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CRADA Final Report
for
CRADA Number Y1292-0136

Machine Tool Evaluation
(Development of Environmentally
Conscious Machining Fluids and
Systems)

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Abstract: The overall purpose of this CRADA is to select or develop as required a group of cutting fluids, for use with metals and/or ceramic materials, which are more environmentally benign and which will reduce or eliminate the environmental problems associated with management and disposal of these cutting fluids. This CRADA was initially funded by DOE/DP, and was expanded to include DOE/ER funding with an added focus on environmental issues related to synthetic cutting fluids. The specific objective of this DOE-ER funded project (one of ten technical tasks within the CRADA) is to determine and demonstrate chemical methods of degrading and/or improving the disposability of synthetic cutting fluids. Photochemical advanced oxidation processes were developed and demonstrated to successfully remove all carbon from new and used cutting fluids, and from surrogate solutions containing up to 15,000 ppm of total organic carbon in the initial solutions. Chemical and energy costs for the process were evaluated. Commercial providers of advanced oxidation process technologies were consulted concerning scale-up, and associated costs in industrial systems were estimated to be well represented by the laboratory bench-scale measured values. Engineering aspects and alternative oxidation methodologies were explored through consultation with an internationally recognized chemical engineer, and it was concluded that no clear alternatives were available for treating aqueous fluids with extremely high initial carbon content (i.e. 15,000 ppm total organic carbon).

CRADA Objectives: The objectives of this CRADA encompassed developing methods of utilizing, handling and disposing of synthetic and/or semi-synthetic cutting fluids such that the total costs related to the use of the coolant is both affordable to small manufacturing operations and acceptable for environmental disposal. The CRADA was broken down into 10 major technical task areas including: (1) development of specific machining validation methods, (2) new fluids formulation, (3) comparative machinability evaluations, (4) alternative fluids (for corrosion testing, part cleaning and protection studies), (5) fluid/machine compatibility studies, (6) fluid physical stability studies, (7) fluid stability to microbes studies, (8) fluid toxicity studies, (9) fluid recyclability studies and (10) development of waste disposal techniques for any coolant system used by industry or by DOE facilities. The objective of this ER funded project was CRADA technical task area 10. The CRADA consisted of three phases: (1) characterization and testing of coolants, (2) development of coolant and best management practices and (3) refinement and optimization of best coolant system management practices. This ER funded project was incorporated into phases 2 and 3. This ER funded project was tasked with determining a technically viable, as well as economically and environmentally acceptable, method for disposal of the synthetic cutting fluids. This objective encompassed refining and optimizing the waste disposal methodology for a variety of cutting fluids.

Meeting the CRADA Objectives: The treatment of aqueous solutions containing organic carbon levels above several hundred ppm had not been critically addressed prior to the work undertaken as part of this CRADA. Our demonstration of total organic carbon removal from new and used cutting fluids, as well as surrogate solutions, containing up to 15,000 ppm total organic carbon meets one of the primary objectives of the CRADA by demonstrating a technically viable method of cutting fluid treatment. Our work has

simultaneously advanced the field of advanced oxidation technology research through our pioneering study of extremely high organic carbon content fluids. Moreover, complete removal of the initial organic carbon from aqueous solutions meets the CRADA objective of finding an environmentally acceptable method of fluid treatment. Fluid treatment by advanced oxidation technology results in water, carbon dioxide and/or small organic acids and metal speciation depending on the initial sample content. The metals can be removed by ion-exchange rendering the final solution environmentally benign. The electrical and chemical costs determined for carbon removal from extremely high carbon content fluids using photochemical advanced oxidation processes was determined to be approximately \$1 per gallon. This cost is high compared to the treatment of typical environmental aqueous wastes which contain much smaller amounts of organic carbon (< 100 ppm total organic carbon); however, the cost is intrinsic to the high carbon content of the fluids and is not economically prohibitive and meets the CRADA economic objective. The technology demonstration, costs determinations and associated publications are the product of this ER funded portion of the CRADA. Commercial equipment is available to implement this technology.

Relationship to DOE/ER's Mission: The knowledge gained from this research will assist DOE/ER in addressing environmental quality issues at facilities involved in machining of metals, ceramics and composite materials. Other benefits include improving the knowledge base in applications of photochemical advanced oxidation processes and in materials processing. Hence, the results of these studies have broad significance in contributing to DOE's environmental quality and science missions. The CRADA project is also synergistic with our study of the "Photochemistry of Hazardous Organics in Multiphase Media" (ERKCC07); which focuses on the photochemical degradation of organics at solid/air and solid/liquid interfaces. The "Photochemistry of Hazardous ..." program is supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy.

Technical Aspects of the Research: The synthetic fluids studied in this project were aqueous-based fluids that typically contained 15000 mg L⁻¹ (ppm) initial total organic carbon (TOC₀) after dilution to the manufacturer's specification for fluid use. The fluids are comprised of a blend of polyglycols, long chain aliphatic components with varying functionality and assorted defoaming and bacteriocidal agents. The fluids are engineered to be biorecalcitrant for increased in-grinder service time. The biorecalcitrant nature of the fluids makes them unresponsive to bioremediation technologies. Other used fluid treatment options can include landfilling, incineration, deep well injection, supercritical water oxidation (SCWO), electron beam, photochemical hydrogen peroxide and ozone methods and semiconductor methods (UV/TiO₂). Incineration and landfilling are possible methods of treatment for fluids with extremely high carbon content; however, the volumes of fluid utilized by end-users can be quite large and less expensive treatment options exist. In a recent survey of advanced oxidation process (AOP) costs, incineration and landfilling were found to be the most expensive waste treatment methods, costing well in excess of \$1 gal⁻¹.¹ Deep well injection and SCWO and electron beam technologies are reported to be applicable to fluids with extremely high carbon content; however, capital costs make

these methodologies unattractive for small manufacturers. Semiconductor-based AOP methodologies are generally not useful at high contaminant levels, presumably due to fouling of the catalyst surface. We tested the use of UV/TiO₂ on extremely high carbon containing fluids and found the methods to be ineffective. Although fluid discoloration was observed, TOC loss did not occur. Photochemical hydrogen peroxide and ozone based AOP methods have been reported to be the least expensive methodologies, but the upper limit of treatable TOC₀ was reported to be 1000 ppm.²

Application of photochemical AOP methodologies to aqueous systems containing TOC₀ levels well in excess of 1000 ppm had not been systematically studied prior to our work on this CRADA. In fact, most research has focused on low concentrations (< 100 ppm) of environmental contaminants in soils, groundwaters, etc. We have addressed the cost of applying photochemical AOP methods utilizing hydrogen peroxide, photo-Fenton and hydrogen peroxide/ozone reagents to solutions of synthetic cutting fluid, ethylene glycol, polyethylene glycol and sodium dodecylsulfate at TOC₀ levels up to 15000 ppm. We refer to TOC₀ levels greater than 1000 ppm as “extremely high” to differentiate them from systems containing TOC₀ levels between 100 ppm and 1000 ppm which are typically referred to as “high” levels.

Our studies of AOP treatment of ethylene glycol, polyethylene glycol and sodium dodecylsulfate are described in a manuscript entitled “Application of Advanced Oxidation Process Technologies to Extremely High TOC Containing Aqueous Solutions,” which has been accepted for publication in *Journal of Advanced Oxidation Technologies*. A copy of the manuscript is attached to this report as Appendix A. In addition, we have examined new and used cutting fluids provided by the CRADA partner, as well as used cutting fluid samples obtained from machines placed at ORNL by the CRADA partner for use in other technical tasks.

We have chosen to employ, as a figure-of-merit, the electrical energy per unit mass (EE/M) required to remove carbon from solution. The EE/M metric has been recommended as a standard figure-of-merit for comparison of data from AOP systems originating in different laboratories.³ This figure-of-merit is related to the electrical energy efficiency of the AOP system (lower values mean higher efficiencies). For a zero-order kinetic process, the EE/M has been defined as the electrical energy in kilowatt hours (kWh) required to bring about the degradation of a unit mass (one kg) of a contaminant. Additionally, the EE/M allows direct comparison of differing AOP technologies, such as those employed in this study, and provides a comparison among the technologies, which is useful to industries and practitioners of AOP. However, EE/M values also reflect intrinsic hardware efficiencies which may vary from one laboratory to the next and reflect differing lamp efficiencies, stirring and/or mass transfer efficiencies in the reactor and efficiencies of O₃ generating systems, among other hardware-specific factors. To better estimate the effect of scale on the costs of fluid treatment, we have consulted engineers at Calgon Carbon Corporation, a major supplier of AOP equipment. After a review of our results for the surrogate fluids, and based on their experience in scale-up of AOP treatments of dilute TOC₀ systems from batch reactors similar to the one used in this work, it was estimated that our measured EE/M values would not change significantly on scale-up.

TOC removal from the surrogate solutions was fastest (least costly) for the glycol fluids (ethylene glycol and polyethylene glycol) and slowest (most costly) for sodium dodecylsulfate (SDS), as described in the attached manuscript (Appendix I). The costs determined for the glycol and SDS fluids bracketed the costs determined for new and used cutting fluids. By way of example, the TOC decrease during photolysis of an aqueous solution is shown as a function of time in Figure 1 for solutions containing

Figure 1

ethylene glycol (filled diamond symbols, $\text{TOC}_0=10,000$ ppm, $\text{H}_2\text{O}_2=9\%$) and a synthetic cutting fluid (open square symbols, $\text{TOC}_0=10,000$ ppm, $\text{H}_2\text{O}_2=9\%$). The linearity of the plots in Figure 1 demonstrate that loss of carbon is a zero-order process. From the data in Figure 1, a difference in the rate of TOC loss is apparent in the different fluids. The rate of TOC loss from solution was determined to be independent of the rate of stirring (stirrer rates from 500-2500 rpm) in the reactor, thereby demonstrating that the efficiency of the reactor was not limited by mass transfer of the solution through the photolytic zone.

Table 1 gives the EE/M values for TOC removal from solutions of cutting fluid, ethylene glycol, polyethylene glycol and sodium dodecylsulfate employing several AOP technologies. Subsections of the table divided by horizontal lines give data for solutions with 10000 ppm TOC_0 containing 9% H_2O_2 , 13000 ppm TOC_0 containing 3% H_2O_2 and 4500 ppm TOC_0 containing 3% H_2O_2 . AOP methodologies involving UV/ H_2O_2 , UV/ $\text{H}_2\text{O}_2/\text{O}_3$, UV/ $\text{H}_2\text{O}_2/\text{Fe}$ (initial $\text{Fe}^{2+} = 2.5 \times 10^{-3}$ mol L^{-1}) and UV/ $\text{H}_2\text{O}_2/\text{O}_2$ were examined. Columns in Table 1 give the EE/M values for each substrate utilizing only UV/ H_2O_2 , and with additives Fe^{2+} , O_2 and O_3 respectively. Calculated costs for removing 95% of the TOC_0 from solution is given in parenthesis in Table 1. These costs only take into account the energy requirements for running the lamp, and the ozone generator where appropriate, and are based on a standard rate of $\$0.06 \text{ kW}^{-1} \text{ h}^{-1}$. For systems utilizing such high H_2O_2 concentrations, the chemical costs for H_2O_2 alone can exceed the energy costs. Using the best available costs for bulk H_2O_2 (50%), we estimate chemical costs of $\$0.99 \text{ gal}^{-1}$ and $\$0.33 \text{ gal}^{-1}$ for preparing 9% and 3% H_2O_2 solutions respectively. The combined chemical and electrical costs are competitive with what the CRADA partner estimates for current waste disposal costs. The costs are considerably less than the average DOE cost for handling RCRA waste. A consulted chemical engineer (Professor Mark Zappi, Mississippi State University) agreed that the costs for treating such extremely high TOC containing fluids by AOP alone was reasonably low and that other AOP technologies were not promising stand-alone choices for treatment of such high TOC_0 fluids. Combined AOP and biological treatment were suggested for follow-up studies.

The mechanism of ethylene glycol degradation in a UV/H₂O₂ system has been examined to some extent. Oxalic acid; glycolic acid and formic acid are observed as intermediate oxidation products during photolysis. However, surprisingly, these intermediate oxidation products are formed in limited amounts and do not build up during the photolysis. We hypothesize that multiple oxidation reactions may occur while chemical species are resident within the photolytic reaction zone, leading to rapid and complete oxidation of the contaminant, thereby preventing the buildup of intermediate oxidation products. Further work would be required to confirm this mechanism.

Table 1. EE/M (kW h kg⁻¹) and energy costs (\$ gal⁻¹) for removing 95% of TOC₀ from the specified fluids utilizing various AOP technologies.

	AOP Method			
	UV/H ₂ O ₂	UV/H ₂ O ₂ /Fe ²⁺	UV/H ₂ O ₂ /O ₂	UV/H ₂ O ₂ /O ₃
3% H₂O₂, 4500 ppm TOC₀				
Cutting Fluid	321 (0.32)	248 (0.24)	--	303 (0.39)
Ethylene Glycol	143 (0.14)	72 (0.07)	198 (0.19)	143 (0.18)
Polyethylene Glycol	142 (0.14)	49 (0.05)	--	--
SDS	468 (0.46)	325 (0.32)	--	--
9% H₂O₂, 10000 ppm TOC₀				
Cutting Fluid	298 (0.65)	--	--	--
Ethylene Glycol	155 (0.34)	76 (0.17)	--	--
3% H₂O₂, 13000 ppm TOC₀				
Cutting Fluid	--	--	--	180 (0.67)
Ethylene Glycol	255 (0.72)	253 (0.71)	435 (1.22)	130 (0.48)
Polyethylene Glycol	375 (1.06)	--	--	81 (0.30)

Patents: Not Applicable.

Commercialization Possibilities: The costs of removing extremely high levels of carbon from aqueous solutions is high simply because of the large amount of carbon which must be removed. Importantly, our work shows that it is possible to remove all of the carbon from these solutions. The commercialization of AOP process for treatment of cutting fluids and related solutions will depend in part on the value associated with treating the fluids. As society and industry places higher value on the treatment of such systems, the higher costs will become more acceptable. The costs observed in this study are considerably less than the current DOE complex-wide cost of handling RCRA waste and only a small fraction of the cost of handling aqueous mixed waste.

Plans for Future Collaboration: None at this time.

Conclusion: Hydroxyl radical-based AOP technologies have been systematically investigated for extremely high carbon content aqueous wastes and found to be effective

remediation technologies. The electrical and chemical costs of applying the technology are the major contributing cost factors and are competitive with current disposal cost.

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Appendix I: Manuscript; "Application of AOP Technologies to Extremely High TOC Containing Aqueous Solutions," M. E. Sigman*, A. C. Buchanan III and S. M. Smith, *J. Adv. Ox. Technol.* 1997, in press.

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