FINAL CRADA REPORT

**UOP
Des Plaines, IL
Unitel Technologies**

**Argonne National Laboratory
Energy Systems Division
Argonne, IL**

Report Date: 2010 February 1

CRADA Number: 0100601
CRADA Title: Membranes for Corrosive Oxidations
CRADA Start/End Date: May 2001 – April 2005

DOE Award Number: FWP 49021 or HQ CPS 1629
Argonne Funding: \$975,000

Argonne PI: Seth W. Snyder
Section Leader, Process Technology Research
Energy Systems Division
630-252-7939
seth@anl.gov

Industrial Partner:
Santi Kulprathipanja
UOP, LLC
50 East Algonquin Road
Des Plaines, IL 60017
847-391-3138
Santi.Kulprathipanja@uop.com

DOE Program Manager:
Dickson Ozokwelu
US DOE - Industrial Technologies Program
1000 Independence SW
Washington DC 20585
202-586-8501
dickson.ozokwelu@ee.doe.gov

Ravi Randhava
Unitel Technologies, Inc.
Suite 111, 411 Business Center Drive
Mt. Prospect, IL 60056-6040
847-297-2265
rr.unitel@gmail.com

The submitted manuscript has been created by Argonne National Laboratory, a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC, under Contract No. DE-AC02-06CH11357 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government

Summary of Major Accomplishments:

The objective of this project is to develop porous hydrophilic membranes that are highly resistant to oxidative and corrosive conditions and to deploy them for recovery and purification of high tonnage chemicals such as hydrogen peroxide and other oxychemicals.

The research team patented a process for membrane-based separation of hydrogen peroxide (US Patent # 5,662,878). The process is based on using a hydrophilic membrane to separate hydrogen peroxide from the organic working solution. To enable this process, a new method for producing hydrophilic membrane materials (Patent # 6,464,880) was reported.

We investigated methods of producing these hydrophilic materials and evaluated separations performance in comparison to membrane stability. It was determined that at the required membrane flux, membrane stability was not sufficient to design a commercial process. This work was published (Hestekin et al., J. Membrane Science 2006).

To meet the performance needs of the process, we developed a membrane contactor method to extract the the we surveyed several commercial and pre-commercial membrane materials. We identified pre-commercial hydrophilic membranes with the required selectivity, flux, and stability to meet the needs of the process. In addition, we invented a novel reaction/separations format that greatly increases the performance of the process.

To test the performance of the membranes and the new formats we procured and integrated reactor/membrane separations unit that enables controlled mixing, flow, temperature control, pressure control, and sampling. The results were used to file a US non-provisional patent application (ANL-INV 03-12)

Summary of Technology Transfer Benefits to Industry:

Hydrogen peroxide is widely used in pulp and paper applications, environmental treatment, and other industries. Virtually all hydrogen peroxide production is now based on a process featuring catalytic hydrogenation followed by auto-oxidation of suitable organic carrier molecules. This process has several drawbacks, particularly in the extraction phase. One general disadvantage of this technology is that hydrogen peroxide must be produced at large centralized plants where it is concentrated to 70% by distillation and transported to the users' plant sites where it is diluted before use.

Advanced membranes have the potential to enable more efficient, economic, and safe manufacture of hydrogen peroxide. Advanced membrane technology would allow filtration-based separation to replace the difficult liquid-liquid extraction based separation step of the hydrogen peroxide process. This would make it possible for hydrogen peroxide to be produced on-site in mini-plants at 30% concentration and used at the same plant location without distillation and transportation. As a result, production could become more cost-effective, safe and energy efficient.

The membrane contactor method (INV-03-012) is available for licensing for either in situ or dedicated production of hydrogen peroxide . CRADA participants were notified of this Subject Invention.

Other Information/Results: (Papers, Inventions, Software, etc.)

Patent applications:

ANL-INV-03-007 SEPARATION OF HYDROGEN PEROXIDE FROM ANTHRAQUINONE WORKING SOLUTION USING INORGANIC MEMEBRANES IN A TWO-PHASE SEPARATION SYSTEM, inventors, Rathin Datta, Ed St. Martin, M. Henry, J. Hestekin, Seth Snyder, S. Kulprathapanja, A. A. Oroskar, P. Pujado and R. Randava, abandoned.

ANL INV-03-012 “MEMBRANE CONTACTOR ASSISTED WATER EXTRACTION SYSTEM FOR SEPARATING HYDROGEN PEROXIDE FROM A WORKING SOLUTION, AND METHOD THEREOF” Seth W. Snyder (Argonne), Yupo J. Lin (Argonne), Jamie A. Hestekin (Argonne), Michael P. Henry (Argonne), Peter Pujado (UOP), Anil Oroskar (UOP), Santi Kulprathipanja (UOP), Ravi Randhava (Unitel), filed by the U.S. Dept of Energy on September 30, 2006.

Publications

J. A. Hestekin, E. G. Gilbert, M. P. Henry, R. Datta. E. J. St. Martin, S. W. Snyder “Modified Porous Nafion 112 Membranes: Characterization, Modeling, and Emulsion Separations”, *Journal of Membrane Science*, **2006**, 281: 268-273

Presentations

Results from this project were presented at:

St. Martin, Edward “Membranes for Corrosive Oxidations” presented at the 2002 Spring AICHE meeting, New Orleans, LA

Snyder, Seth “Membranes for Corrosive Oxidations” presented at the 2005 Spring AICHE meeting, New Orleans, LA