THE USE OF ADVANCED ACOUSTIC CAVITATION FOR APPLICATIONS IN THE OIL AND NATURAL GAS INDUSTRY

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ABSTRACT

Argonne National Laboratory (ANL) has conducted research involving acoustic cavitation (sonication) combined with advanced oxidation techniques for several applications for the oil and natural gas industry. Acoustic cavitation involves the application of high intensity sound waves (having strong oxidation potential) to a liquid phase. Microbubbles form which grow to a critical size (on the order of a few angstroms) which then implode. At the collapsing bubble interface, temperatures in the order of ~5,000° K and pressures on the order of 500 to 1,000 atmospheres have been estimated, while the bulk solution stays near ambient. This creates conditions that are very effective for cleaning industrial equipment. This process can be enhanced by the combination with other advanced oxidation techniques such as ozone injection, vapor stripping, and/or the addition of hydrogen peroxide.

ANL has conducted research into mineral scale removal using this advanced acoustic cavitation technique. Barium sulfate ($BaSO_4$) scale was used as the surrogate scale. During these tests, ANL was able to break up scale with as large as 5/8-in thickness. Preliminary results to date indicate that better than 90% of surrogate scale was removed, after a 15-min application of sonication (20 kHz) at 20 W/cm^2. Additional research (for the textile and forest products industries) conducted at ANL included the removal of solidified polyethylene from spinnerette heads and polypropylene from scaled glassware (for application to spinnerette heads). In these applications, the removal of the solidified waste form reached nearly 100% using sonication techniques. The sound waves effectively chiseled the waste forms from the equipment, breaking the scale into many, many fine particulates, effectively forming a slurry of the original solid "hockey-puck-like" monolith. The acoustic cavitation effectively scoured the equipment surface free of the solidified waste form.

ANL is currently investigating the use of this advanced acoustic cavitation technique to remove paraffin build-up from production wells and lateral piping in the field. FNI, ANL, and Nicor Technologies are currently examining the possibility of using this technique to remediate blocked or plugged underground natural gas storage wells. Other potential applications of this advanced acoustic cavitation technique being studied include: disablement and neutralization of land mines and unexploded ordinances, *in-situ* removal of chlorinated solvents (volatile organic compounds) from groundwater, enhanced oil/water separation, development of a hand held device for decontamination and decommissioning of buildings, and removal of oil and cutting lubricants from scrap aluminum.

ANL has been researching the combination of acoustic cavitation (sonication) with advanced oxidation (air, oxygen, ozone, and hydrogen peroxide) techniques for the past five years. Furness-Newburge, Inc. (FNI) has been working with the foundry industry to solve environmental emissions problems and optimize sand/clay/binder reuse for the past eight years. ANL and FNI joined forces in May of 1998 to begin examining the synergies of their independent work efforts and focus on new applications for the joint technology interests. The following text summarizes these efforts by application and give a brief summary of the approach.

Groundwater and Soil Remediation

ANL has been investigating an integrated (sonication coupled with vapor stripping) system in a current project funded by the U.S. Department of Energy's (DOE's) Environmental Management Science Program (EMSP) to partially degrade and/or destroy volatile organic compounds (VOCs). An experimental pilot-scale, in-well system is being designed and installed in a high-bay area at ANL. ANL and its industrial partner, FNI, are fabricating the test system for the pilot demonstrations.

Preliminary laboratory-scale results obtained from the EMSP project indicate the system is capable of partially degrading and destroying VOCs. The combination of sonication and vapor stripping can remove up to 97% of the chlorinated solvents with a 5-10 minute contact time. ANL believes that this system can destroy chlorinated solvents and petroleum hydrocarbon contaminants at a very high rate with minimum contact time.

ANL is currently working on a research project to determine the efficiency and economics of employing an integrated (acoustic cavitation combined with advanced oxidation) treatment system to destroy/remove hydrocarbons at levels encountered in contaminated groundwater at oil refineries. The objective of this effort is to conduct a pilot-scale demonstration of an integrated treatment system that couples in-well sonication and in-well vapor stripping augmented with ozone/hydrogen peroxide to effectively treat groundwater contaminated with petroleum hydrocarbons [e.g., polyaromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene and total xylenes (BTEX)]. This treatment scheme enables the contaminated water to be treated in well (i.e., below grade), thereby minimizing the regulatory concerns and economic issues associated with pump-and-treat technologies.

ANL and FNI have had discussions with personnel at McClelland Air Force Base in California; Warren Air Force Base in Cheyenne, Wyoming; and Badger Army Ammunition Plant in Wisconsin about the groundwater problems at their respective sites. These sites have typical groundwater problems with contamination due to chlorinated solvents such as 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), dichloroethane (DCA), chloroethylene (DCE), carbon tetrachloride, vinyl chloride, and dinitrotoluene (DNT).

Scale Removal for the Oil and Gas Industry

<u>Radioactive Scale (Naturally Occurring Radioactive Materials-NORM)</u>

Within DOE's Gas Research Program, the management of naturally occurring radioactive materials (NORM) in natural gas production is a high priority environmental research area. Petroleum production NORM is generated in three waste streams: scale, sludge, and produced water. Scale and sludge accumulate primarily in water-handling equipment, such as pipelines, tubing, pumps, filters, oil/water separators, and storage vessels.

The purpose of this project is to examine a new technology involving sonication/dissolution aimed at treating naturally occurring radioactive materials (NORM) waste. Barium sulfate ($BaSO_4$) scale was used as the surrogate waste for this study. This project investigated the sonication/dissolution of NORM wastes. During the first part of this study, barium sulfate ($BaSO_4$) scale was formed in glass beakers; the $BaSO_4$ scale was spiked with various non-radioactive co-contaminant forms such as strontium and cesium. The strontium and cesium used in these studies were of the non-radioactive form. Future activities involve the sonication/dissolution of $BaSO_4$-scale containing radium.

Barium-sulfate scale (potentially contaminated with radioactive materials) is a common byproduct of oil and natural gas production. The baseline technology for removing this scale from industrial equipment involves using a proprietary dissolver operated at a solution temperature of 190 to 200^{o}F at pH ~13. A decrease of 20 to 30^{o}F as a result of sonication would be extremely beneficial and would be more cost effective than the current operations for removing barium sulfate scale. This project also will determine whether the combination of sonication techniques coupled with the use of chelating agents could effectively remove NORM-type scale from industrial equipment. The focus of this study is to determine whether sonication techniques can enhance the dissolution of $BaSO_4$ scale either using sonication alone or using sonication in conjunction with chelating agents (such as ethylenediaminetetraacetic acid (EDTA), citric acid, etc.). The objective of this project is to determine whether sonication alone or using sonication in conjunction with chelating agents can enhance the dissolution of $BaSO_4$ scale. Preliminary results are shown in Fig. 1.

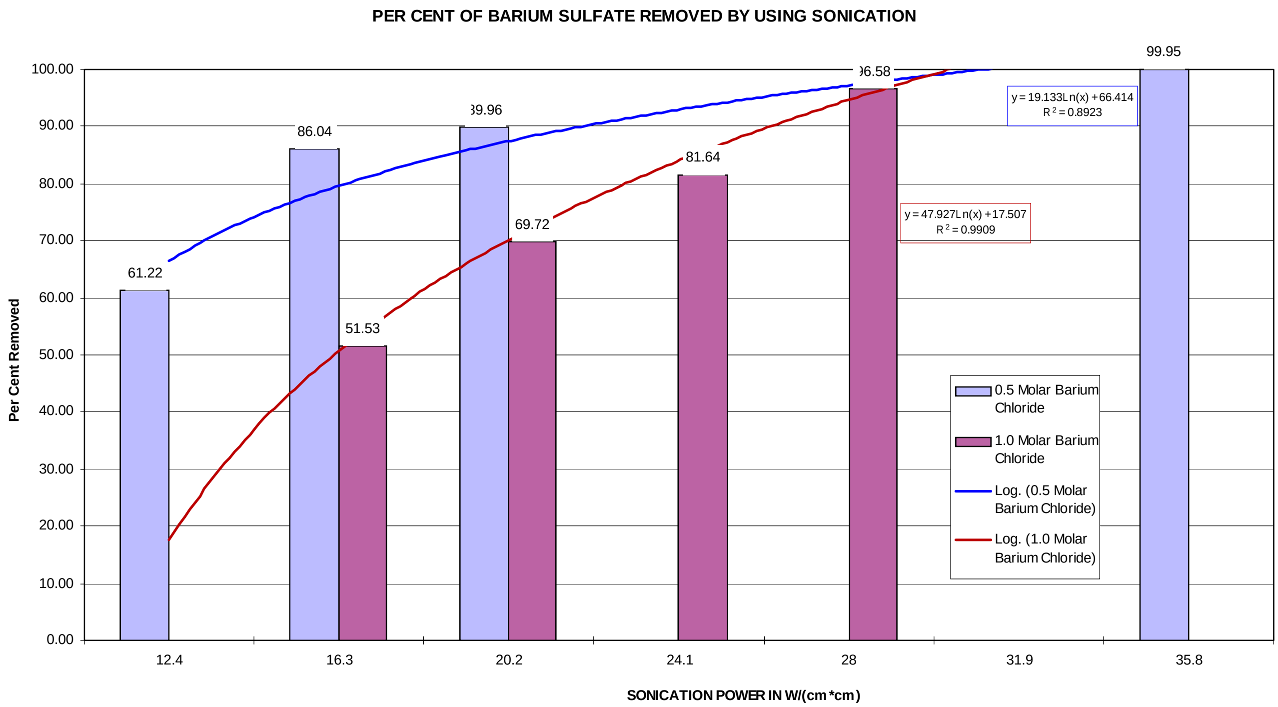

Figure 1 Preliminary results of barium sulfate removal using sonication.

Mineral Scale (Within Production and/or Storage Wells, Laterals, and Equipment)

FNI, ANL and Nicor Technologies are currently examining the possibility of utilizing sonication to locate and remediate underground natural gas storage well damage. The diagnostic portion of the research effort will utilize a high frequency transponder and a receiver to locate the damaged areas within the underground storage well. Once the problem area has been located, the actual remediation of the damage to the underground storage area will be conducted using sonic transducers contained within the same small (coffee cup size) unit used to locate the problem area. The acoustic waves generated by these transducers will actually break up any scale, inorganic precipitate, organic or hydrocarbon residue, fouling or plugging caused by either particulates or bacteria.

The use of sonic waves to locate, size, and identify objects is well known, mature technology. Sonication has also been shown to break up mineral scale and other scaling/fouling build-up within natural gas and oil field piping/wells. This project proposes to adapt sonication for the detection and remediation of damaged underground natural gas storage wells. Initially a "surrogate" underground storage well environment would have to be created in the lab. Both the locating and remedial functions of sonication would be tested in the "surrogate" storage well created in the lab. The ability of the sonicator to break-up the various types of blockages (inorganic, organic/hydrocarbon, and fouling/plugging caused by particulate and bacteria) will be tested in the lab. Additionally, more tenacious types of scale will be tested to determine the limits/capabilities of the various power intensities and frequencies used in the first year's efforts.

The field test partner, Nicor Technologies, will provide fouled/scaled tubing from actual underground storage wells. If the proposed system can remove the actual scale/fouling from the tubing provided, an actual down-hole "pre-field test" can be conducted in an actual observation well (located within a storage reservoir system) as the final test of the system prior to beginning the actual field trials scheduled as part of the second phase of activities.

Process Optimization within the Foundry and Steel Industries

In the production of iron castings, molten iron is poured into a "green" sand mold comprised of sand, clay, powdered coal, water, and organic binders. The heating of the coal and other organics in the mold during casting causes the release of volatile organic compounds (VOCs) such as benzene. In order to reduce these emissions, advanced oxidants (AO) were introduced as a "sand additive" to these molds by way of a Sonoperoxone™ (SP) system that uses ozone, hydrogen peroxide, and sonication. This SP/AO-containing water replaces ordinary water as a mold ingredient. These Sonoperoxone™ systems have been operating at more that four working foundries for the last 1 to 4 years.

Records from these foundries have shown reductions in VOCs and benzene emissions after installation of the Sonoperoxone™ system. FNI is working with the Pennsylvania State University to test and evaluate the emissions from green sand and green sand components using thermogravimetric analysis (TGA). In these TGA tests, sand samples were heated under nitrogen; and mass losses were tracked to determine the amount and temperature where emissions occur. Two full-scale foundry lines running the same casting types in parallel have been compared: one using AO/SP and one not using this AO/SP. Over a full year of operation, the AO foundry's sand had consistently lower mass losses that would translate into lower VOC emissions. In addition, pilot-scale casting trials were conducted on molds whose only difference was that one mold used this AO treated water and the other mold used ordinary water. Mold autopsies and TGA tests characterized the effect of AO on these emissions during the casting event, and generally found emission reductions with water containing AO.

Compaction and Stabilization of Wastes for Recycle/Reuse

The current disposal option of choice by the steel and foundry industry involves sending metal fines/particulates (called "swarfs") to either a landfill or to a scrap metal yard. Included in these wastes are manufacturing process "swarfs" (metallic particulates from grinding, polishing, honing, etc.); pollution control wastes (e.g., baghouse wastes and other pollution control residues); and mill scale or slags. Even though the landfills accept these wastes, the landfill owners recognize that these are really undesirable wastes, due to their tendencies to rapidly oxidize and create spot flare-ups (fires). Because of these problems, the steel industry often pays premium to dispose of the swarfs at a landfill. The "swarfs" typically contain high metallic content (>40% iron and other recyclable metals such as nickel, copper, etc.), and, therefore, have some intrinsic recyclable/reuse value. The handling of these metallic wastes (particulate and other solid forms) is difficult. By packaging these metallic wastes into a more manageable form, value is created where only cost existed before. These wastes need to be converted into a different form so that they can either be recycled or formed into a marketable byproduct.

This project investigates the use of various chemical-binding agents, used either singly or in combination with one another, in order to form dense, hard recyclable forms of the metallic particulates. The objective of this phase of ANL's work with Solvent Systems International, Inc. (SSI) is to "optimize" the compressive strengths of the newly formed by-products. ANL and SSI will examine how the additives (binders) can by combined with advanced oxidation techniques (including sonication) in order to maximize the compressive strengths of the recycled by-products.

FUTURE APPLICATIONS

The following two topic areas are applications that are not fully developed and need further study to bring them into the prototype/field testing phases of development.

Decommissioning and Decontamination of Buildings

The objective of this approach is to demonstrate the potential of multiple advanced oxidation delivery systems to deactivate viruses and kill bacteria in biological systems and to render less toxic in chemical warfare agents. The proposed delivery systems of advanced oxidants are as follows: (1) Foams or foamed gels with the bubbles containing advanced oxidants and the bubble wall structure designed in such a way to extend the stability of the advanced oxidants, such as UV/ozone/high humidity gases used to generate the microbubble structure (i.e., lamellae) in a foam or foamed gel; (2) Gas phase delivery of advanced oxidants in the form of high humidity, UV-irradiated ozone containing gas and/or the same device used as a recirculating biological or chemical destruction system; (3) Advanced oxidant containing steam-cleaning system for decontamination of buildings, rooms, or laboratories, or other structures containing chemical or biological agents. This would involve the use of advanced oxidants in the water used to generate steam. This would be a synergistic approach in that the steam in and of itself could be used to sterilize the bacteria, spores, viruses, or other microorganisms in a biological system directly and then due to the heat more rapidly decompose the toxic “skeleton” (i.e., the potentially more toxic daughter byproducts of biological death). In a chemical system employing an A/O steam decontamination approach, the A/O steam tends to speed chemical dissociation of the chemical agent. The potential use of reactive metals such as vanadium, titanium, and iron could further enhance A/O steam decontamination when finally irradiated with ultraviolet light. This creates a scenario of advanced oxidation chain reactions that have already been verified by the scientific/technical community familiar with advanced oxidation systems. The end state will be a building, facility, or site that is completely reusable, non-toxic, steam-cleaned, and in terms of public perception, “sterilized.” A fourth objective would be in the creation of an advanced oxidant decontamination device to be used for hospital workers caring for victims of biological terrorism. A downdraft or side-draft device would capture the bacterial aerosol from breathing and coughing of a victim and kill the organism and hence deny a pathway for disease propagation.

The proposed approach to the problem of decontaminating chemically and biologically contaminated surfaces by deactivating viruses and killing bacteria in biological systems and rendering chemical warfare agents less toxic is unique because: (1) each sub-element of the proposed system has a proven technical basis in other applications; (2) the delivery system can be deployed in a simple manner: and (3) the project team has both a strong scientific research and development track record and proven industrial successes.

Conventional treatment of solid structures generally includes chemical extractions such as with steam cleaning systems or chelating agents, and render to rubble contaminated structures. The approach being offered has the ability to completely remove the chemical or biological agents, and thereby enable the structure to once again be used. The technology of advanced oxidation has already been proven by the scientific community to kill pathogens and dissociate chemicals. What is being proposed is a focused expansion of existing technology into a technology that is adaptable, flexible, portable, and applicable to chemical and biological agents by relatively low-tech delivery systems and maintainable, reliable, and already proven components. Current approaches using advanced oxidation are already being used in extremely large-scale applications such as drinking water treatment and reduction of air pollutants such as benzene and other VOCs in the foundry industry.

Disablement and Neutralization of Ordinances/Land Mines/Explosives

The objective of this approach is to demonstrate the potential of multiple advanced oxidation delivery systems to deactivate viruses and kill bacteria in biological systems and to render less toxic in chemical warfare agents. The proposed delivery systems of advanced oxidants are as follows: (1) Foams or foamed gels with the bubbles containing advanced oxidants and the bubble wall structure designed in such a way to extend the stability of the advanced oxidants, such as UV/ozone/high humidity gases used to generate the microbubble structure (i.e., lamellae) in a foam or foamed gel; (2) Gas phase delivery of advanced oxidants in the form of high humidity, UV-irradiated ozone containing gas and/or the same device used as a recirculating biological or chemical destruction system; (3) Advanced oxidant containing steam-cleaning system for decontamination of buildings, rooms, or laboratories, or other structures containing chemical or biological agents. This would involve the use of advanced oxidants in the water used to generate steam. This would be a synergistic approach in that the steam in and of itself could be used to sterilize the bacteria, spores, viruses, or other microorganisms in a biological system directly and then due to the heat more rapidly decompose the toxic “skeleton” (i.e., the potentially more toxic daughter byproducts of biological death). In a chemical system employing an A/O steam decontamination approach, the A/O steam tends to speed chemical dissociation of the chemical agent. The potential use of reactive metals such as vanadium, titanium, and iron could further enhance A/O steam decontamination when finally irradiated with ultraviolet light. This creates a scenario of advanced oxidation chain reactions that have already been verified by the scientific/technical community familiar with advanced oxidation systems. The end state will be a building, facility, or site that is completely reusable, non-toxic, steam-cleaned, and in terms of public perception, “sterilized.”

This approach provides a very versatile compact transportable and low-tech decontamination family of processes that can be tailored to specific applications and locations such as targets of terrorism, triage centers, and extended care facilities. The operational personnel will require minimal training and relatively standard personal protective equipment. The maintenance personnel would require a slightly higher level of training but certainly not beyond what is considered normal and prudent in our relatively high-tech society. The transient nature of advanced oxidation would also help to allay fears of long-term decontamination residuals, such as would be found in chlorine or other long-term potential high-risk chemical approach to chemical decontamination.

This approach focuses on the exact goals and needs of the current climate of terrorism because: (1) it focuses on a unique solution to the problem of decontaminating chemically and biologically contaminated surfaces by deactivating viruses and killing bacteria in biological systems and rendering chemical warfare agents less toxic; (2) each sub-element of the proposed system has a proven technical basis in other applications; (3) the delivery system can be deployed in a simple manner; and (4) the project team has both a strong scientific research and development track record and proven industrial successes.

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In summary, seven different applications of combing advanced acoustics (sonication) with advanced oxidation techniques have been presented. At least three of these applications have direct linkages to oil and gas industry applications: (1) mineral scale removal (paraffins, underground storage well remediation, improving performance of stripper wells, etc.); (2) radioactive scale removal (NORM); and (3) groundwater and soil remediation (e.g., at oil or gas processing plants). Two other applications have been discussed that have applications in the steel and foundry industries (process optimization and compaction/stabilization of wastes for recycle/reuse). Finally two more futuristic application in the decommissioning and decontamination (D&D) areas (disablement/neutralization of ordinances and D&D of buildings) have been presented as areas that need more development work. ANL is working closely with their industrial partners (FNI, Nicor Technologies, and Solvent Systems, Inc.) in all of these areas to further advance the technology of combing acoustic cavitation with advanced oxidation techniques.