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Project Title: **Basic Engineering Research for D&D of R. Reactor Storage Pond Sludge: Electrokinetics, Carbon Dioxide Extraction, and Supercritical Water Oxidation**

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Research Objective

Collaborating researchers at the University of South Carolina (USC), Clemson University (CU), and the Savannah River Site (SRS) are investigating the fundamentals of a combined extraction and destruction process for the decontamination and decommissioning (D&D) of PCB-contaminated materials as found at DOE sites. Currently, the volume of PCBs and PCB-contaminated wastes at DOE sites nationwide is approximately 19,000 m^3. While there are a number of existing and proposed processes for the recovery and/or destruction of these persistent

pollutants, none has emerged as the preferred choice. Therefore, this research focuses on combining novel processes to solve the problem. The research objectives are to investigate benign dense-fluid extraction with either carbon dioxide (USC) or hot water (CU), followed by destruction of the extracted PCBs via either electrochemical (USC) or hydrothermal (CU) oxidation. Based on the results of these investigations, a combined extraction and destruction process that incorporates the most successful elements of the various processes will be recommended for application to contaminated DOE sites.

Research Progress and Implications

This report summarizes work after nine months of a three-year project. This project involves personnel from two Universities and the SRS. Bi-monthly progress reports are submitted to SCUREF, and quarterly meetings at alternating sites have been held to share progress, make presentations, and plan future activities.

At USC, tracer diffusion experiments have been conducted with model contaminants, including some chlorinated compounds. Two papers are being prepared on the tracer work. The supercritical carbon dioxide extraction system is up and running, including two ISCO syringe pumps, allowing continuous extraction. A promising surfactant has been chosen and is on-hand for initial extraction experimentation. A search is underway to find additional commercially available surfactants that are both soluble in supercritical carbon dioxide and UV-detectable. A schematic of the extraction system is shown in Figure I.

A high-pressure cell for electrochemical destruction experiments has been constructed. Complications have arisen concerning high-pressure sealing of electrodes and manufacture of a custom high-pressure cell. Electrolytes will be added to the system to enhance the conductivity in carbon dioxide. One new electrolyte has been synthesized and additional electrolytes are being researched. A schematic of the electrochemical reaction system is given in Figure II. Some commercially available PCB surrogate compounds have been chosen and ordered for initial extraction and electrochemical experiments. A gas chromatograph has been prepared for PCB analysis and will be used to evaluate both extraction and electrochemical destruction results. In addition, a dialogue has been initiated with University Health and Safety officers to discuss the special requirements and hazards associated with working with PCBs.

At CU, a supercritical water oxidation (SCWO) reactor design has been completed. The design includes a specialized mixing tee, which will be custom designed and fabricated at Clemson. The heat source for the reactor, a Techne sand bath oven, has been installed and is being optimized for the desired experimental conditions. Heat transfer analyses have revealed the depth to which the reactor coil should be immersed into the sand bath and customized holding brackets are being designed. A schematic of the SCWO reactor is given in Figure III. A Hewlett-Packard mass spectral analyzer has been ordered. The analyzer is planned for installation and operation in June 1999, and to be connected to a PC for control and data acquisition. Drawings have been developed for a high-pressure view cell with variable path lengths. This vessel will be used for in-situ measurements of PCB solubility at elevated pressures in hot and supercritical water if existing equipment proves insufficient.

SRS personnel have been providing support to the project by attending all quarterly meetings, providing regulatory compliance information regarding PCB handling and usage, and providing model matrix material. This model material, used in the field to absorb PCB-contaminated liquids, will be contaminated in the lab and used for extraction experiments.

Planned Activities

USC:

Summer 1999: Finish construction and pressure testing of electrochemical cell
Begin basic conductivity experiments and cyclic voltammetry
Explore the use of electrolytes to enhance carbon dioxide conductivity
Compile voltammetry data and analyze system effectiveness and efficiency
Explore purchase and implementation of a new electrochemical batch reactor provided from a commercial vendor
Begin extraction experiments with surrogate compound(s) and surfactant
Perform extraction experiments with model matrix materials provided by SRS
Continue to search for additional surfactants based on initial extraction results
Continue extraction experiments

Long Term: Design a continuous-flow electrochemical destruction system
Determine PCB destruction efficiencies / kinetics, correlate data, prepare models
Perform PCB + surfactant extraction experiments

CU:

Summer 1999: Continue literature search for SCWO and PCB solubility data
Connect mass spectrometer for reaction byproduct analysis
Fine tune heat transfer model
Build custom mounting bracket and reactor assembly

Long Term: Begin PCB solubility experiments
Construct SCWO system
Examine oxidation reaction kinetics
Compare the performance of different oxidizing agents (O_2 vs. H_2O_2)

Information Access

Publications and Presentations

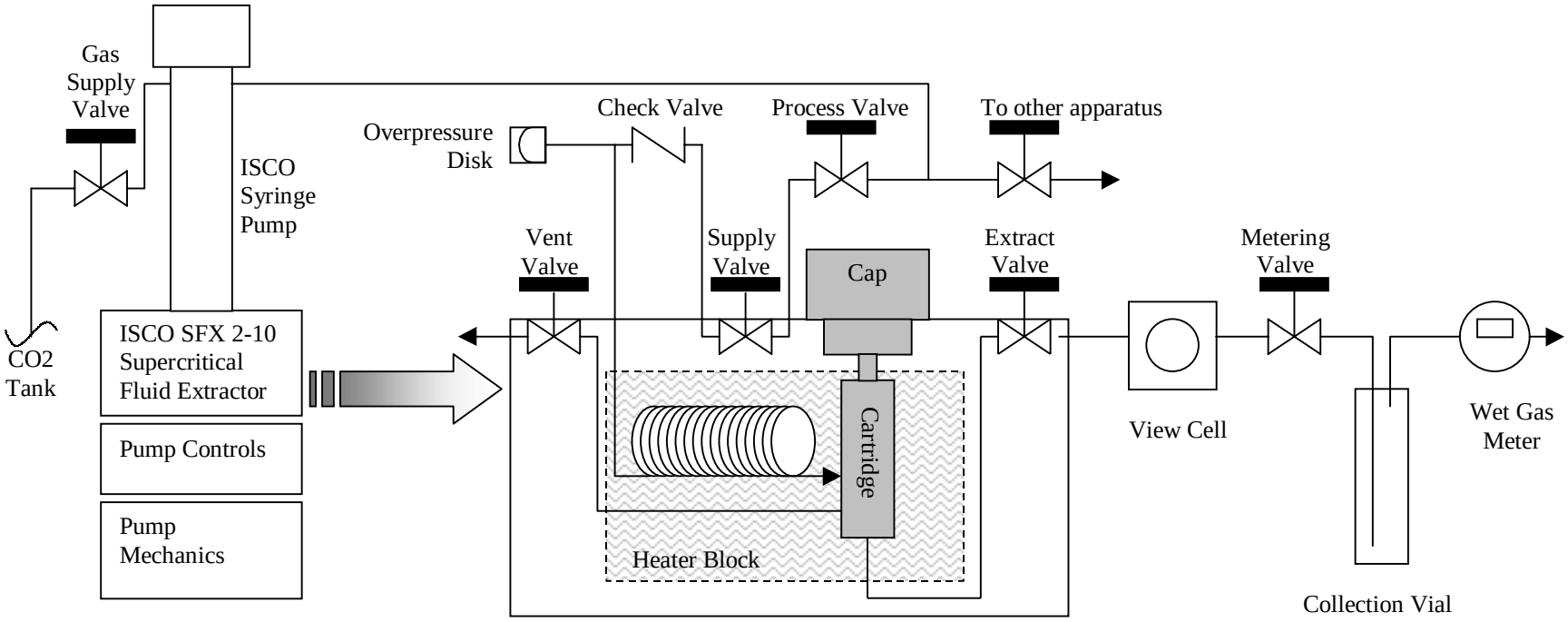
"Decontamination & Decommissioning of PCB Sites at SRS." J. Pickett, L. Oji, M. Matthews, R. White, J. Weidner, D. Bruce, M. Thies. Poster paper given at the Workshop on Integration of End User Needs with Research Projects for the Environmental Management Science Program, Savannah River Site, November 17-18, 1998.

"Mass Transfer in CO_2/Surfactant Systems", M. Matthews, Presented at the 1998 AIChE Annual Meeting, Miami Beach, FL, November 15-20, 1998.

"Sonochemical Oxidation of Organic Contaminants in Waste Water", Bruce, D., Presented at the AIChE Annual Meeting, Miami Beach, FL, November 15-20, 1998.

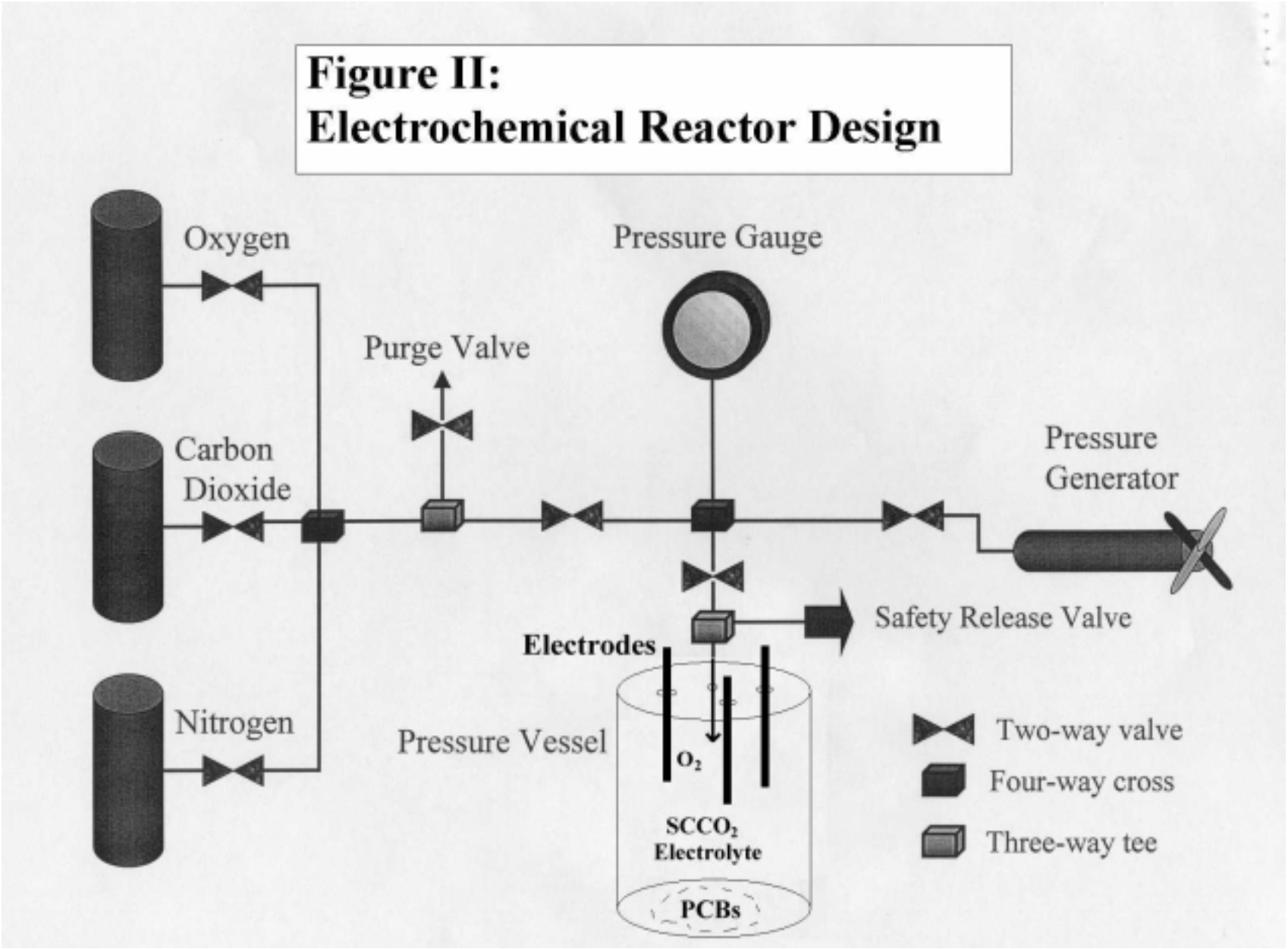
Figure I

Supercritical Carbon Dioxide Extraction Apparatus



Expanded View of Supercritical Fluid Extractor

Figure II:
Electrochemical Reactor Design



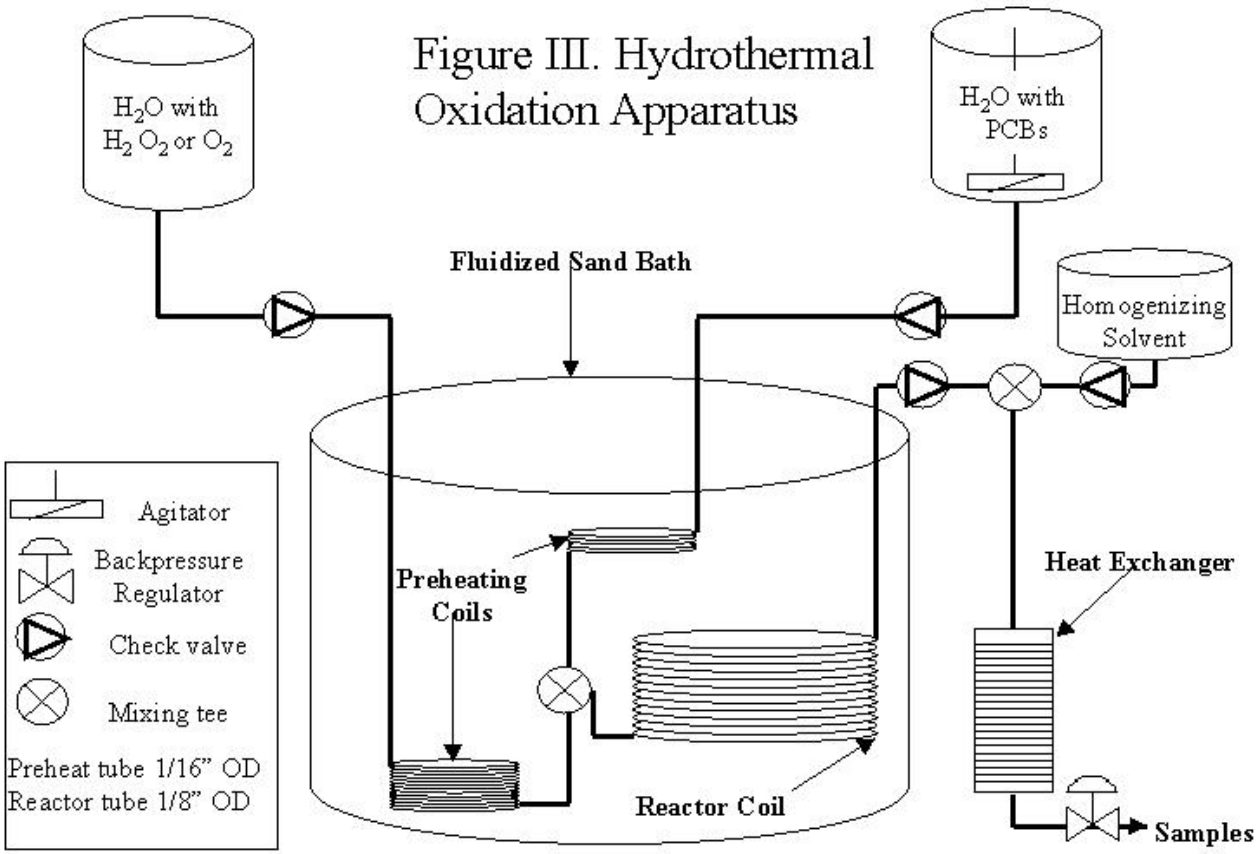


Figure III. Hydrothermal Oxidation Apparatus
H_2O with H_2 O_2 or O_2
H_2O with PCBs
Fluidized Sand Bath
Homogenizing Solvent
Agitator
Backpressure Regulator
Check valve
Mixing tee
Preheat tube 1/16" OD
Reactor tube 1/8" OD
Preheating Coils
Heat Exchanger
Reactor Coil
Samples