Catalytic Destruction of PCE and TCE in Soil Vapor – Laboratory and Field Studies

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Motivation

- Superfund sites spread throughout the US
  - Often contaminated through commercial ventures
- Pose risk to human and ecological health
  - Groundwater contamination
- Clean-up methods for contaminated soils
  - Soil-vapor extraction with activated carbon adsorption
  - Pump-and-treat for contaminated groundwater
  - Soil dredging and treatment

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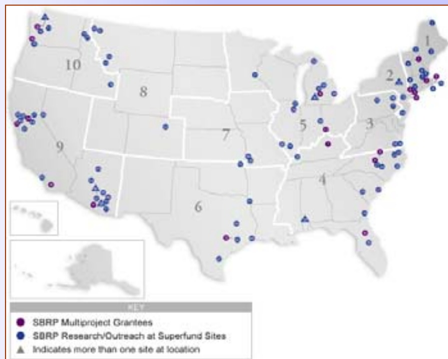
Superfund Sites

- 1246 Superfund Sites on National Priority List
- Common Contaminants
  - Semi-volatile chlorinated organic chemicals
    - Trichloroethylene (TCE)
    - Tetrachloroethylene (PCE)
  - These contaminants are present in ~90% of Arizona Superfund sites



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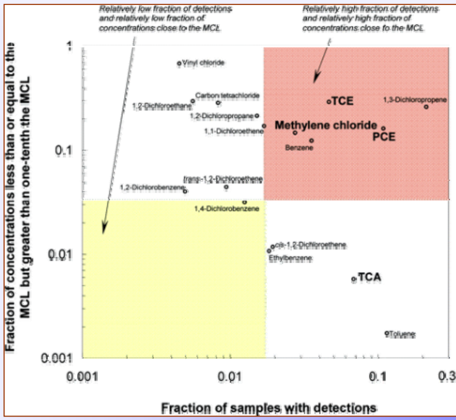
Prevalence of PCE and TCE



Fraction of samples with detections versus fraction of concentrations less than or equal to the MCL but greater than one-tenth of the MCL (5068 wells sampled). Moran et al., *ES &T* (2006).

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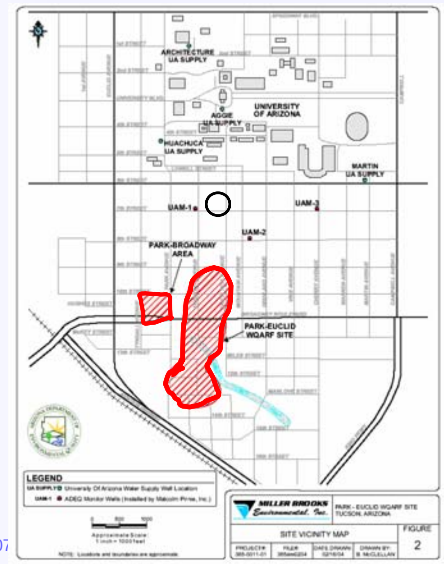
Park-Euclid Plume

1000 ft



Yellow contours represent PCE concentration in groundwater from 100 ppb to 1 ppb

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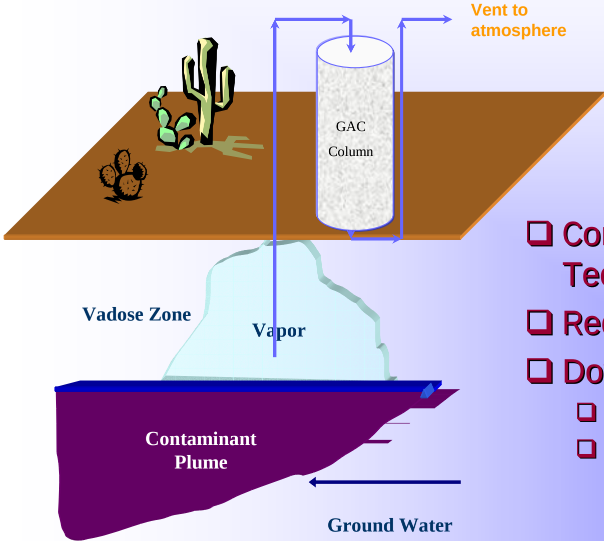
Activated Carbon Adsorption



- Common Remediation Technology
- Requires SVE
- Downside
  - Non-destructive
  - Regeneration/disposal costs

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Catalytic Oxidation

$$C_2Cl_4 + 2O_2 \xrightarrow{\text{catalyst}} 2CO_2 + 2Cl_2$$

$$2HCl + \frac{1}{2} O_2 \xrightarrow{\text{catalyst}} H_2O + Cl_2$$

poisons

- Issues with destruction through oxidation
  - High temperatures (>500°C)
  - Cl_2 poisoning occurs above 450°C
    - Blocks active Pt sites on catalyst
  - Production of furans and dioxins

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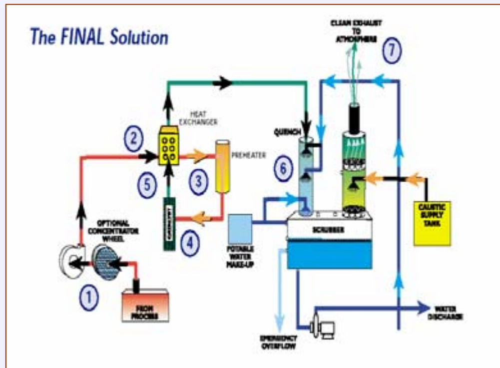

Schematic (taken from Catalytic Combustion Corporation) showing the major components of the redox catalytic system proposed for pilot-scale testing at the Park-Euclid site. Our system will differ from this in one important way: we propose introducing propane into the catalyst (4) in order to facilitate both reduction and oxidation reactions (not just oxidation), and to prevent catalyst poisoning.

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Catalytic Reduction

$$C_2Cl_4 + 5H_2 \xrightarrow{\text{catalyst}} C_2H_6 + 4HCl$$

$$2C_2Cl_4 + 7H_2 \xrightarrow{\text{catalyst}} C_2H_6 + 8HCl + 2C$$

coking

- Issues with destruction through reduction
  - Deactivation through coking
  - High price of H_2

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Objectives

- Hypothesis
  - Near Stoichiometric Redox Conditions
    - Poisoning reduced
    - Temperatures lowered
- Reduction-Oxidation (Redox) Conditions
    - $H_2 : O_2 = 2:1$
    - $O_2 + C \longrightarrow CO_2$
    - $H_2 + Cl_2 \longrightarrow 2\ HCl$
- Alternate Reductants
  - Propane
  - Methane, ethane, butane

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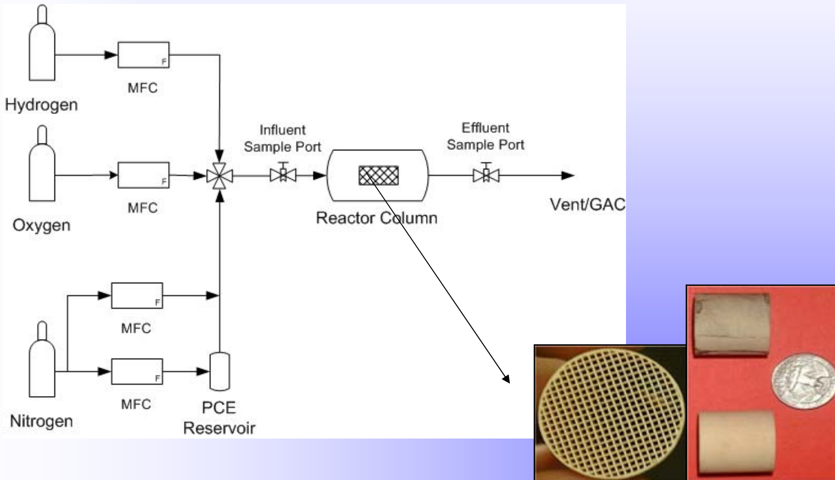
Lab Process Flow Diagram



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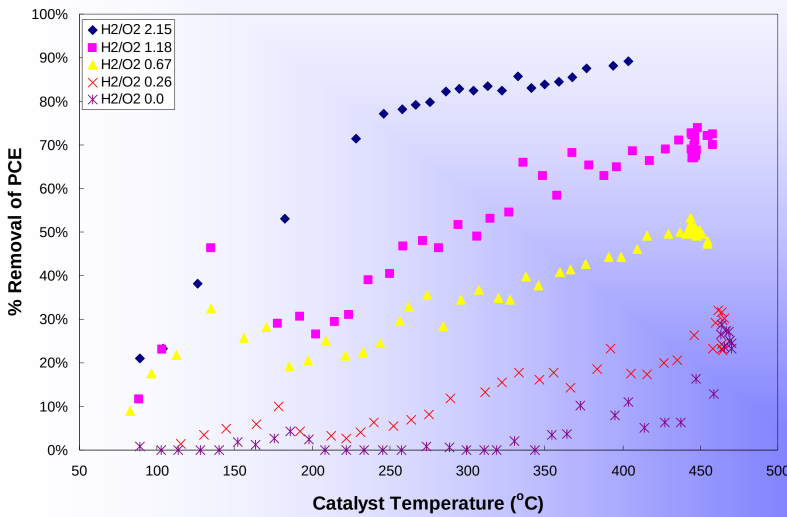
Lab – H_2 / O_2 Effect



- 0.5 Lpm Flow Rate
- 5% O_2 (vol)
- Varying H_2
- N_2 Remainder
- 0.50 sec Residence Time
- 800 ppm PCE

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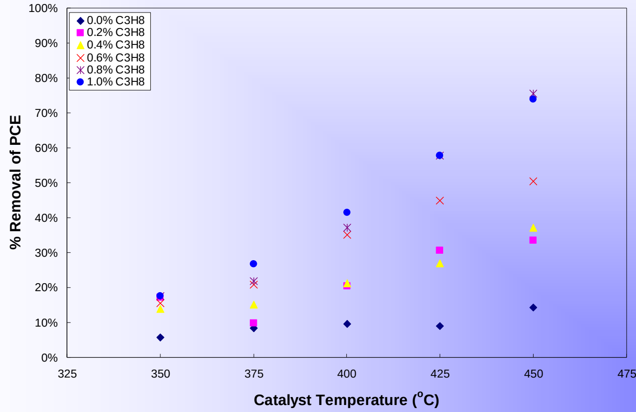
Propane as Reductant

$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$



- •1.0 Lpm flow rate
- • 5% O_2 (vol)
- •Varying C_3H_8
- •N_2 Remainder
- •0.25 sec residence time
- •200 ppm PCE

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Reactor Model

- Assumptions
  - Reaction is first order
  - Adsorption represented by Langmuir isotherm
  - Fast adsorption/desorption
  - No interspecies competition for sites

k = 1st order reaction constant
r = reaction rate
τ = reactor residence time
x = target compound conversion
C = concentration of target compound
C_0 = initial concentration
b = equilibrium constant

$$r_{PCE} = -k\theta_{PCE}$$

$$\theta_{PCE} = \frac{bC_{PCE}}{1+bC_{PCE}}$$

$$\frac{dC_{PCE}}{-r_{PCE}} = \tau$$

$$C_0 \ln(1-x) - \frac{x}{b} = -C_0 kb\tau$$

$$x = 1 - \frac{C_{PCE}}{C_0}$$

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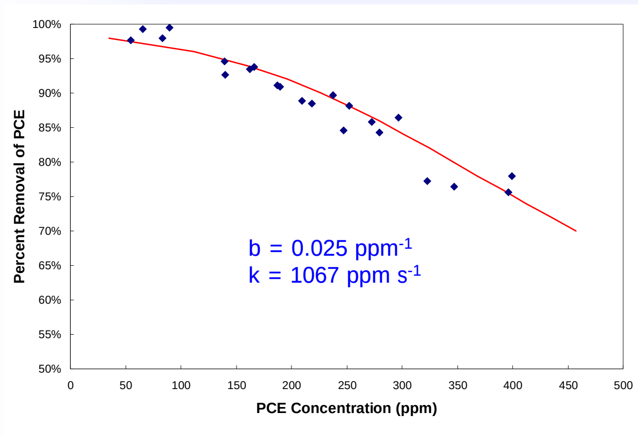
Lab – Effect of H_2 / O_2



- 1.0 L/min
- 1.3% O_2
- 2.7% H_2
- N_2 remainder
- 0.25 s residence time
- 200 °C

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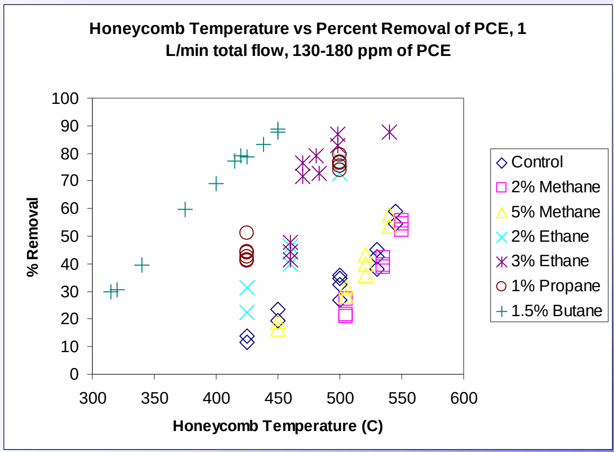
Alkane Reductants

(weakest) C-H bond dissociation energy: butane < propane < ethane < methane



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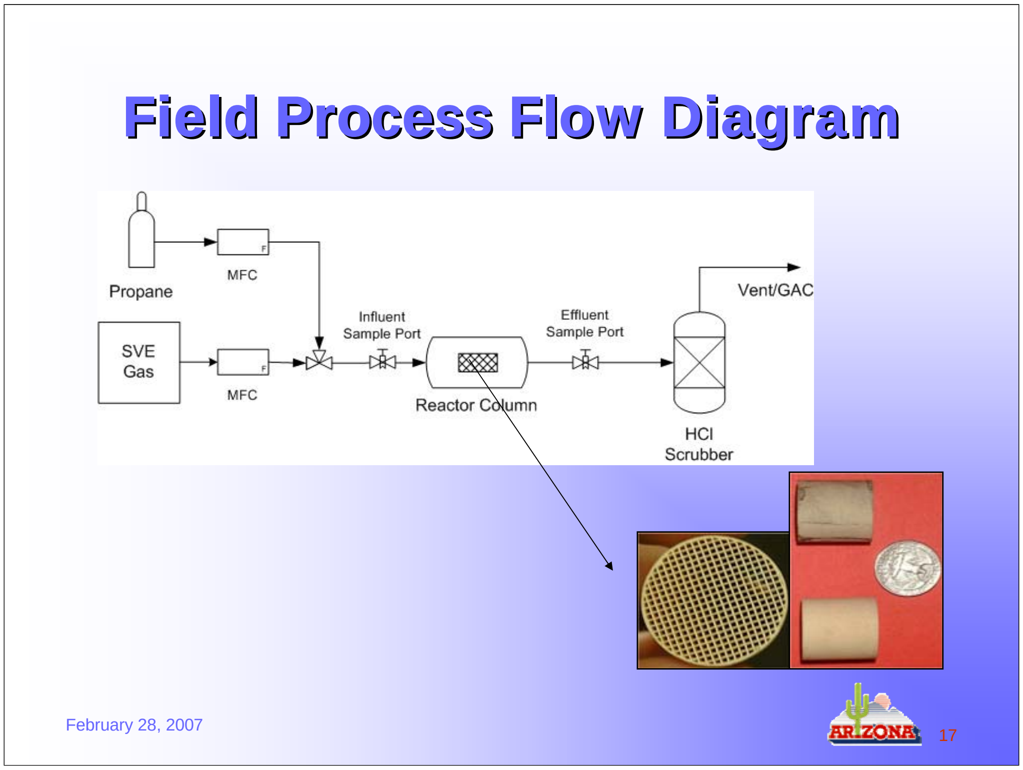
Field Process Flow Diagram
Propane
MFC
SVE
Gas
MFC
Influent
Sample Port
Reactor Column
Effluent
Sample Port
Vent/GAC
HCl
Scrubber
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Catalytic Converter

- 2 alumina honeycomb monolith support s (2" long x 4.7" major axis 3.15" minor axis).
- Pt/Rh or Pd/Rh with cerium/zirconium oxygen storage additives.
- Surface area = 4400 m^2
- Normal automotive flow rate: 20 cfm to 300 cfm.
- Minimum temperature for 50% activity = 415 ^0C

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Park-Euclid Field Site

Catalytic converters

Effluent stream

Scrubber

100 L/min through each reactor (3.5 cfm)

Effluent stream

Heater control

Propane

Catalytic converters

SVE pump

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Field Conditions

- 2 Alumina supported Pt/Rh catalysts
  - 2" long x 4.7" major axis; 3.15" minor axis
- 450 – 650^{o}C Temperature Range
- 25 – 200 ppmv PCE
  - 10 – 50 ppmv TCE
- 100 Lpm total flow rate
  - 0.2 sec Residence Time
- 1.0 – 2.0% propane by volume

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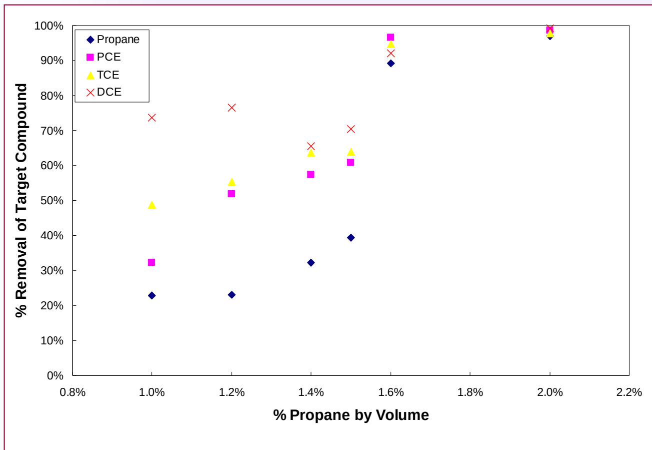
Field – Propane Effect



- 100 L/min
- SVE Gas
- 1-2% C_3H_8 (vol)
- 0.2 s residence time
- 20-200 ppm PCE
- 450-650 ^oC

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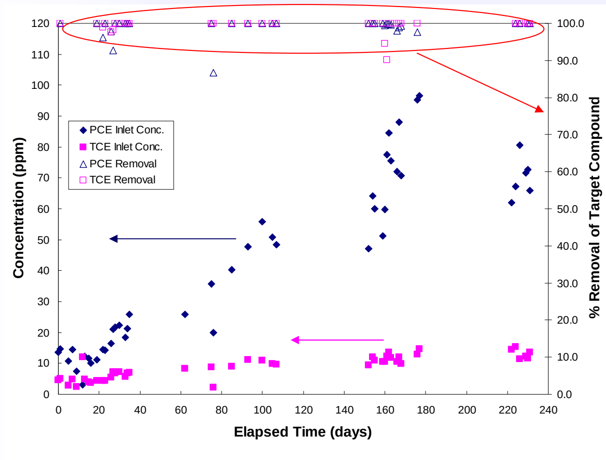
Field – Extended Operation



- 100 L/min
- SVE gas
- 2% C_3H_8 (vol)
- 0.2 s residence time
- ~520 °C

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Treatment Costs

- Catalytic Converter
  - ≈ 200 ppm PCE
  - 10^6 L soil vapor treated
  - 2% v/v propane @ $1.70/gal (DOE, 2005)
  - Propane-only treatment costs
    - ≤ $10/lb PCE destroyed (PCE-dependent)

- Granular Activated Carbon
  - ≈ 100 ppmv PCE, 50 cfm, 85 °F
  - GAC-only treatment costs:
    - ≈ $3.50/lb PCE absorbed
    - (Siemens Water Technologies, Sept. 2006)

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Future Directions Field Work

- SBIR Phase I ($100k/6 months)
- SBIR Phase II ($750k/2 y)
  - Hydro Geo Chem
  - Improved scrubber design
  - Larger flow rates (150 cfm; Phoenix area)
  - UA Page Ranch (relocate existing system; Freon 11, 12; solar)
- Provisional patent application - Dec. 2006

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Conclusions

- Catalytic destruction w/ redox conditions viable remediation technology
  - Available for long term applications
  - Resolves previous issues with catalytic destruction
- Propane an effective alternate to hydrogen gas as reductant
- Works under wide range of conditions

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Stoichiometry and Bond Dissociation Energy

$CH_4 + 2O_2 = CO_2 + 2H_2O$ **439.3 kJ/mol**

$1\, mol + 2\, mol\ O_2 = ...$

$1\, mol + 9.5\, mol\ air = ...$

$i.e., 10.5\%\ CH_4\ in\ air$

$C_2H_6 + 3.5O_2 = 2CO_2 + 3H_2O$ **420.5 kJ/mol**

$1\, mol + 3.5\, mol\ O_2 = ...$

$1\, mol + 16.7\, mol\ air = ...$

$i.e., 6.0\%\ C_2H_6\ in\ air$

$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$ **410.5 kJ/mol** **$CH_3CH_2CH_3$**

$1\, mol + 5\, mol\ O_2 = ...$

$1\, mol + 23.8\, mol\ air = ...$

$i.e., 4.2\%\ C_3H_8\ in\ air$

$C_4H_{10} + 6.5O_2 = 4CO_2 + 5H_2O$ **411.1 kJ/mol** **$CH_3CH2CH_2CH_3$**

$1\, mol + 6.5\, mol\ O_2 = ...$

$1\, mol + 30.9\, mol\ air = ...$

$i.e., 3.2\%\ C_4H_{10}\ in\ air$

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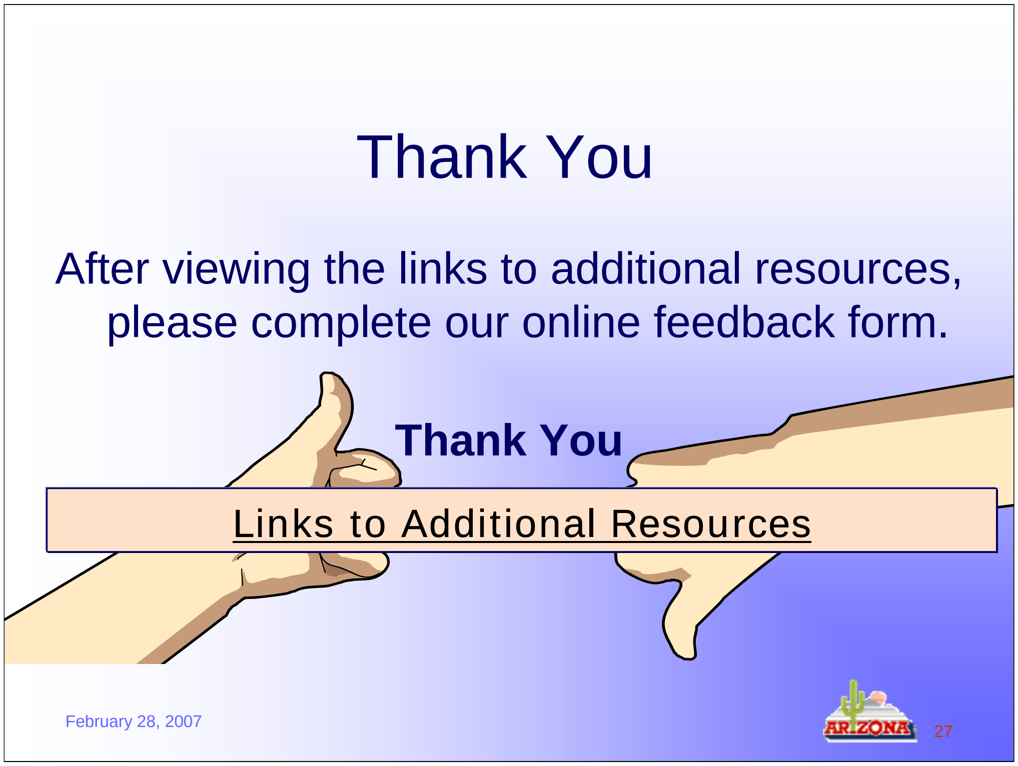
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