Project No. 64979: Basic Engineering Research for D&D of PCB-Contaminated Wastes at DOE Sites: Electrokinetics, Carbon Dioxide Extraction, and Supercritical Water Oxidation

Edward A. Hamilton, SC Universities Research and Educational Foundation

Michael A. Matthews, John W. Weidner, Ralph E. White, University of South Carolina

David A. Bruce, Mark Thies, Clemson University

Lawrence Oji, John B. Pickett, Nancy Lowry, Savannah River Site

The PCB Problem

- More than 19,000 m^3 of polychlorinated biphenyl (PCB) contaminated waste exists at DOE sites nationwide:
  - *e.g.* SRS & Hanford reactor storage basins; Oak Ridge K-25
- D&D activities generate additional PCB-laden job control wastes:
  - *e.g.* mopheads, absorbent material, clothing
- Thermal incineration is only legal means of destruction

Project Goal

To develop new processes for the combined extraction and destruction of PCBs for D&D of DOE matrix materials, such as reactor pond sludges, as well as organics solids that constitute job control waste.

Anticipated Benefits

- Basic science understanding of PCB adsorption, extraction, destruction kinetics
- New process options for separating PCBs from solid matrices and other pollutants (e.g. MLLW)
- Combined extraction/destruction methods that are alternatives to thermal incineration

Project Team

- University of South Carolina
  - CO2 extraction and electrochemical oxidation
- Clemson University
  - Hot water extraction and HTO
- SRS Tech Center/Westinghouse
  - Provide regulatory guidance; characterize water, sludge and job control wastes;develop simulant waste “recipes”
- SC Universities Research & Ed. Foundation
  - Coordinate all activities

Extraction and Oxidation: Parallel Research Tracks

1. Dense CO_2 PCB extraction: Use of additives to enhance extraction from solid matrices
2. Hot water PCB extraction: Use of high temperature to enhance extraction from solid matrices
3. Electrochemical oxidation of PCBs in CO_2: Electrochemistry as an alternative to thermal incineration
4. Hydrothermal oxidation of PCBs: Hot or supercritical water oxidation as an alternative to thermal incineration

Dense CO_2 and Hot Water PCB Extraction: Scope of Research

- Measure diffusion coefficients and adsorption/ desorption constants for PCBs on solid matrices
- Determine extraction dynamics and PCB removal efficiencies
- Correlate extraction data with a transport-based model to be used for extraction process scale-up

Dense CO_2 PCB Extraction: Scientific Principles

- Above the critical point, CO_2 solvent properties can be controlled for exacting separations
- CO_2-soluble additives will be investigated to help overcome the strong PCB - solid matrix surface interactions
- The adsorptive and convective transport processes of pure and modified dense CO_2 will be measured

Hot Water PCB Extraction: Scientific Principles

- Though ambient water is not a PCB solvent, hot water (250 - 300°C) is.
- Hot water may be a more effective solvent than CO_2 for certain matrices
- Organics are highly soluble in supercritical H_2O

Electrochemical Oxidation and Hydrothermal Oxidation: Scope of Research

- Investigate superoxide chemistry or hydrothermal oxidation chemistry to selectively attack C-Cl bonds
- Find best reaction conditions
- Determine kinetics
- Model reaction data with kinetic models to be used for reactor design/scale-up

Electrochemical Oxidation: Scientific Principles

- Oxygen in dry, aprotic solvents is converted to superoxide (O_2^-) upon application of electric field
- O_2^- reduces PCBs to bicarbonate and chlorides (known chemistry in aprotic solvents)
- Dense phase CO_2 + electrolyte should enhance rate of destruction of PCBs at low temperature and with no secondary solvent waste.

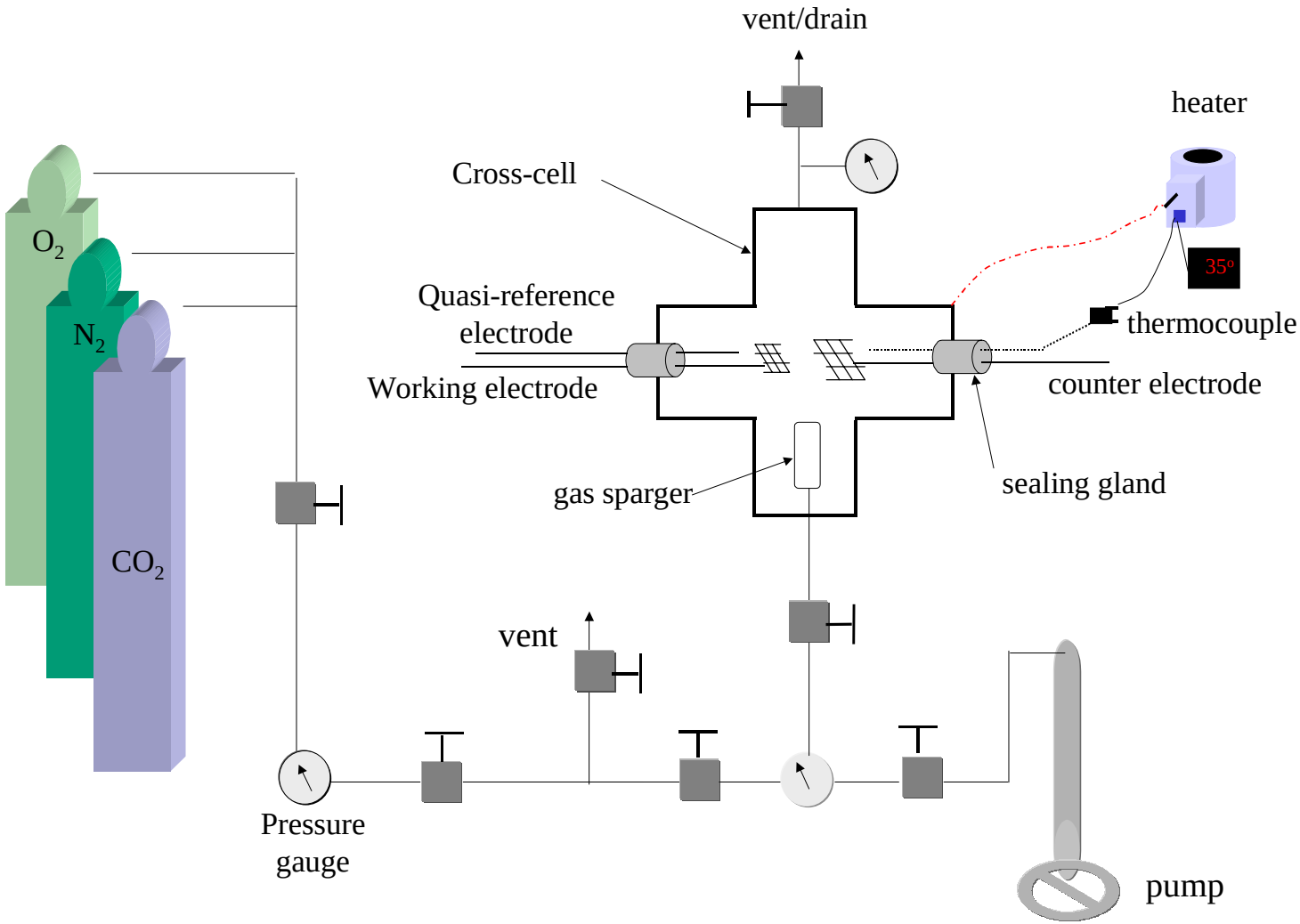
HTO: Scientific Principles

- Above or near the critical point of water (374°C and 218 atm), organic wastes, O_2, and water form a single homogeneous phase
- Reaction is not mass transfer limited in the homogeneous phase
- PCBs are oxidized to CO_2, H_2O, and HCl with an efficiency > 99.999%

Electrochemical Oxidation: Technical Approach

- A high pressure batch reactor will be used for initial studies of:
  - Supercritical fluid/electrolyte conductivity
  - Cyclic voltammetry of the oxygen/superoxide couple
- Kinetic data will be collected using chlorinated benzenes as model compounds

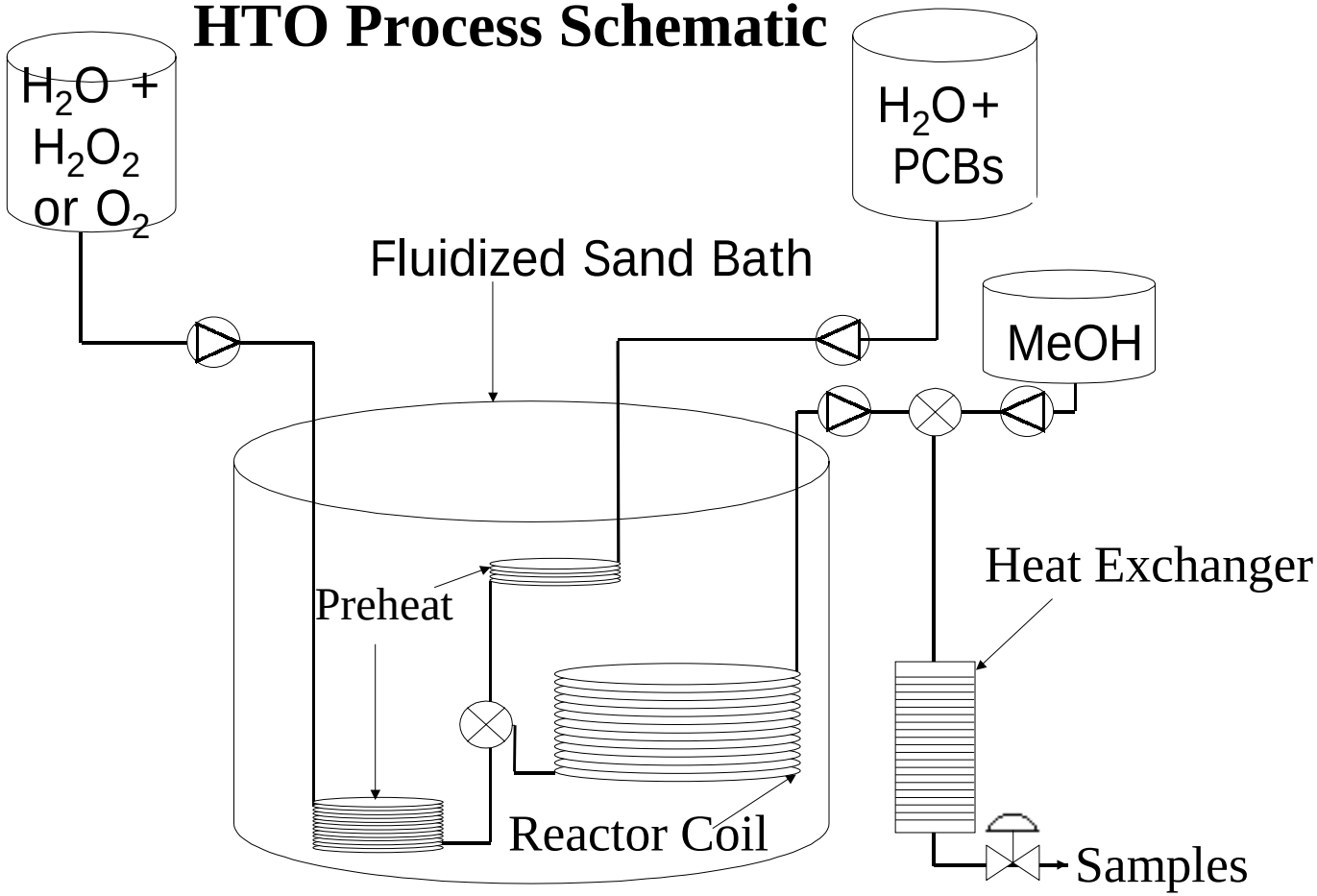
Pressurized Electrochemical Cell Schematic



SCWO: Technical Approach

- A plug flow reactor will be used for the kinetic studies
  - scale-up will be simplified
  - flow reactors are ideal when the required residence time is short
  - steady-state operation allows multiple samples to be obtained under identical conditions
- Kinetic data are crucial for rational reactor design and economic evaluations

HTO Process Schematic



Discussion: Hydrothermal or Electrochemical Oxidation of PCBs

•Have reviewed existing literature on supercritical water oxidation (SCWO) of PCBs and on superoxide chemistry in aprotic solvents. Some commercial installations of SCWO may provide basis for design of processes for DOE wastes

•Developed a new, continuous-flow hydrothermal oxidation apparatus has been constructed.

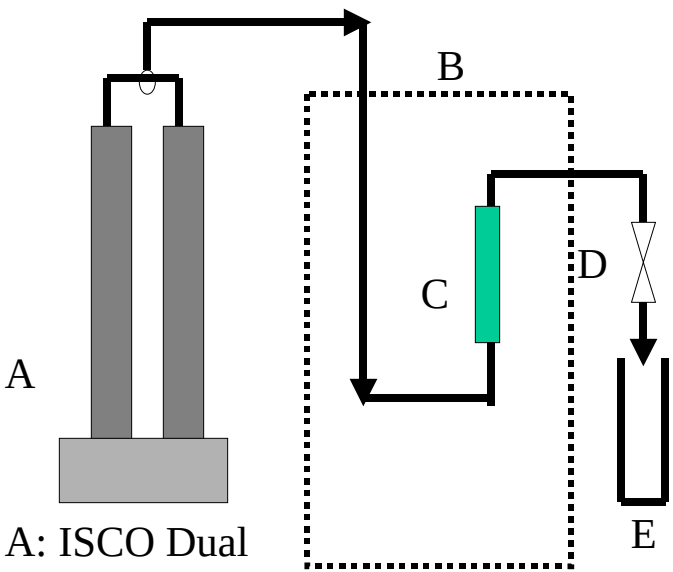
• Conducted HTO screening tests with both *tert*-butanol and 1,2,4 trichlorobenzene as model contaminants, obtaining decompositions between 80 and about 90 %. H_2O_2 was the oxidant.

•Developed a low-cost reactor and electrode system for rapid screening of electrochemical reactions under high pressure. Validation of conductivities of model aqueous systems has been accomplished; high pressure conductivity studies are underway.

CO_2 Extraction: Technical Approach

- Solid matrices identified by SRS (*e.g.* adsorbents) are spiked with chlorinated aromatics at known levels
- Supercritical CO_2 (or CO_2 + additives) extraction is done and extraction efficiency computed
- Mathematical models of the extraction will be developed for analysis and scale-up

CO_2 Extraction System



A: ISCO Dual Syringe Pump

B: Isothermal chamber

C: 10-ml extraction vessel

D: Pressure let-down valve

E: Chilled solvent collection vial

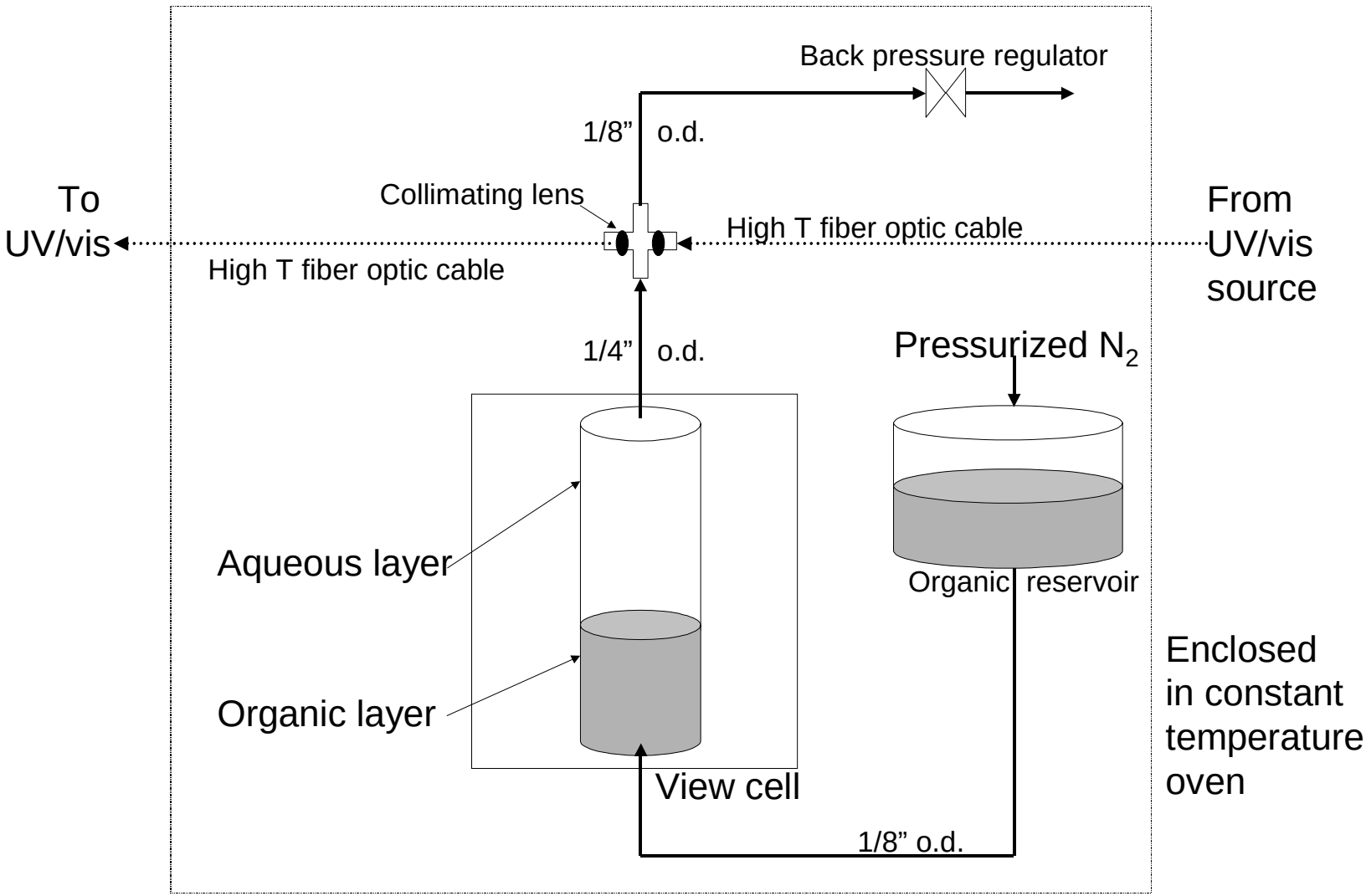
Procedure:

- Adsorbent samples are impregnated with chlorinated aromatic (1,2,4 TCB) from CH_2CL_2 solution; solvent is evaporated.
- 1,2,4 TCB concentration on adsorbent is verified by Soxhlet extraction in acetone. Target range is ~2000-4000 ppm.
- CO_2 extraction performed at fixed T&P; extract is collected in chilled solvent vial.
- Post-extraction analysis of solvent and of extracted adsorbent is used to obtain material balance closure.
- A GC/FID is used for determining 1,2,4 TCB concentration

Hot Water Extraction: Technical Approach

- Initial studies will focus on solubility of PCBs in hot water, as data are scarce
- A static, continuously mixed, high T & P view cell will be used in conjunction w/ UV fiber optic spectroscopy to determine solubilities
- Thermodynamic models will be developed to support extraction studies.

High Temperature, High Pressure PCB / Water Solubility Apparatus



Discussion: Extraction of PCBs using CO_2 or Hot Water

•Have reviewed existing solubility and vapor pressure data for certain PCB congeners in both CO_2 and water. Data in hot water are particularly scarce; we will collect additional solubility data in the new apparatus.

•SC CO_2 extraction of 1,2,4 TCB from plant-based adsorbent material at 4000 psia, 40 ^oC (ρ= 0.91 g/cc) gives extraction efficiencies of 25-30%. Extraction at 4000 psia, 80 ^oC (ρ= 0.38 g/cc) gives >60% extraction efficiency. Evidently 1,2,4 TCB is strongly bound within the plant matrix; higher temperature (higher vapor pressure) appears to be more important for extraction than CO_2 density.

•Developed a high pressure, high temperature apparatus for measuring solubilities of chlorinated compounds in hot water or supercritical water.

•Previous work on extraction of PCBs from soil will be modeled as a prelude to developing extraction models for DOE matrices.