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Metal Recycling through Ultrasound Enhanced Precipitation and Coagulation, 1st yr report

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First year report
Metal Recycling Through Ultrasound Enhanced Precipitation and
Coagulation

A Small Business Pollution Prevention Center Project

Patrick E. Wheat

Definitions

Adsorbate - Any chemical species that undergoes an interphase transfer from one medium to the surface of a second, especially when the second medium is a solid.

Adsorbent - For this report the primary adsorbent is a metal hydroxide/oxyhydroxide.

Adsorption - The interphase transport of a chemical species resulting in the surface limited accumulation of that chemical species. While adsorption can be theoretically defined, the distinction between adsorption and co-precipitation in hydrous metal oxide (HMO) systems is frequently blurred (Leckie et al., 1980)

Co-precipitation - a solution phenomenon where two or more chemical species are removed from solution simultaneously in response to factors reducing their solubility. For example, above $\text{pH} \approx 7.0$ both ferric ion and cupric ion undergo a hydrolysis reaction resulting in the formation and simultaneous precipitation of both hydroxides ($\text{Fe}(\text{OH})_3$ and $\text{Cu}(\text{OH})_2$)

Ferric hydroxide ($\text{Fe}(\text{OH})_3$) - Is the product of the reaction of ferric cation (Fe^{3+}) with hydroxide anion (OH^-). In this work the ferric hydroxide is formed in water solution and exists as a hydrated species known as hydrous ferric oxide (HFO).

Ferric oxyhydroxide (hydrous ferric oxide - HFO) - An imaginary chemical species that is believed to exist in aqueous solution as a polymeric hydrated species and is generally represented by the speculative chemical formula (FeOOH). Various proposed structural representations of the complex have been investigated but none appears to accurately describe this dynamic chemical species' composition in solution (Schugar et al., 1967).

Floc - In the case of freshly formed HFO, an amorphous (non-crystalline) coagulated mass of adsorbent. For this project HFO is the primary flocculant upon which adsorption can occur although other hydrous metal oxides (HMOs) can also act in this capacity when they occur in solution.

Internal Adsorption Capacity (IAC) - This is a term I have coined to describe the internal pore and channel adsorption sites of a flocculant particle (Anderson and Rubin, 1981; Benjamin and Leckie, 1981). As the floc forms, channels permeate the core and apparently become kinetically isolated from the body of solution containing the adsorbate (metal contaminant).

Project Overview

The original project formulation was based on work performed by the principal investigator (Patrick Wheat) for his Ph.D. research and the findings of Kruus et al. (1991). A solution color change observed in reactions mixtures containing ferric chloride and a polycyclic aromatic hydrocarbon (PAH) at acidic pH (ca. 3.0) led to the hypothesis that HMO was forming in water solution upon exposure to high intensity ultrasound. The work of Kruus et al. (1991) seemed to support this interpretation with their detection of zinc hydroxide ($Zn(OH)_2$) in mixtures of water, cobalt, and zinc metal (Zn^0) exposed to intense ultrasound. The combination of these two findings led to this study of ultrasound's ability to induce either hydrolysis or free radical addition reactions with metal ions to form HMOs in aqueous solution. This is an attractive research goal since HMOs are generally less soluble than the analogous metal ions and it was hoped that treatment would amplify the efficiency of heavy metal removal via precipitate formation at reduced pHs. Moreover, it was suspected that HMOs' known ability to serve as adsorbents for additional metallic ions in solution could be used to amplify the removal of contaminating metallic ions via a complex series of linked coprecipitation/adsorption mechanisms.

At the outset of the project two questions were posed. First, is an ultrasonic field of high intensity capable of inducing rapid chemical alteration of dissolved metallic ions leading to the accelerated formation and precipitation of HMOs in solutions of varying pH? Second, is an ultrasonic field of varying intensity capable of enhancing coagulation of suspended material through electrokinetic, perikinetic, and orthokinetic modification as a result of free radical and/or anionic reactions, thermal excitation, and acoustic streaming, respectively?

Progress Summary

A model system to study the effects of high intensity ultrasound on enhanced removal of metallic ions from aqueous solutions via precipitation and coagulation continues as we enter the second year of this two year project. The model system under investigation continues to focus on an ultrasonic modification of heavy metal adsorption on ferric hydroxide flocs.

Calorimetry

The first goal in the project was to determine the energy output of the ultrasonic transducer. The calorimetric method of Mason (1991) was utilized to make the necessary measurements after a suitable calorimeter was constructed from available materials. A thermocouple temperature sensing device was used to measure the temperature rise and from a graph of temperature vs time a tangent to the curve was constructed at time equal to zero seconds. The slope of the tangent line is represented by dT/dt , where T = kelvin

temperature and t = time in seconds. The formula for calculating the power (P) is then given by:

$$P = (dT/dt)c_p(M)$$

Where:

- DT/dt = the change in temperature (K) per unit of time at $t=0$ sec.
 C_p = the heat capacity of the water utilized at the initial temperature tested (298K) ($Jkg^{-1}K^{-1}$)
 M = Mass of the water (kg)

Intensity is defined as the power radiated per unit area of probe tip. The probe tip utilized in this work has an area of one square centimeter (1.0 cm^2). Using this methodology a working intensity of 27.2 Watts/cm^2 was obtained.

Ultrasound and Fe^{3+}

Previous experimental results have demonstrated that ultrasonic radiation is capable of promoting the rapid hydrolysis of ferric ion to HFO in acidified aqueous solutions (Wheat, 1992). However, a number of questions concerning the mechanism by which the HFO forms in response to ultrasonic stimulation remained unanswered by this earlier work. In order to explore these areas a series of experiments using ultrasound to treat solutions of ferric ion (Fe^{3+}) in aqueous solution were conducted.

The experimental results presented below (see figures #1 & 2) are the outcome of the sixth in a series of experimental trial reactions in which ferric chloride solutions were exposed to ultrasound of varying intensity for different periods of time. The ultrasound reaction was cooled with an ice bath to attempt to minimize temperature excursions that accompany energy input. The control reaction was cooled by immersion of the reaction flask in a cool water bath ($T \approx 21.7^\circ C$). The blank reaction flask was allowed to stand in the open air and warmed slightly during the time of the reaction, apparently due to an exothermic reaction.

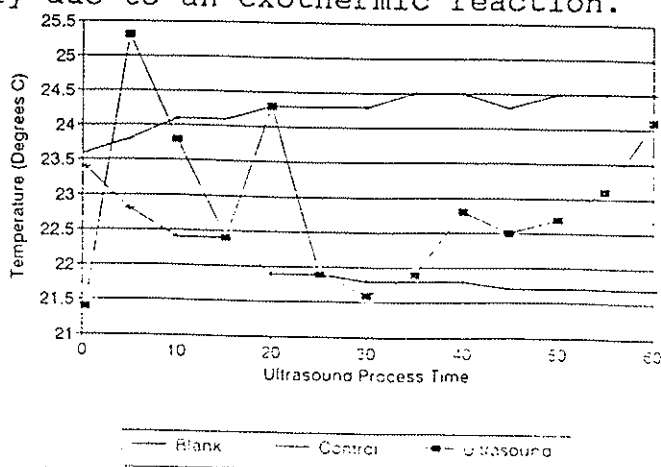


Figure #1: Reaction temperature vs time

Figure #1 depicts the temperature profile as a function of reaction time derived from the three simultaneous trials. Notable is the slight temperature rise for the blank, the irregular temperature profile for the ultrasound reaction (evidence of the difficulty with which temperature is maintained during ultrasonic reactions), and the slight decrease in temperature of the control reaction as it cooled to the temperature of the water bath @ 21.7°C). Figure #2 shows the absorbance at 375 nm for aliquots of the same ultrasound, control, and blank mixtures as a function of reaction time. The blank reaction, maintained at the highest steady temperature ($24 \pm 1^\circ\text{C}$), shows the greatest absorbance as a function of reaction time while the control sample, with the lowest overall temperature ($22.7 \pm 1^\circ\text{C}$) shows the smallest increase in absorbance during the trials. The intermediate absorbance obtained for the ultrasound treated solution probably reflects the temperature excursions exhibited by that system, in spite of attempts to maintain the temperature constant with external cooling.

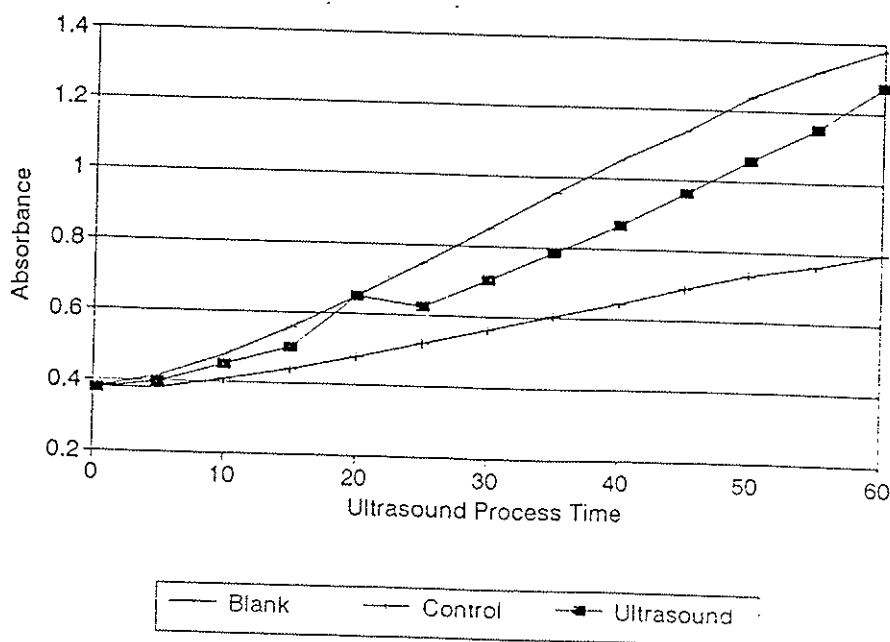


Figure #2: Solution absorbance vs reaction time

These experimental findings support a mechanism consistent with a thermally induced hydrolysis of the ferric ion. The data indicate that, regardless of the source of energy (an exothermic reaction in the case of the blank or ultrasonic heating for the treated sample) the principal mechanism driving the process is thermal in nature. The reaction that predominates appears to be the following:



Thus, in response to question #1, whether ultrasonic treatment can enhance the formation of HMO: it appears, in the iron system, that ultrasound promotes the formation of HFO via a thermal mechanism. Moreover, this result seems to suggest that a free radical mechanism, which would be expected to exhibit a lack of temperature dependence, probably does not play a major part in the formation of HFO under the reaction conditions utilized.

The question posed in objective #1 has a second part: does ultrasound have the ability to affect the precipitation of ferric oxyhydroxide from mildly acidic solution? This question was not addressed completely by these first experimental trials, however, from additional results obtained to date it is evident that precipitation of the oxyhydroxide is largely driven by a change (an increase) in pH and is apparently not affected by the presence of ultrasonic radiation under moderately acidic (pH ≤ 3.0) conditions.

Kruus et al. (1991) Findings

The experiments of Kruus et al. (1991) were not replicated but the direct formation of zinc hydroxide from zinc metal observed by these workers is likely to be an enhanced hydrolysis reaction as well. In this case, however, the presence of zinc hydroxide in solution is probably due to a two stage process.

In stage one the hydroxide forms on the surface of the metal via a water hydrolysis linked mechanism:



In stage two liquid microjets induced by the asymmetric collapse of ultrasound linked cavitation bubbles probably scours the zinc hydroxide from the surface of the metal causing it to be released into solution. This scouring action "renews" the zinc metal's surface enhancing further formation of hydroxide. Additional contributions to enhanced hydroxide formation by ultrasound include accelerated mass transfer of solvent to the surface via acoustic streaming, shock wave induced velocity field disruption in the proximity of the surface/water interface, and localized heating in the proximity of microjet impacts.

Experiments to investigate the ability of high intensity ultrasound to scour zinc(II) hydroxide from the surface of the parent metal, while interesting because they may help explain the observed rate enhancement of Diels-Alder synthesis (Pindur et al.,

1993), are currently outside the scope of the original proposal and will not be pursued further in this project.

The experimental trials with ferric ion described above revealed new information, clarified some outstanding questions, and raised many new questions about heterogeneous reactions, however, they failed to fully explore the second major question to be answered by this investigation: what is the effect of ultrasound on precipitation, coagulation, and flocculation? In addition, questions about the validity of the currently accepted literature model (Girvin et al., 1991) for surface adsorption on metal hydroxide flocs arose during a preliminary analysis of the system in preparation for the first set of ultrasound modified adsorption trials. From this preliminary analysis it became clear that ultrasound holds promise as a probe with which to investigate this poorly understood system.

Humberto Campos

It is noteworthy that a graduate student (Homberto Campos) joined the project in the fall of 1994. With the addition of this new team member, whose background in marine chemistry has added great depth to our system analyses, progress on the project has begun to accelerate and gain new focus.

Project Reformulation

In light of the results obtained from the first experimental trial, and extensive conversations with personnel at the John Deere Waterloo Wastewater Treatment Facility (JDWWTF) who have expressed a preliminary interest in the work, a reformulation of the research plan to shift the project's focus from the mechanism of HFO generation to ultrasound modified adsorption and coagulation is being conducted. This reformulation represents a significant shift towards research targeted for the second year of the project and, we believe, will sharpen the project's focus on applied research of direct utility to Iowa's industrial base.

In its reformulated form the project retains two features in common with the original project:

(1) It remains focused on providing useful information to industries concerned with the removal and recovery of metallic contaminants from aqueous waste streams, and

(2) It renews its focus on applied research, being modelled after existing industrial waste stream treatment technology currently utilized in the State of Iowa.

John Deere and Company

As was stated above John Deere and Company have expressed an preliminary interest in becoming involved in the project because of possible linkages to their existing process. John Deere's treatment facility, in downtown Waterloo, Iowa, currently treats a variety of heavy metal containing wastewater streams from a number

of different firms around the state of Iowa using a proprietary phosphate modified HFO precipitation methodology. The method utilized is based on coprecipitation of heavy metal contaminants as opposed to adsorption on HFO. In the first step of the process oily wastewater containing heavy metal contaminants is segregated from those containing high concentrations of hexavalent chromium (Cr^{6+}) from plating operations.

The oily contaminated wastewater is acidified ($\text{W}/\text{H}_2\text{SO}_4$) in the first treatment step to $\text{pH} \approx 3.0-3.5$. After this initial acidification additions of phosphate, cationic polymers, ferric chloride, and anionic polymers, are made and the resulting mixture is flocculated by a pH modification ($\text{pH} \rightarrow 8.9$) with calcium hydroxide. A similar procedure is utilized for wastewater containing hexavalent chromium, however, in the case of this waste stream an initial acidification to $\text{pH} \approx 4.0$ is followed by reduction with bisulfite ($\text{Cr}^{6+} \rightarrow \text{Cr}^{3+}$), additions of cationic polymer, ferric chloride, anionic polymer, and subsequent precipitation using pH modification to 8.9, again with calcium hydroxide.

The acidification followed by neutralization is both costly and results in the formation of excessive sludge which ultimately requires landfill disposal. The rationale for the costly initial acidification and subsequent neutralization (resulting in coprecipitation of HMOs) is to ensure that a uniform distribution of hazardous metallic ions are adsorbed throughout the HFO floc. Current application theory holds that the "internal adsorption capacity" of a pre-formed floc (as opposed to a co-precipitated floc) is kinetically inaccessible to metallic contaminant ions and that the best available technological solution is to co-precipitate metals from solution by acidification followed by neutralization. This formulation arises from the belief that metal oxyhydroxide flocs have a labyrinthal structure inundated with pores and channels of narrow diameter within which diffusion is restricted (Kinniburgh and Jackson, 1981; Benjamin and Leckie, 1981).

Based on this information it seems reasonable to assume that if the full internal adsorption capacity of a pre-formed HFO floc could be made as accessible to metallic contaminants in solution as adsorption sites on the co-precipitated floc are it would be possible to eliminate the need for the original acidification and the excess $\text{Ca}(\text{OH})_2$ required to neutralize it. The result should then be reductions in contaminated sludge requiring transportation, economic savings on raw materials (H_2SO_4 and $\text{Ca}(\text{OH})_2$) and landfill costs, minimization of John Deere's future legal exposure from spills and landfill leakage, and liberation of landfill space designated for hazardous waste disposal. Unfortunately, given current technology, it is difficult to rapidly access the internal adsorption capacity of HFO flocs.

In order to address these problems we have begun to utilize ultrasound to attempt to access the internal adsorption capacity of pre-formed HFO floc by disrupting the floc particles with short (three [3] second) bursts high intensity ultrasonic radiation. This shift in focus to pre-formed floc disruption as a mechanism to

access the internal adsorption capacity is a direct outcome of fragmentation studies conducted in aqueous solution (Wheat, 1992) and a review of the literature that revealed work performed by Koltchoff and Moskovitz (1937) and Gadde and Laitinen (1973). Koltchoff and Moskovitz demonstrated a 7% difference in copper adsorption capacity between co-precipitated and pre-formed HFO in the presence of ammonia while Gadde and Laitinen demonstrated a variable adsorption capacity difference for pre-formed and co-precipitated ferric oxyhydroxide flocs that was dependent upon the concentration of lead in solution. In all cases, at pH = 6, Gadde and Laitinen found that the capacity of HFO for lead was greater for co-precipitated material than for adsorption on pre-formed floc implying a significant unutilized internal adsorption capacity.

Experimental Plan

In response to the changing needs of the reformulated project two avenues of investigation are being explored in year two of the project. The first focuses on a comparison of our experimental results obtained through replicated literature experiments (Leckie et al., 1980), as controls, and ultrasound modified treatment of the system. A second avenue of exploration involves the use of ultrasound to probe fresh and aged HFO flocs to alter their settling behavior and, perhaps, their adsorption capacity. This second area of focus is derived from a series of unplanned experimental flocculation trials that yielded some unanticipated findings of interest (See figure 3).

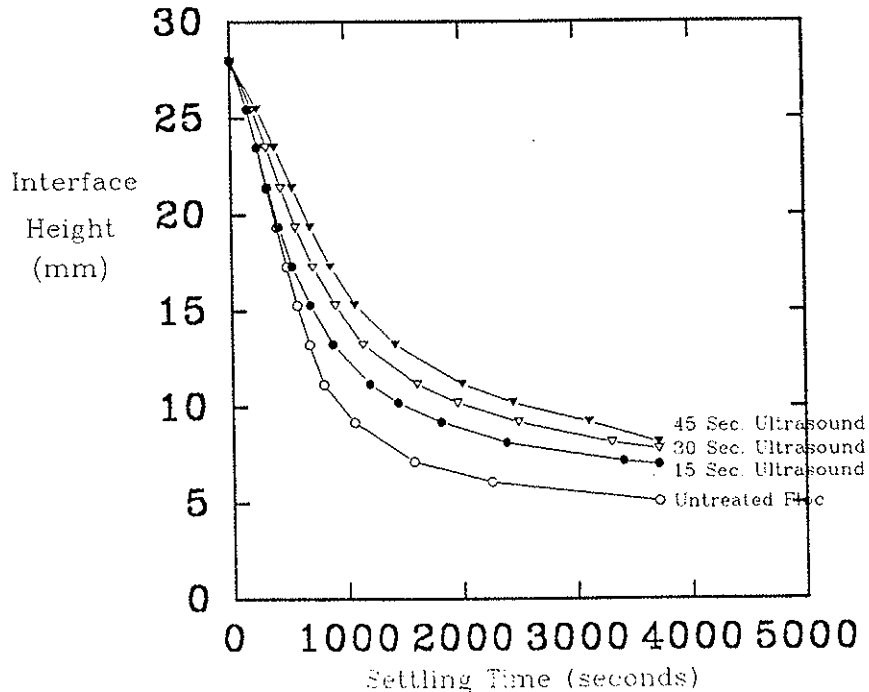


Figure #3: Settling curves for ultrasound treated aged HFO flocs

From the data in figure number #3 the effects of ultrasonic treatment on a continuously stirred, aged, HFO floc with ultrasonic radiation can be seen. The rate of settling in the ultrasound treated system is initially slower than the untreated floc and the settling rate difference increases with sedimentation time. Moreover, each incremental ultrasonic treatment (15 seconds at 27.2 Watts/cm²) yielded a floc with slower settling velocities and shorter transitions times to type II, III, and IV settling (Reynolds, 1982). Visual inspection of the floc resulting from ultrasonic treatment revealed that after initial disruption of particulate material in solution a voluminous floc rapidly (within 3 minutes) forms. The changes in the physical appearance of the floc, its settling behavior, its compaction settling volume, and the clarity of the supernatant that result from treatment are all quite dramatic, however, the mechanism by which the transformation is occurring remains obscure at this time. Our current hypothesis is that the disruption of the floc destabilizes the existing floc matrix equilibrium toward one favoring the formation of larger particles. The large floc particles resulting from U.S. treatment apparently undergo an early transition to type (II-III - zone or hindered) settling behavior and hence the observed lower rates of sedimentation. In addition, the floc seems to enter type IV (compression settling) earlier, a fact that contributes to the overall poor settling results and large compacted sludge volumes obtained.

In mitigation of these somewhat disappointing settling results is the observed significant decrease in turbidity of the solution remaining above the floc during numerous settling trials. This observation has been supported by preliminary atomic absorption (AA) analysis of the supernatant which indicates that the concentration of iron in the supernatant remaining after ultrasonic treatment is approximately 95% lower (0.89 mg Fe/L for the treated supernatant and 17.9 mg Fe/L for the untreated solution). Unfortunately, the concentration of copper in the treated supernatant did not exhibit a similar decrease. A comparison of the two supernatants revealed that there was a decrease in copper concentration of only about 3%.*

* It should be noted that although a number of replicate experimental trials of treated and untreated floc settling behavior have been conducted, only one trial of copper adsorption on the treated and untreated floc has been conducted and this preliminary data should be considered as anecdotal until further tests can be performed.

Some additional general notes are in order. The character of the U.S. treated floc during and after the settling experiment appears to be significantly different than that of the untreated material. The treated floc particles are clearly larger during and after settling and the interface of the treated floc forms almost immediately and is quite sharp throughout the entire settling experiment while that of the untreated material is diffuse. Moreover, the differential appearance of the two compacted sludges has led us to begin a comparative exploration of the filterability of the treated vs the untreated flocs. Based on the economic importance of settleability and filterability in industrial treatment we are cautiously optimistic about the ultimate utility of ultrasonic treatment for modification of HFO coagulation and sedimentation

Work Remaining

Work that remains to be performed in year two of the project promises to be voluminous. Below is outlined what I consider to be an ambitious plan for the second year of the project:

- (1) To elucidate, to the extent possible, the mechanism by which clarification of floc supernatants occurs in response to ultrasonic treatment
- (2) To continue experiments designed to compare and contrast untreated and ultrasound treated flocs using literature described adsorption processes (Leckie et al, 1980). These experiments are tailored to explore the effect of ultrasonic treatment upon pre-formed HFO flocs in an attempt to determine if ultrasonic disruption of the freshly prepared pre-formed floc will allow access to the internal adsorption capacity. Initial trials at 10% and 20% copper/iron have been conducted to date but data analysis is incomplete at this time. Control of the system's pH instability is the greatest difficulty currently, and addressing this problem may force us to utilize a batch type method of floc preparation instead of a fresh floc preparation (Swallow et al., 1994). An additional recurring problem is instrument (AA) insensitivity and instability which is affecting the reproducibility of our results. We are attempting to address this issue with the recent acquisition of additional volumetric glassware making dilutions more facile but we will continue to lack access to metal concentration data for very dilute solutions resulting from effective copper removal at high floc to copper ratios. Notwithstanding the difficulties, work in this area is progressing slowly with Humberto Campos conducting most of the experimental trials. We remain optimistic that we will be able to access at least some of the internal adsorption capacity of the floc based on the work of Kolthoff and Moskovitz (1937) and Gadde and Laitinen (1973). However, to date, the anticipated difference has not materialized or has been shadowed by variability in the system or instrumentation.
- (3) To extend #2 above by using the developing methodology to attempt enhanced removal of nickel (Ni^{2+}) ions from solution and perhaps lead (Pb^{2+}). Lead is an interesting candidate for study but may not be appropriate at this stage of the project because:
 - (a) lead adsorption has been shown to exhibit great sensitivity to minor fluctuations in pH which promises to make this system difficult to control in the laboratory scale process, and
 - (b) the high toxicity of lead and the cost of hazardous waste disposal makes work with this metal less attractive

On the other hand nickel (Ni^{2+}):

- (a) is a waste stream component of great concern to a number of local iron and steel foundry industries and investigation of its behavior seems consistent with IWRC program goals, and
 - (b) has allowable discharge levels that are anticipated to decrease in response to regulatory mandate in the near future.
- (4) To further characterize the settleability, filterability, and final compacted volumes of U.S. treated flocs vs untreated flocs.
 - (5) To continue to develop a theoretical basis for adsorption in the ultrasound modified system. Of interest are systems at low adsorption surface coverage, comparisons of pre-formed vs co-precipitated flocs, aged flocs vs freshly prepared material, competition for adsorption sites by cations of similar charge, and the role of ligand complexation in adsorption dynamics.

Relevance to Program Priorities

The proposed second year activities continue to focus on practical waste treatment concerns of industries in Iowa by attempting to develop novel technological solutions to existing problems.

Through extensive discussions with personnel at the JDWWTF we have begun the process of technology transfer and hope to broaden efforts in this area in the coming year. I am optimistic, based on these discussions, that a strong linkage between UNI and John Deere, based on our shared strengths, will provide enhanced opportunities to graduate students enrolled in the UNI Environmental Science Graduate Program.

Dissimination of information

It is anticipated that the outcome of this investigation will be presented during the winter of 1995/1996, both locally (UNI) and nationally as poster sessions and presentations offered by the principal investigator and the graduate student(s) involved in the project. A completion report will be submitted at the conclusion of the project. Publication of these research findings in peer review journal(s) is anticipated during the winter of 1995/1996.

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Budget - Year Two
Travel and Salary

(1) Principal investigator - salary (2/9 year):	\$ 9,334.00
(2) Principal investigator - benefits (0.1763 x \$9334.00):	\$ 1,646.00
(3) Two (2) graduate student stipends (yr)	\$ 24,000.00
(4) Travel to national meeting for student presentations of research findings (two graduate students and PI)	\$ 1,500.00

Instrumentation

(1) 20 KHz, 475 Watt, Ultrasonic generator with 1/2 inch titanium Horn type transducer with replaceable tips. Capable of programmed pulsed or continuous operation. Stainless steel reactor adapter	\$ 4500.00
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Supplies

(1) Glassware: (Beakers, flasks, graduated cylinders, volumetric flasks, pipettes, separatory funnels, etc.)	\$ 1,300.00
(2) Miscellaneous laboratory supplies, atomic absorption accessories	\$ 1,250.00
(3) Chemicals	\$ 1,050.00
Total	\$ 44,580.00

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