

ANNUAL DOE GRANT PROGRESS REPORT

DOE Program: EMSP

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"Cavitation Hydrothermal Oxidation:
A New Remediation Process"

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I certify that to the best of my knowledge (1) the statements herein (excluding scientific hypotheses and scientific opinions) are true and complete, and (2) the text and graphics in this report as well as any accompanying publications or other documents, unless otherwise indicated, are the original work of the signatories or individuals working under their supervision.

PI Signature:



1. Brief Summary of Progress:

During the past year, we have continued to make substantial scientific progress on our understanding of cavitation phenomena in aqueous media and applications of cavitation to remediation processes. Our efforts have focused on three separate areas: sonoluminescence as a probe of conditions created during cavitation collapse in aqueous media, the use of cavitation for remediation of contaminated water, and an addition of the use of ultrasound in the synthesis of novel heterogeneous catalysts for hydrodehalogenation of halocarbons under mild conditions.

In order to gain further understanding of the conditions present during cavitation, we have continued our studies of sonoluminescence [1]. We have made recent breakthroughs in the use of emission spectroscopy for temperature and pressure measurement of cavitation events, which we expect to publish shortly. We have been able to measure *for the first time* the temperature of cavitation *in water* during multi-bubble cavitation in the presence of aromatic hydrocarbons [2]. The emission from excited states of C_2 in water gives temperatures that are consistent with adiabatic compressional heating, with maximum temperatures of 4300 K. Our prior measurements of cavitation temperatures in low vapor pressure nonaqueous media gave somewhat higher temperatures of 5000 K [1]. This work lays permanently to rest exotic mechanisms for cavitation chemistry, at least for cavitation fields.

In a new avenue of research, we have recently explored the generation of cavitation by hydrodynamic techniques and demonstrated for the first time that chemical reactions occur during turbulent flow of water and of water containing chlorocarbons [3]. This work received substantial publicity. While the chemical effects of *acoustic* cavitation (i.e., sonochemistry and sonoluminescence) have been extensively investigated during recent years, little is known about the chemical consequences of *hydrodynamic* cavitation created during turbulent flow of liquids. Hydrodynamic cavitation is observed when large pressure differentials are generated within a turbulent liquid flow and is accompanied by a number of physical effects, erosion being most notable from a technological viewpoint. It has the potential advantage of facile scale-up: there already exist commercial high pressure flow mixing units capable of generating hydrodynamic cavitation with flows of 50 gpm (Microfluidics, Inc., Newton, MA). However, prior reports of hydrodynamically induced chemistry or luminescence and direct comparisons to sonochemistry or sonoluminescence have been extremely limited. The oxidation of iodide to triiodide in aqueous solutions containing halocarbons (e.g., CHCl_3 or CCl_4) under hydrodynamic cavitation conditions was examined in order to determine the origin of this hydrodynamic chemical reaction. This reaction also serves as a model for remediation of halocarbon contaminated water using hydrodynamic cavitation, a previously unexplored approach to remediation. The effects of several experimental variables on the I_3^- production rate were investigated. Increasing the reaction temperature inhibits the I_3^- production due to increased vapor pressure, which leads to reduced efficacy during cavitation collapse; the rate decreases exponentially with vapor pressure. The production of I_3^- is sensitive to the nature of the dissolved gas and decreases exponentially with increasing gas thermal conductivity. Thus, the chemistry observed and its response to external parameters is remarkably similar to ultrasonically induced cavitation, albeit the sonochemical rates are significantly higher at least with our current experimental configurations.

We have stumbled across another research area that has led to a recent discovery relevant to remediation chemistry: the catalytic *hydrodehalogenation* of halocarbons. In work not funded by the DOE, we have been actively involved in the development of sonochemical preparations of active heterogeneous catalysts [4-6]. The localized hot-spot created during acoustic cavitation is sufficient to strip ligands completely from metal complexes. This process also produces enormous cooling rates ($>10^9$ K/s) and so allows the formation of colloidal, amorphous metal aggregates. We have very recently used ultrasound to produce nanostructured MoC_2 with very high surface areas and excellent catalytic activity [7]. Our most recent discovery is very relevant to our DOE project, however: this sonochemically prepared MoC_2 is an extremely effective and stable *hydrodehalogenation* catalyst. In gas flows with H_2 , we can remove both Cl and F from essentially all halocarbons, replacing the halogen with hydrogen quantitatively and quickly without degradation of the MoC_2 catalyst (in spite of the release of HCl or HF which rapidly destroy most other catalysts), under mild conditions (<300 °C). We have examined quantitatively the catalytic properties of supported catalysts produced sonochemically from using gas/solid microreactor kinetics monitored by GC/MS. We expect to publish this work in the near future.

1. Suslick, K. S.; Crum, L. A. "Sonochemistry and Sonoluminescence," in *Encyclopedia of Acoustics*; Crocker, M. J., ed.; Wiley-Interscience: New York, 1997; vol. 1, ch. 26, pp. 271-282.
2. Suslick, K. S.; Didenko, Y. T.; McNamara III, W. B. "Sonoluminescence Temperature of Aqueous Cavitation", submitted for publication.
3. Suslick, K. S.; Mdleleni, M. M.; Ries, J. T. "Chemistry Induced by Hydrodynamic Cavitation" *J. Am. Chem. Soc.*, **1997**, *119*, 9303-9304.
4. Suslick, K. S. "Sonocatalysis," in *Handbook of Heterogeneous Catalysis*; Ertl, G.; Knozinger, H.; Weitkamp, J.; eds.; Wiley-VCH: Weinheim, 1997; vol. 3, ch. 8.6, pp. 1350-1357.
5. Suslick, K. S.; Hyeon, T.; Fang, M.; Cichowlas, A. A. "Sonochemical Preparation of Nanostructured Catalysts," *Advanced Catalysts and Nanostructured Materials*; Moser, W. R., ed. Academic Press: New York, 1996, pp. 197-211.
6. Suslick, K. S.; Fang, M.; Hyeon, T. "Sonochemical Synthesis of Iron Colloids" *J. Am. Chem. Soc.*, **1996**, *118*, 11960-11961.
7. Hyeon, T.; Fang, M.; Suslick, K. S. "Nanostructured Molybdenum Carbide: Sonochemical Synthesis and Catalytic Properties," *J. Am. Chem. Soc.*, **1996**, *118*, 5492-5493.

2. Current Funding.

Status	Source and Project Number Title Major Goals Overlap	Dates of Project	% PI Effort
		Annual Direct Costs	Academic Summer
Active	NSF, CHE9420758 "Chemical Effects of Ultrasound" To examine and develop applications of sonochemistry to materials and inorganic synthesis. No overlap with current proposal.	1/15/95 - 11/30/98 \$80,531	12 25
Active	NIH "Heme Proteins, Microspheres, and Their Synthetic Analogs" Investigation of heme protein and metalloporphyrin chemistry. No overlap of personnel with current proposal.	12/1/96 - 11/30/01 \$187,162	12 25
Active	DOE, DE-AC276ER01198, Block Grant to the UIUC MRL "Field Responsive Porphyrinic Materials" Goals: To develop porphyrins as nonlinear optical and ferroelectric materials through organized arrays. No overlap with current proposal.	1/1/91 - 12/31/95 \$38,373 (KSS portion)	5 5
Active	VivoRx, Inc. "Proteinaceous Microspheres" Development of protein microspheres for pharmaceutical and drug delivery. No overlap of personnel with current proposal.	10/1/96 - 9/31/97 \$30,000	5 5
Active	DOE "Cavitation Hydrothermal Oxidation: A New Remediation Process" Use of ultrasound for remediation of contaminated water and soil. No overlap with current proposal.	9/1/96 - 8/31/99 \$150,386	12 25
Active	DOD, Army "MURI: Dendritic Materials Systems" Multi-PI thrust for development of new dendrimer & hyperbranched polymers, No overlap with current proposal.	6/1/97 - 5/30/00 \$17,852 (KSS portion)	12 25

6. Education and Human Resource Development.

Current Group Members involved in sonochemical research:

Gennady Dantsin

B.S., State Univ. of New York, Binghamton, 1995.

Yury Didenko**

B.S., M.S., Moscow State University, 1970-75.

Ph.D., Moscow State University, 1985.

Head of Laboratory, Pacific Oceanological Institute,
Vladivostok, Russia.

Research Associate, Univ. of Illinois, 1995-97.

Kenneth Kolbeck

B.S., University of New Mexico, 1991.

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B. S., Illinois Wesleyan, 1995.

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B.S., University of California, Santa Barbara, 1992.

Millan M. MdIeleni

B.Sc., University of Fort Hare (S. Africa), 1987.

Ph.D., Univ. of California at Santa Barbara, 1995.

Postdoctoral Associate, Univ. of Illinois, 1995-97.

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B.A., Northwestern University, 1995.

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