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SONOCATALYTIC WET OXIDATION FOR WATER PURIFICATION(U)  
TAYLOR (S R) AND ASSOCIATES BARTLESVILLE OK  
S R TAYLOR ET AL. OCT 91 DAAK70-91-C-0018

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SONOCATALYTIC WET OXIDATION FOR WATER PURIFICATION

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STRBE-FSE  
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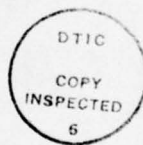


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## PROJECT SUMMARY

Currently, the Army uses water purification systems based on reverse osmosis (RO). RO is effective, but considerable energy is required to overcome the osmotic pressure of raw water. Also, elaborate pretreatment systems must be used to prolong the life of expensive RO elements. The Army desires a system that is at least as effective as RO for water purification, yet is smaller, lighter, more economical, and longer-lived than the current systems.

This program was directed toward development of a suitable ultrasonic reactor design that will allow rapid oxidation of contaminant species under mild conditions thus reducing the capital cost for the equipment as well as the operating costs associated with the high temperature and pressure operations. Additionally, a novel desalination method using ultrasonic atomization to promote vaporization with subsequent condensation was tested. S. R. Taylor and Associates have been actively developing applications of ultrasonics to chemical and material processing problems and have been working on the development of a novel ultrasonic reactor that promotes bulk mixing, via an ultrasonically induced high shear mechanism (in addition to normal cavitation forces). We proposed that this dual action reactor could dramatically reduce the overall process temperature and pressure requirements for wet oxidation. We also proposed that ultrasonic atomization could provide a highly efficient means to achieve desalination prior to wet oxidation.

The following accomplishments have been achieved during Phase I:

- Initial tests showed that the cavitation zone occurs near the face of the waveguide, but not into the screen itself.
- There is a synergistic effect of ultrasound coupled closely with a screen to achieve excellent mixing and resultant dispersions. However, increasing the distance between the waveguide and the screen reduces the mixing and dispersion but appears to afford better cavitation.
- Reverse flow tests showed about the same dispersions as forward flow tests.
- Initial oxidation tests show that ultrasonic cavitation has no effect on TDS from inorganic sources; ultrasonic cavitation does lead to a reduction in turbidity for samples containing organic species.
- Oxidation tests showed that ultrasonic enhancement greatly improved oxidation and removal of organic contaminants under very mild conditions. Increasing pressure, however, had a negative effect on ultrasonically enhanced oxidation. Although the oxygen partial pressure is increased by higher operating pressures, cavitation significantly inhibited thus reducing the overall extent of oxidation.
- Ultrasonic atomization can provide a very energy efficient means to vaporize water for distillation to desalinate brackish and sea waters. So long as the thermal energy required can be derived from the surroundings, energy efficiency can be very high.

Phase II research and development will focus on further scaleup and optimization of both the wet oxidation reactor and the ultrasonic atomization/desalination technique. Prototype equipment will be produced for subsequent full-scale testing.

## 1.0 INTRODUCTION

Currently, the Army uses water purification systems based on reverse osmosis (RO). RO is effective, but considerable energy is required to overcome the osmotic pressure of raw water. Also, elaborate pretreatment systems must be used to prolong the life of expensive RO elements. The Army desires a system that is at least as effective as RO for water purification, yet is smaller, lighter, more economical, and longer-lived than the current systems. Such water purification must be able to treat a wide range of incoming waters, including but not limited to, fresh, brackish, and seawater desalination, raw waters and nuclear, biological and chemical contaminated waters.

In many respects, water treatment needs in isolated regions like polar regions or on shipboard are similar in that systems must be self-contained and independent of outside support for long periods of time. For this reason, wet oxidation for waste handling has been studied for shipboard use. This includes waste water from heads, showers, lavatories, scullery, galley, laundry, and below water deck drains [1]. The dilute wastes result in a high hydraulic loading but if high oxidation efficiencies can be achieved, a single step wet oxidation plant is an attractive simple solution. However, even with added catalysts, the temperatures and pressures required were 450-600°F and 600-900 psi respectively. If ultrasonic catalysis can be used to lower these conditions, the process would become much more economically attractive and useful for bulk water purification.

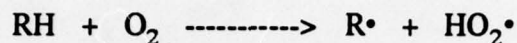
This program was directed toward development of a suitable ultrasonic reactor design that will allow rapid oxidation of contaminant species under mild conditions thus reducing the capital cost for the equipment as well as the operating costs associated with the high temperature and pressure operations. Desalination can then be accomplished via vaporization/condensation or by RO once the contaminant load is significantly reduced by wet oxidation. The novel desalination method proposed for initial testing during Phase I utilized energy efficient, ultrasonic atomization to produce a mist of ultrafine water droplets. Vaporization then occurs by extraction of heat from the surrounding atmosphere. Cyclone separation of the salt dust from the aerosol and subsequent condensation of the water vapor achieved effective desalination while deriving most of the energy to accomplish this from the surroundings.

The second key step is the use of wet oxidation to remove contaminants and reduce subsequent loads to the RO membrane. S. R. Taylor and Associates have been actively developing applications of ultrasonics to chemical and material processing problems and have been working on the development of a novel ultrasonic reactor that promotes bulk mixing via an ultrasonically induced high shear mechanism in addition to normal cavitation forces. We proposed that this dual action reactor could dramatically reduce the overall process temperature and pressure requirements for wet oxidation.

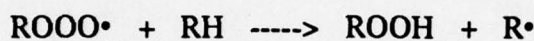
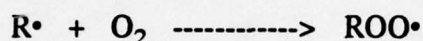
## 1.1 Background

### 1.1.1 Wet Oxidation

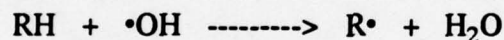
Wet oxidation is essentially an auto-oxidation process. In the absence of any catalyst, chain initiation takes place mainly through the thermal process where RH represents the organic substrate [2]:



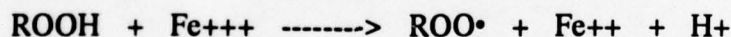
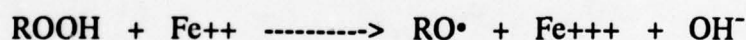
followed by the propagation step with the reactions



Thus, the higher oxygen pressure resulting in an increase in the oxygen concentration in water means increased production of free radicals, which, in turn, will increase the effectiveness toward overall oxidation. In the presence of metal ion-peroxide systems as catalysts, the rapid reaction between hydroxyl radicals, produced by interaction of the metal ion and hydrogen peroxide, and the organic substrate



completely outweighs the thermal initiation process. Also, the chain propagation step is greatly influenced because of the reaction of Fe<sup>++</sup> and Fe<sup>+++</sup> ions with ROOH to produce more free radicals (RO<sup>•</sup> and ROO<sup>•</sup>) according to:



Thus, the O<sub>2</sub> pressure does not influence the COD reduction with catalysts as it does in the situation with no catalysts. It is necessary that the pressure be above the corresponding vapor pressure at the particular temperatures so that the reaction proceeds in liquid phase.

If sonocatalysis can mimic metal catalysts, then pressures may be reduced even further. Additionally, as will be discussed below, sonolysis of water can provide the oxidants thus reducing even further the need for external thermal activation.

### 1.1.2 Sonochemistry

The use of ultrasound to enhance chemical reactivity is becoming a common laboratory technique with wide applicability. So much so that an entire issue of the Journal, Ultrasonics [3], was devoted to the subject of sonochemistry. However, these methods have yet to be applied to actual industrial scale operations primarily due to the batch type treatment schemes that have been considered to date; continuous treatment methods have yet to be developed. In fact, in a very recent report, Pugin [4] states:

"We conclude that the treatment of suspensions of powders should be conducted in continuous flow cells as they force the reaction mixture into the cavitation zone."

Sonochemistry is the use of ultrasound to catalyze and promote chemical reaction (ultrasound is sound with a frequency greater than 17 kHz, above the range of human hearing). Practical applications of ultrasound--medical imaging and mechanical processes such as homogenization, cell lysis, plastic welding, and cleaning surfaces of materials and instruments--have been outside the fields of chemistry and chemical processing. In the 1980's, chemists began to reexamine the effect of high-frequency sound waves on chemical reactions. Their efforts have led to new ways to carry out important reactions.

High intensity ultrasound causes solutions to cavitate. The solution cavities are created during the rarefaction half-cycle of the ultrasound. Liquids differ in their susceptibility to cavitation; liquid vapor pressure is a factor. In general, if the sonic intensity is high enough, cavities will be formed. These cavities will collapse when the pressure half-cycle of the ultrasound is experienced [5,6]. Several diverging theories of post cavity collapse exist: shock-wave; charge separation [5,7]. In the shock-wave theory, the cavities are squeezed and compressed during the pressure half-cycle of the acoustic waves. When a threshold pressure is exceeded, the cavities catastrophically collapse. Local shock waves are created; local temperatures and pressures have been estimated to exceed  $7 \times 10^3\text{K}$  and 80,000 psi [7]. Alternatively, the spherical cavities may be deformed during the pressure half-cycle into a lens shape. Charges may be generated and stabilized when the cavity deforms. Dielectric breakdown occurs upon further compression; light and heat are released. Thermal and photochemical effects result [5]. Regardless of the precise mechanism of energy generation, some remarkable chemical effects are produced.

### 1.1.3 Relevant Atomization Background

Early work related to fuel combustion by the American Petroleum Institute led to the development of an atomizer relying on the high instantaneous accelerations obtainable by ultrasonics. The vibrating transducer exerts a radiation pressure within the drop being fed onto the transducer tip. This radiation pressure causes vibrations on the surface of the liquid in such a way that capillary waves are formed. The amplitude of strain within the large droplet which is in contact with the vibrating transducer is sufficient at certain times to

exceed the surface tension and tensile strength of the liquid and a free droplet forms, approximately the size of the half-wavelength of the capillary waves. This technique permitted the use of light fuel oils at flow rates of 0.2 gph in domestic heating units, compared to the usual 0.75 gph that was the minimum possible without clogging.

Other systems have used gas driven ultrasonic atomization of the Hartmann whistle type. Here, ultrasonic standing waves generated in a gas around the nozzle tips are allowed to interact with a thin film of liquid which is fed to them. Our personnel have been extensively involved in early investigations of these and other nozzles [8-14] and several variations are now commercially available [15]. Nozzles of this type very efficiently produce somewhat more uniform droplet sizes and smaller droplets than do the common "two-fluid" and "single fluid" pressure nozzles commonly used; good summaries of atomization may be found in several references [16,17].

Very little new had taken place in the ultrasonic atomization field over the last 20 years until a new breakthrough by our personnel [8,18,19] solved a persistent problem common to all nozzles, namely presenting the liquid in a uniform and optimized form to the atomization forces. In this case, a large surface is vibrated ultrasonically with standardized presentation of the fluid to the atomizer in the form of small volume elements of liquid contained in the open spaces of known size porous media (eg. screens, perforated, sheets, or cloth) moving across the activated area. Under a Navy SBIR contract, we have begun development of this novel atomizer. The ultrasonic screen-style atomizer is a highly energy efficient atomizer characterized by very narrow droplet size distributions which maximize the number of particles in the desired size range.

## 1.2 Phase I Technical Objectives

The overall objective of this program was to determine the feasibility of using a novel ultrasonic atomization/vaporization/condensation cycle for energy efficient distillation and the technical and economic utility of ultrasonically enhanced wet oxidation for the destruction and decomposition of contaminants during bulk water purification. The specific objectives addressed in this program were:

- Identify and characterize the relative contributions of ultrasonically-induced cavitation and shear in the proposed continuous flow reactor.
- Measure the observed oxidation rates of bulk water simulants as a function of both reactor physical design and processing conditions.
- Perform extended oxidation tests with characterization of the products of reaction based on processing conditions suggested by completion of the above objectives.
- Determine the effectiveness of desalination using ultrasonic atomization/vaporization/condensation.

1.2 Phase I Work Plan

The Individual Tasks along with the anticipated Milestones/Accomplishments for each are shown below:

Task 1 - Ultrasonically-induced cavitation and shear force measurement

- Fabricate and Verify Reactor Operation
- Determine Cavitation Zone
- Determine Shear Force
- Evaluate Synergism

Task 2 - Wet Oxidation Process Characterization

- Determine Power Effects
- Evaluate Screen Size Effects
- Determine Liquid-dependent Effects

Task 3 - Preliminary Desalination Tests

- Ultrasonic Atomization/Vaporization/Condensation

Task 4 - Engineering Specification and Program Reporting

- Monthly Reporting
- Completing Final Report

**2.0 EXPERIMENTAL**

2.1 Materials

The Aluminum foils used for cavitation testing are described below, in Table 1:

Table 1 - Aluminum Test Specimen Geometries

<u>Foil No.</u>	<u>Area, cm<sup>2</sup></u>	<u>Weight, g</u>	<u>Calculated thickness using 2.65 g/cm<sup>3</sup> density</u>
1	6.29	0.0323	1.94/1000 cm=0.76/1000 inch(mils)
2	6.29	0.0440	2.64/1000 cm=1.04/1000 inch(mils)
3	6.29	0.1491	8.96/1000 cm=3.53/1000 inch(mils)

Metal powders were obtained from Goodfellow Co., Cambridge, England. The powders that were tested and their properties are listed in Table 2:

The sea-water used for wet oxidation and desalination testing was mixed per directions on the package of Sea Salt, from Lake Products Co., Inc. of Maryland Heights, MO. Sea water has approximately 32,000 mg/L Total Dissolved Solids (TDS). For brackish water, sea water was diluted with tap water to one-fourth the concentration (8,000 mg/L).

Table 2 - Metal Powder Properties

<u>Metal</u>	<u>Mfg.Method</u>	<u>Density, g/cc</u>	<u>Max Particle Size, m</u>	<u>Melting Point, °C</u>
Copper	Electrolytic	8.92	50	1083
Chromium	---	7.2	38	1857

Simulant organic contaminants obtained for wet oxidation testing are listed below in Table 3 along with the source.

Table 3 - Organic Compounds

Anthracene: 97%, Aldrich Chemical Co., Milwaukee, WI

Lindane (1,2,3,4,5,6-Hexachlorocyclohexane,  $\gamma$ -isomer): 97%, Aldrich Chemical Co.

2,4,6-Trichlorophenol: 98%, Aldrich Chemical Co.

Phenol: Redistilled, 99+%, Aldrich Chemical Co.

Trichloroethene: 99+%, Aldrich Chemical Co.

## 2.2 Equipment

The continuous flow reactor process array is shown in Figure 1. The reactor array was essentially the same for the various experiments. A detailed engineering drawing of the reactor is shown in Figure 2. The reactor has a outside diameter of 2 inches and is 3-inches long. It is made of aluminum with 7/32-inch wall thickness. The reactor is attached to a transducer whose 1-inch diameter wave guide extends into the reactor. The cavitation zone

occurs at the circular end face of the wave guide. The reactor vessel end has a thickness of 1/16-inch and a 3/4-inch diameter outlet.

A 40x40 mesh screen of 1-inch diameter is placed between the reactor outlet and the 3/16-inch thick reactor outlet end plate. Both the reactor inlet and outlet have 1/2-inch diameter threads for connecting tubing to the reactor. An alternate liquid outlet of 3/8-inch diameter was plugged for the cavitation and shear experiments.

The test array that was used for the metal powder experiments was also as given in Figure 1. The reactor feed/effluent vessel for these runs was either a 2000 cc beaker or a 1000 cc beaker depending on the amount of distilled water used for the metal/water slurry. For the run with 800 cc water, the former was used and for the 400 cc runs, the latter was used. The pump suction was taken from the beaker and discharged to the reactor. The liquid slurry was irradiated by the ultrasound reactor, passed through a screen closely coupled with the wave guide, and discharged to the beaker. For all of the runs, nitrogen was bubbled through the liquid that was in the beaker and in the system to alleviate metal oxidation.

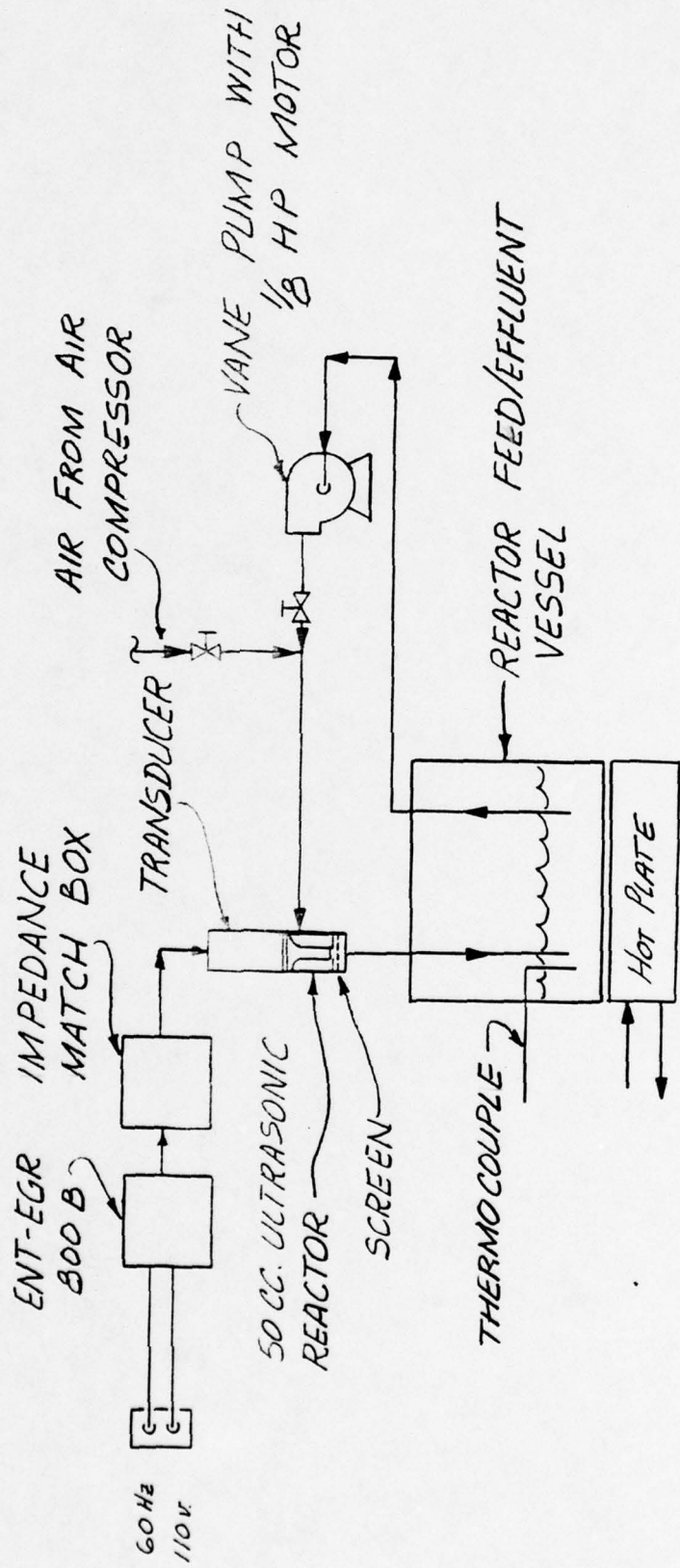


Figure 1. Schematic Drawing of the Process Flow Array.

		CONTRACT A-10
SCHEMATIC OF PROCESS FLOW FOR WET OXIDATION		NO. 1
SCALE: NONE		DWG NO.
SH NO.		1-0
NC.		



Except for the reverse flow tests, the flow inlet was into the 1/2-inch reactor side opening and the outlet was from the 1/2-inch diameter end plate outlet (see Figure 1). This flow gives a specific residence time distribution through the reactor. In this direction, it is possible that a dead zone might exist adjacent to the waveguide face. Reverse flow would overcome such a dead zone, if it exists.

The pressure array for wet oxidation testing is shown in Figure 3. The pump and reactor are the same as used in the earlier testing. However, for the pressure tests, the entire system was closed, and pressurized to 50 psi by an air compressor. Solutions of organics to be tested were added from the top of the steel pressure mix tube until the coils and half the chamber were full. The tube was then sealed and the air was pumped into the system to 50 psi. The valve between the gauge and the air hose was adjusted periodically to keep the pressure of the system constant.

The desalination array is shown in Figure 4. The ultrasonic humidifier used was a Holmes-Air 2-gallon ultrasonic humidifier. A fan was used at the end of the duct to provide airflow through the system. The humidifier reservoir was filled with the sea water simulant described above and the humidifier was set on high speed and medium-high mist volume. The mist created entered the duct work, where the water evaporated, leaving salt dust in the air. The dust and water vapor were blown through the filter where the dust was trapped. The vapor passed through the filter to condense on the cold coils circulating at the base of the duct below the filter. The condensate dripped into the collection pot and was retained for later analysis.

Turbidity measurements were made with a Engineered Systems & Designs Model 800 Turbidimeter. TDS, conductivity and pH were measured with the Checkmate Deluxe Field System by Corning. TOC measurements were performed by Metlab of Tulsa, OK.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Cavitation and Shear Force Measurement

##### 3.1.1 Determine Cavitation Zone

The objective of these tests were to determine where the cavitation zone was occurring within the reactor. This was attempted by measuring aluminum foil weight loss due to erosion which is a simple test for the intensity of cavitation [7] The foil samples were placed over the 3/4-inch reactor outlet such that one-half of the circular area was covered by the foil. The foil samples were placed between the reactor end and the screen over which the end plate was bolted. Foil samples were also tried below the screen and within the reactor zone itself. Figure 5 shows these locations schematically. The foil samples all were rectangular with dimension of 1.7 cm x 3.7 cm or 6.29 cm<sup>2</sup> each but with three different thicknesses as give in Table 1.

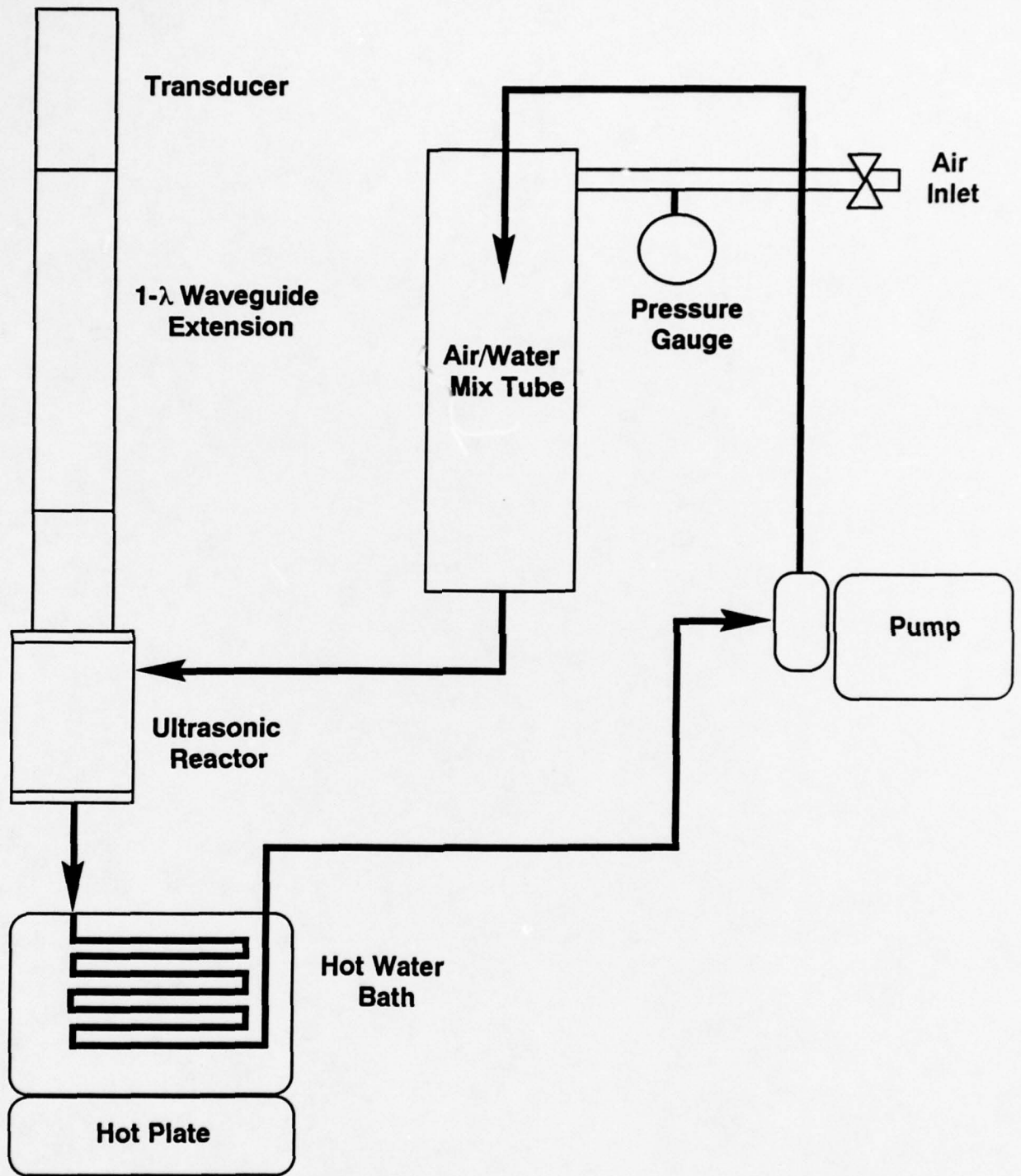


Figure 3. Schematic of the Flow Through Pressure Array.

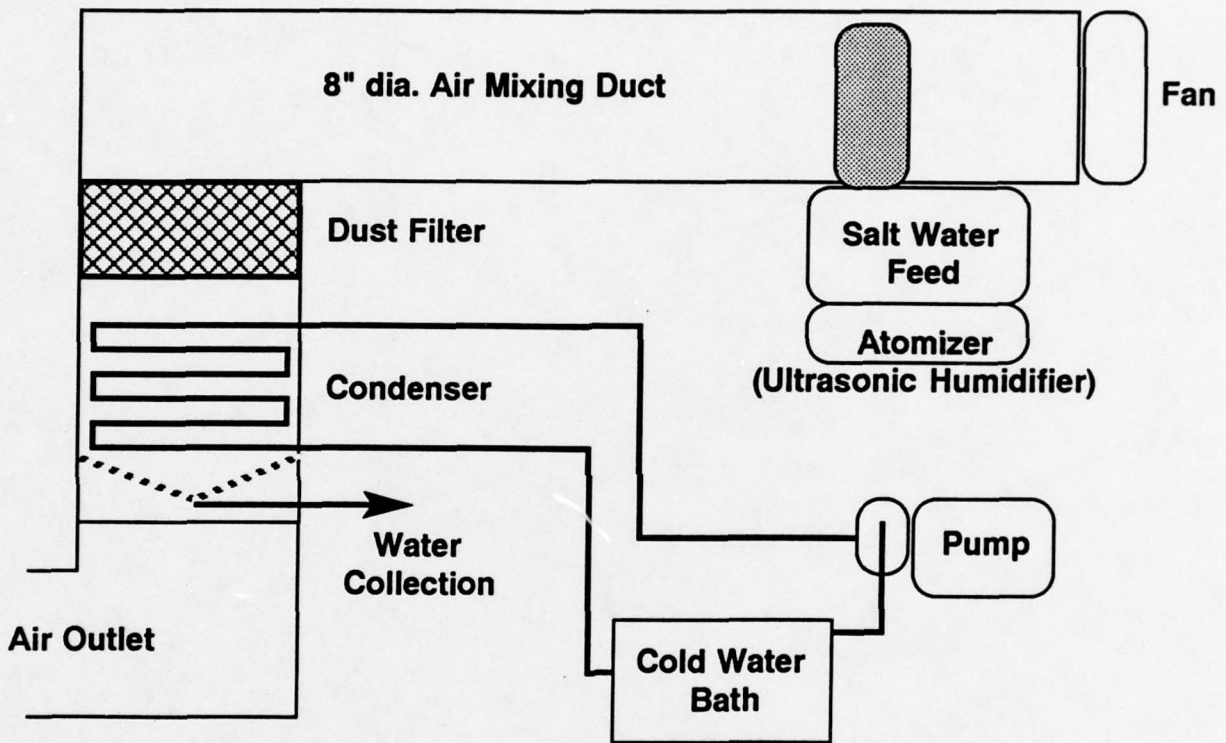


Figure 4. Schematic of the Phase I Desalination Test Array.

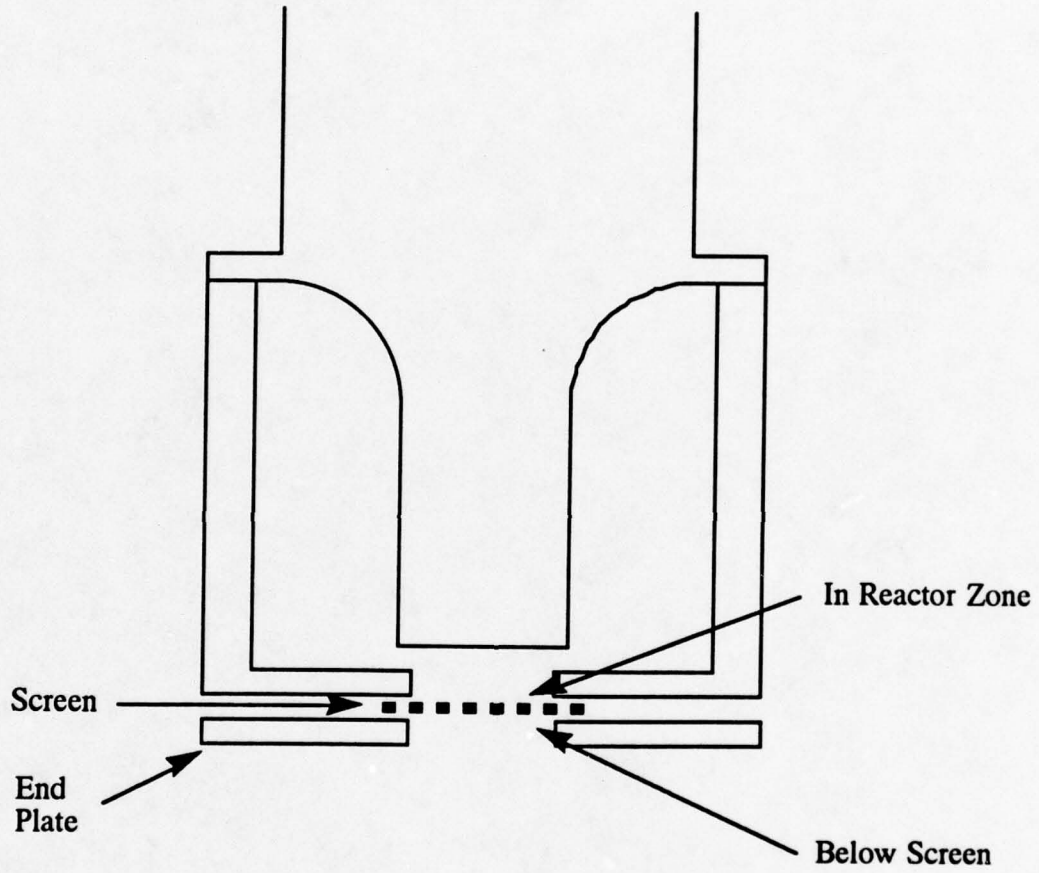


Figure 5. Schematic of Aluminum Foil Test Locations.

For foil No. 1, tests quickly showed that stress fatigue, with essentially complete removal of the sample, occurred when the foil was either put into the reactor or when placed below or above the screen for ultrasonic power levels from 5 to 25 watts. It was concluded from these initial tests on thin foil that stress fatigue and tearing were leading to break up of the foil. Foil sample No.2 responded similarly.

To achieve erosion by cavitation only and to measure it, only the heavier foil No. 3 was used. It was tested at three conditions above the screen, at a flow rate of approximately one gpm: 25 watts ultrasonic power (ultrasonics) for 5 minutes run time; at 50 watts for 10 minutes and then with no flow (reactor full of water) at 100 watts ultrasonics for 18 minutes.

The results are shown in Figure 6. The results show that there was essentially no erosion due to cavitation where the foil was placed (above the screen). Apparently, for this flow configuration, cavitation occurred at the face of the wave guide as evidenced by erosion of the waveguide surface. Thus, at the screen, there was no cavitation. This means that phenomena that depend upon cavitation solely, such as oxidation of dissolved organics, will be little effected by the screen. Alternatively, processes that are dependent upon the screen should be relatively independent of whether cavitation is occurring.

### 3.1.2 Determination of Shear Force

The specific objective of this task was to gain knowledge about the mechanism of shear generation within the reactor under flow conditions. The method that was used for shear effectiveness measurement was to compare slurry stability effects using dispersions of ultrafine silica (cabosil) into a liquid. Dispersion, homogenization and emulsification are processes that have been shown to be dramatically improved via ultrasonic treatment [7]. Hence, dispersion can be used as a sensitive test of the effectiveness of an ultrasonic treatment method. Ultrafine particulate, such as cabosil silica, requires very high shear to promote dispersion of the fine solids into a slurry. Hence, the stability of the slurry can be used as a direct measurement of the effectiveness of dispersion.

A series of test points were obtained for pressure drop across the reactor screen. Figure 7 shows that the screen does provide a slight pressure drop. This may be important for liquid flow geometries throughout the reactor since this holdup may ensure that the liquid all passes through the cavitation zone directly adjacent to the waveguide surface.

Three sets of tests were then made using a 38/62 vol % solution of isopropanol/water into which about 0.5 wt% of cabosil was dispersed. This liquid solution promoted wetting and hence dispersion of the cabosil to form a more stable sol than 1 wt% cabosil in water. The results from these runs are given in Figures 8, 9, and 10. All were mixed for three minutes at a control valve setting on the pump discharge gate valve of 2 and 3/4 turns (or equivalent to about 0.4 gpm total flow rate of circulation through the reactor). After mixing for 3 minutes; the pump then was shut off. The beaker containing the dispersion was poured into a graduated cylinder and the dispersion was allowed to settle. The settled clear liquid volume was measured versus time of settling in hours.

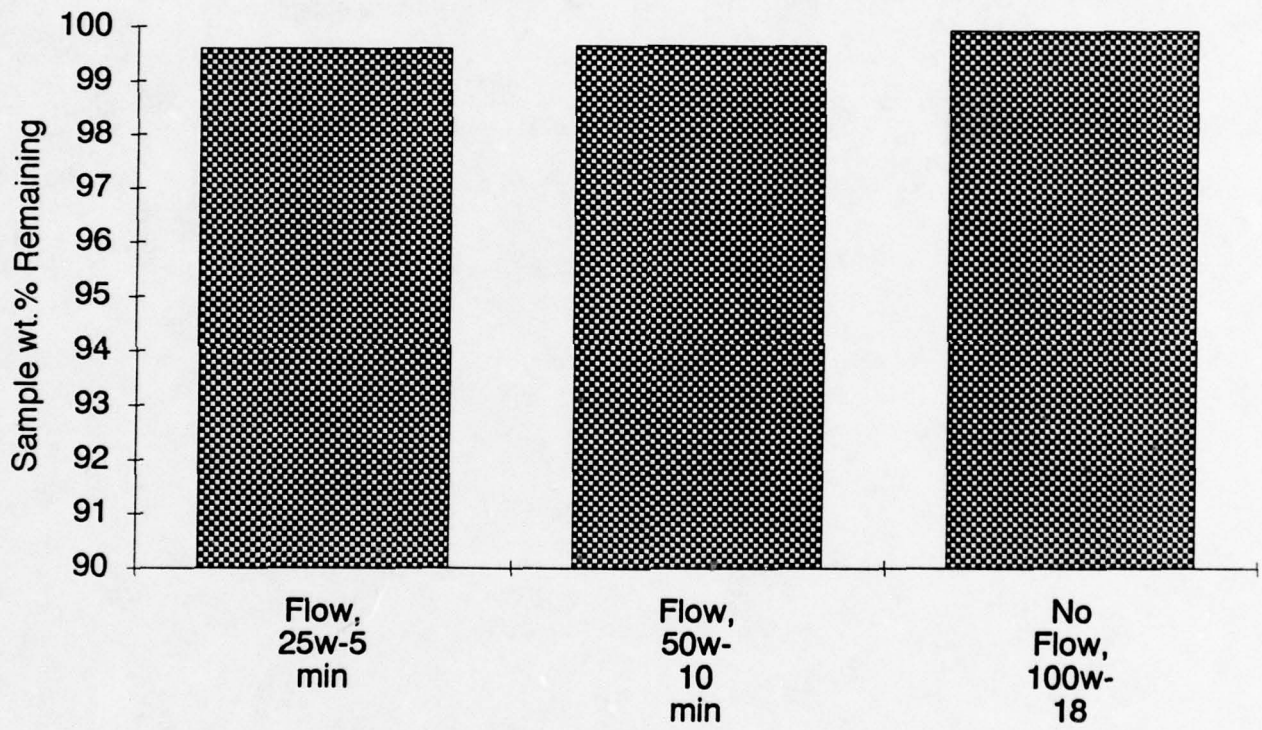


Figure 6. Effect of Cavitation on Aluminum Foil Weight.

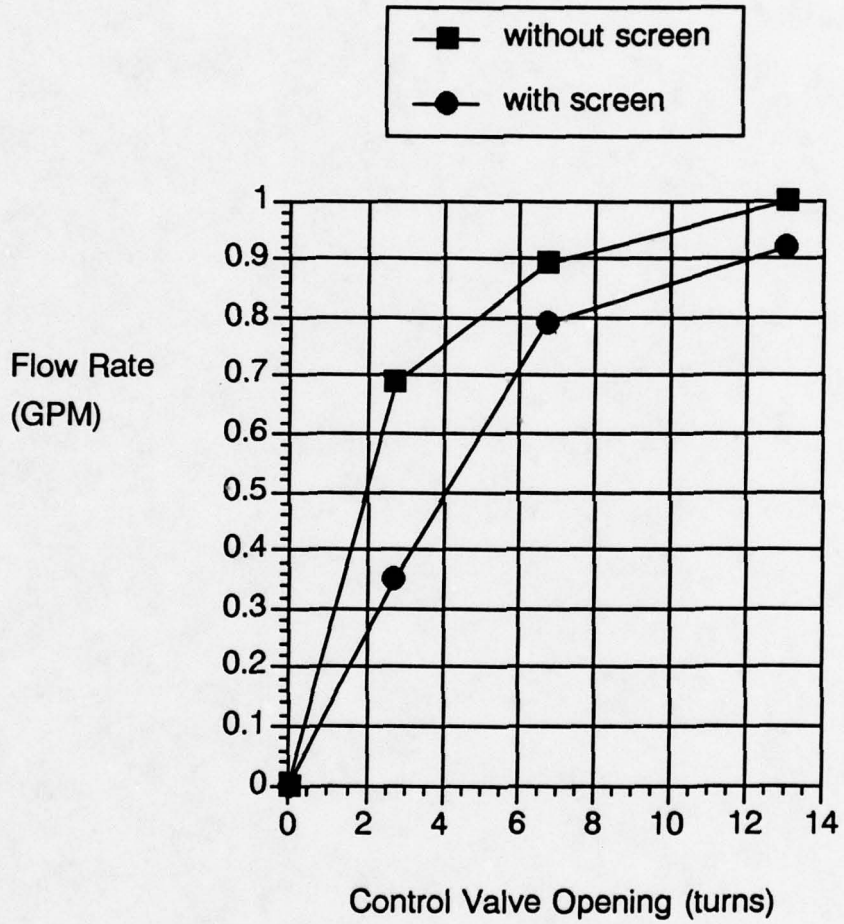


Figure 7. Effect of the Screen on Flow Rate.

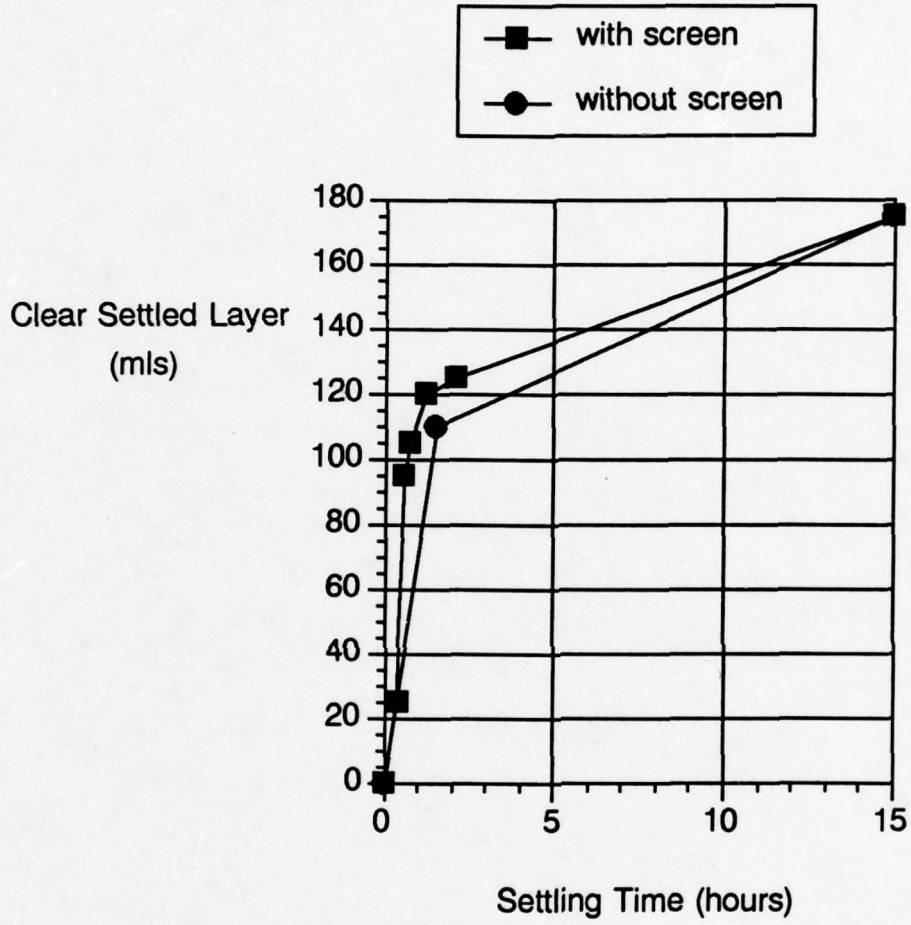


Figure 8. Effect of the Screen Alone on Cabosil Dispersion Stability.

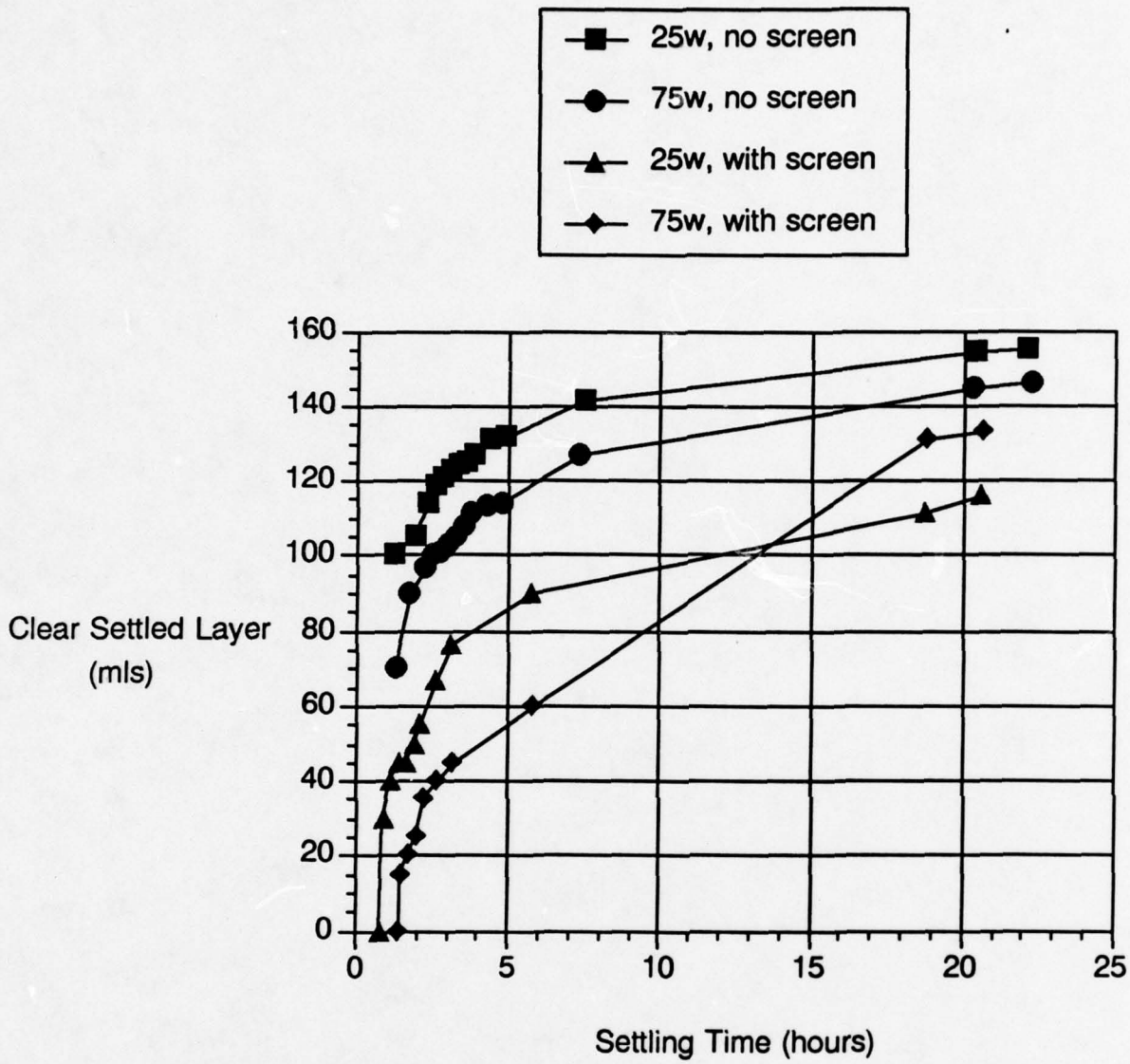


Figure 9. Effect of Ultrasonic Power and Screen Presence on Dispersion Stability.

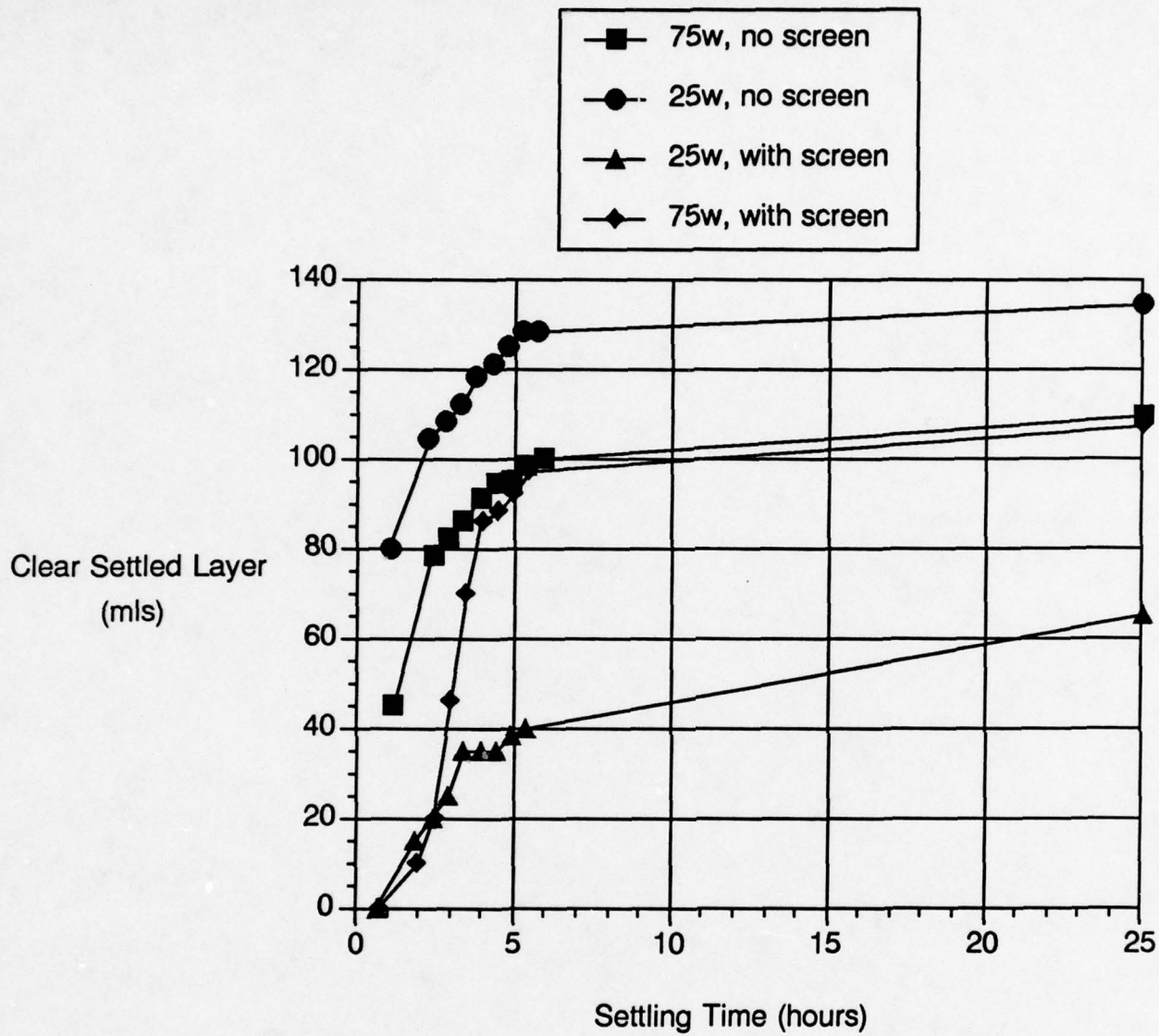


Figure 10. Effect of Ultrasonic Power and Screen Presence on Dispersion Stability.

In Figure 8, the tests were done with no ultrasonic activation both with and without the screen in the reactor. There was no significant difference in settling time for no activation with and without a screen in the reactor. This indicates that at the low volumetric flow rates used for these tests, turbulence across the screen due to the flowing liquid was not sufficient to significantly affect mixing and dispersion of the cabosil into the liquid phase. ultrasonics

A second set of experiments were performed with the same basic conditions except that all 4 runs of this set were done with ultrasonic treatment; first 25 watts with no screen in the reactor; next with 75 watts with no screen; then 25 watts with a screen and 75 watts with a screen in the reactor. A plot of settled clear liquid volume (cc) versus hours of settling time, is shown in Figure 9. The results demonstrate the synergistic effect of the shear screen in conjunction with cavitation. Namely, the tests made with a screen in the reactor at 25 and 75 watts of power were distinctly more stable than the same conditions without a screen in the reactor.

A repeat test was made to confirm the reproducibility of the previous test. The results are shown in Figure 10. Here again, the dispersions made with the screen in the reactor showed the formation of a more stable sol or gel. It is noted that the 25 watts ultrasonics with the screen in reactor was more stable than 75 watts with screen. Repeat tests showed a crossover with time indicating a less stable sol or gel for the 75 watt test with the screen. This can be interpreted in the following manner. Cavitation tests have already indicated that the primary cavitation zone is directly adjacent to the surface of the waveguide and that very little cavitation is occurring at the screen. Therefore, the improvement in dispersion with the screen in place is due to the synergistic effect of the vibrational wave being transmitted across the screen. Since vibrational energy transmission is reduced through a cavitating liquid, increasing power leads to less vibrational wave transmission to the screen.

### 3.1.3 Reactor Geometry Modification

In order to evaluate how the reactor geometry might affect the interaction of the shear generation and cavitation mechanisms, the same dispersion tests were conducted after modifying the reactor by incorporation of a 1/16-inch gasket in the upper flange of the ultrasonic reactor. This gasket increased the distance between the ultrasonic waveguide and the downstream shear screen from 1/8 inch distance to 3/16 inch. This caused the cavitation at the surface of the wave guide to be moved away from the shear screen. The results of the repeat tests were distinctly different and are given in Figure 11. In this graph the four curves were much closer together and showed less dispersion differences than Figures 9 and 10.

Essentially, the ultrasonic tests without the screen in the reactor showed improved stability while those with the screen in place showed reduced stability. One explanation is that with the gasket, cavitation mixing improved over the previous month because there was a larger cavitation volume. It is not believed that the rubber itself caused a dampening of the ultrasound because the gasket was located at a nodal (zero displacement amplitude) point. Also, with the gasket, ultrasound, and screen, mixing was less because the increased distance

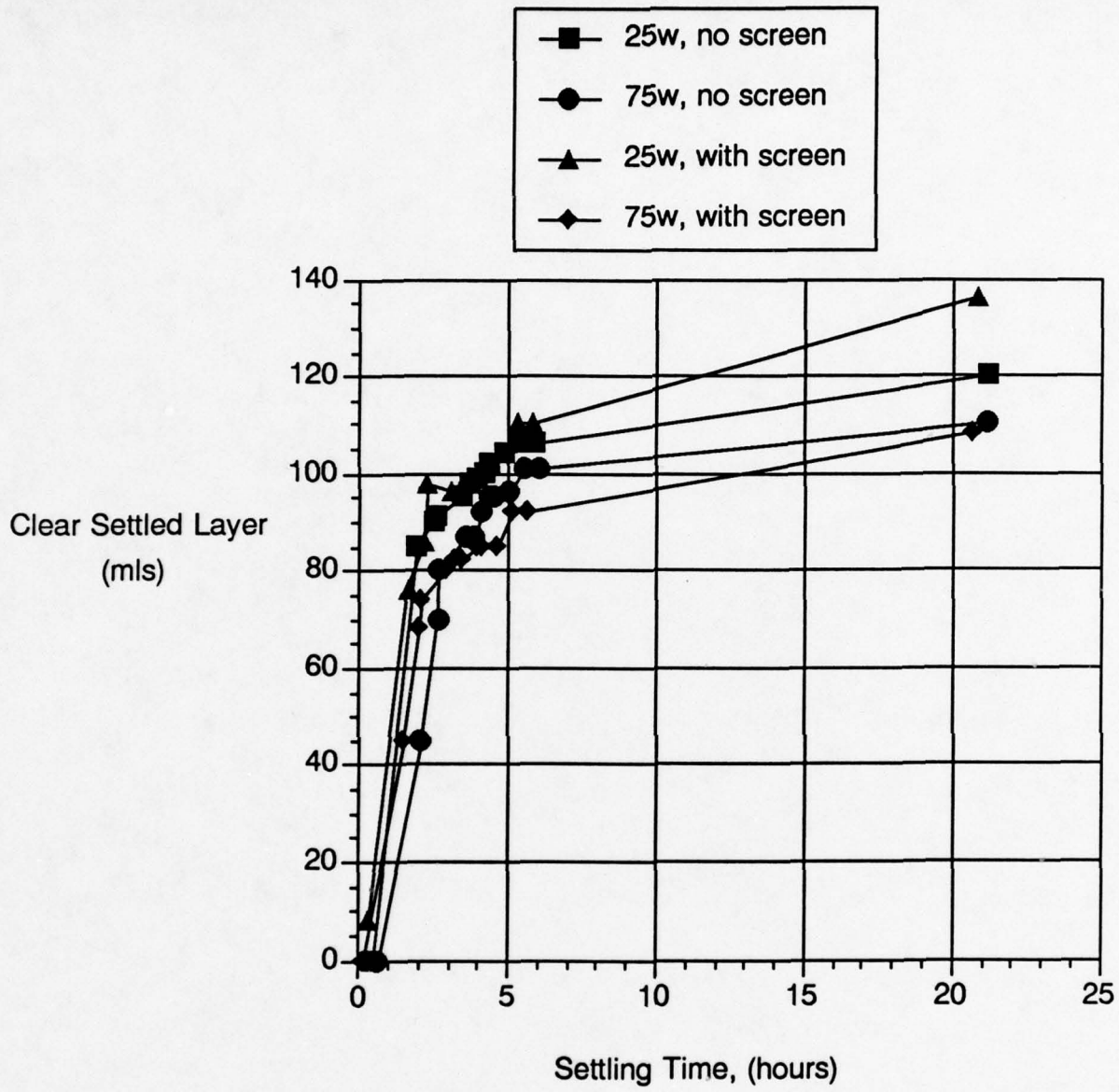


Figure 11. Effect of Modified Reactor Geometry on Dispersion Stability.

between waveguide surface and screen reduced the vibrational energy available at the screen due to attenuation effects.

A subsequent test was run immediately after these tests wherein the gasket was removed and dispersion stability was measured for three conditions: no ultrasonic activation, screen in place, ultrasonic activation and no screen, ultrasonic activation and screen. The results from this test, shown in Figure 12, duplicated the results observed in the earlier tests without the gasket in place. Hence, the small modification to the basic reactor geometry did indeed have a large impact on the relative contributions of cavitation and shear generation to the observed dispersion stability.

In an attempt to quantify the contribution of ultrasonic mixing to total mixing, a control test was run to simulate essentially zero mixing. Isopropanol/water was added to 2.8 grams of cabosil and mixed vigorously for 18 seconds by hand. Half of the mixture was poured into a 250 cc graduate and settling time was measured versus clear settled layer volume. The results in Figure 13 show that the dispersion was poor and settled quickly to a clear liquid. By comparison with data from Figure 12 (110cc clear layer in 1 hr for ultrasonic power with no screen; 70 cc in 1 hr for 25w ultrasonics power with the screen versus 190 cc hand mixed) one can estimate the percent of the dispersion increase due to ultrasonic power. There was a 58% increase in dispersion stability when the screen and cavitation are combined:

$$\frac{\text{Vol. clear - hand mixed} - \text{Vol. clear - cavitation}}{\text{Vol. clear - hand mixed} - \text{Vol. clear - cavitation and shear}} = 190 - 110 / 190 - 70 = 70 / 120 = 0.58$$

### 3.1.4 Reverse Flow Tests

As a result of the gasket tests, it was decided that flow geometry tests of the reactor needed to be performed. There was concern with the ultrasonic residence time distribution of fluids within the reactor. Since distance from the waveguide end to the screen proved to be critical, it was decided to reverse the flow in the reactor and run added mixing tests.

The flow array used for these tests is the same as that shown in Figure 1, except that the direction of flow was reversed. The pump discharge entered the reactor at the screen and flowed upward, impinging upon the waveguide and exiting the reactor at the former inlet.

The pump controller was set to give about 1 gpm of liquid flow as was done in previous tests. The 1/16-inch gasket was not used in these tests. Instead, a very thin paper gasket was used in the upper flange of the reactor. All of these tests used about 1/2 wt% cabosil in 500 cc of a 38/62 vol % mixture of isopropanol/water. All tests were run for 3 minutes.

The results are shown in Figure 14 and compare reverse and forward flow for 25w power with the screen. The conclusion was that there was essentially no difference between reverse flow and forward flow. Tests were also conducted without the screen and with and without the gasket. In all cases, there was no significant difference between forward and reverse flow.

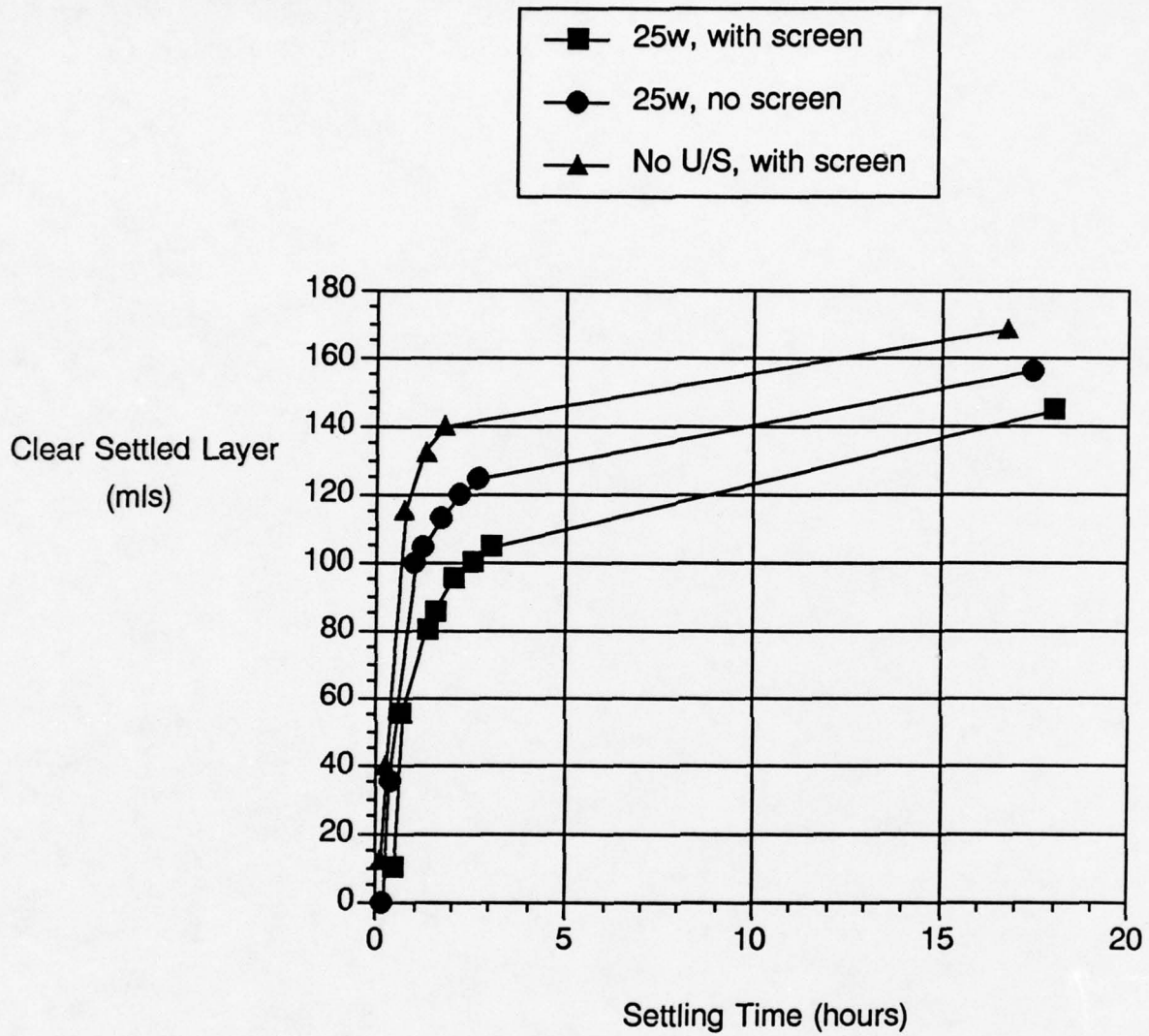


Figure 12. Repeat Dispersion Tests without Gasket.

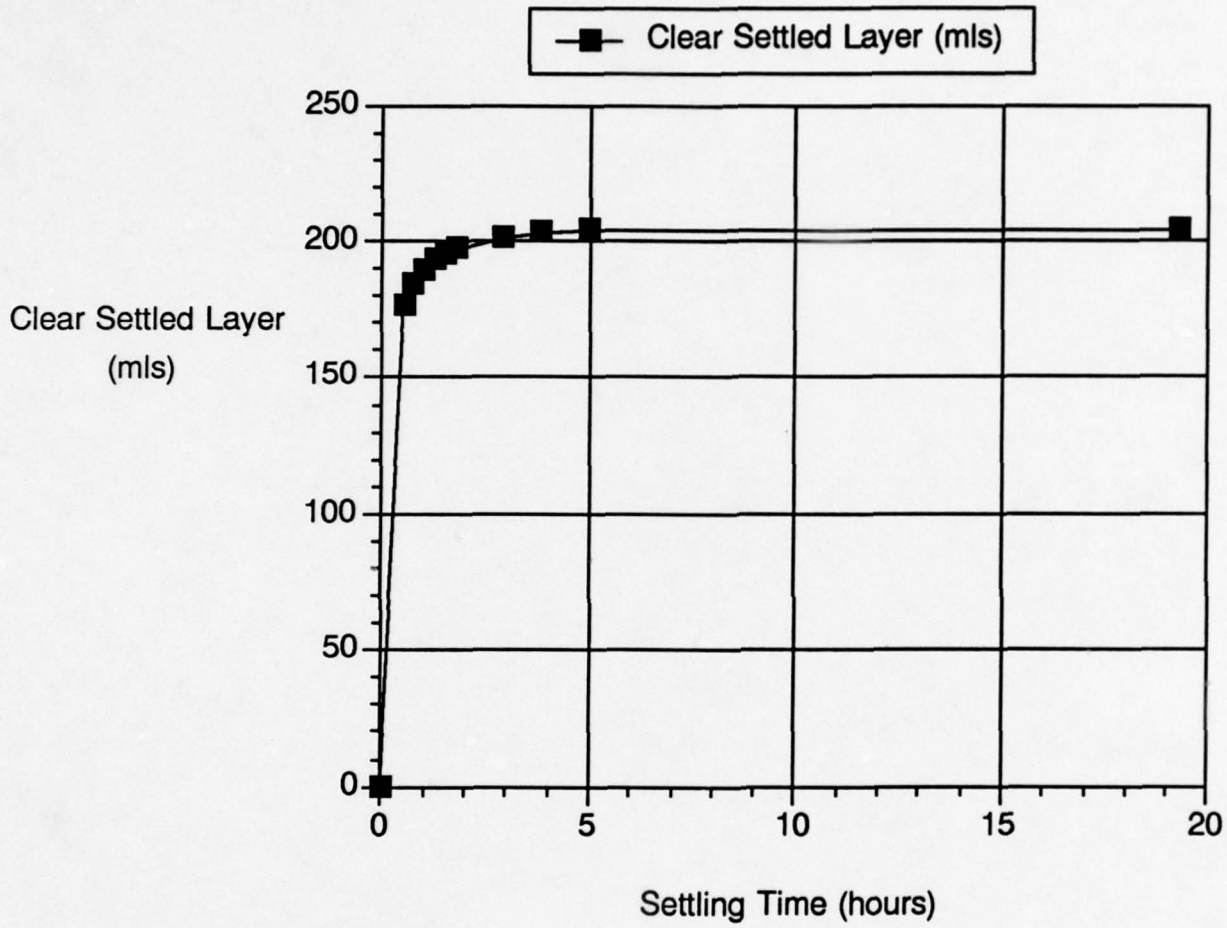


Figure 13. Effect of Hand Mixing on Dispersion Stability.

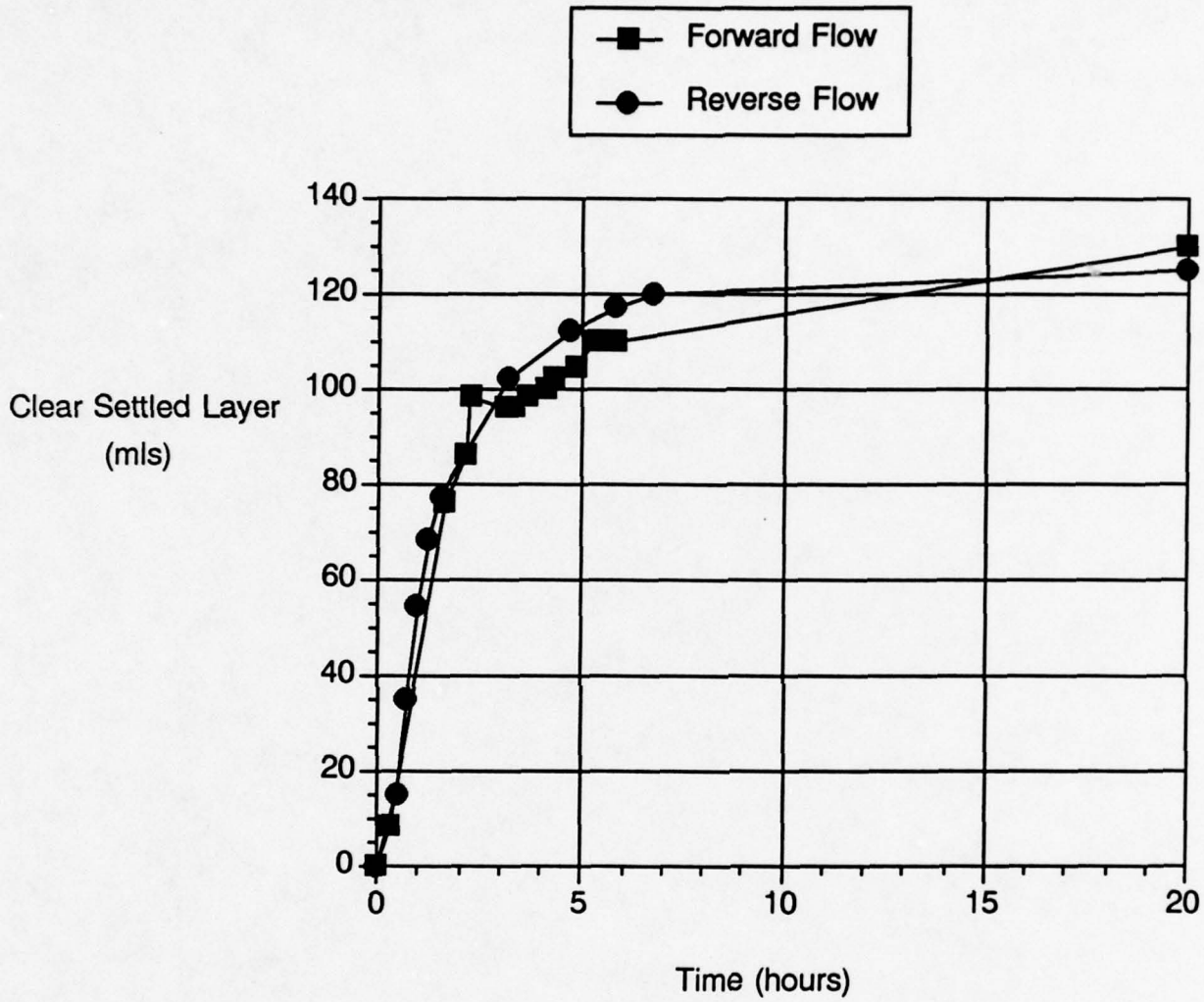


Figure 14. Effect of Reverse Flow on Dispersion Stability.

### 3.1.5 Evaluation of Process Synergism

Apparently, while the increased ultrasonic cavitation promotes formation of a gel that is more stable initially, the shear generated by the synergistic effect of the compressional wave with screen actually provides better dispersal as evidenced by better long term stability for the 25 watt with screen tests.

If one superimposes Figures 8, 9, and 10, a clear consistent picture is shown of the effect of screen and the effect of ultrasonic vibration on the stability of the sols. There is a clear synergistic effect resulting from the exceptional shear generation caused by the interaction of the compressional wave across the screen, resulting in much greater dispersion than either ultrasonic cavitation or screen shear alone can produce.

## 3.2 Wet Oxidation Process Characterization

### 3.2.1 Metal Powder Tests

In order to verify that actual cavitation was occurring within the reactor zone and to measure its extent, tests were made preliminary to actual wet oxidations by air of unpurified water. These preliminary tests consisted of suspending elemental metal powders in distilled water under nitrogen and irradiating them with 50 watts of ultrasound for various reaction times and at room temperature. Copper and chromium metal powders were used. The purpose was to parallel work done by S. J. Doktycz and K. S. Suslick [20] who showed that turbulent flow and shock waves produced by acoustic cavitation caused the metal particles to be driven together at sufficiently high velocities to induce melting upon collision. This resulted in fusion of the particles. After drying, these fused pairs of micron sized particles could be observed under a scanning electron microscope. They thus deduced the localized effective temperatures of the acoustic cavitation produced by the irradiation conditions by knowing the melting temperatures of the metal powders.

The metal powders used are described in Table 2. Two tests were made with the copper powder in a water slurry. The first test used 1/2 wt% Cu powder in water and was run for 10 minutes at 50 watts of ultrasound, while the second test used 1.3 wt% cu slurry and 30 minutes at 50 watts of ultrasound.

Test 1 - 800 ml of distilled water purged of oxygen with nitrogen gas was used with 4.0224 grams of copper powder weighed under nitrogen atmosphere. Circulation was begun at 1.5 gallons per minute and, the ultrasound power was run for 10 min. at 50 watts. The slurry was then vacuum filtered and dried in an oven for 24 hours. Dried samples of the irradiated copper were examined microscopically (400x) and there appeared to be no fusion. This run had been made at 40 times more dilute condition and 1/3 of the ultrasound irradiation than the above referenced article by Doktycz and Suslick. They had used 20 wt% metal powders in freshly distilled decane under argon

with direct immersion ultrasonic horn irradiation at 20 kHz and 50 W/cm<sup>2</sup> for 30 minutes, at 15°C.

Test 2 - Test 1 was repeated but with 5.3025 g Cu in 400 cc distilled water and run for 30 minutes at 50 watts. The sample was filtered and the product metal powder dried for 1 hr at about 220°F, allowed to cool and then observed under the microscope. The conditions of the increased concentration to 1.31 wt % slurry and 3 times the time of ultrasonic irradiation appeared to give much more fusion. Several fused particles could be seen (400x) although the number of fused particles was small. While this demonstrates that cavitation is occurring within the reactor zone, the short residence time limits the effectiveness of the cavitation zone.

Test 3 - This test was performed with chromium powder, with properties given in Table 2, and test conditions identical to those of test 2. That is, 4.6433 g of Cr powder was put in 400 cc of distilled water with nitrogen bubbled in while using 30 minutes of 50 watts of ultrasonic irradiation. Similarly, the slurry was vacuum filtered, and the metal powder product was dried overnight at 200-220°F.

Under the microscope, the irradiated product appeared to be smaller than the original chromium powder before irradiation. The treatment appeared to have ground the chromium to a smaller size than the 38 microns listed on the original sample label. This is consistent with prior work on ultrasonic comminution [7]. We did not observe any fused chromium particles. This indicates that the relative energy density of the cavitation was sufficient to fuse copper but not sufficient to fuse chromium. Two methods are available to increase the net cavitation energy. The ultrasonic power can be turned up and while this will increase cavitation energy but not the size of the cavitation zone. An alternative is to recycle the solution through the reactor in a pump-around loop. This provides a longer residence time in the cavitation zone. Based on the above tests, it appears that both increased power input and residence time will be needed for effective treatment.

### 3.2.2 Liquid-Dependent Effects

Based on the dispersion and metal powder tests described above, the following procedure was used for all subsequent wet oxidation tests. The total volume of liquid to be treated was added to the array and the total volume then pumped around in a loop between the heating bath and the reactor. This increased the residence time within the reactor cavitation zone so as to maximize the sonocatalytic effects. While batch tests were conducted during this Phase I effort, continuous flow could easily be accomplished by taking off a product stream from the loop equal to a continuous input feed. The shorter the residence time required to achieve oxidation, the greater the capacity of the reactor system.

Ultrasonically enhanced wet oxidation tests were run on simulated sea-water and simulated wastewater to determine the effect of cavitation on inorganic versus organic

systems. The systems were run in two liter batches, at atmospheric pressure, while varying temperature, ultrasonic power, and exposure time. The reactor was setup in configuration II with the rubber gasket in place as described previously. This configuration provided a larger cavitation zone over configuration I which provided better screen mixing. Conductivity, pH, Total Dissolved Solids (TDS), and turbidity were measured before and after the test runs for comparison.

First, three sea-water batches were run and analyzed. The test results (Trials 1-3, Table 4) showed little change comparing before and after exposure to ultrasonic activation. This was expected since the cavitation should not be sufficient to cause decomposition of the inorganic materials but rather lead to selective oxidation of the organic species.

Following the sea-water tests, three organic systems were tested. The contents and test conditions for these tests are listed in Tables 4 and 5 (Trials 4-6). Appropriate amounts of anthracene, lindane, trichlorophenol, and phenol were weighed and dissolved in the listed amount of acetone. 20 ml of 1g/l trichloroethene was added to each of the solutions which were then diluted to 2L with either distilled water or simulated sea-water. The pH, conductivity, and TDS of the three systems after cavitation were again consistent with the conditions before ultrasonic activation was applied. However, for trials #4 and 6 (temperature = 180°F), a significant (approximately 50%) decrease in turbidity was measured after cavitation. Trial #5, conducted at room temperature showed a slight increase in turbidity.

Table 4. Composition of Organic Constituents in Trials 4-6.

<u>Compound</u>	<u>Trial Conc., mg/l</u>		
	<u>4</u>	<u>5</u>	<u>6</u>
Anthracene	13.6	17.6	19.1
Lindane	11.0	14.5	12.1
Trichlorophenol	13.9	11.1	12.3
Phenol	19.8	10.9	9.9
Trichloroethane	10.0	10.0	10.0
Acetone, ml	20	30	10
Diluent	sea water	D.I. water	D.I. water

In industry, turbidity measurements are commonly used to determine the clarity or concentration of suspended materials in wastewaters; quantitative measurement is made of TSS as well [21]. The reduction of turbidity in trials #4 and 6 would indicate that the cavitation-induced reactions are more effective at higher temperature. Samples from all three trials were sent to Metlab of Tulsa, OK, for Total Organic Carbon (TOC) determination. These initial test waters were made up by dissolving the required amount of the organic components in acetone and then diluting with water. The end result was that the major organic contaminant in these tests was acetone. In fact, approximately

Table 5. Wet Oxidation Data

Trial	Conditions				Results											
	Time (min)	Temp. (F)	U/S pwr (watts)	pH	Cond. (mS)		TDS (/L)		Turb. (NTU)		TOC (mg/L)		TOC decr.			
					before	after	before	after	before	after	before	after				
1	10	room*	100	7.9	8.3	65.9	64	32.6g	31.8g	3.1	2.5	**	**	-		
2	60	room*	50	8	8.2	64	64.6	31.9g	32.2g	5.4	4.1	**	**	-		
3	10	180	50	8.1	8.4	65.4	69.3	32.5g	34.6g	2.1	1.1	**	**	-		
4	15	180	50	8.3	8.5	63.2	66.8	31.4g	33.3g	11.5	5.1	**	505	-		
5	10	room*	100	7.9	7.8	0.022	0.033	11mg	16mg	15.4	17.6	**	5253	-		
6	5	180	100	8.3	8.1	0.015	0.022	7.8mg	11mg	82.7	37.8	**	286	-		
7	15	180	0	8.2	8	0.006	0.053	2.6mg	26mg	0.08	9.6	**	**	-		
8†	15	180	100		8.2		0.068		34mg		11.45	**	**	-		
9	15	180	0	7.39	8.4	14.1	16.1	7.39g	8.03g	1.5	2.3	328	110	66%		
10†	15	180	100		8.3		17.1		8.53g		0.58		87.5	73%		
11	30	180	100	8.8	8.5	0.006	0.011	2.8mg	5.7mg	0.95	7.6	328	74.6	77%		
12	60	180	100	8	8.2	0.004	0.04	2.1mg	20mg	-	8.2	328	31.9	90%		
13	15	180	100	7.6	7.8	0.341	0.302	169mg	150mg	2.67	2.2	140	159	-		
14	5	180	200	7.6	8	0.341	0.425	169mg	212mg	2.67	2.08	140	121	14%		
15	15	180	100	7.9	7.9	16.1	15.5	8.05g	7.71g	5.01	1.25	159	144	9%		
16	15	180	100	8.2	7.9	50.9	48.6	25.53g	24.63g	0.8	0.32	170	161	5%		
17	5	180	200	8.2	7.9	50.9	52	25.53g	26.19g	0.8	4.6	170	140	18%		

† continuation of previous test

\* 80°F - 95°F

\*\* not measured

99% of the total organic carbon initially was acetone. These results then simply indicate that heating leads to greater removal of the acetone.

To eliminate this situation for further testing, solutions were made without initial acetone dissolution. The organic components were added to flasks of distilled water and stirred to allow as much dissolution as possible. The solutions were left to settle and restirred for several days to let the solution become saturated.

To determine the effect of heating and stirring on the reduction of TOC, a sample was made of the organic solutions. It was heated and mixed for 15 min., tested for TOC, ultrasonically oxidized and then rechecked for TOC. The results of these trials are shown in Table 5, Trials 7-10. The first set of tests (7-8) were done in the same set up as used previously (i.e. copper tubing). It was possible that the copper was contributing to the increasing conductivity and TDS, so the second set (9-10) was run using PVC tubing. Due to the decreasing TOC values, it is believed the PVC plasticizers (which could possibly leach to the system) were not factors in the measured TOC.

Trials 11 and 12 were run to determine the effects of longer ultrasonic exposure time on the organic samples. The TOC decrease was significant for these two runs. Due to the "batch" nature of the treatment, the longer run time allows more cycles through the reactor and therefore more exposure to the effects of cavitation. These test results indicated that long exposure times are desired for increased oxidation.

Next, tests were run to determine the effects of high system pressures on ultrasonic oxidation. The pressure array was used as described earlier in Figure 3. Approximately 500 ml of organic solution was used in each test, and each test was run at 50 psi. It was noticed, during these tests, that the cavitation sounds were not as loud as in earlier tests. The tuning frequency of the system also changed significantly as pressure was applied to the system. In fact, when the ultrasonics were left on and the pressure was released, the cavitation sound volume gradually increased as the pressure of the system slowly returned to the atmospheric pressure. It is believed that the high pressures were actually hindering the cavitation process. The small changes in TOC also support this assumption. Although increasing the ultrasonic power input led to increased organic removal even at shorter residence times (test 16 vs. 17), the actual amount of organic material removed was very small. The results of the pressure tests are listed as Trials #13-17 on Table 5.

### 3.3 Preliminary Desalination

#### 3.3.1 Ultrasonic Atomization/Vaporization/Condensation

Although reverse osmosis can effectively desalinate even sea water, the high dissolved solids content puts a heavy load on the membranes. Alternative methods to efficiently and economically desalinate waters would help provide a more effective overall system by reducing the load on the RO unit. While distillation is a very old method for desalinating waters, it is an effective but costly method, particularly if fuel is required to boil the water.

Our proposed modification is to use a highly energy efficient means (e.g., ultrasonic atomization) to provide an aerosol of very fine water droplets. Sufficient heat for vaporization is then readily available from the surroundings. Vaporization of the water leaves an aerosol consisting of the dissolved solids which can then be filtered to separate them from the moisture-laden airstream. After filtration, the water vapor is recondensed again using the surroundings to provide the required heat sink.

Figure 15 shows a flow chart representing such a process. Based on the parameters shown in Figure 15, it should be possible to recover 0.582 gallons of desalinated water for each gallon vaporized (atomized). Appendix A provides the detailed calculations to obtain this result. These temperatures and relative humidities represent a poor case, i.e., any increase in the temperature differential and/or relative humidity differential will both increase the amount of water recovered as a function of the amount of water evaporated and will also reduce the airflow required to achieve the required heat transfer. The only energy required is for atomization of the water and pumps and blowers to move the air and cooling water. So long as the pressure drops throughout the system can be kept low, these process steps are relatively low energy consumers. The bulk of the energy required can be derived from the surroundings. Obviously, this is only true so long as a sufficient temperature difference can be maintained. In very cold climates, it will be necessary to heat the input air sufficiently to get the proper temperature difference relative to the water temperature which will probably be close to freezing. In very hot climates there will only be a problem if the water and air temperatures are relatively close.

The key step in the process is the ultrasonic atomization step. There are several methods for ultrasonically atomizing liquids. The requirements for atomization are that the atomizer should produce very fine sized droplets, preferably in the 2-5 micron size range in order to promote rapid vaporization. Traditional ultrasonic atomizers rely upon the frequency of vibration to control and determine the final droplet size wherein the droplet size is inversely proportional to the frequency. A key advantage to ultrasonic atomization is its very low energy requirement. Typical energy requirements for atomization are in the range of 0.05 to 0.1 kwh (170 - 341 Btu) per gallon. Other nonultrasonic atomizers are either incapable of delivering the fine sized droplets required or require very high energy input to achieve this fine size. The thermal energy required to evaporate water under the conditions in Figure 15 is 1015.8 Btu/lb H<sub>2</sub>O evaporated (8468.7 Btu per gallon). Obviously, if most of this thermal energy required to vaporize and then condense the water can be obtained from the surroundings, the proposed method has the potential to be very energy efficient. One key disadvantage to these traditional atomizers is the fact that as the frequency is increased to achieve the desired droplet size, the atomizer size and atomization rate drops significantly. Hence, atomizing large volumes of water would require a large number of atomizers. This has limited development of such a process.

Low cost ultrasonic atomizers, however, are now available in the form of ultrasonic humidifiers. Although the volumetric atomization rates for such atomizers is very low, they are effective at producing droplets in the right size range. Higher atomization rates are

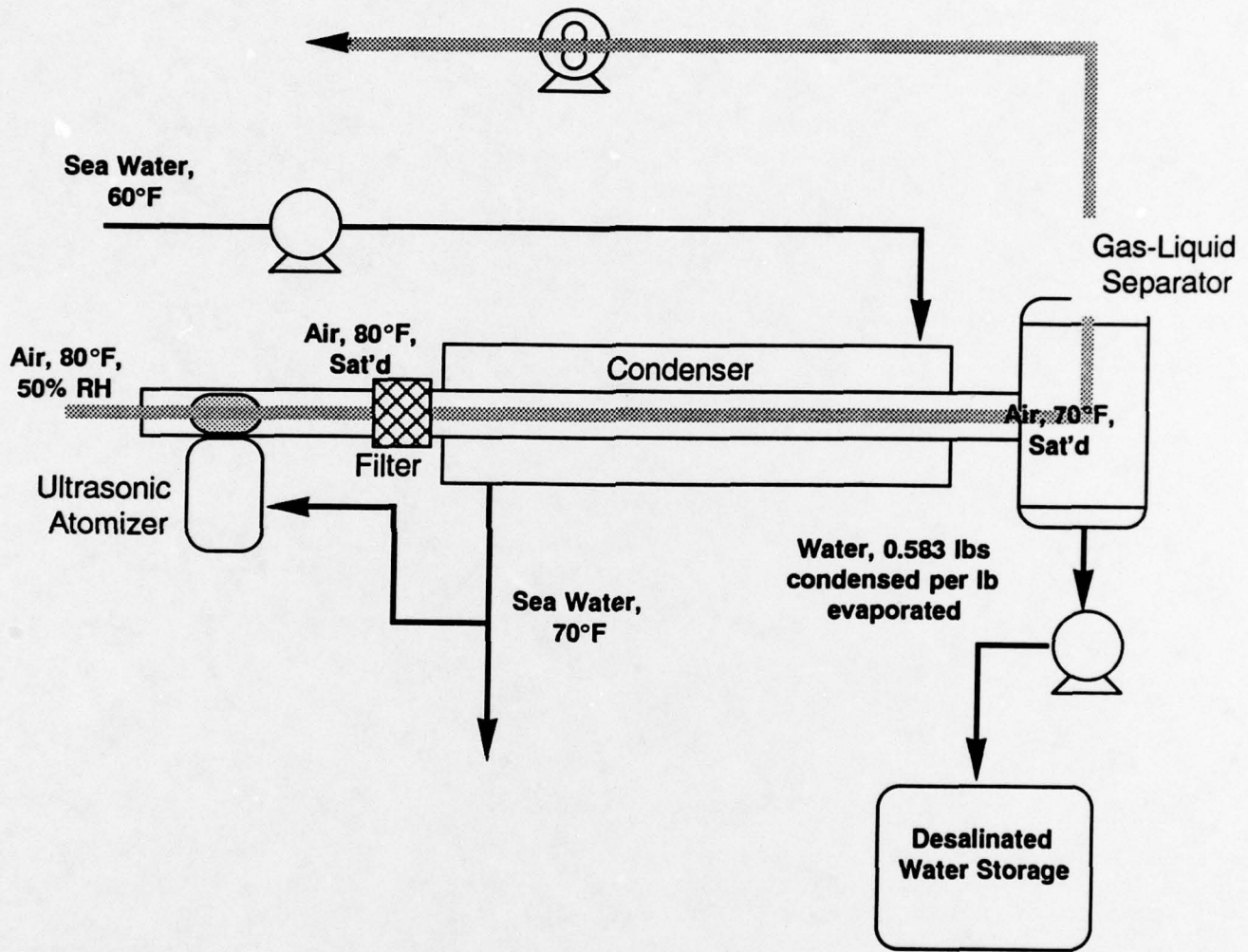


Figure 15. Desalination Process Model.

possible through the use of a new atomizer. Under separate contract with the U.S. Navy [19], S. R. Taylor and Associates is developing a novel atomizer which produces up to 10 times the atomization rate as existing atomizers while maintaining very high energy efficiency. Although not used for Phase I studies (the array was unavailable during this test program), it can be used in future work. For these Phase I studies, an existing ultrasonic humidifier/atomizer was used to produce the fine sized water droplets.

The desalination array as described earlier is shown in Figure 4. The system was erected on a laboratory bench, open to the atmosphere. Condensation from the cooling coils was collected for testing.

However, in an open system, condensation will occur simply from the natural humidity. To take atmospheric moisture into account, two samples were taken. The system was run for a total of four hours without the humidifier. The volume of condensation was saved for comparison. The system was then run for four hours with ultrasonic humidifier running. Total Dissolved Solids (TDS) of the two samples were used in calculations below:

condensation from atmosphere only (without ultrasonics) => a  
 condensation with ultrasonics => b  
 condensation from effects of sea water, only => c

$$\frac{(\text{vol}_b)(\text{TDS}_b) - (\text{vol}_a)(\text{TDS}_a)}{\text{vol}_b - \text{vol}_a} = \text{TDS}_c = 274 \text{ mg/L}$$

The results of these calculations, as well as other tests run on the two samples, are listed in Table 6. The ultrasonic desalination treatment of the sea water decreased the TDS by 99%. According to Mr. Shalewitz, RO desalination typically produces a TDS reduction of 97-99%, hence, the proposed ultrasonic atomization method has potential on the basis of product water quality.

Table 6. Desalinated Water Quality

<u>Sample</u>	<u>pH</u>	<u>TDS, (mg/L)</u>	<u>Cond., (mS)</u>
Raw water sample	8.16	33,080	65.9
Condensed without atomization	-	145	0.303
Ultrasonically atomized	5.34	233	0.470

This result is even more promising when the low efficiency of the filtration is taken into account. Obviously, the best desalination will occur when all of the salt dust is separated from the airstream. However, this will require a higher pressure drop and, hence, greater energy cost. In the tests above, it was visually apparent that a large portion of the ultrafine solids passed through the filter but were not re-absorbed in the condensation stage. Reducing the need for a difficult separation step further enhances the potential of the process.

3.3.2 Energy Consumption for Desalination

During this Phase I testing, effort was focused more on demonstrating successful desalination rather than on constructing an efficient laboratory system. Because of this, a low efficiency condenser section was used although this meant that the volume of water recovered was a very small percentage of the water evaporated. The following energy data is based on the volume of water atomized; the volume produced is based on the thermodynamic efficiencies described in Figure 15.

Table 7. Energy Consumption for Desalination

<u>Task</u>	<u>Energy Consumption, kwh/gal</u>
Atomization	0.05 - 0.10
Fan or Blower for Air Movement <sup>1</sup>	3.5 - 7
Pump to Provide Water Flow <sup>2</sup>	2 - 5
TOTAL	5.55 - 12.1

<sup>1</sup>5-10 HP Blower for 15,000 cfm

<sup>2</sup>2-5 HP Pump for 150 gpm

Clearly, atomization represents only a small portion of the total energy required for desalination thus the overall process becomes very energy efficient by utilizing the surroundings for all of the thermal energy requirements. A variety of desalination procedures have been developed and Table 8 provides a summary of their relative economic standing [22]. While RO is favored for brackish waters, distillation is favored for sea water applications.

Table 8. Relative Economic Standing of Desalting Processes\*

<u>Process</u>	<u>Brackish Water</u>	<u>Sea Water</u>
Multistage Flash		
Distillation (MSF)	7	8
Vertical Tube		
Distillation (VTE)	7	8
Combined MSF & VTE	7	8
Vapor Compression		
Distillation	6	7
Electrodialysis	8	0
Reverse Osmosis	8	4
Freezing Processes	6	5
Ion Exchange	7	0

\*Based on 0 for least competitive and 8 for most competitive

Actual costs are dependent upon the production rate but, as a comparison, operating costs for a 100 gpm acid-dosed, multi-stage flash distillation unit are approximately \$6.61 per gallon [23]. Based on the energy data shown for the ultrasonic atomizer concept, operating costs would range from \$0.56 to 1.21 per gallon assuming an electrical energy cost of \$0.10 per kwh. This suggests that the ultrasonic atomization desalination process has the potential to be very energy efficient for sea water applications in particular.

#### 4.0 CONCLUSIONS AND RECOMMENDATIONS FOR PHASE II

Water purification requires alleviating both inorganic and organic constituents. The overall goal of this project is to develop a system that can effectively handle both types of contaminants in a system that is more attractive than current RO systems. Since several of the key problems with RO purification systems are related to membrane clogging, an improved purification system might also include processes that significantly reduce the load on the RO membranes thus dramatically improving the lifetime and maintainability of the RO elements. It appears that the proposed processes can accomplish such a function.

First, the novel atomization/vaporization/condensation processes may solve the desalination problem and thus reduce almost entirely the TDS load on the RO membrane. This has particular application to cases where sea water is the feed. Second, sonocatalytic wet oxidation can achieve up to 90% reduction of organic contaminants in water under very mild conditions. However, significant disadvantage is the apparently long residence time required to achieve this reduction. A good potential use of the sonocatalytic process would be to neutralize CBR hazards so that any subsequent polishing could be accomplished with standard RO elements without having to then handle the elements themselves as hazardous wastes.

Finally, the sonocatalytic process appears to affect a reduction in turbidity and such a reduction could also help reduce the load on the RO membranes significantly. This is perhaps more important than the actual oxidation since it is the suspended species which lead to high turbidity that can rapidly lead to membrane fouling.

Overall, these Phase I results are very encouraging and suggest a potential for success in Phase II. To summarize, the following accomplishments have been achieved during Phase I:

- Initial tests showed that the cavitation zone occurs near the face of the waveguide, but not into the screen itself.
- There is a synergistic effect of ultrasound when coupled closely with a screen. Excellent mixing and dispersion was achieved.
- Increasing the distance between the waveguide and the screen reduces the mixing and dispersion but appears to afford better cavitation.

- Reverse flow tests showed about the same dispersion as forward flow tests.
- Initial oxidation tests show that ultrasonic cavitation has no effect on TDS from inorganic sources; ultrasonic cavitation does lead to a reduction in turbidity for samples containing organic species.
- Oxidation tests showed that ultrasonic enhancement greatly improved oxidation and removal of organic contaminants under very mild conditions. Increasing pressure, however, had a negative effect on ultrasonically enhanced oxidation. Although the oxygen partial pressure is increased by higher operating pressures, cavitation significantly inhibited thus reducing the overall extent of oxidation.
- Ultrasonic atomization can provide a very energy efficient means to vaporize water for distillation to desalinate brackish and sea waters. So long as the thermal energy required can be derived from the surroundings, energy efficiency can be very high.

Phase II research and development will focus on further scaleup and optimization of both the desalination process and the sonocatalytic oxidation process to treat larger volumes (up to 10 gpm). Additionally, the systems will be mated with a standard RO system so that the effects of the pretreatment on membrane fouling can be determined. Key Phase II objectives will be 1) to verify the desalination model and to measure the actual energy consumption as a function of variation in the operating parameters of feed air and water temperature and atomized droplet size; 2) to scale up and further optimize the ultrasonic reactor to enhance both wet oxidation and solids dissolution to reduce water turbidity.

Scaleup of the desalination system to 30-60 gpm is believed possible using the new ultrasonic atomizer developed by SRTA to achieve the required atomization rates with the desired droplet size. The primary unknown for scaleup is the actual airflow required to achieve successful heat transfer. Requirements could be as high as 10,000 cfm per gallon which would mean very large ducts and condensers thus raising the capital costs and the size of the system. Phase II operational testing will allow definition of the optimum operating regimes.

Scaleup of the sonocatalytic oxidation system is limited by the long residence time requirements to achieve successful oxidation. For 90% oxidation, approximately 3600 gallons of reactor volume would be required to achieve 60 gpm treatment rate. Alternatively, as a pretreatment to aid dispersion of the suspended solids, approximately 300 gallons of reactor volume would be required at a residence time of 5 minutes. Power consumption for the ultrasonic components would be relatively small but overall energy consumption may be high due to the requirement to heat the water. It is believed that the long residence times will prohibit the use of the sonocatalytic reactor for complete oxidation.

The operating characteristics of the overall system will be determined over the full range of potential operating conditions. Tests will be conducted with simulants and actual samples.

Samples of treated waters will be fully characterized including analysis of the individual organic component concentrations. As a result of the experimental work, a prototype system will then be fabricated and performance evaluated prior to shipment to the Sponsor for actual onsite testing.

Finally, the results of all testing will be analysed and correlated in order to provide engineering specifications for Phase III prototype system fabrication.

REFERENCES

1. Jagow, R. B., "Investigation of the Feasibility of Using Wet Oxidation to Process Dilute Onboard a Coast Guard Vessel," ASME Publication 71-ENAs-4, presented at Intersociety Conference on Environmental Systems, July 1974.
2. Uri, N., Autoxidation and Antioxidants, Lundberg, W. V. ed., Vol. 1, Chap. 2, Interscience, New York, 1961.
3. Ultrasonics, 25, January 1987.
4. Pugin, B., "Qualitative Characterization of Ultrasound Reactors for Heterogeneous Sonochemistry," Ultrasonics, 25, p.49, (1987).
5. E. I. El'piner, Ultrasound: Physical, Chemical and Biological Effects, trans. by F. L. Sinclair, Consultants Bureau, New York (1964).
6. A. R. Williams, Ultrasound: Biological Effects and Potential Hazards, Academic Press, New York (1983).
7. J. R. Frederick, Ultrasonic Engineering, J. Wiley & Sons, New York (1965).
8. Tarpley, W.B., Jr., et al., "Development and Test of Generators for Aerosolization of Liquids (U)," Contract DA-18-064-404-CML-3 (1955).
9. Tarpley, W.B., Jr., et al., "Development and Test of Nozzles for the Dissemination of Particulates (U)," Contract DA-18-064-404-CML-94 (1956).
10. Tarpley, W.B., Jr., Baddorf, P.E. and R. Pheasant, "Fine Particle Agent Dissemination (U)," ATL-TR-65-9, Contract AF 08(635)-4024, CONFIDENTIAL (1956).
11. Tarpley, W.B., Jr., Pheasant, R. and C.D. McKinney, Jr., "Gel-Stabilized Suspensions (U) (A New Dissemination Technique)," AF Contract AF 08(635)-4998, CONFIDENTIAL (1966).
12. Tarpley, W.B., Jr., et al., "Microencapsulation of High Energy Compounds by Ultrafine Atomization Techniques," Final Report under Contract No. NORD-18976 (1961).
- 13a. Tarpley, W.B., Jr., Jones, J.B. and J.L. Straughn, "Aerosolization and Coating Apparatus," U.S. Patent No. 2,993,469 (1961).
- 13b. Tarpley, W.B., Jr., Jones, J.B. and J.L. Straughn, "Aerosolization Unit," U.S. Patent No. 2,998,391 (1961).
- 13c. Jones, J.B. and J.L. Straughn, "Aerosolization Process," U.S. Patent No. 2,944,029 (1960).
- 14a. Tarpley, W.B., Jr., and J.L. Straughn, "Process of Forming a Dispersion of Aerosol Particles and Process for Coating Solid Particles with said Dispersion," U.S. Patent No. 3,009,826 (1961).

- 14b. Jones, J.B. and K.H. Yokom, "Method and Apparatus for Generating Aerosols," U.S. Patent No. 3,084,874 (1963).
- 14c. Jones, J.B., "Process for Generating Aerosol and Apparatus Therefor," U.S. Patent No. 2,929,563 (1960).
- 15a. Sonicore Atomizing Nozzle, Sonic Development Co., Literature and Discussions, 1965-1984.
- 15b. FloSonic Division, Fluid Kinetics, Inc., Literature and Discussions, 1973-1984.
- 15c. SonoMist Ultrasonic Spray Nozzle, Heat Systems Ultrasonics Inc., Literature and Discussions, 1979-1984.
16. Marshall, W.R., Jr., "Atomization and Spray Drying," Chemical Engineering Progress Monograph Series, (%), No. 2 (1954).
17. Handbook on Aerosols, R. Dennis, Ed., p. 9 et seq., TID-26608, Prepared for Division of Biomedical and Environmental Research, ERDA (1976).
18. Tarpley, W.B., Jr., Taylor, S.R. and E.N. Twesme, "Piezoelectric Ultrasonic Atomization for Home Heating Combustion," U.S. DOE (1983).
19. Taylor, S. R., Hoffman, A. A., Collins, S. A. and E. E. Farmer, "Novel Atomization for Efficient Liquid Filtration", Final Technical Report, Navy Contract No. N61533-91-C-0006, August 1991.
20. Doktycz, S. J., and Suslick, K. S., "Interparticle Collisions Driven by Ultrasound," Science, 247, pp. 1067-1070, 2 March, 1990.
21. Willard, H. H., Merrit, L.L., Dean, J.A., and Settle, F.A., "Instrumental Methods of Analysis," seventh ed., Wadsworth Publishing Co., Belmont, CA, 1988, pp. 186-9.
22. Homer, W. A. and C. A. Scharpf, "Principal Factors Relating to the Selection of Single-Purpose and Dual-Purpose Desalting Plants", Chem. Eng. Prog. Symp. Ser., v. 67, No. 107, 1970, p. 184.
23. Principles of Desalination, Eds. K. S. Spiegler and A. D. K. Laird, 2nd Edition, Academic Press, New York, 1980.

APPENDIX AWater Vaporization/Condensation Calculations

The following calculations are based on the temperatures and relative humidities shown in Figure 17.

Table 1. Air Moisture Levels<sup>1</sup>

<u>Temperature, °F</u>	<u>Relative Humidity, %</u>	<u>lb H<sub>2</sub>O/lb dry air</u>	<u>Enthalpy, Btu/lb dry air</u>
70	100	0.016	31.50
80	50	0.011	43.69
80	100	0.023	34.09

<sup>1</sup>data taken from Perry's Handbook of Engineering, 3rd Edition.

Based on the above data, it would be necessary to atomize and evaporate 0.012 lb H<sub>2</sub>O/lb dry air and it should be possible to obtain 0.007 lb H<sub>2</sub>O (condensed)/lb dry air. Thus:

$$0.007/0.012 = 0.583 \text{ lb H}_2\text{O condensed/lb H}_2\text{O evaporated}$$

Evaporation

Enthalpy required is  $43.69 - 31.50 = 12.19$  Btu/lb dry air

Air required/lb H<sub>2</sub>O evaporated =  $1/0.012 = 83.3$  lb dry air/lb H<sub>2</sub>O evaporated

Therefore, energy required =  $12.19 \times 83.3 = 1015.83$  Btu/lb H<sub>2</sub>O evaporated; at 0.0807 lb/ft<sup>3</sup>, will need 1032 ft<sup>3</sup>/lb H<sub>2</sub>O evaporated.

Condensation

Enthalpy is  $43.69 - 34.09 = 9.6$  Btu/lb dry air

Therefore, energy required is  $83.3 \times 9.6 = 799.68$  Btu/lb H<sub>2</sub>O evaporated; at 10 Btu/lb cooling water, will need 79.968 lb cooling water/lb H<sub>2</sub>O evaporated; at 8.337 lb/gallon, will need 137.2 gal cooling water/gal H<sub>2</sub>O condensed.

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