

# Kinetics of Thermally Activated Persulfate Oxidation of Trichloroethylene (TCE) and 1,1,1- Trichloroethane (TCA)



**Chenju Liang, Clifford J. Bruell**  
**University of Massachusetts Lowell**



**Michael C. Marley, Ken Sperry**  
**Xpert Design and Diagnostics (XDD),  
LLC**

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# Selected Target Contaminants:

Trichloroethylene (TCE)  $C_2HCl_3$

1,1,1-Trichloroethane (TCA)  $C_2H_3Cl_3$

# Selected Oxidant for In Situ Chemical Oxidation (ISCO) :

Sodium Persulfate  $Na_2S_2O_8$



# Persulfate Anion

- At ambient groundwater temperatures (15° C) the persulfate anion ( $S_2O_8^{2-}$ ) is a strong two-electron oxidizing agent.
- Reduction of the persulfate anion ( $S_2O_8^{2-}$ ) results in the production of sulfate anions as follows:



## Notes

- When dry Sodium Persulfate is added to water at ambient temperatures, it behaves as a fairly strong oxidant with a standard oxidation potential of 2.01 volts.
- This is an important reaction for the destruction of soil organic carbon.
- At ambient groundwater temperatures (5 degrees C.), relatively little TCE or TCA degradation is likely to be observed.

# Thermally Activated Persulfate Oxidation

- Thermal activation conditions (i.e., 40 - 99°C) result in the production of highly reactive sulfate free radicals ( $\text{SO}_4^{\cdot-}$ ):



- When the sulfate free radical serves as an oxidant it accepts a single electron resulting in the production of sulfate anions as follows:



## Notes

- The major product resulting from the reduction of persulfate is sulfate anions ( $\text{SO}_4^{2-}$ ) which are relatively harmless.
- The National Secondary Drinking Water Regulations (NSDWRs) for sulfate is 250 mg/L.

# Oxidation Potential for Selected Oxidants

Oxidant	Oxidation Potential (E°) (Volts)
Fluorine	3.03
Hydroxyl radical	2.8
<b>Sulfate radical</b>	<b>2.6</b>
Ozone	2.07
Persulfate anion	2.01
Hydrogen peroxide	1.70
Permanganate	1.68



# Experimental Design

- Experiments were designed to determine the influence of temperature and persulfate concentration on thermally activated persulfate oxidation of target contaminants.
- Pseudo-first-order reaction rates and activation energies were used to compare the experimental results.
- Aqueous phase experiments were first conducted to determine feasibility. Subsequent soil slurry experiments were conducted to better understand the influence of soil constituents such as soil minerals and soil organic carbon.



- A series of sealed 60 mL bottles were filled with a target contaminant solution at 50 to 70 mg/L and oxidant at the desired oxidant/contaminant molar ratio. A phosphate buffer was used to maintain a pH of 6.0 .

## Amber Boston-Round 60 mL Screw Cap Borosilicate Glass Bottles



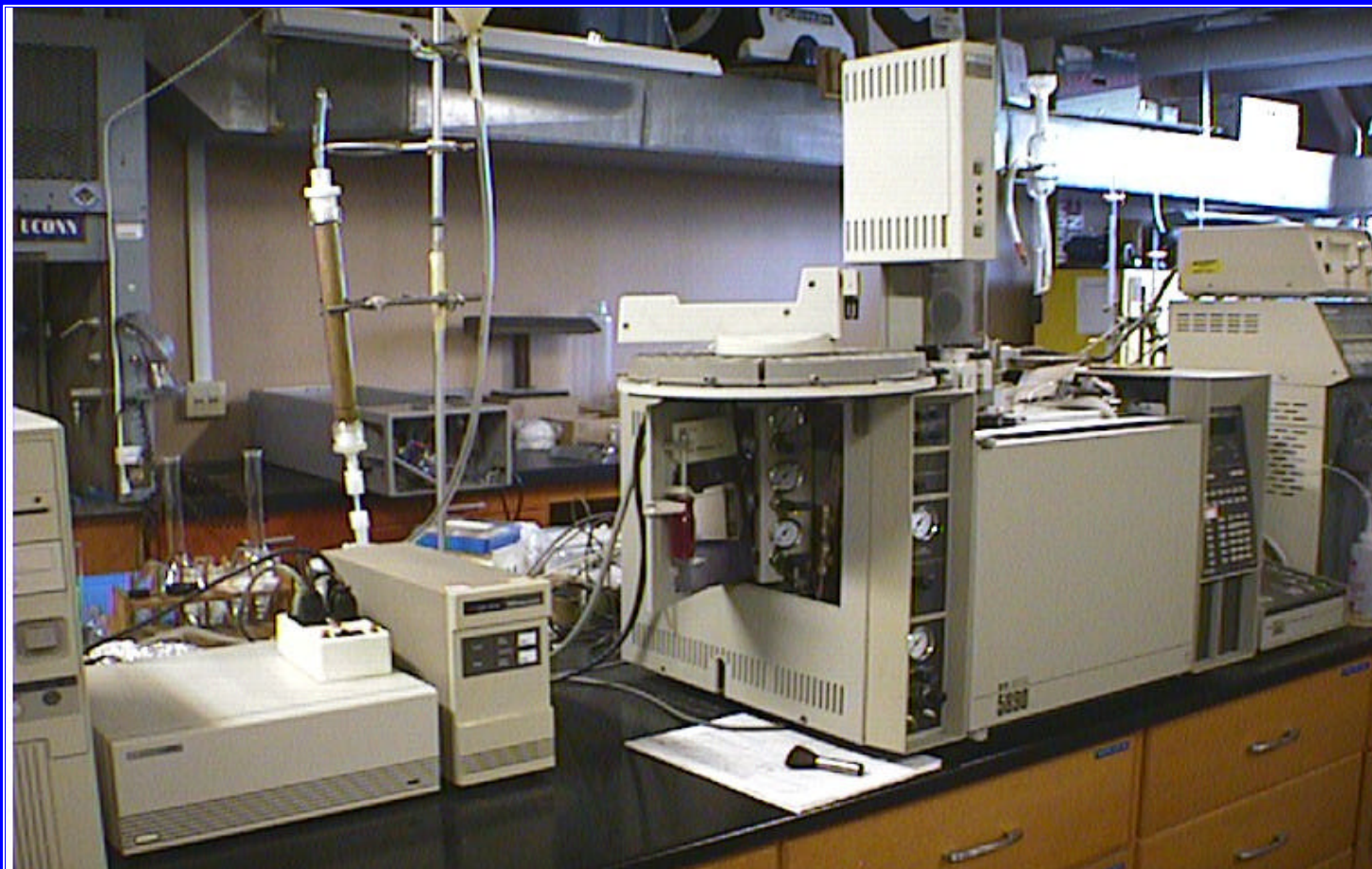
# Temperature Controlled (20-99°C) VWR Model 1227 Water Bath Reciprocal Shaker Containing Sample Bottles



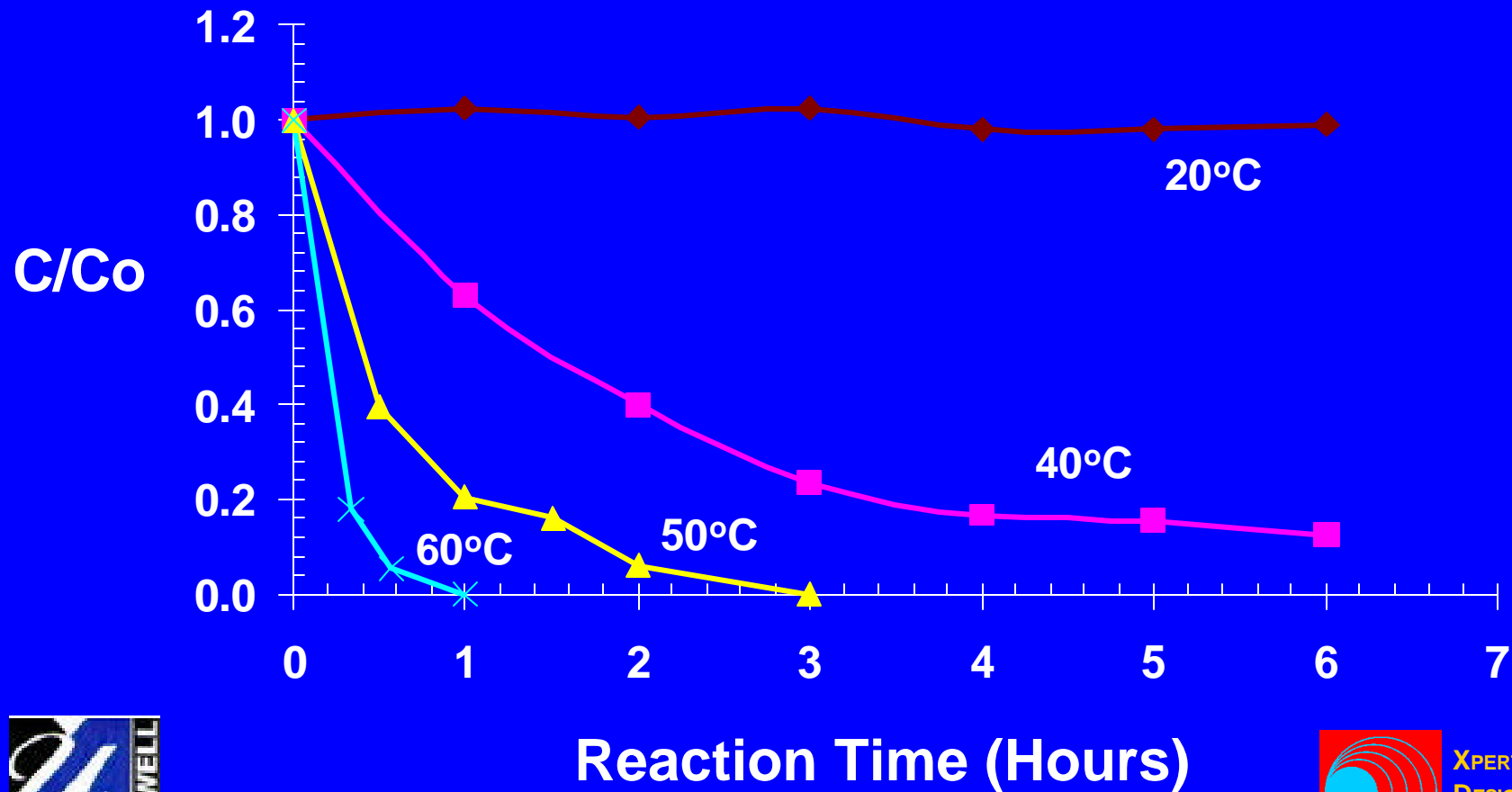
## Notes

- At various time periods, bottles were sacrificed, chilled in an ice-bath to quench the reaction, extracted with pentane and analyzed for target contaminant content.
- If degradation by-products were present, they most likely would have eluted within the solvent peak and therefore would not be seen.
- The pH, chloride ion and persulfate concentration were also measured.

# HP Model 5890 Gas Chromatograph (GC) with a Flame Ionization Detector (FID) Used to Quantify TCE and TCA Content



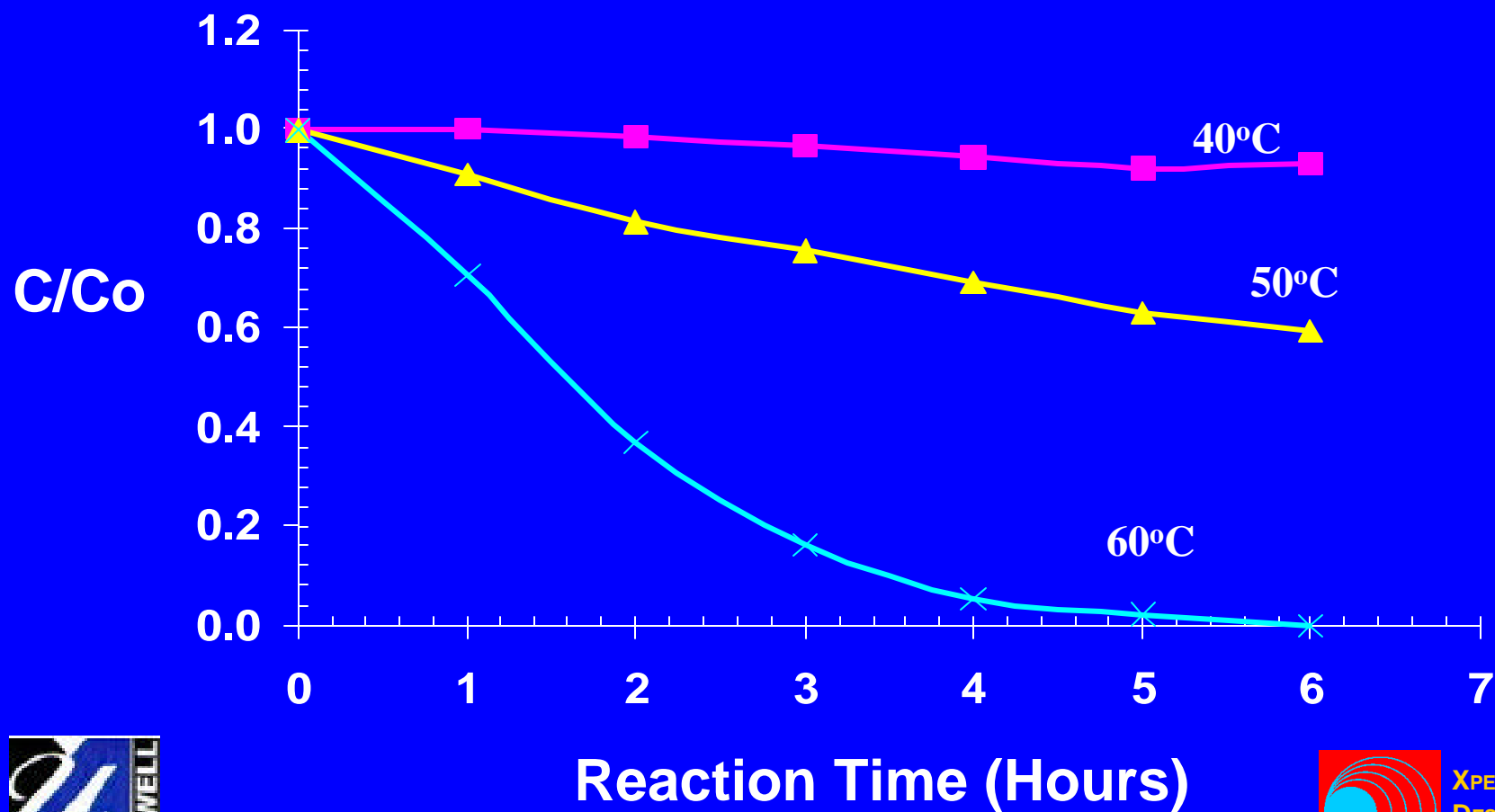
# Aqueous Phase TCE Degradation at an Oxidant/Contaminant Molar Ratio of 10/1 as a Function of Temperature



## Notes

- Control tests were run for all experiments but are not shown because they were horizontal lines over the time periods shown.
- Plots of raw data are shown. Within each experiment 2 bottles were sacrificed, analyzed and averaged. Each experiment was repeated two times at separate times. Therefore, each data point shown represents an average of four data points.
- There was very little degradation at 20° C. However, as temperature was increased, significant increases in degradation rates were observed.

# Aqueous Phase TCA Degradation at a Oxidant/Contaminant Molar Ratio of 10/1 as a Function of Temperature



# Kinetic Model

$$\ln [ C/C_0 ] = - k t$$

where:

C = Target contaminant concentration at time t, (mg/L).

C<sub>0</sub> = Initial target contaminant concentration, (mg/L).

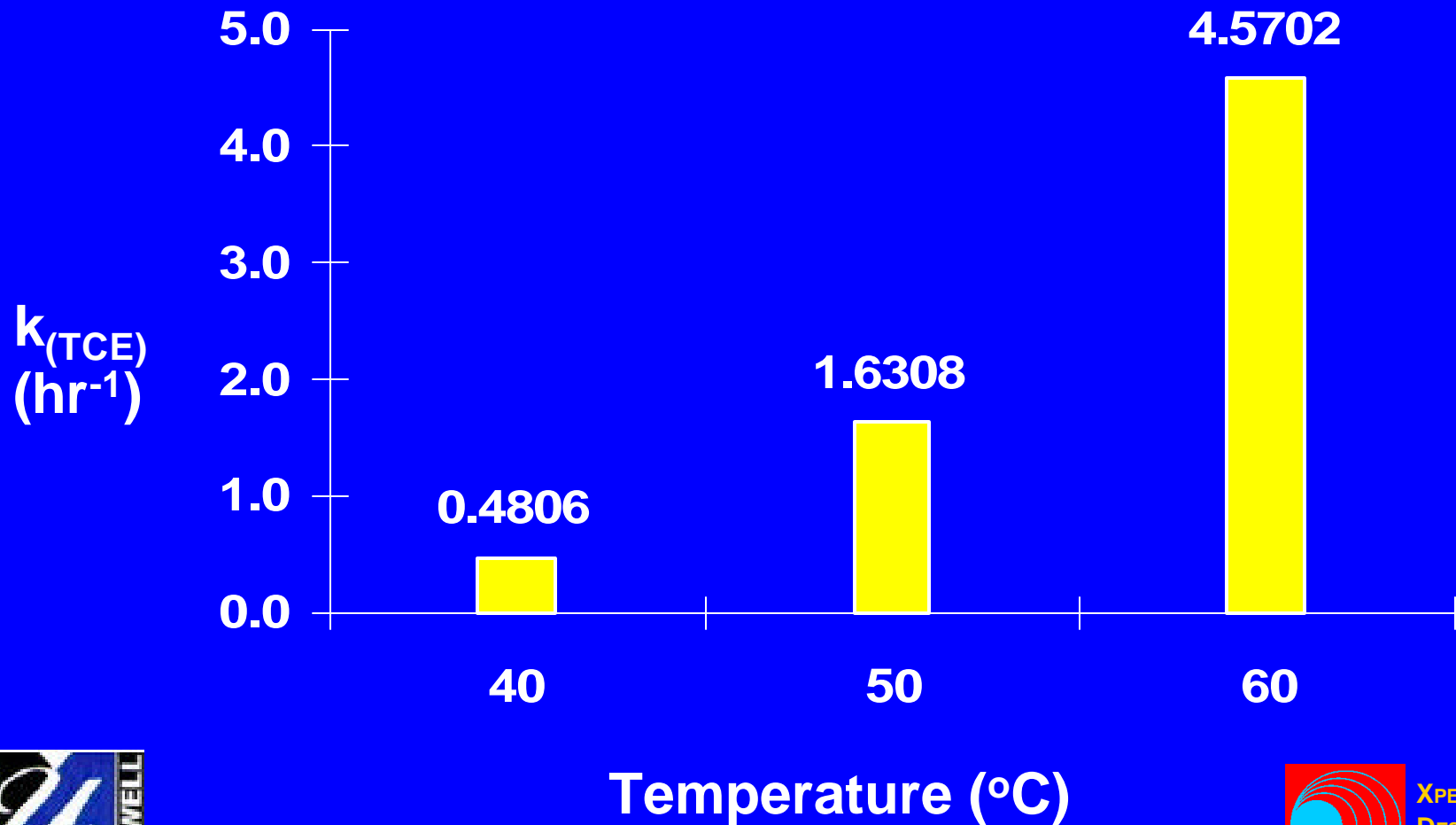
k = Pseudo-first-order reaction rate, (hr<sup>-1</sup>).



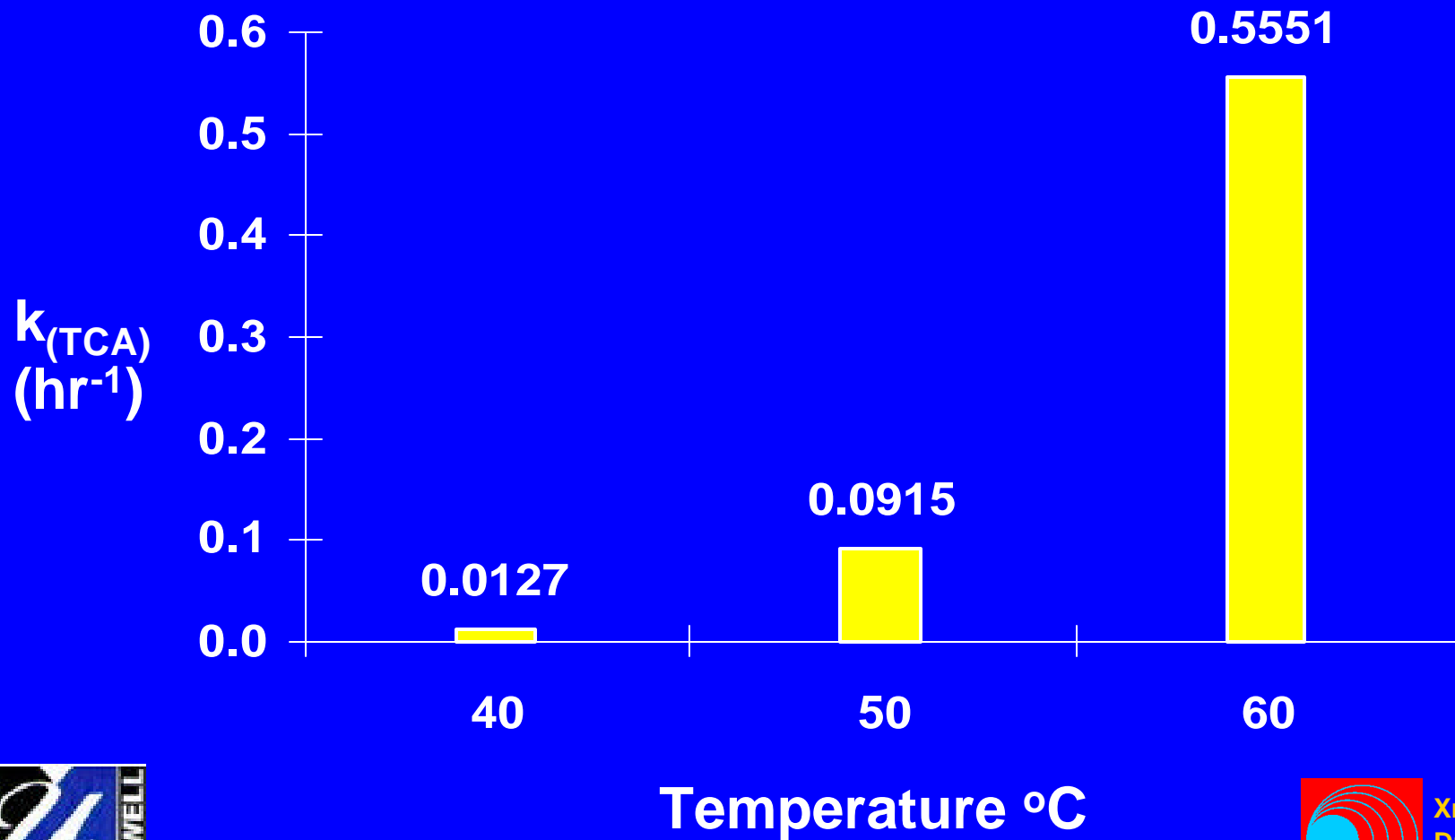
## Comparison of Aqueous Phase TCE and TCA Degradation at an Oxidant/Contaminant Molar Ratio of 10/1 as a Function of Temperature.

Target Contaminant	Temp. (°C)	k (hr <sup>-1</sup> )	t <sub>1/2</sub> (hrs)
TCE	20	0.0018	385.0
	40	0.4806	1.44
	50	1.6308	0.42
	60	4.5702	0.15
TCA	40	0.0127	54.57
	50	0.0915	7.57
	60	0.5551	1.25

# Comparison of Pseudo-First-Order Reaction Rates ( $k$ ) for TCE at Different Temperatures



# Comparison of Pseudo-First-Order Reaction Rates ( $k$ ) for TCA at Different Temperatures



# Activation Energy

Arrhenius equation:

$$\ln k = \ln A - E_a/RT$$

where:

k = Rate Constant (hr<sup>-1</sup>)

A = Frequency Factor (hr<sup>-1</sup>)

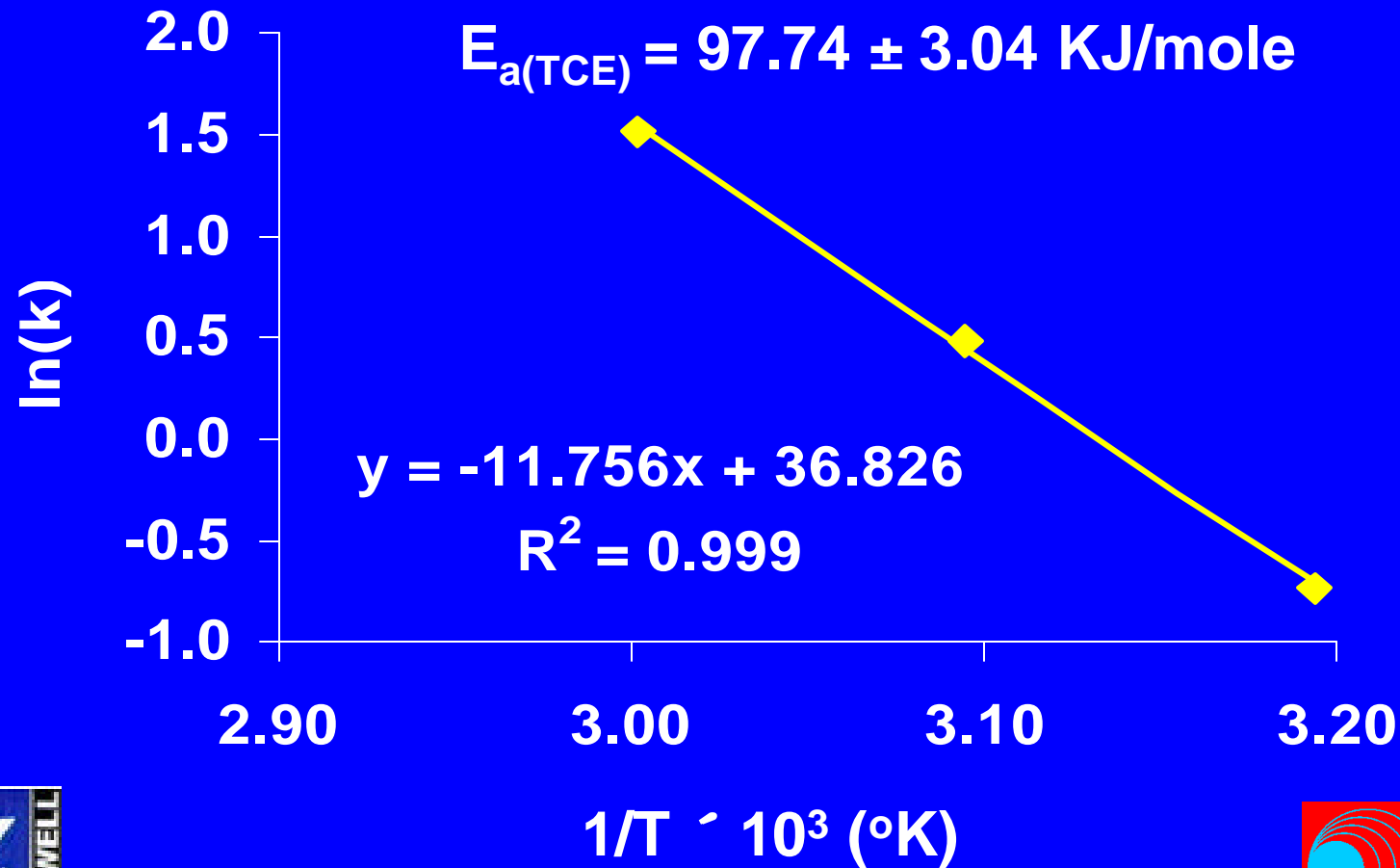
R = Universal Gas Constant (8.314 J mole<sup>-1</sup> °K<sup>-1</sup>)

T = Temperature (°K)

E<sub>a</sub> = Activation Energy (KJ/mole)



# Activation Energy for TCE Degradation.



# Activation Energies

- Reactions with high activation energies are very temperature-sensitive.
- Reactions with low activation energies are relatively temperature insensitive.
- A knowledge of activation energies allows estimation of reaction rates at desired system temperatures.



# Activation Energies

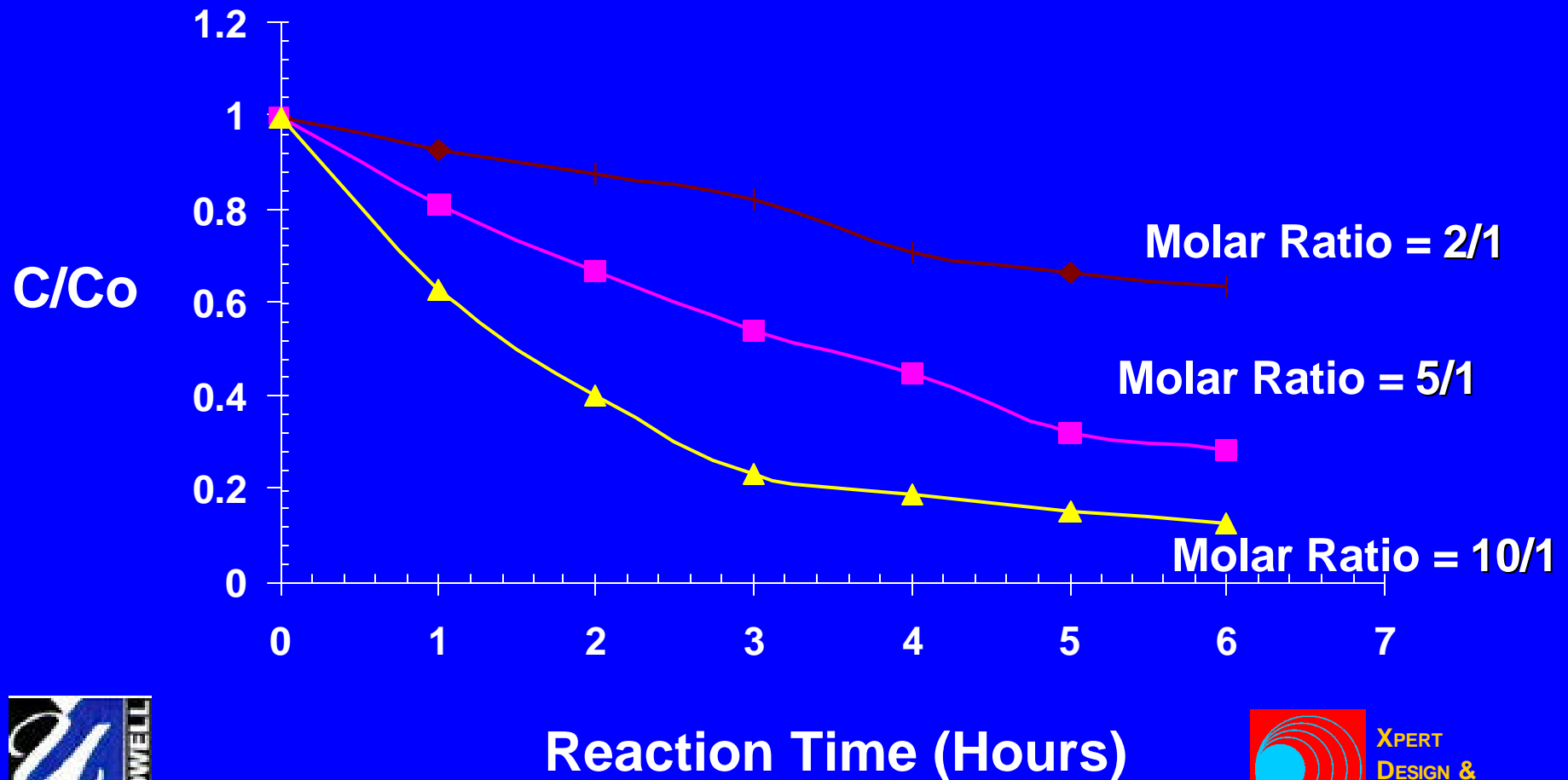
Contaminant - Oxidant	Activation Energy (KJ/mole)	Relative increase in reaction rate, resulting from a 10°C increase in system temperature
TCE – KMnO <sub>4</sub>	35 ± 2.9	1.7 X
TCE – Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	97.74 ± 3.04	3.04 ~ 3.62 X*
TCA – Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	163.86 ± 1.38	5.22 ~ 6.49 X*



\* 40-50 ~ 50-60 °C.



# Aqueous Phase TCE Degradation at 40°C as a Function of Oxidant/Contaminant Molar Ratio.

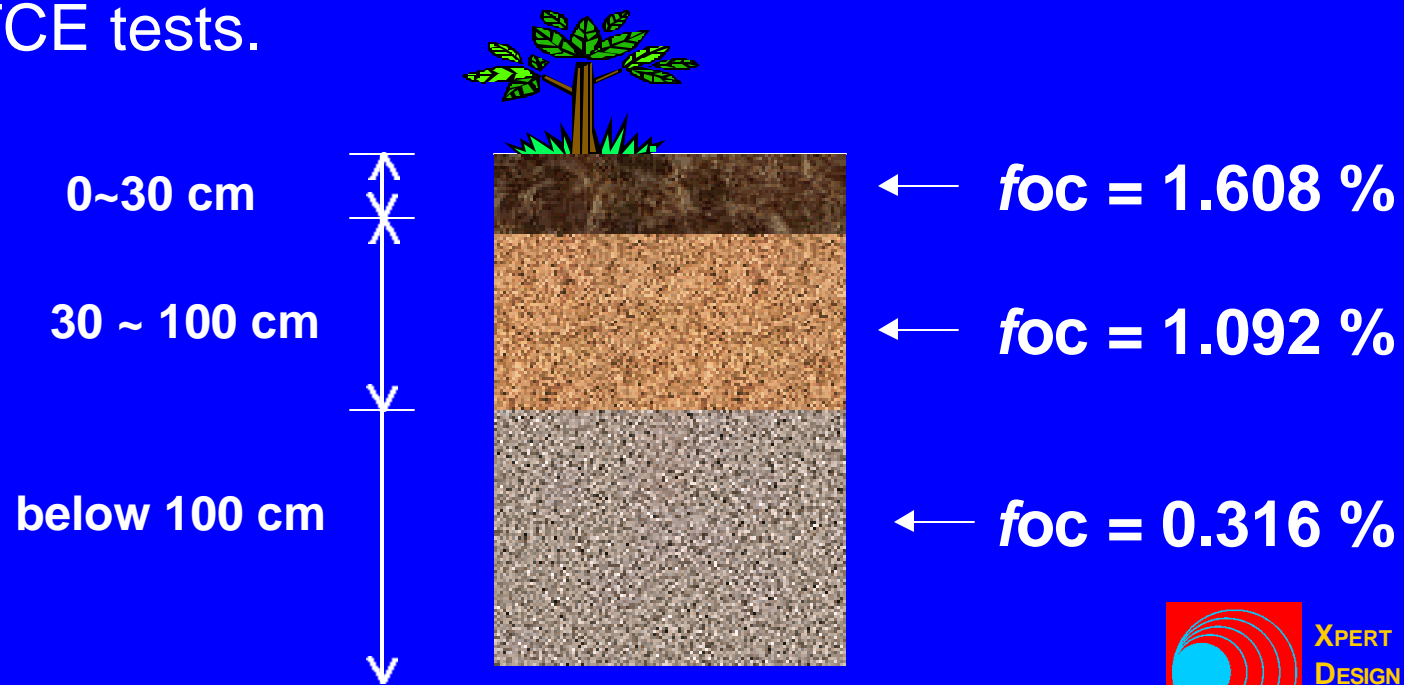


# Comparison of Aqueous Phase TCE and TCA Degradation as a Function of Oxidant/Contaminant Molar Ratio.

Target Contaminant	Temp. (°C)	Oxidant / Contaminant Molar Ratio	k (hr <sup>-1</sup> )	t <sub>1/2</sub> (hrs)
TCE	40	2/1	0.0780	8.88
		5/1	0.2100	3.30
		10/1	0.4806	1.44
TCA	50	2/1	0.0120	57.75
		5/1	0.0420	16.50
		10/1	0.0900	7.70

# Soil Slurry Experiments

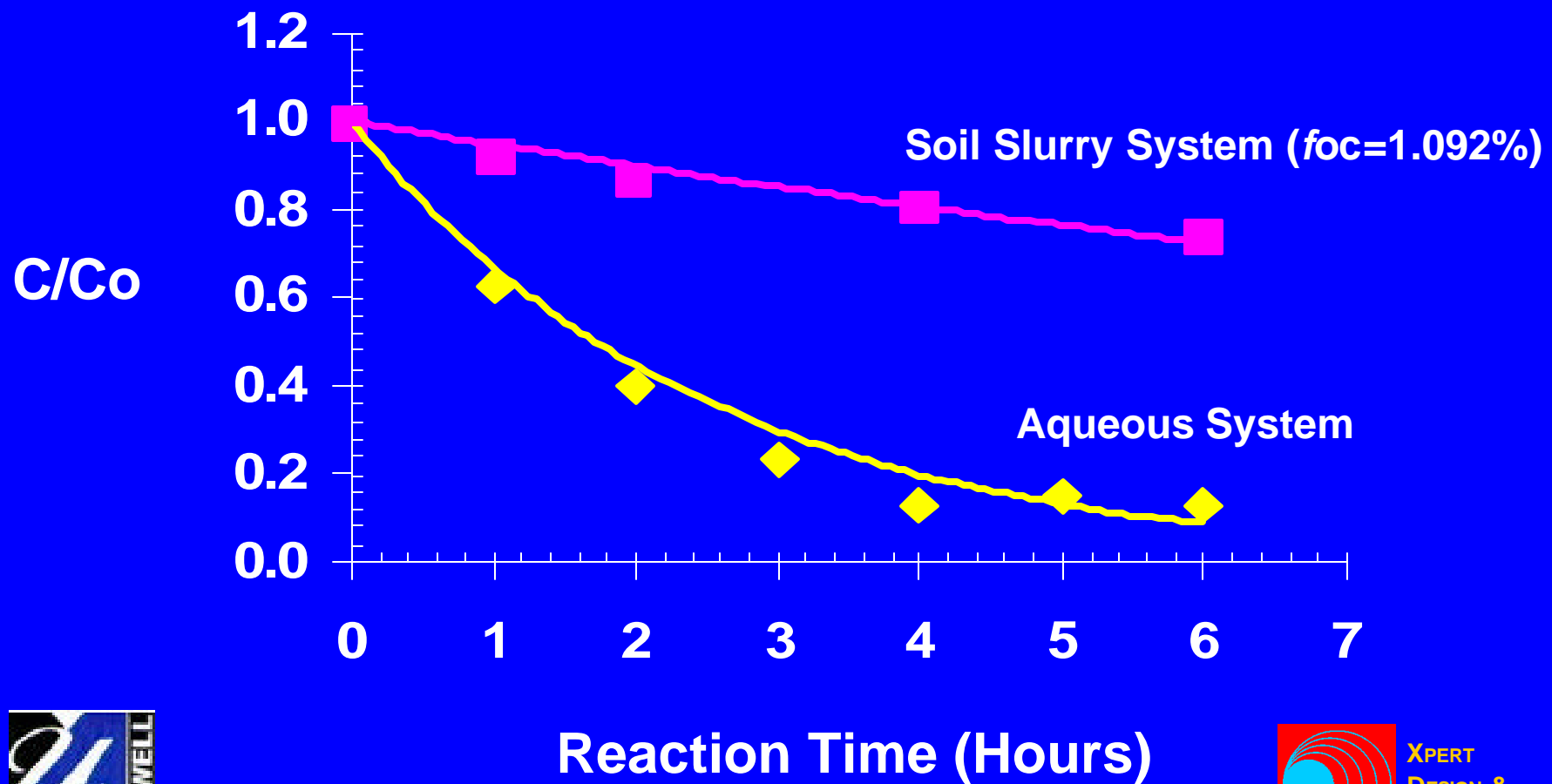
- Soil samples with a range of fraction of organic carbon (*foc*) levels were used.
- A soil to water mass ratio of 1/5 was used in all tests.
- An oxidant/contaminant molar ratio of 10/1 was used in all TCE tests.



## Notes

- Soil was a silty sand.
- All soils were: passes 30 - retained 200 sieve size.
- This system was un-buffered.  
The initial pH was approximately 5.  
The final pH was approximately 3.

# Comparison of TCE Degradation in Aqueous and Soil Slurry Systems at 40°C



# Relative Treatment Efficiency for TCE in Soil Slurries at 50 °C as a Function of *foc*.

Soil <i>foc</i> (%)	$k_{(TCE)}$ (hr <sup>-1</sup> )	$k_{(Persul.)}$ (hr <sup>-1</sup> )	$t_{1/2}$ (TCE) (hrs)	$t_{1/2}$ (Persul.) (hrs)	$k_{(TCE)}/k_{(Persul.)}$ or $t_{1/2}$ (Persul.)/ $t_{1/2}$ (TCE)
1.608	0.2059	0.0792	3.37	8.75	2.60
1.092	0.1497	0.0737	4.63	9.40	2.03
0.316	0.1536	0.0311	4.51	22.28	4.94



## Notes

- Pseudo-first-order coefficients in soil are much slower than observed in aqueous systems.
- Both TCE destruction and Persulfate destruction were monitored within the soil systems and pseudo-first-order coefficients were determined.
- Treatment efficiency is expressed as the ratio of  $k(\text{TCE})/k(\text{persulfate})$  because it is desired to destroy the target contaminant while maintaining oxidant persistence.

## Notes

- The ratio of  $t_{1/2}$  (persulfate) /  $t_{1/2}$  (TCE) is an equivalent measure of efficiency.
- The highest value of this ratio (i.e., 4.94) occurred in the soil with the lowest  $f_{oc}$  (i.e., 0.316). Therefore, persulfate degradation would be most effective in this soil.

## Notes

- Within soil slurries, elevated levels of TCE and persulfate degradation were observed at elevated *foc* levels.
- Increased degradation rates of both TCE and Persulfate was observed at the highest *foc* level (1.608%). It is postulated that this occurs because of the elevated iron levels associated with the highest *foc* soil.

# Iron Catalyzed Persulfate Oxidation



Where

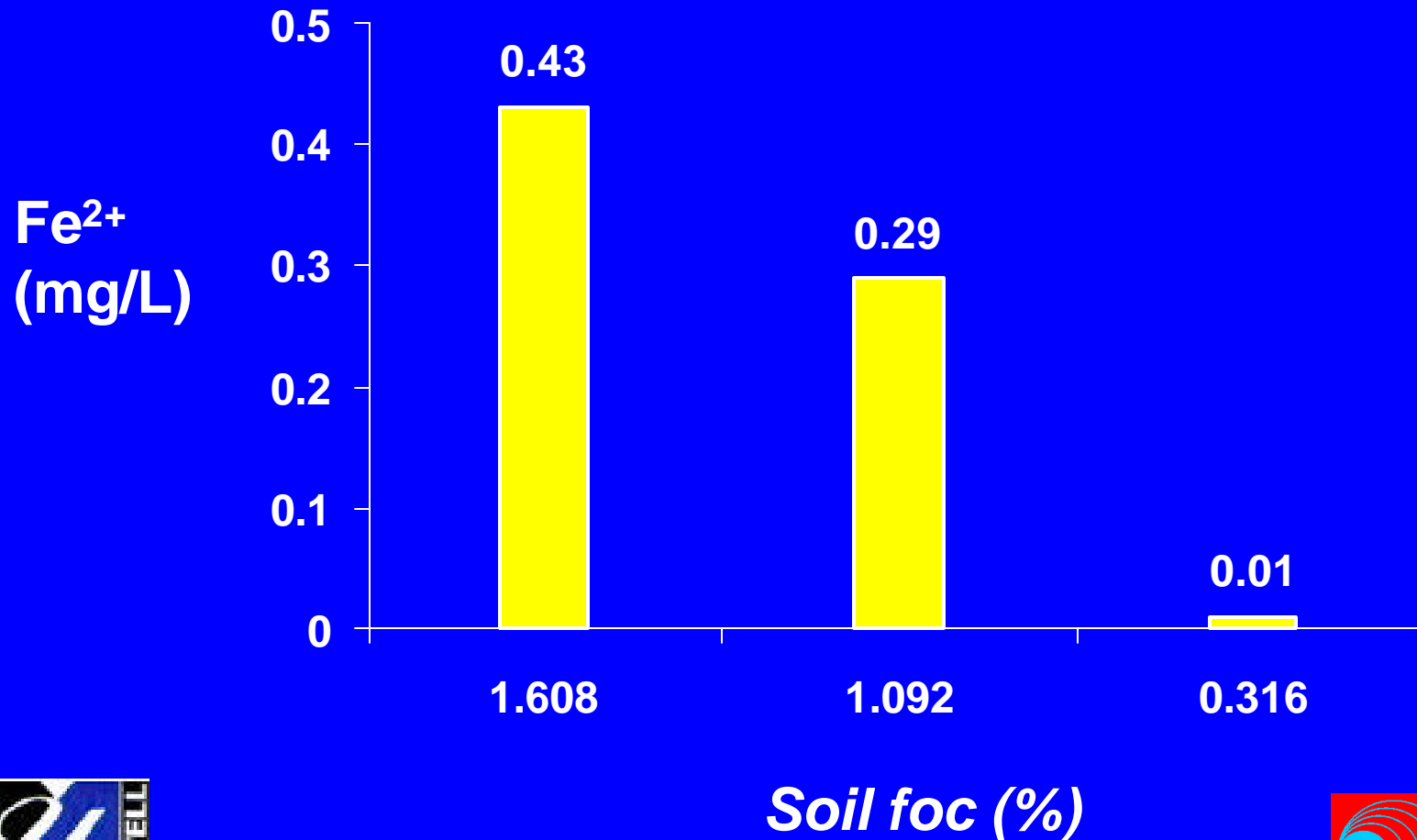
Me = Metal Catalyst



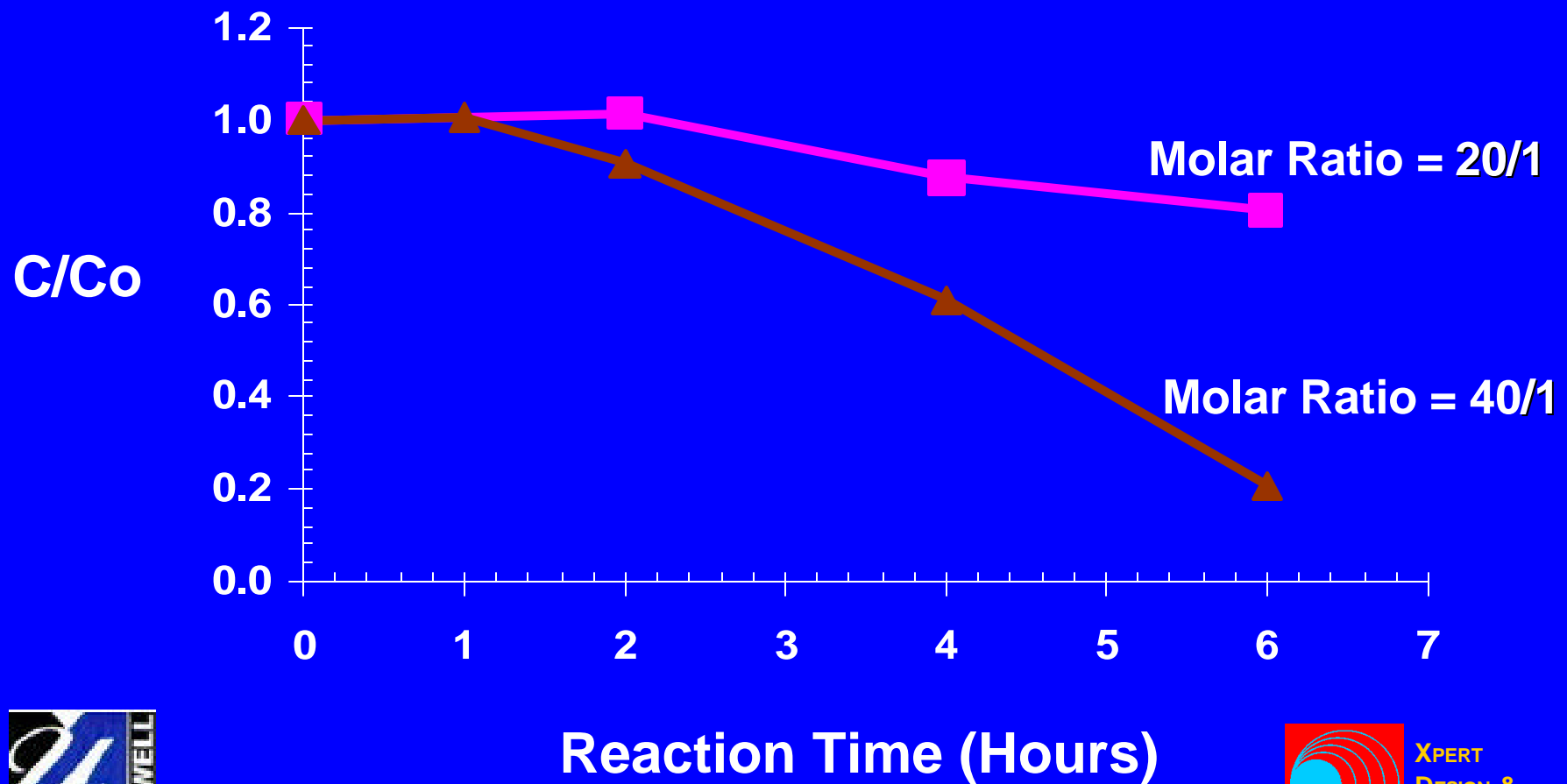
## Notes

- The results presented here for the soil slurry tests represent persulfate oxidation resulting from sulfate free radicals produced from a combination of thermal activation and iron catalysis.
- Transition metals such as Mn could produce a similar result.

# Initial Soluble Fe<sup>2+</sup> Content vs. Soil foc.



# TCA Degradation in Soil Slurry Systems with an *foc* 0.316% at 60°C



## Notes

- Previously we had observed significant degradation of TCA in aqueous systems at a 10/1 molar ratio at 50 degrees C. However, when these same conditions were used in a soil slurry system using a soil with a 1.092% foc, virtually no TCA destruction occurred (not shown). This is probably due to competition by the soil constituents for the sulfate free radicals formed.

## Notes

- To prove it was soil constituents that were exhibiting an oxidant demand we repeated the experiment using a soil that had been previously oxidized within a muffle furnace at 550 degrees C. and found that when using this oxidized soil we could then achieve TCA destruction (not shown).

## Notes

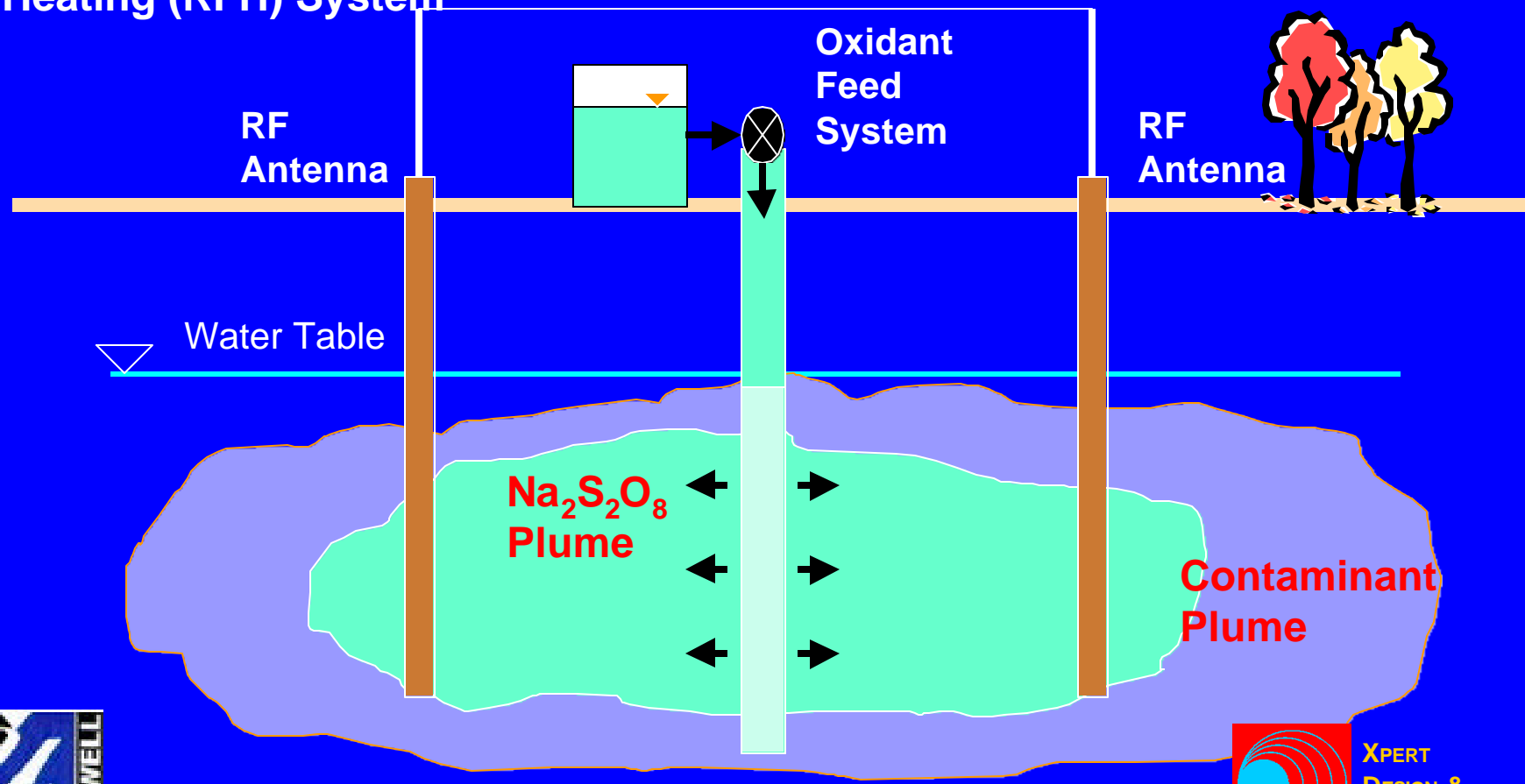
- This figure shows that using a natural soil with the lowest foc at an elevated temperature, and elevated molar ratios, that TCA destruction could be achieved.
- A pre-experiment was conducted to estimate required sampling intervals (not shown).

## Notes

- At a 20/1 molar ratio there is a lag time of several hours before TCA destruction begins. It is believed that this lag time is the time required to first destroy any soil organic carbon before TCA destruction can begin.
- At 40/1 molar ratio, which represents twice the oxidant, the lag time is about 1/2 as long, before TCA destruction occurs.

# Field Application of Thermally Activated Persulfate

Radio Frequency Heating (RFH) System



## Notes

- In the field, *in situ* heating can be used to warm up select portions of a contaminated aquifer, which has been dosed with persulfate, to generate sulfate free radicals. Any thermal technology should work.
- Because the sodium persulfate solution is relatively unretarded, this material can be injected within the TCE / TCA plume and only activated after the persulfate plume encompasses the TCE/TCA plume.

# Patented Process

- The use of soluble peroxygen compounds, such as persulfate for *in situ* chemical oxidation of volatile organic compounds (VOCs) is a patented process:

United States Patent 6,019,548

Hoag et al. Feb. 1, 2000

- Xpert Design and Diagnostics (XDD), is a patent licensee.



# Summary and Conclusions

- Persulfate compounds have the ability to degrade TCE and TCA under thermally activated conditions in aqueous and soil slurry systems.
- Increases in system temperatures and oxidant / contaminant molar ratios resulted in increases in pseudo-first-order reaction rates.
- TCE is more readily degraded than TCA.



# Summary and Conclusions

- Higher temperatures, higher oxidant/contaminant molar ratios and longer reaction times are required to achieve TCE and TCA degradation in soil systems vs. aqueous systems.
- Within soil slurries, elevated levels of TCE and persulfate degradation were observed at elevated *foc* levels. This may be due to the fact that soils with elevated *foc* levels also exhibited elevated soluble iron levels ( $\text{Fe}^{2+}$ ).

