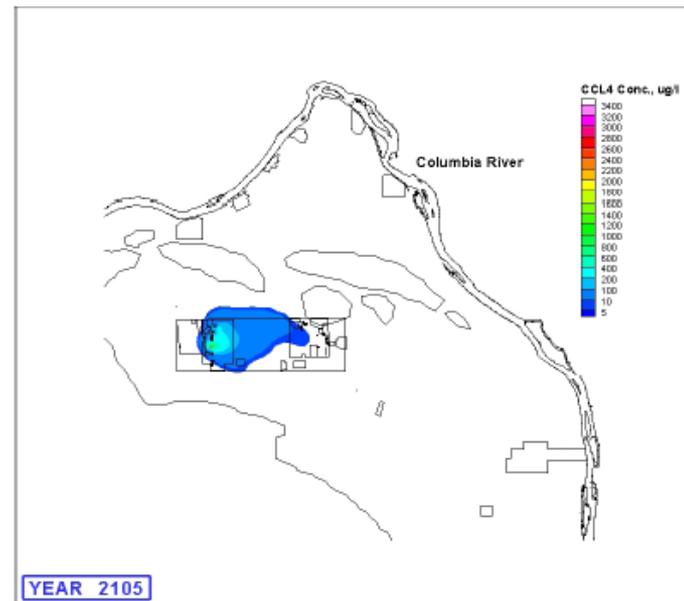
Natural Attenuation Parameters

- Previous studies (e.g., ITRD, fate and transport modeling) identified potential for natural attenuation to meet goals
- K_d and **attenuation reaction rate (k_a)** are key parameters to success; if K_d and k_a are high enough, attenuation may meet remediation goal

Best estimate
 k_a , K_d



No
 k_a , K_d



Abiotic Attenuation Pathways (k_a)

- Electron transfer [reduction by Fe(II) or sulfide, oxidation by Fenton reagents, microbial action, etc.)]
 - usually yields hazardous products (e.g., CF from CT)
 - moderate to very fast
 - usually requires manipulation to ensuring reagent contacts contaminant
- Hydrolysis (nucleophilic substitution of Cl by oxygen from water)
 - yields innocuous products
 - very slow
 - “guaranteed” natural process

Hydrolysis

- For CT:



- For CF:



Neutral hydrolysis (dominant at pH <4)



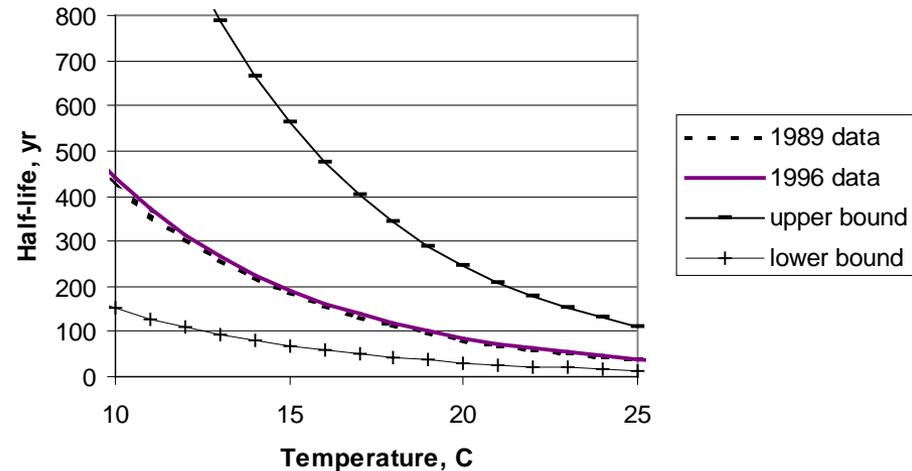
Base-catalyzed hydrolysis (dominant at pH >8)

Natural Attenuation by Hydrolysis

- Abiotic hydrolysis rates have been measured in DI water at high temperatures (> 70 C)
- Extrapolation to groundwater temperature results in large uncertainty in rate
- Further uncertainty arises from the possibility that sediment surfaces or groundwater constituents may catalyze hydrolysis rates

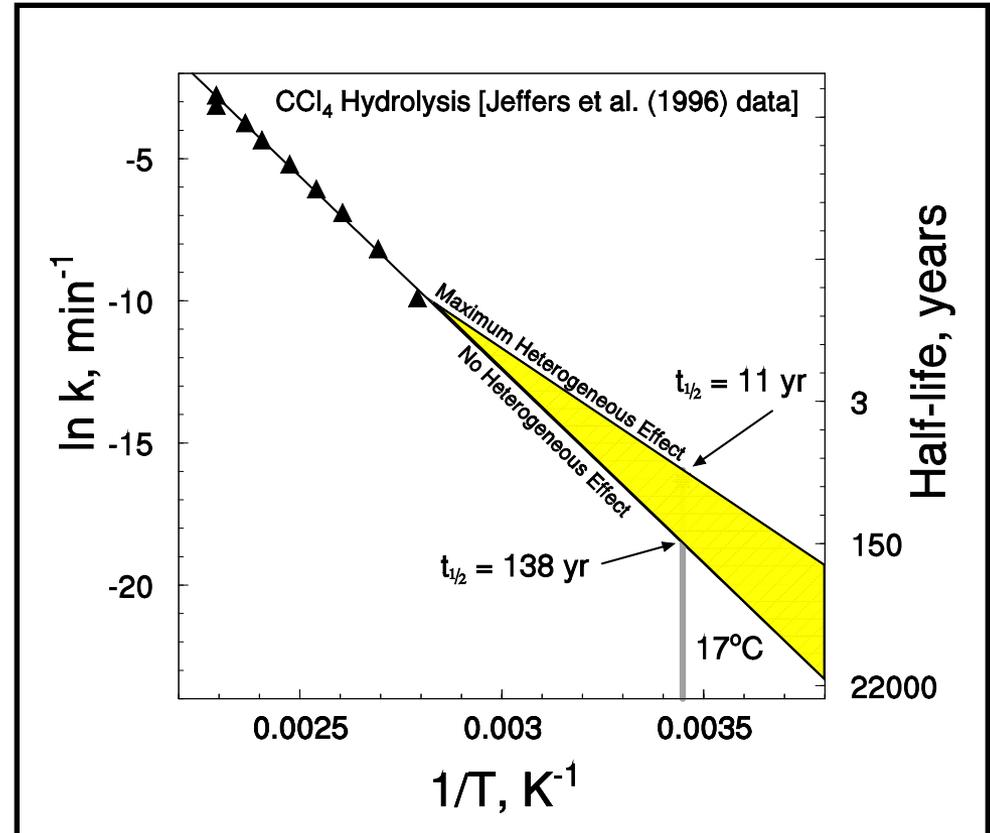
Figure 2. Neutral Homogeneous Hydrolysis of Carbon Tetrachloride in Distilled Water

Data of Jeffers et al. (1989, 1996)



Heterogeneous Catalysis Hypothesis

- Heat released during sorption raises local temperature and effectively lowers the activation energy
- Other factors such as accessibility and strain may also affect reaction rate

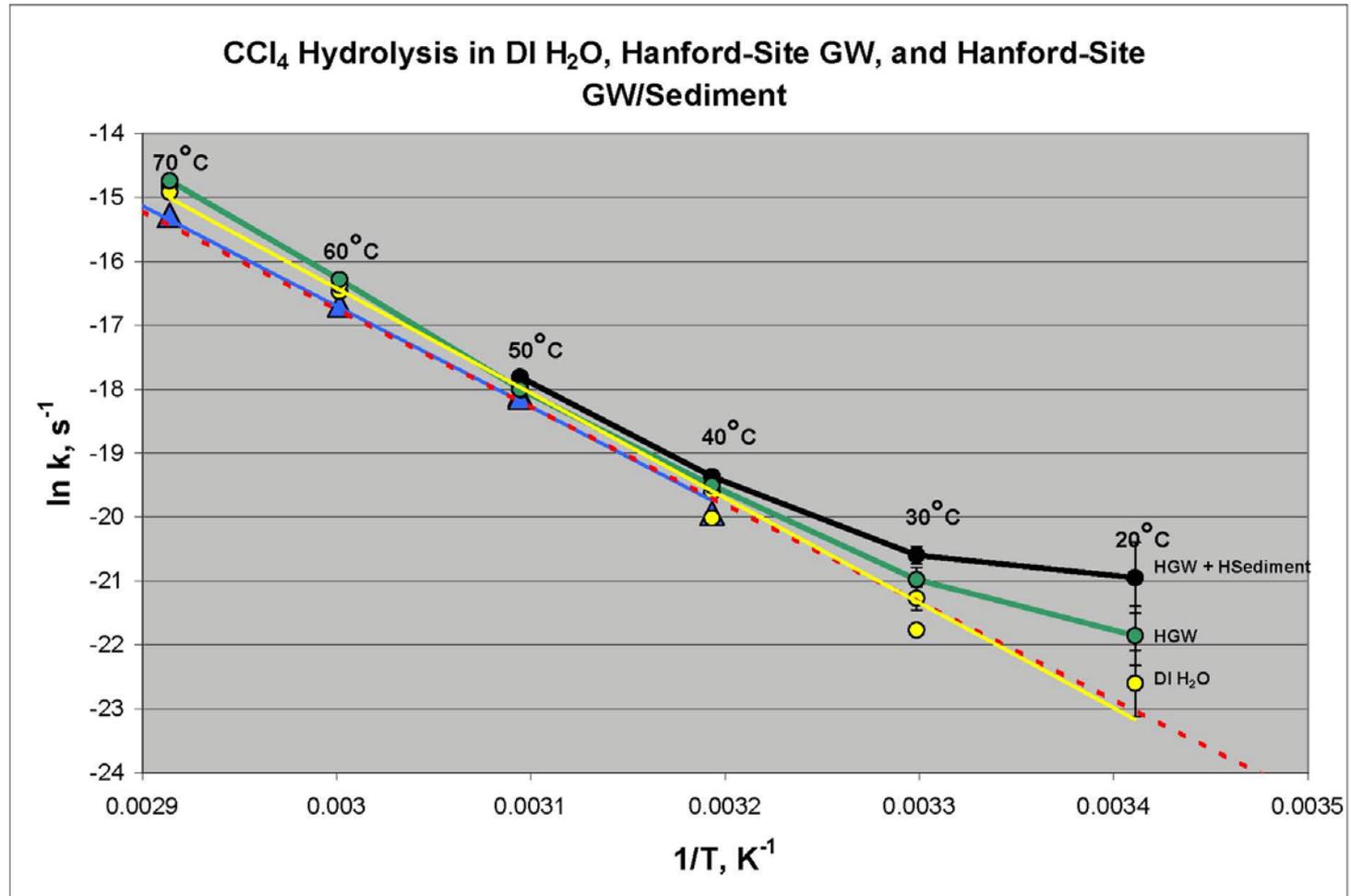


We estimated a maximum rate increase of about 8-fold for a 1 ppm solution of CT at 17 C due to sorption effects alone.

Prior and Related Work

- Literature data for homogeneous hydrolysis only at high temperatures for CT and CF
- No literature has shown heterogeneous effects on CT and CF hydrolysis
- Sister project funded by Fluor-Hanford starting in FY2006 initiated 5-year experiments for low-temperature CT hydrolysis under homogeneous conditions and in the presence of Hanford-Site sediment

Preliminary Evidence for Heterogeneous Effects on Hydrolysis Rate



Data from sister project funded by Fluor-Hanford (PNNL Support to Remediation Decision Support for FY08); Error bars are 95% Confidence Intervals.

Overview of Project

Large uncertainty in abiotic degradation rates (k_a) limits the ability to predict fate and transport and to develop cost-effective remediation plans for CT and CF plumes in 200 West Area

Project will provide critical physical-chemical data for CT and CF hydrolysis reactions under groundwater conditions (T, surfaces)

- First determination of $k_a(\text{Het})$ for CT and CF
- Maximum increase for k_a from Het could be 8x for 1000 ppb CT
- Clarification of $k_a(\text{Hom})$ for CF
- Improved k_a 's will strengthen technical basis for remediation decision

Type of Hydrolysis	CT		CF	
	Hom	Het	Hom	Het
Neutral	X*	?	X	?
Basic			X	?

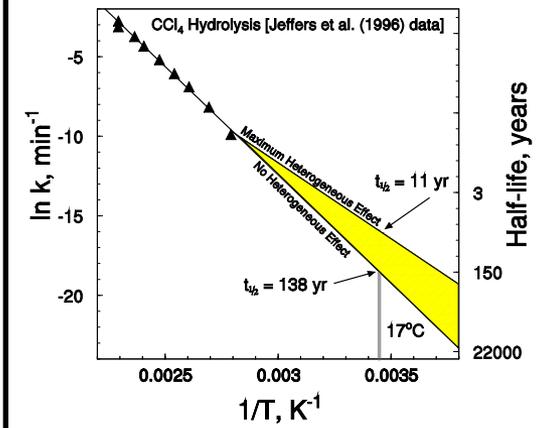
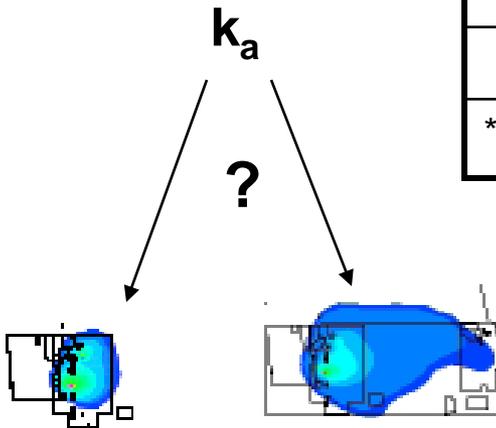
*Currently funded by Fluor-Hanford

Homogeneous (Hom)—Occurring in solution phase only

Heterogeneous (Het)—Involves interface between solution and solid phase

Neutral—Insensitive to pH (H_2O is active agent)

Base-catalyzed—Rate increases with pH (OH^- is active agent)



Problem



Project Approach



Potential Impact

Specific Project Objectives

- Determine the neutral and base-catalyzed homogeneous hydrolysis rates for CF under near-ambient temperatures.
- Determine the impact and mechanisms of representative Hanford mineral surfaces on the hydrolysis of CT at near-ambient temperatures.
- Determine the impact and mechanisms of representative Hanford mineral surfaces on the neutral and base-catalyzed hydrolysis of CF at near-ambient temperatures.

Approach

- Conduct experiments in sealed ampoules (headspace:fluid ratios of 1:2) at PNNL
- Conduct selected experiments in parallel at SUNY-Cortland (Dr. Peter Jeffers) using zero-headspace reactors
- Determine liquid/vapor partition coefficients at elevated temperatures for CT and CF

Sediment and Minerals

- Hanford-Site sediment (silt loam, 422' depth, 216-Z-9/C3426, uncontaminated, collected on 4 Jan 2005)

Particle Size Class	----- weight percent -----
Sand (>53 μm)	0
Silt (2-53 μm)	78
Clay (<2 μm)	22
Bulk Mineralogy	
Quartz	49
Plagioclase (60:40 An:Al)	10
Potassium feldspar	1
Smectite	30
Mica/illite	6
Kaolin/serpentine	5

Mineral	Source Locale
Montmorillonite	Newcastle Formation, Crook County, Wyoming (SWy-2, Source Clay of The Clay Minerals Society)
Kaolinite	Bath, SC (Peerless #2)
Albite	Kona, SC (SRM 99a, Soda Feldspar, National Institute of Standards and Technology)
Muscovite	Stoneham, ME (ground to silt size)

Groundwater

- Uncontaminated Hanford-site groundwater (Well 699-49-100C located near the Yakima barricade west and up-gradient of the 200-West Area at the Hanford Site, collected on 12 July 2006)

Constituent/Property	Value ($\mu\text{g L}^{-1}$ unless otherwise indicated)
SO_4^{2-}	75000
NO_3^-	13000
Cl^-	19000
F^-	300
Ca^{2+}	60000
Mg^{2+}	21000
Na^+	25000
K^+	7500
Fe (valence unspecified)	30
Alkalinity	175000
Total Organic Carbon	1000
Electrical Conductivity ($\mu\text{S cm}^{-1}$)	570
pH (log units)	7.75

Typical PNNL Experiment

Analysis	Sampling Time									
	t0	t1	t2	t3	t4	t5	t6	t7	t8	t9
Cl ⁻ by IC	1	8	17	26	33	42	51	58	67	76
Cl ⁻ by IC	2	9	18	27	34	43	52	61	68	77
Cl ⁻ by IC	3	10	19	28	37	44	53	62	69	78
Cl ⁻ by IC	4	13	20	29	38	45	54	63	70	79
Cl ⁻ by IC	5	14	21	30	39	46	55	64	73	80
CT,CF,MC by GC	6	15	22	31	40	49	56	65	74	81
CT,CF,MC by GC	7	16	25	32	41	50	57	66	75	82

	100 C	Reference	4 C	
Cl ⁻ by IC	11	Reference	12	<div style="display: flex; flex-direction: column; gap: 5px;"> <div style="background-color: #d9ead3; width: 20px; height: 10px; margin-bottom: 5px;"></div> <div style="background-color: #f4cccc; width: 20px; height: 10px; margin-bottom: 5px;"></div> <div style="background-color: #fce4d6; width: 20px; height: 10px; margin-bottom: 5px;"></div> <div style="background-color: #fff2cc; width: 20px; height: 10px; margin-bottom: 5px;"></div> <div style="background-color: #d9ead3; width: 20px; height: 10px; margin-bottom: 5px;"></div> <div style="background-color: #f4cccc; width: 20px; height: 10px; margin-bottom: 5px;"></div> <div style="background-color: #fce4d6; width: 20px; height: 10px; margin-bottom: 5px;"></div> </div>
Cl ⁻ by IC	23	Reference	24	
Cl ⁻ by IC	35	Reference	36	
Cl ⁻ by IC	47	Reference	48	
Cl ⁻ by IC	59	Reference	60	
Cl ⁻ by IC	71	Reference	72	
Cl ⁻ by IC	83	Reference	84	

Incubated at nominal temperature (20, 30, 40, 50, 60, or 70 C)
 Incubated at 100 C for initial concentration determination
 Incubated (quenched) at 4 C for reference values
 Selected at random to determine fluid:headspace ratio

PNNL Experimental Matrix

- CF Homogeneous and Sediment

PNNL Chloroform (CF) Hydrolysis Experiments					
Temperature, °C	pH=3.0		pH= 8.0		HW
	DI, 40 ppm CF	DI, 400 ppm CF	DI, 400 ppm CF	DI, 400 ppm CF	HSed, 400 ppm CF
20	NA	X	X	X	X
30	NA	X	X	X	X
40	X	X	X	X	X
50	X	X	X	X	X
60	X	X	X	X	NA
70	X	X	X	X	NA

- CT Heterogeneous (Mineral-Specific)

PNNL Mineral-Specific Carbon Tetrachloride (CT) Hydrolysis Experiments				
Temperature, °C	HW, 400 ppm CT			
	Montmorillonite	Kaolinite	Albite	Muscovite
20	X	X	X	X
30	X	X	X	X
40	X	X	X	X
50	X	X	X	X
60	NA	NA	NA	NA
70	NA	NA	NA	NA

- CF Heterogeneous (Mineral-Specific)

PNNL Mineral-Specific Chloroform (CF) Hydrolysis Experiments				
Temperature, °C	HW, 400 ppm CF			
	Montmorillonite	Kaolinite	Albite	Muscovite
20	X	X	X	X
30	X	X	X	X
40	X	X	X	X
50	X	X	X	X
60	NA	NA	NA	NA
70	NA	NA	NA	NA

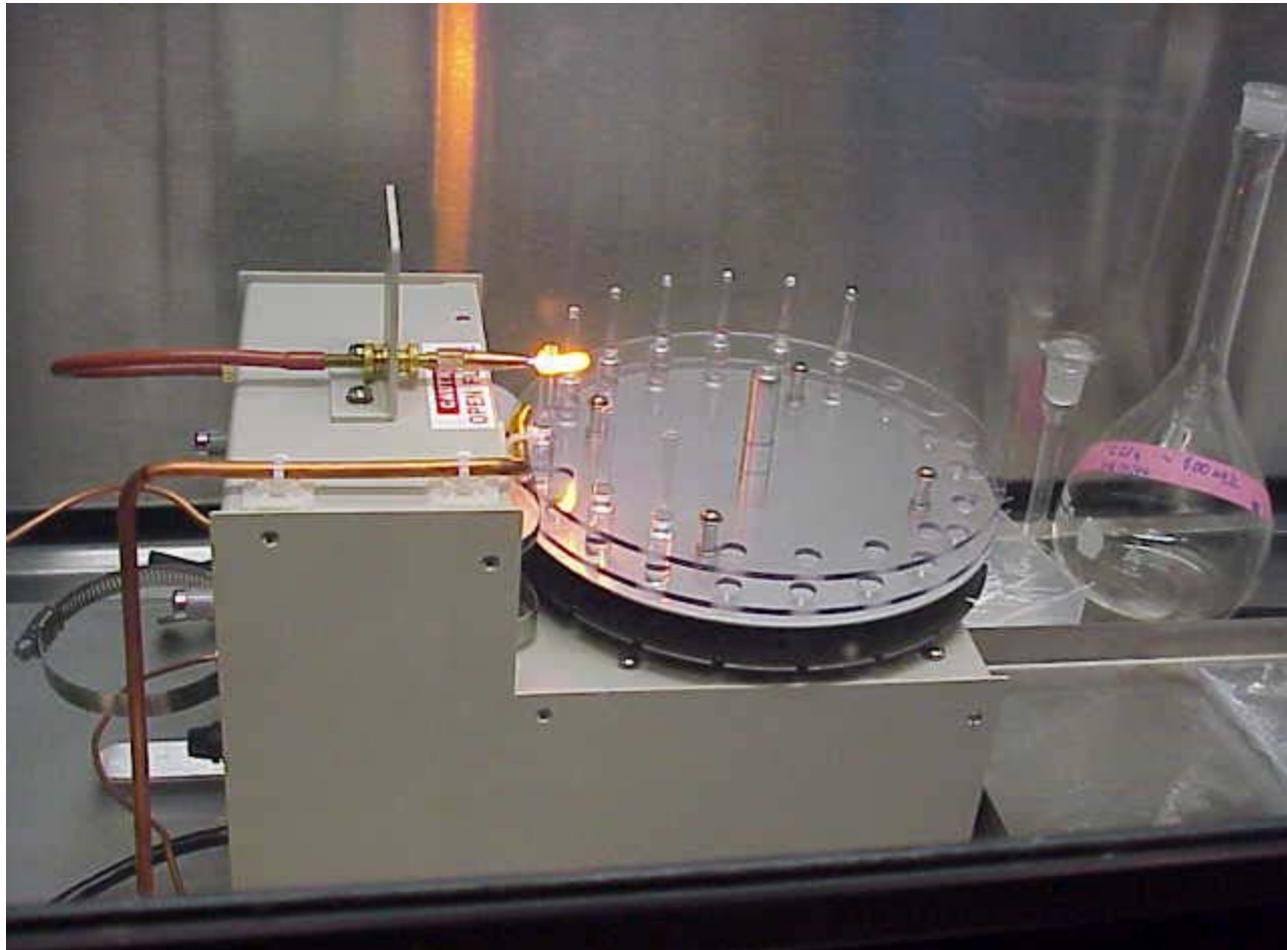
Large Headspace Ampule



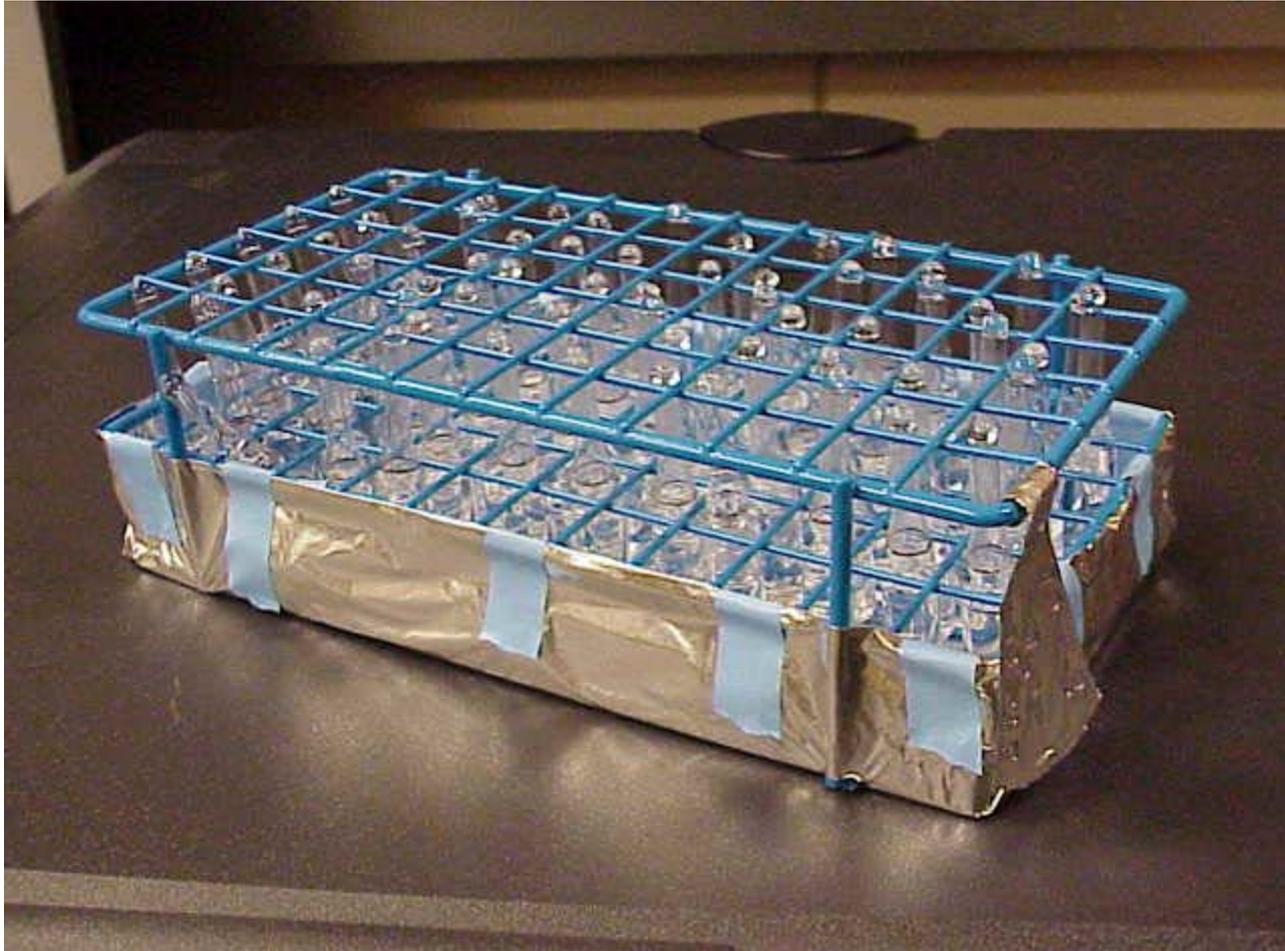
Ampule Filling



Ampule Sealing



Rack of Sealed Ampules



Incubator Array



SUNY-Cortland Experimental Matrix

- CF homogeneous, pH 12
- CT and CF mineral-specific (kaolinite, montmorillonite)
- Liquid-vapor partition coefficients

Zero-headspace reactor (top) and liquid-vapor partition coefficient bulb (bottom) developed and used at SUNY-Cortland by Dr. Peter Jeffers



Current Status of Experiments

PNNL Chloroform (CF) Hydrolysis Experiments						
Temperature, °C	pH=3.0		pH= 8.0		pH= 12.0	HGW
	DI, 40 ppm CF	DI, 400 ppm CF	HSed, 400 ppm CF			
----- Fraction of experiment sampled as of July 25, 2008 -----						
20	NA	20	20	100	40	
30	NA	30	20	100	40	
40	30	30	40	100	40	
50	40	40	90	100	90-completed	
60	60	60	100	100	NA	
70	90	90	100	100	NA	

PNNL Mineral-Specific Carbon Tetrachloride (CT) Hydrolysis Experiments				
HGW, 400 ppm CT				
Temperature, °C	Montmorillonite	Kaolinite	Albite	Muscovite
	----- Fraction of experiment sampled as of July 25, 2008 -----			
20	50	50	50	50
30	60	60	60	50
40	70	70	70	60
50	100	100	100	100
60	NA	NA	NA	NA
70	NA	NA	NA	NA

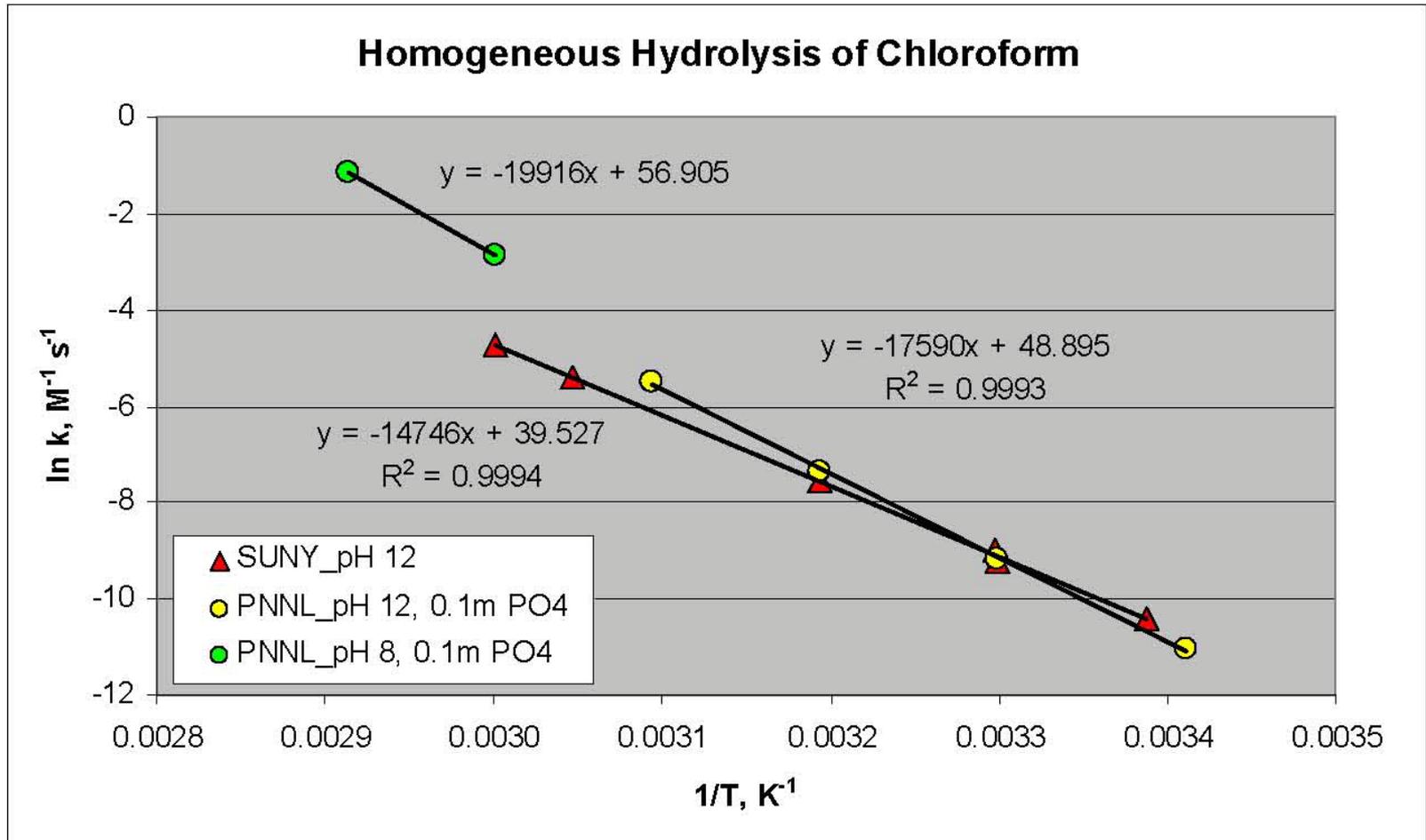
PNNL Mineral-Specific Chloroform (CF) Hydrolysis Experiments				
HGW, 400 ppm CF				
Temperature, °C	Montmorillonite	Kaolinite	Albite	Muscovite
	----- Fraction of experiment sampled as of July 25, 2008 -----			
20	30	30	30	30
30	30	30	30	30
40	30	60	60	30
50	60	60	60	60
60	NA	NA	NA	NA
70	NA	NA	NA	NA

Base-Catalyzed Homogeneous Hydrolysis Rates for CF

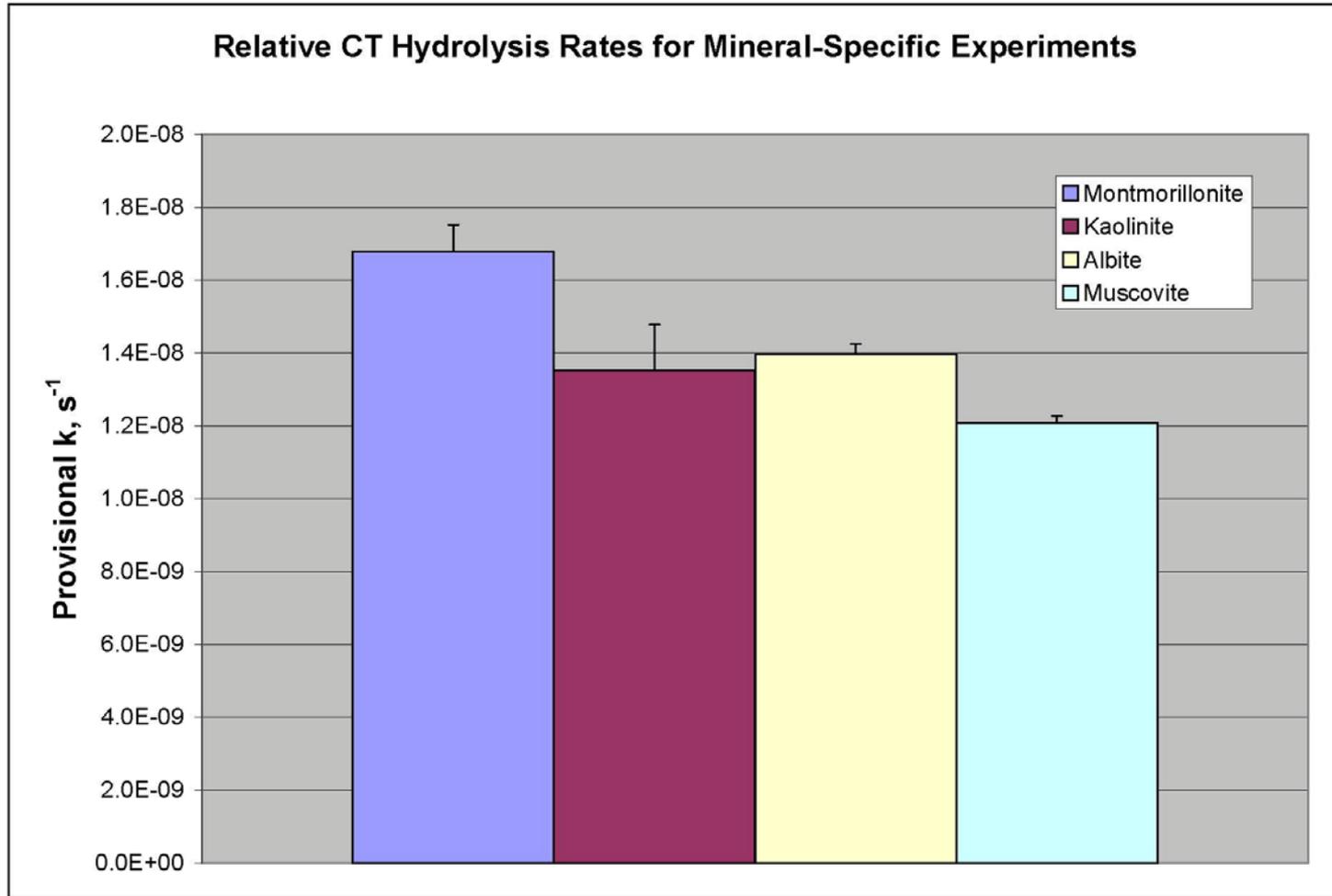
Table 3. Provisional rate constants for base-catalyzed homogeneous hydrolysis of CHCl_3 .

Temperature, °C	Initial CHCl_3 Concentration, mg kg^{-1}	Initial OH^- Concentration, mol kg^{-1}	k_B , SUNY, $\text{kg mol}^{-1} \text{s}^{-1}$	k_B , PNNL (0.1 m phosphate), $\text{kg mol}^{-1} \text{s}^{-1}$	K_H' (Gorgenyi et al., 2002)
70	182	1.72e-6	--	3.22e-1	0.663
60	182	1.72e-6	--	5.64e-2	0.541
60	58	9.74e-3	8.70e-3	--	--
55	157	9.59e-3	4.55e-3	--	--
50	285	2.44e-2	--	4.19e-3	0.417
40	157	9.59e-3	5.18e-4	--	--
40	58	9.74e-3	5.18e-4	--	--
40	285	2.44e-2	--	6.46e-4	0.296
30.15	50	1.01e-2	1.22e-4	--	--
30	190	9.74e-3	1.00e-4	--	--
30	285	2.44e-2	--	1.05e-4	0.209
22	157	9.59e-3	2.98e-5	--	--
20	285	2.44e-2	--	1.57e-5	0.137

Base-Catalyzed Homogeneous Hydrolysis Rates for CF



Mineral Effects on CT Hydrolysis Rates at 50 C

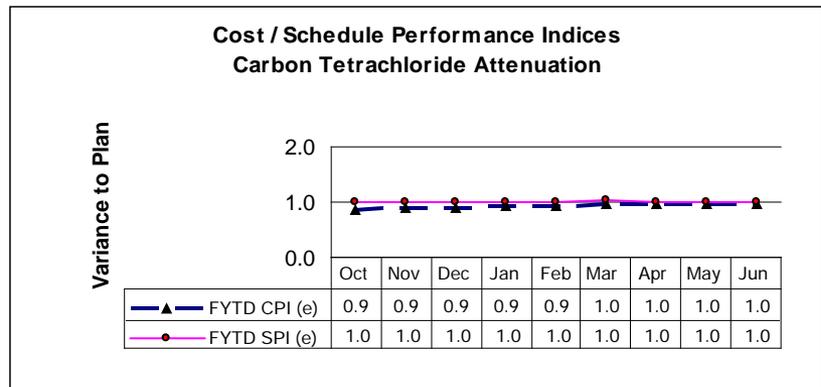
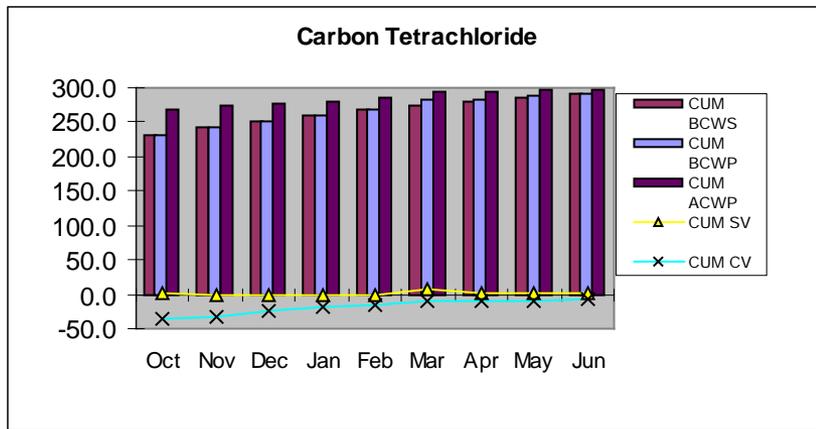
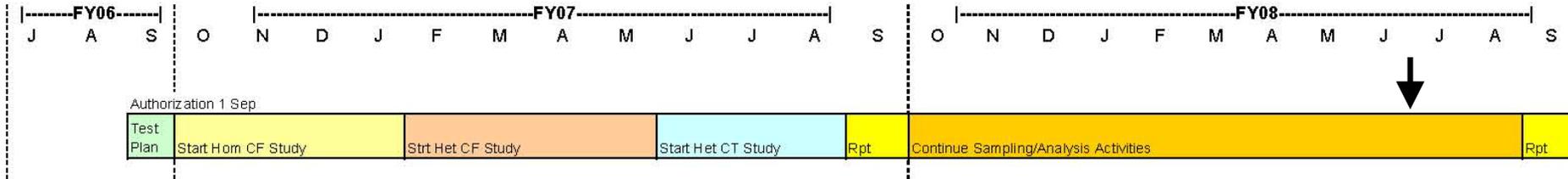


28 mg montmorillonite, 20 mg of other minerals; Error bars are 95% Confidence Intervals

Summary

- 58 individual long-term hydrolysis rate experiments started at PNNL
- 13 have completed sampling, although some analysis remains
- Reasonable agreement between PNNL and SUNY-Cortland data for base-catalyzed homogeneous CF hydrolysis
- Some evidence for phosphate effect (strong nucleophile) on rates
- Some evidence for mineral specificity, although need to adjust for surface area differences
- Work continues at SUNY-Cortland on liquid-vapor partition coefficients and heterogeneous rate experiments
- Sampling and analysis expected to continue at PNNL for next 3-4 years with follow-on funding from Fluor-Hanford

Schedule and Performance



Carbon Tetrachloride	FY07	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
CUM BCWS	214.8	230.1	243.0	252.0	260.9	269.0	275.6	281.2	286.0	290.1	294.0	298.0	309.0
CUM BCWP	217.8	232.0	242.7	251.8	260.6	268.7	283.0	284.1	287.3	291.3	0.0	0.0	0.0
CUM ACWP	252.3	268.3	274.1	277.3	279.1	284.9	292.9	293.7	296.4	297.3	0.0	0.0	0.0
CUM SV	3.0	1.9	-0.3	-0.3	-0.3	-0.3	7.4	2.9	1.2	1.2	0.0	0.0	0.0
CUM CV	-34.5	-36.3	-31.4	-25.5	-18.5	-16.2	-9.9	-9.5	-9.2	-6.0	0.0	0.0	0.0

Total Earmark Funds: \$309K

Acknowledgments

- Dr. Peter Jeffers developed the zero-headspace reactor concept and performed experiments at SUNY-Cortland
- Odeta Qafoku and Colleen Russell set up and operated the PNNL experiments
- Tom Wietsma performed the ion chromatographic analyses for Cl⁻ at PNNL