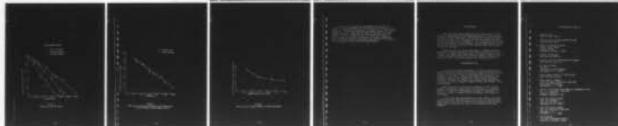AD-A045 351   NAVAL ACADEMY ANNAPOLIS MD ENERGY-ENVIRONMENT STUDY GROUP   F/G 13/2
              AN EVALUATION OF THE ENGINEERING DESIGN PARAMETERS OF HYDROGEN --ETC(U)
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AN EVALUATION OF THE ENGINEERING DESIGN PARAMETERS
OF HYDROGEN PEROXIDE, ULTRA-VIOLET OXIDATION OF
REFRACTORIES IN WASTE WATER.

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The capability of oxidizing refractories in waste water by hydrogen peroxide ultra-violet treatment had been dmonstrated by laboratory experiments. The purpose of this project was to dtermine data which will permit an engineer to design a full-scale hydrogen peroxide-ultra-violet treatment facility. This data was developed for the most difficult refractory, acetic acid/acetate, in waste water and the results show that the engineer may design for minimum time or minimum energy utilization.

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INTRODUCTION

Dr. Edward Koubek of the Chemistry Department, U. S. Naval Academy, investigated a method of oxidizing certain refractory organics utilizing hydrogen peroxide activated by ultra-violet light. He also considered the advantages of this method over metal ion-catalyzed hydrogen peroxide oxidation. Dr. Koubek's conclusions were that the ultra-violet hydrogen peroxide system has several advantages over the metal ion-hydrogen peroxide system.[6] He also concluded that the ultra-violet light might have beneficial side effects when treating wastes containing viruses which are difficult to destroy.

As a result of Dr. Koubek's conclusion, the author was assigned the task of applying ultra-violet hydrogen peroxide treatment to waste waters, in particular those which might be generated aboard a ship. However, there were no design data available so the assignment became one of determining design data.

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[6]Ind. Eng. Chem., Process Des. Develop. 14 348 (1975)

DESIGN PARAMETERS

Source of Ultra-violet Radiation

The source of ultra-violet radiation is, of course, one of the primary parameters. The standard source, a mercury bulb in the form of a long slender tube, was selected as the most efficient configuration. Further, the temperature of the bulb or tube wall is critical and must be maintained at 40 to 42°C.[1]

Thickness of Reactants

The distance the ultra-violet radiation will effectively penetrate the reactants surrounding the tube is also a primary parameter to be evaluated. The depth of penetration of ultra-violet radiation from mercury vapor lamps has been studied relative to bactericidal action, and effective penetrations to several inches have been reported.[2] Based on this reference and the fact that ultra-violet water sterilizers are commercially available, the decision was made to start with an off-the-shelf sterilizer, but with the condition that the design of the sterilizer be such that the thickness or depth of the reactants could be varied with minimum modification to the sterilizer.

Ultra-violet Reflectors

Some of the ultra-violet radiation could be expected to pass through the reactants and strike the metal surface at the outer wall of the reactor chamber. Therefore, the possibility of reflecting this radiation back into the reactants is a parameter to be evaluated particularly when the reactant depth or thickness is small. "Aluminum is one of the most satisfactory reflectors for most purposes."[3] This reference then goes on to discuss the effects of manufacturing on the reflectivity, pointing out that rolled or extruded surfaces are generally smooth, bright and good reflectors. Iron is less expensive when used to fabricate equipment, so the decision was made to utilize both materials (iron and aluminum) to determine the influence each has on the effectiveness of the ultra-violet-hydrogen peroxide oxidation process.

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[1]Koller, Lewis R. Ultra-violet Radiation, 2nd Ed.(1965) John Wiley & Sons, p. 52.

[2]Hoather, Roy C. Journal of the Institute of Water Engineers, Vol. 9, p. 191-207 (1955).

[3]Koller, Lewis R. Ultra-violet Radiation, 2nd Ed. (1965) John Wiley & Sons, p. 201.

TEST SAMPLE

It was decided that for the purposes of this investigation, the material to be oxidized would be the most difficult, acetic acid, the material Dr. Koubek utilized in his investigation. Houston Research, Inc.[4] has developed a method of determining a "refractory index" in terms of the oxygen available to the oxidation process, the time required to oxidize 50% of the reactant, and the initial amount of the reactant components. The refractory index values (RFI values) for several compounds are given in Table 1. These are included as a method of ranking refractories, should there be further work in the area of ultra-violet-hydrogen peroxide oxidation.

The source of the acetic acid was sodium acetate. Each sample was an equal part by volume of 1.25 mols of hydrogen peroxide in 1 liter of water and of .25 mols of sodium acetate in 1 liter of water.

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[4]Houston Research, Inc. "Oxidation of Refractory Materials by Ozone with Ultra-violet Radiation," paper presented at 2nd Int'l. Ozone Symposium, Int'l. Ozone Institute, May 11-14, 1975. Montreal , Canada.

TABLE 1

REFRACTORY INDEX VALUES FOR VARIOUS COMPOUNDS

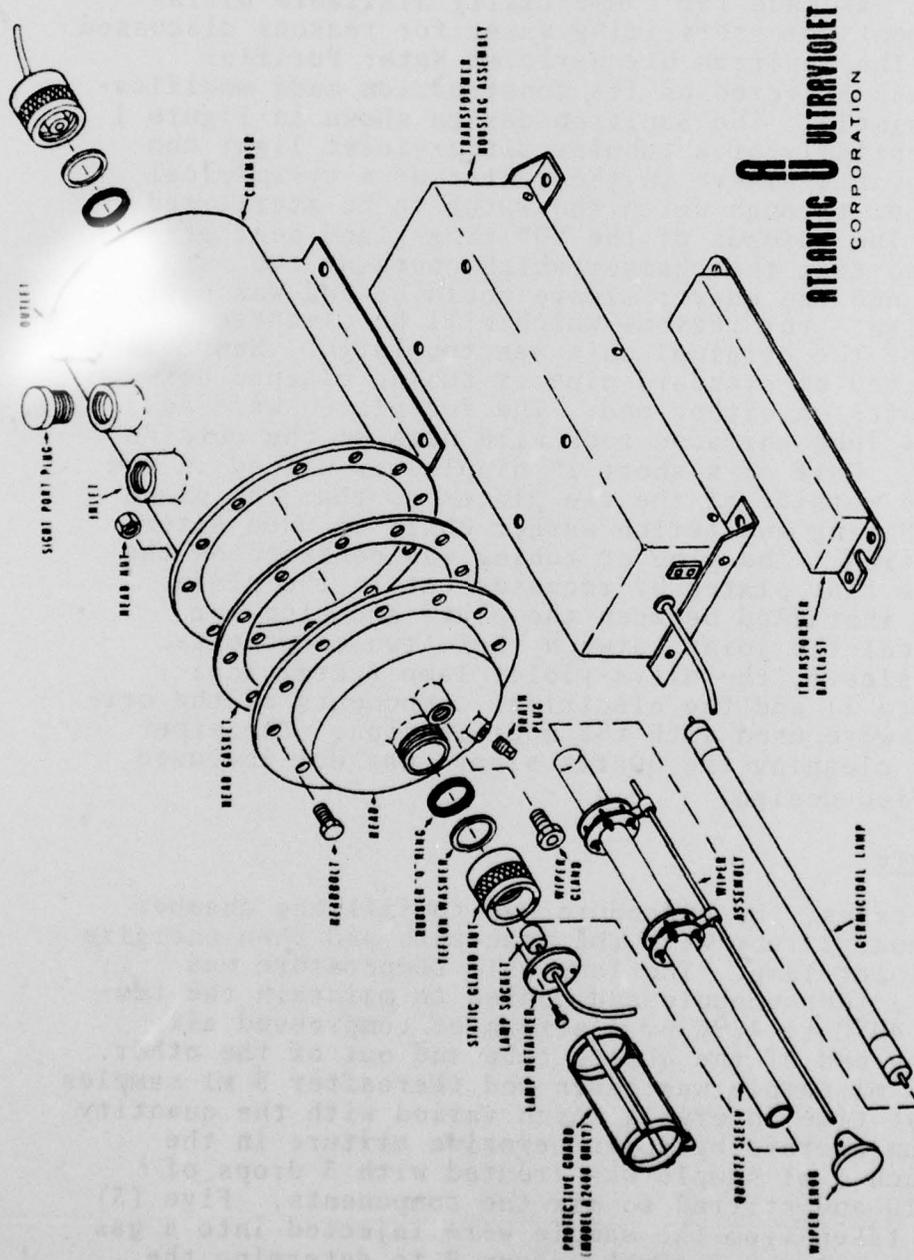|	Compound	RFI-Value	Qualitative Scale
1)	KCN	0.41	Slightly Refractory (RFI < 1)
2)	Complexed Cd-Cyanide	0.96	Slightly Refractory (RFI < 1)
3)	Glycine	19.7	Refractory (RFI, 1 → 100)
4)	Palmitic Acid (as NH_4-Salt)	27.3	Refractory (RFI, 1 → 100)
5)	Glycerol	112	Highly Refractory (RFI > 100)
6)	Ethanol	245	Highly Refractory (RFI > 100)
7)	Complexed Ferricyanide	270	Highly Refractory (RFI > 100)
8)	Acetic Acid	> 1000	Very Highly Refractory

PROCEDURE

Equipment

A search was made for commercially available ultra-violet equipment for sterilizing water for reasons discussed previously. The Sanitron Ultra-violet Water Purifier Model A2400 was selected as its construction made modifications quite simple. The Sanitron design shown in Figure 1 consists essentially of a tubular ultra-violet light contained in a quartz sleeve in the center of a cylindrical tank or chamber through which the water to be sterilized was passed. The threads of the "O" ring gland seal are 2" pipe threads so that the chamber which contains the reactants around the quartz sleeve could be and was easily changed in size. For reasons which will be discussed later, the chamber of the original unit was too large. New chambers were constructed of standard pipe or tubing clamped between two steel plates on either end. The two plates were held together by 4 long threaded rods with nuts on the outside of the plate. Half of a short 2" nipple was welded in the center to the outside of the two plates so that the gland seal nut, "O" ring and teflon washer could be used after the modification. The pipe or tubing was centered on the inside of the flat plates by recesses cut in the plate. Gaskets were installed between the plate and pipe, or tubing, to seal the joint between those two components. The quartz sleeve, the ultra-violet lamp (germicidal lamp in Figure 1) and the electrical components of the original design were used with the modification. The wiper assembly for cleaning the quartz sleeve was not included in the modified design.

Test Procedure

In all cases, the procedure was to fill the chamber around the quartz tube with the reactants and then energize the ultra-violet lamp. The lamp wall temperature was measured by a thermocouple and cooled to maintain the temperature at 40°C to 42°C by a stream of compressed air forced in one end of the quartz tube and out of the other. An initial 5 ml sample was taken and thereafter 5 ml samples were taken at time intervals which varied with the quantity of the sodium acetate-hydrogen peroxide mixture in the chamber. Each 5 ml sample was treated with 3 drops of sulfuric acid and stirred to mix the components. Five (5) microliters taken from the sample were injected into a gas chromatograph using a Parapak column R to determine the percent of acetic acid remaining in the sample relative to the untreated or initial sample.

FIGURE 1

Exploded View of the Sanitron Water Sterilizer

ATLANTIC **U** ULTRAVIOLET
CORPORATION

OUTLET

SIGHT PORT PLUG

CHAMBER

INLET

HEAD NUT

HEAD GASKET

HEAD

HEADBOLT

RUBBER "O" RING

TEFLON WASHER

STATIC GLAND NUT

LAMP SOCKET

LAMP RETAINER

PROTECTIVE GUARD
(MODEL A2400 ONLY)

WIPER KNOB

QUARTZ SLEEVE

WIPER
GLAND

WIPER
ASSEMBLY

GERMICIDAL LAMP

DRAIN
PLUG

TRANSFORMER
HOUSING ASSEMBLY

TRANSFORMER
BALLAST

Tests with Sanitron Unit

The first test was performed with the Sanitron Water Purifier of Figure 1. The chamber was filled with the reactants and the ultra-violet lamp energized. Two thermocouples had been taped to the lamp and an air hose placed in a hole cut off-center in the lamp retainer on each end. It was quite easy to hold the lamp wall temperature to 40°C to 42°C by varying the air flow through the quartz sleeve. Further, there was negligible temperature difference between the two thermocouples, one at the end of the lamp and one at the middle of the length of the lamp so only one thermocouple was used after the initial test.

After two hours of operation, there had been an insignificant decrease in the acetic acid of each sample, as determined by the gas chromatograph, so the test was discontinued and work initiated to make small chambers as described earlier.

Tests with Small Chambers

In order to compare the effect of the improved reflectivity of aluminum, test chambers were made of both aluminum tubing and galvanized pipe. Three chamber diameters were utilized for both steel and aluminum in order to have more than two data points for graphing. Table 2 below tabulates the internal diameters for the 6 chambers.

TABLE 2

INTERNAL DIAMETER AND CAPACITY* OF THE SIX TEST CHAMBERS

	Steel Chambers		Aluminum Chambers	
Size	Diameter	Capacity*	Diameter	Capacity*
Small	5.26cm (2.07in)	430 ml	5.13cm (2.02in)	280 ml
Medium	5.89cm (2.32in)	900 ml	5.26cm (2.17in)	570 ml
Large	6.25cm (2.46in)	1210 ml	5.89cm (2.32in)	890 ml

The chambers were fabricated of commercially available tubing and pipe. All were of different capacity, except for the medium steel pipe and large aluminum tubing.

* measured, not computed.

RESULTS

The results of the test on these 6 chambers are given on Figures 2 and 3. Both graphs show percent of acetic acid remaining in the 5 ml samples after a period of treatment in minutes shown on the horizontal axis. Figure 2 is the results for the steel pipe chambers. Figure 3 is the results for the aluminum tubing chambers.

In order to compare the results for steel and aluminum surface, the data for the medium steel pipe and for the large aluminum tubing, both of which have the same internal diameter and capacity, was plotted on one graph, Figure 4. The data for each of these two materials fit the same graph so only one line has been drawn.

Discussion of Results

The rate of reaction of the ultra-violet-hydrogen peroxide oxidation increases during the first 20 minutes. This part of the graphs is shown by the dotted line. The increase in the rates of the oxidation in the chamber during the initial 20 minutes or so is the induction period during which the oxidation process comes to equilibirium.

Contrary to what was expected, the aluminum tubing chambers did not increase the rate of reaction of the oxidation as compared to that in the iron chamber, as shown in Figure 4. The quantity of reactants, 890 ml for the aluminum chamber and 900 ml for the steel chamber, required the same time period to achieve the same percentage of removal of sodium acetate for each type of metal of the chamber wall. The inside surface of the steel pipe was galvanized or coated with zinc which is not recommended as an ultra-violet radiation reflector.[5] As a result of this experiment, it appears that the reflective quality of the inner surface of the chambers is not important.

Figures 2 and 3 summarize the experimental data, but the designer can select the diameter of the chamber only on the basis of the time required to complete the reaction. Therefore, a graph was generated to show energy consumption as a function of diameter, or capacity, of the chamber. This graph, Figure 5, shows that the efficiency of the electrical energy into the ultra-violet mercury lamps increases with chamber diameter. The energy required per milliliter of reactants decreases by almost 65% at the larger diameters. These two sets of graphs now give the designer a choice of minimum time or minimum energy.

[5]Koller, Lewis R., Ultra-violet Radiation, 2nd Ed. (1965) John Wiley & Sons, p. 205.

Internal Chamber Diameter

△ 5.26 cm diameter

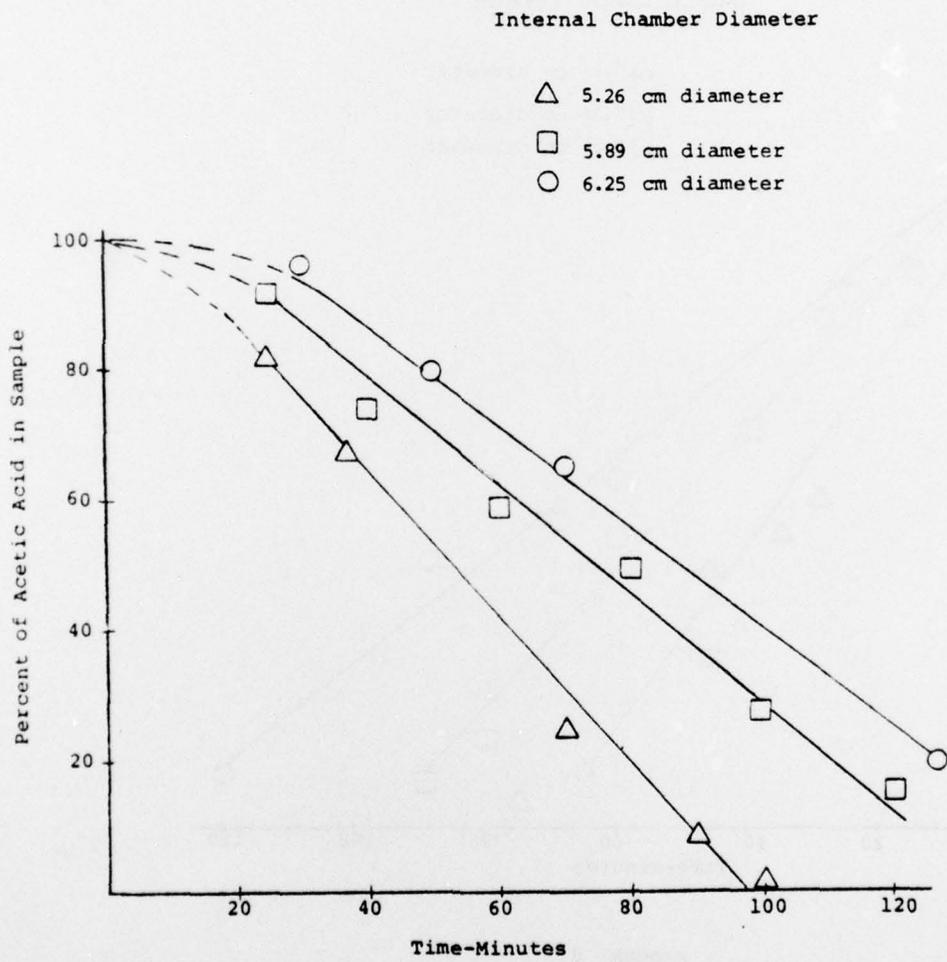□ 5.89 cm diameter

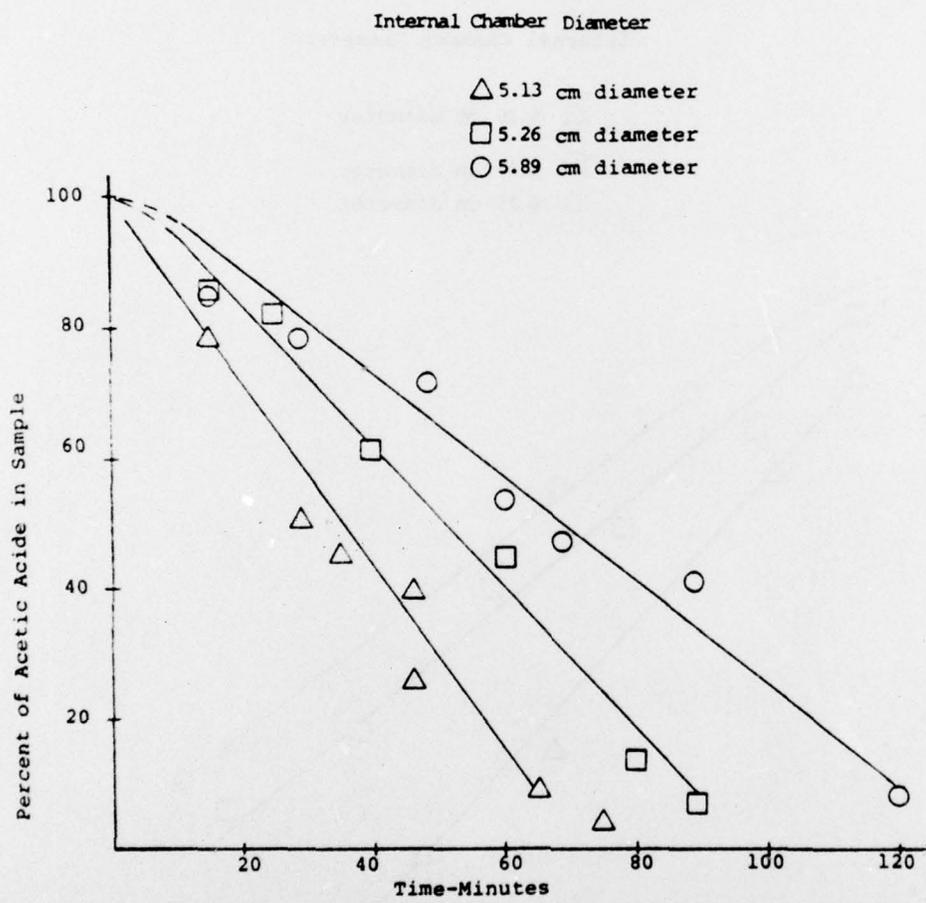○ 6.25 cm diameter

FIGURE 2
Chamber Wall Galvanized Pipe
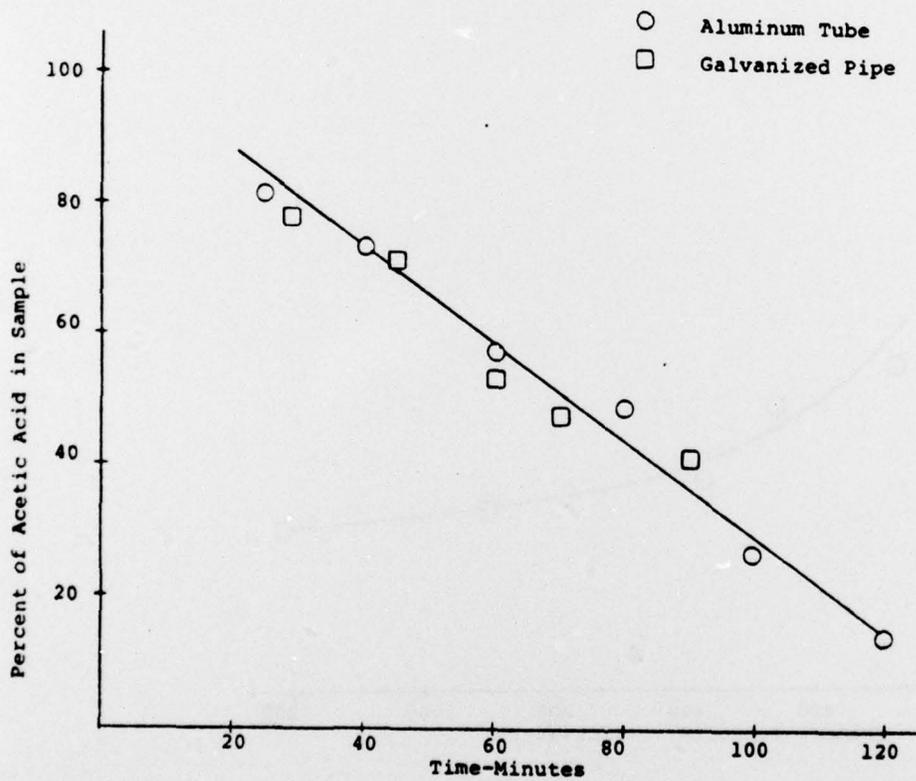
FIGURE 3
Chamber Wall Aluminum Tubing

FIGURE 4

Comparison of Aluminum and Galvanized Steel Chamber Wall
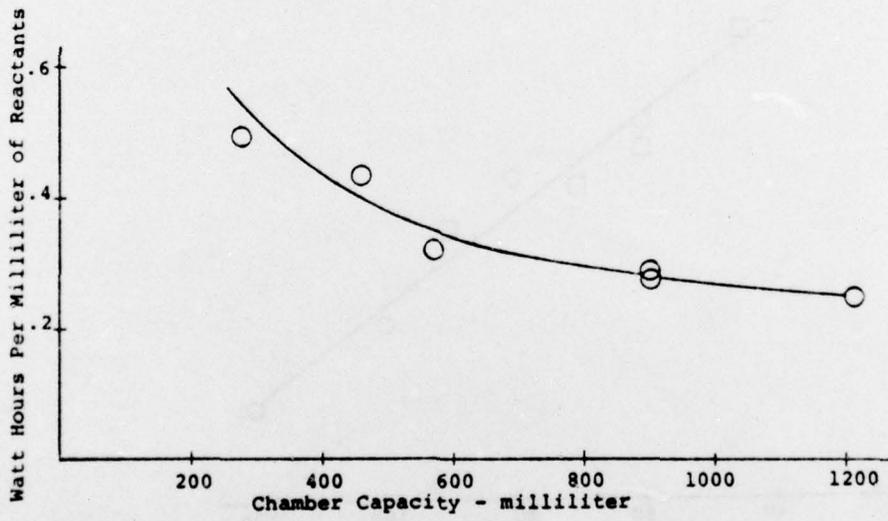Internal Diameter of Both Chambers 5.89 cm.

FIGURE 5

Effect of Reactor Chamber Diameter on Energy Requirement

An interesting question concerning the graph of Figure 5 is what happens to the curve as the diameter continues to increase? It appears to level out at the largest diameter. If it continues at that energy level to even larger diameters, then the designer's options are even greater. If its slope reverses so that the energy per unit volume of reactants increases at larger diameters, then very definitely the designer can optimize the diameter of the chamber based on power requirements.

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CONCLUSIONS

The most difficult refractories in waste water can be oxidized completely with hydrogen peroxide in the presence of ultra-violet radiation. The design of oxidizing chambers either minimizes the treatment time or the energy required per unit volume of the reactants. It is assumed that because of the increasing cost of energy, the designer would utilize the second choice to minimize the energy required per unit volume of reactants.

Based on the use of two materials, aluminum surfaces produced by normal manufacturing processes and galvanized surfaces of commercial steel pipe, it appears that the ultra-violet radiation reflectivity of the reactor chamber wall does not affect the rate at which the oxidation occurs.

RECOMMENDATIONS

In order to design equipment to oxidize refractories other than acetic acid by the ultra-violet-hydrogen peroxide method, design data must be developed similar to that of Figures 3, 4, and 5. These data should be centrally maintained so that if the demand for ultra-violet hydrogen peroxide oxidation is sufficient, generalized design data in terms of time, refractory index values, and energy could be developed.

The relation of the outside diameter of the reactor chamber and energy required per unit volume of reactants, Figure 4, should be investigated further to determine if there is indeed a diameter which minimizes the energy requirement.

A more detailed investigation of the effects of ultra-violet radiation reflectivity on the rate of reaction may well lead to the use of a material or surface finish which appreciably increases the rate of oxidation within the chamber.

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