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Ozone Mass-Transfer and Kinetics Experiments

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and
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OZONE MASS TRANSFER AND KINETICS EXPERIMENTS

Prepared for Rockwell Hanford Operations

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ABSTRACT

Experiments were conducted at the Hanford Site to determine the most efficient pH and temperature levels for the destruction of complexants in Hanford high-level defense waste. These complexants enhance migration of radionuclides in the soil and inhibit the growth of crystals in the evaporator-crystalizer. Ozone mass transfer and kinetics tests have been outlined for the determination of critical mass transfer and kinetics parameters of the ozone-complexant reaction.

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INTRODUCTION

A set of exploratory experiments has been completed, under Rockwell's Long-Term High-Level Defense Waste Program (AR-01-15-10), to examine the effect of pH and various catalysts and additives on the ozone treatment of residual liquor for the removal of ethylenediaminetetraacetic acid (EDTA) and other organic complexants by oxidation. Once the complexants are removed, the radionuclides can be separated and recovered from the residual liquor.

The oxidation experiment discussed in the report by W. I. Winters^a and reviewed in our Task 1 through 5 reports suggests, as a preliminary conclusion, that the most efficient ozonation is at a pH of ~14 and ~60°C. Under these conditions, the reaction is rapid and homogeneous throughout the course of the experiment.

The experiments carried out under acidic conditions, i.e., pH ~1.2, are also homogeneous and consume very little ozone. The EDTA-ferric complex reacts very rapidly under these conditions in an aqueous solution, however, the EDTA reaction was found to be very slow in the synthetic residual liquor or "Buckey Mix." Experiments are in progress to determine the cause of this slow reaction.

The ozonation appears to be most efficient under the conditions of a pH of ~14 and ~60°C. This report is intended to review the existing data available under these conditions, consider the question of mass transfer, recommend experiments to sort out the mass transfer and reaction rate, and determine the enhancement factor.

OZONATION OF SYNTHETIC RESIDUAL LIQUOR AT A pH of ~14

Two experiments were carried out under the conditions of a pH of ~14 and ~60°C. The data of these experiments are summarized in Table 1.

^aW. I. Winters, Extrusion of Ceramic Materials for Immobilization of Hanford Nuclear Waste, RHO-SA-208, Rockwell Hanford Operations, Richland, Washington (1981).

TABLE 1. Summary of a pH of ~14 Data.

Chemical Components	pH ~14	pH ~13.8
EDTA	0.031	0.029
Aluminum	0.657 mol/L	0.597 mol/L
Iron	3.29×10^{-3} mol/L	1.48×10^{-3} mol/L
CO_3^{2-}	0.15 mol/L	0.12 mol/L
NO_2^-	1.33 mol/L	1.28 mol/L
O_3 feed conc.	3.0 wt%	3.7 wt%
O_3 feed rate	10.6 g/hr	29.43 g/hr
$\text{O}_2\text{-O}_3$ flow	4.5 L/m	9.45 L/m
$(\Delta\text{O}_3/\Delta\text{EDTA})_{0.005\text{M}/\text{EDTA}}$	19.0	36.6
$t_{0.005\text{M}/\text{EDTA}}$	4.35 hrs	2.5 hrs

Reactor liquid volume: $V = 1.5$ L

The pH ~14 experiment was one of the first experiments carried out by Mr. Winters. Some parts of the experimental procedures and equipment were still being perfected so there are no data available on the pH, NO_2^- , and CO_3^{2-} concentrations as a function of reaction time.

The major difference between the pH ~14 and pH ~13.8 experiments was the ozone feed rate was higher in the pH ~14 experiment and the ozone concentration was higher for the pH ~13.8 experiment.

The reaction time was much shorter, 2.5 hours, to reduce the EDTA concentration to 0.005 mol/L ($t_{0.005\text{M}/\text{EDTA}}$) for the experiment with the higher ozone feed rate (pH ~14) as compared to 4.35 hours for the other experiment with higher concentration (pH ~13.8). The data on the ozone requirement, $(\Delta\text{O}_3/\Delta\text{EDTA})_{0.005\text{M}/\text{EDTA}}$, indicate that the shorter reaction time was accomplished at the expense of the ozone requirement.

A summary of the key process parameters as a function of reaction time is shown in Figure 1 and Figure 2 for the two experiments.

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FIGURE 1. First pH ~ 14 Run. O₃ Feed:
4.5 L/min, 10.6 g/L, 39.3 mg/L = 3.0 wt%.

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FIGURE 2. Repeat Run pH ~ 13.8. O₃ Feed:
 9.45 L/min, 29.43 g O₃/hr, 49.05 mg/L = 3.74 wt%.

The disappearance of EDTA and the ozone utilization curves are generally similar for both experiments; however, the $\Delta O_3/\Delta \text{EDTA}$ curves are very different. The difference is possibly due to a more rapid ozone decomposition at the higher ozone feed rate.

The disappearance of NO_2^- concentration and the appearance of CO_3^{2-} concentration is shown in Figure 3 for the pH ~ 13.8 experiment. The disappearance of NO_2^- seems to be a zero order reaction. It is probably controlled by the feed rate of ozone, i.e., the reaction is mass transfer controlled. This observation is in agreement with the known extremely rapid reaction of ozone with the nitrite ion. The rate constant is $k_{\text{NO}_2} = 0.168 \text{ mol/L-hr}^{-1}$.

The formation of carbonate appears to be a first order reaction as shown by Figure 4. The rate constant is $k = 0.097 \text{ hr}^{-1}$.

The disappearance of EDTA appears to be a pseudofirst order reaction as shown by Figure 5. There is a rate change after 2.5 hours for the pH ~ 13.8 reaction and after 2.75 hours for the pH ~ 14 reaction. These rate changes are frequently observed in ozone treatment reactions as indicated by the Ishizaki data in Figures 6 through 9 and Tables 2 and 3.

The explanation for the rate change during the ozone reactions is the initial more reactive compound is converted to less reactive aldehydes and acids after the first step of the ozone reaction. After the rate change, the ozonation of these compounds is observed. In a rate change of this type the second rate is slower.

The second reaction after the rate change is faster in our case. We believe that a very likely explanation for this observation is that the steady-state concentration of ozone (A_{ss}^O) is smaller during the first part of the reaction because the very rapid reaction of NO_2^- with ozone depletes the ozone concentration. Therefore, the pseudofirst order reaction of EDTA is slower before the rate change. Once most of the nitrite is consumed A_{ss}^O rises and the pseudofirst order reaction of EDTA will be more rapid.

FIGURE 3. The Concentration of NO_2^- and CO_3^{2-} During the pH ~ 13.8 Experiment.

FIGURE 4. Concentration of CO₃²⁻ During the pH ~13.8 Experiment.

FIGURE 5. EDTA versus Time at pH $\approx$ 14.

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FIGURE 6. COD Reduction by Ozonation of Diethylene Glycol. (Data of Ishizaki).

FIGURE 7. COD Reduction by Ozonation of Triethanolamine.

FIGURE 8. COD Reduction by Ozonation of Benzidine.
(Data of Ishizaki).

FIGURE 9. Oxidation Efficiency of Ozonation of Naphthol and Nitrobenzene.

TABLE 2. Ozone Utilization to Rate Change at pH ~9.

Compound	% Chemical Oxygen Demand (COD) Reduction at the Rate Change	O ₃ Utilized to Rate Change mg O ₃ /mg COD
Acetone cyanohydrin	50	3.8
Diethylene glycol	88	3.1
Triethanolamine	90	5.3
Phenol	92	1.6
Nitrobenzene	87	2.2
Dimethyl phthalate	78	2.7
α -Naphthol	89	1.7
Benzidine	77	2.6
N-nitroso-diphenylamine	87	2.2
Benzothiazole	95	1.8

TABLE 3. Rate Change in COD Reduction of Various Compounds^a.

Compound	pH	Apparent First Order Rate Constant $\times 10^2(\text{min}^{-1})$	% COD Reduction at the Rate Change
Acetone cyanohydrin	4	---	---
	7	0.9	50
	9	1.0	50
	11	1.6	60
Diethylene glycol	4	---	---
	7	1.3	85
	9	3.5	88
	11	4.2	89
Triethanolamine	4	1.8	70
	7	2.2	80
	9	4.2	90
	11	4.0	90
Phenol	4	3.8	87
	7	5.7	91
	9	6.7	92
	11	6.9	93
Nitrobenzene	4	2.9	80
	7	4.1	87
	9	5.2	87
	11	5.0	88
Dimethyl phthalate	4	2.0	50
	7	5.0	75
	9	4.8	78
	11	6.0	83
α -Naphthol	4	3.3	86
	7	3.7	85
	9	4.5	89
	11	4.5	89
Benzidine	4	3.2	77
	7	3.5	77
	9	3.3	77
	11	3.7	78
N-nitroso-diphenylamine	4	3.7	77
	7	4.5	76
	9	5.0	87
	11	5.5	85
Benzothiazole	4	3.0	70
	7	4.3	90
	9	4.8	95
	11	4.5	95

KINETICS

Ozone Input: A = ozone concentration in solution

A^* = concentration of dissolved ozone at interface in
equilibrium with ozone gas interface

$$\frac{dA}{dt} = k_L a (A^* - A)$$

Ozone Decomposition:

$$\frac{dA}{dt} = -k_d(A)$$

Ozone Reaction with NO_2^- :

$$\frac{dA}{dt} = -k_{\text{NO}_2} (A) (\text{NO}_2^-)$$

Change of Ozone with Time:

$$\frac{dA}{dt} = k_L a (A^* - A) - k_d (A) - k_{\text{NO}_2} (A) (\text{NO}_2^-)$$

At Steady-State:

$$(A)_{ss} = \frac{k_L a A^*}{k_L a + k_d + k_{\text{NO}_2} (\text{NO}_2^-)}$$

THE REACTION OF OZONE WITH EDTA

This reaction is believed to be a second-order reaction similar to the reaction of most organic compounds with ozone, e.g.,

$$- \frac{d \text{ EDTA}}{dt} = k \text{ EDTA (A) (EDTA)}$$

under steady state conditions:

$$\frac{dA}{dt} = 0 \text{ and the reaction becomes a pseudofirst order,}$$

$$- \frac{d \text{ EDTA}}{dt} = k' \text{ EDTA (EDTA)}$$

OZONE REQUIREMENT

The ozone is consumed by the decomposition reaction and by the reaction with oxidizables present. At pH ~14, the ozone decomposition is very rapid and produces hydroxyl radicals which, in turn, react with the EDTA.

If too much ozone is fed into the solution, the ozone decomposes near the interface and the EDTA does not have time to diffuse to the hydroxyl radical before it reacts with water and is unavailable. This leads us to believe that the excessive ozone feed is responsible for the much higher ozone requirement in the pH ~13.8 experiment.

CONCLUSION

A study of ozone mass transfer and reaction kinetics is necessary to optimize the reaction and to permit the design of a large-scale plant.

MASS TRANSFER OF OZONE INTO SYNTHETIC RESIDUAL LIQUOR

The residual liquor is an electrolyte solution that contains a number of dissolved complexed and uncomplexed organics. The solubility of ozone and the diffusion of the various reacting species are different from those observed in pure water.

Under the strongly alkaline condition of pH ~ 14 , the achievable ozone concentration, A_{ss}^0 , will be strongly affected by the decomposition rate along with solubility, i.e., Henry's Law constant.

The mass transfer parameters that affect A_{ss}^0 include the following:

- Gas-liquid interface (a')
- Reactor pressure (P)
- Gas flow to reactor volume ratio (G/V).

However, there is a limit to all these parameters beyond which their increase is ineffective. These limits for water in a batch reactor are as follows: $a' = 5 \text{ cm}^2/\text{cm}^3$, $P = 5 \text{ atm}$, and $G/V = 5 \times 10^{-7} \text{ g mol/cm}^3$.

The pH is known to have a powerful effect on A_{ss}^0 , severely limiting the achievable ozone concentration. The data available for water solutions only cover the range of pH = 7 to 11.

Increasing pressure does not necessarily lead to higher ozone concentration. Above 5 atm in water the ozone decomposition accelerates, limiting the value, A_{ss}^0 .

REACTORS

Two reactors might be considered for the ozonation of residual liquor, based on the experimental data already available under pH ~ 14 , $\sim 60^\circ\text{C}$ conditions. They are the stirred-batch reactor and the constant-flow, stirred-tank reactor. The latter one appears to be the most likely choice for a full-scale plant at this time.

The bubble column often used for large-scale ozonation cannot be used here due to the large estimated gas holdup, $\Sigma = 0.6$. (The gas holdup is the fractional volume of gas in the gas-liquid mixture.)

OZONE CONCENTRATION VERSUS TIME

It is possible to derive the expressions describing the ozone concentration in the two reactors of interest as follows:

Batch Reactor:

$$A = \frac{\frac{G}{V} m_o (1 - e^{-PRh})}{k_1 + \frac{G}{VP} H_e (1 - e^{-PRh})} \left[1 - e^{-\left(k_1 + \frac{GH}{VP} e (1 - e^{-PRh})\right)t} \right]$$

where

$$R = \frac{V}{Gh} \left(\frac{k_L k_G a'}{k_L + k_{GHe}} \right)$$

Constant Flow Reactor:

$$A^o = \frac{\frac{G}{V} m_o (1 - e^{-PRh})}{k_1 + \frac{G}{VP} H_e (1 - e^{-PRh}) + \frac{Q}{V}} \left[1 - e^{-\left(k_1 + \frac{G}{VP} H_e (1 - e^{-PRh}) + \frac{Q}{V}\right)t} \right]$$

Steady-State Ozone Concentration:

$$A_{ss}^o = \frac{\frac{G}{V} m_o (1 - e^{-PRh})}{k_1 + \frac{G}{VP} H_e (1 - e^{-PRh})}$$

EXPERIMENTAL MEASUREMENTS REQUIRED

In order to determine important parameters of mass transfer the following measurements and determinations have to be made in the two chosen reactors using a synthetic residual liquor that contains no materials oxidizable by ozone: First use the batch reactor:

1. Solubility of ozone as a function of time A.

Procedure: Charge the reactor with synthetic residual liquor free of oxidizable materials. Adjust pH and feed ozone into the reactor. Monitor the following: ozone concentration as a function of time; pH; pressure; agitator speed; liquid volume; gas volume; ozone concentration in and out. Maintain temperature at $\sim 60^{\circ}\text{C}$.

Variables: Vary ozone concentration in the range of 2, 3, and 4%, ozone flow in the range of $G/V = 10^{-5}$, 10^{-6} , and 10^{-7} g mol/cm³, the pH = 11, 13, and 14 and agitator speed, L = 1/3 maximum rpm, M = 2/3 maximum rpm, H = maximum rpm.

A set of experiments should be carried out at all three pH values as outlined below:

Run	pH	O ₃ %	G/V	RPM
1	11	2	10^{-5}	L
2	11	3	10^{-5}	L
3	11	4	10^{-5}	L
4	11	3	10^{-5}	M
5	11	3	10^{-5}	H
6	11	3	10^{-6}	M
7	11	3	10^{-7}	M

2. Determine the ozone decomposition rate by shutting off ozone feed to the reactor once maximum ozone solubility is achieved (usually after 30 minutes ozone addition) and record ozone concentration as a function of time.

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FIGURE 10. Agitated Absorber (after Reith, 1968).

3. The gas-liquid interfacial area, a' , can be estimated from established relationships between reactor dimensions and agitator size and speed (See Figure 7). A direct and preferred way is to determine the size and number of bubbles by a photographic method.
4. The liquid film conductance, k_L , can now be calculated using the above data and the equation above for, A , as a function of time for the chosen reactor.

The Henry's Law constant for ozone in pure water is,

$H_e = 67,680 \frac{\text{atm cm}^3}{\text{g mol}}$ at 20°C, as reported in the International Critical Tables.

There are methods available to estimate the effect of electrolytes on H_e when they are present in the solution.

The gas film conductance, k_G , is usually considered to be very large for ozone systems, i.e., the liquid film resistance is controlling. Therefore, the expression for R becomes:

$$R = \frac{V k_L a'}{Gh H_e}$$

CONCLUSION

With the above measurements and calculations, the mass transfer of ozone into the synthetic residual liquor will be well understood in the absence of the oxidation reaction. These data will be needed to study mass transfer in the presence of oxidation reactions.

OZONE MASS TRANSFER IN THE PRESENCE OF EDTA OXIDATION

The effect of chemical reactions on the mass transfer in general are discussed in the Appendix.

The oxidation of EDTA is a pseudofirst order reaction under the reaction conditions of interest here (pH ~14, ~60°C). For design purposes, it is important to know if the EDTA reaction affects the mass transfer. Such effect is usually measured in terms of the enhancement factor, E, which is the ratio of liquid film resistance in the presence and absence of reaction.

$$E = \frac{k_L}{k_L}$$

The enhancement factor may be measured experimentally by repeating the experiments outlined above in the presence of EDTA using the synthetic residual liquor.

The enhancement factor may also be estimated from Danckwerts' relationship if the pseudofirst order reaction rate, k, is known. In our case it is known.

$$E = \sqrt{1 + M},$$

where

$$M = \frac{D_{O_3} k}{k_L^2}$$

where

D_{O_3} - diffusivity coefficient

VERY SLOW REACTION

In the case of the very slow reaction the ozone diffuses into the solution and there is no reaction in the interface.

$$E = 1$$

$$\frac{D_{O_3} k'}{k_L^2} < < 1$$

Then the following equation applies:

$$\frac{dA}{dt} = k_L a (A_{ss}^0 - A)$$

SLOW REACTION

Slow reaction is when the reaction is slow but enough to maintain the ozone concentration, $A \sim 0$, in the bulk of the liquid. Then the following equation applies:

$$\frac{dA}{dt} = k_L a A^*$$

In this case E is slightly larger than one.

FAST REACTION

In the case of the fast reaction a significant fraction of ozone reacts in the liquid near the interface. If all the ozone reacts in the interface the following applies.

$$A = 0$$

$$E = (M)^{1/2} > 1$$

$$k_L a = (D_{O_3} k)^{1/2} a$$

In this case, the amount of ozone transferred into the solution is independent of k_L and is determined by the rate constant of the chemical reaction.

CONCLUSION

Therefore, it is very important to know the value of the efficiency factor E , for the optimization of the process parameters and the design of the reactor vessel.

The values of the following parameters can be measured directly:

k_L , k'_L , a' , k_d , A , A_{ss}^0 , k_{EDTA} , k'_{EDTA} .

The values of the following parameters may be estimated from literature, data, and correlations: a' , k_d , D_{O_3} , H_e .

LIST OF ABBREVIATIONS

- A - ozone concentration in the liquid g mol/cm³
- A^* = dissolved ozone concentration at the interface in equilibrium with ozone gas interface g mol/cm³.
- A_{ss} = steady state concentration of ozone in the liquid g mol/cm³.
- A_{ss}^0 = achievable ozone concentration in the absence of chemical reaction g mol/cm³.
- a' = gas liquid interface cm⁻¹.
- G = inert gas flow rate g mol/s.
- H_e = Henry's Law constant atm cm³/g mol.
- h = height of liquid from diffuser to top cm.
- m_O = mole fraction of ozone in the feed.
- k' = rate constant for ozone decomposition at a constant pH, s⁻¹.

k_L = liquid film mass transfer coefficient cm/s

k_G = gas phase mass transfer coefficient, g mol/cm²s atm

P = reactor operating pressure atm.

$$R = \frac{V}{Gh} \frac{k_L k_G a'}{k_L k_G H_e} \text{ atm}^{-1} \text{ cm}^{-1}$$

V = volume of reactor cm³

RECOMMENDATIONS

We recommend that the necessary experiments for mass transfer in the absence or presence of oxidizables be carried out first in the batch reactor. Then, test the model with a couple of experiments. Later, the results can be adapted for the constant-flow, stirred-tank reactor and the necessary additional experiments can be carried out. The outlined experiments may need to be adjusted or modified if experimental difficulties or other problems require it. In that case, contact Bollyky Associates.

DETERMINATION OF INTERFACIAL AREA

The primary parameters affecting the interfacial area in a stirred sparged reactor are:

- a - Reactor dimensions: reactor diameter
- b - Impeller type and dimensions: impeller diameter (d)
- c - Impeller speed: rpm = (N)
- d - Volumetric gas flow rate: Q
- e - Viscosity
- f - Surface tension
- g - Ionic strength
- h - Gas holdup.

Correlations are available between the interfacial area, the power consumption of the impeller, superficial gas velocity (μ), the velocity of rise of bubbles, and the surface tension. These correlations can be used to estimate the interfacial area; however, the simplest and probably the most reliable approach available is the one developed by Reith as shown in Figures 7 and 9.

The values of interfacial area obtained by estimating are only approximate. The composition of the liquid can change the interfacial area by a factor of 3 to 5. Therefore, to obtain reliable data for design and scale-up, the interfacial area should be measured in the actual reaction solution, or the synthetic residual liquor.

To measure the interfacial area directly by the photographic method follow the procedure of W. Varveclir, T. Reith, J. W. Van Hewen, and W. J. Beek, as published in the American Engineering Science, number 22, p. 1519-23 (1967).

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FIGURE 11. Interfacial Area in Agitated Absorbers (after Reith, 1968).

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FIGURE 12. Interfacial Area in Agitated Absorbers (after Reith, 1968).

APPENDIX

THE MASS TRANSFER OF OZONE INTO WATER - ENERGY
REQUIREMENTS STATE OF THE ART^a

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Ozone is normally produced in an electric discharge field type generator from air or oxygen on an industrial scale. (1) The output of ozone generators typically contains 1 to 3% ozone by weight when it is generated from air, and 2 to 5% when oxygen is used. The balance is air or oxygen depending on which of them was used as the feed gas.

The first question that emerges when ozone is used for the treatment of water or wastewater is how to transfer into the water all the ozone from this dilute gas mixture. An added problem to deal with is the relatively low solubility of ozone in water. The solubility is 2.5 to 4.0 mg/L under conditions normally encountered in water and wastewater treatment.

Secondly, the ozone treatment of water and wastewater is a relatively energy intensive process. As a part of that process some of the mass transfer devices themselves may consume significant amounts of energy.

The objective of this paper, is to assess the present state of ozone mass transfer technology and to critically compare the available ozone contactors in terms of efficiency, energy consumptions and utility.

^aPresented at the Symposium on Advanced Technology of the International Ozone Institute, Toronto, Canada, November 16-18, 1977.

THE MASS TRANSFER PROCESS

The basic engineering study of ozone mass transfer was neglected in the past (2). This field has suffered for a long time from two problems:

- The basic mass transfer properties of ozone from gas to water have not yet been determined for many contacting devices.
- Much of the available data combined mass transfer properties and reaction kinetics into one overall rate constant.

This latter approach seriously complicates the use of the data for the following purposes:

- The comparison of different mass transfer devices.
- Carrying out mass transfer calculations.
- Calculating mass transfer in combination with other reactions.

Recently, mass transfer measurements have been made on a few ozone mass transfer devices (3,4,5,8). They shall be discussed in this report in some detail.

The mathematical model that describes the mass transfer process of ozone from air or oxygen into the water is analogous to heat transfer or conduction of electric charge through resistances. The flux equations used are analogous to Ohm's Law, and the ratio of the potential or driving force to the flux represents a resistance.

The resistances on the two sides of the interface are additive. The two-film (double resistance) theory of mass transfer (6) expresses the rate of mass transfer as: N_A (lb. mole/hr) or flux of ozone gas "A" through a unit area of interface "a" in terms of Equations 1 and 2.

$$N_A = k_G a (Y_{A,G} - Y_{A,I}) \quad \text{E. -1}$$

$$N_A = k_L a (C_{A,I} - C_{A,L}) \quad \text{E. -2}$$

where $k_G a$ and $k_L a$ are the mass transfer coefficients for a unit area or resistances in the gas and in the liquid phases respectively. $Y_{A,G}$ and $Y_{A,I}$ represent the mole fractions of A in the gas phase, and at the gas side of the two film interface, whereas $C_{A,I}$ and $C_{A,L}$ are concentrations of A in the liquid side of the interface and in the bulk liquid.

The above equations are usually rewritten as E. -3 and -4 because of the difficulty of measuring interfacial concentrations.

$$N_A = k_G a (Y_{A,G} - Y_A^*) \quad \text{E. -3}$$

$$N_A = k_L a (C_A^* - C_{A,L}) \quad \text{E. -4}$$

where $K_G a$ and $K_L a$ are overall transfer coefficients based on their respective phases, Y_A^* is the gaseous mole fraction of A which is in equilibrium with the concentration of A in the bulk of the liquid, and C_A^* is the concentration of A in the liquid in equilibrium with the gaseous mole fraction of A in the bulk of the gas. Both Y_A^* and C_A^* can be calculated from equilibrium relationships.

The values of $K_G a$ and $K_L a$ have practical importance for the purposes of calculations and designs. In a system where Henry's Law holds $K_L a$ and $K_G a$ are related as:

$$K_L a = H K_G a \quad \text{E. -5}$$

Where H is the Henry's Law constant.

If a gas is highly soluble, H will be small and the liquid side resistance is negligible and the transfer is largely vapor phase controlled e.g. carbon dioxide $H = 1,420$ atm/liquid mole fraction at 20°C . If the gas is sparingly soluble, H will be large and the gas phase resistance is negligible and the transfer is largely liquid phase controlled e.g. oxygen $H = 40, 100$ atm/liquid mole fraction at 20°C . The $H = 3,760$ atm/ liquid mole fraction for ozone at 20°C lies in between (4). It is not known which interface controls or to what extent each contributes.

It is important to point out that E. -5 becomes invalid when,
 (1) additional resistance to mass transfer is introduced e.g. surfactants at the interphase, (2) ripples or interfacial turbulence which could change the single phase mass transfer constant values (3) the occurrence of chemical reaction near the phase boundary not present when the individual constants were measured.

Very few K_{Ga} or $K_L a$ values have been reported in the literature for ozone. The value of K_{Ga} was reported by Richard and Fleishman for static mixers (4). For a 21 element 1/4 in. diameter, Kenics Mixer K_{Ga} ranges from 148 to 643 mg/min (mole fraction) over a range of liquid and gas flow rates from 0.5 to 1.9 liters/min. The mass transfer coefficients can be correlated to the flow parameters of the mixer as follows:

$$K_{Ga} = 0.0264 \phi (Re/(1+1.22\phi))^{1.358} \quad E. -6$$

where

$$\begin{aligned} \phi &= \text{volume fraction of the dispersed phase} \\ Re &= \text{Reynolds number} \end{aligned}$$

Equation 6 allows the calculation of K_{Ga} values for any condition of a 21 element Kenics mixer 1/4 in. diameter provided the mixer chamber pressure is known for the flow rates considered.(4)

The ozone mass transfer coefficient $K_L a^*$ was also determined for agitated reactors (8). It is shown in Table A1.

A mathematical model was developed for an agitated batch reactor with ozone diffusion (5). The achievable ozone concentration (A_{ss}^0) was found to be dependent on interfacial area (a) reactor pressure (P) and a ratio of gas flow to reactor volume (G/V) as shown by E. -7.

$$A_{ss}^0 = \frac{\frac{G}{V} M_o (1 - e^{-PRh})}{K_1 + \frac{GH}{VP} (1 - e^{-PRh})} \quad E. -7$$

TABLE A-1. Ozone Mass Transfer Coefficients.

Contactor	$K_G a$	$K_L a$
Bubble Column		$7.1 \frac{\text{lb mol}}{\text{ft}^2 \text{ hr}}$
Stirred Reactor		$1.43 \frac{\text{lb mol}}{\text{ft}^3 \text{ min}}$
Stationary Mixer	148-643	
Kenics (1/4 in., 21 Elem.)	$\frac{\text{mg}}{\text{min mol fraction}}$	

Where

G = inert gas flow rate (g mol/s)

V = volume of reactor (cm^3)

M_0 = mole fraction of ozone in the inert gas feed

P = reactor pressure (atm)

$$R = \frac{V}{Gh} \frac{K_L K_G a^1}{K_L + K_G H} \quad (\text{atm}^{-1} \text{ cm}^{-1})$$

h = height of water above the diffuser (cm)

K_1 = first order rate constant for ozone decomposition (s^{-1})

H = Henry's Law constant ($\text{atm cm}^3 / \text{g mol}$)

K_L = liquid film mass transfer coefficient (cm/s)

K_G = gas phase mass transfer coefficient ($\text{g mol/cm}^2 \text{ sec atm}$)

The liquid film conductance was determined as $K_L = 0.0142 \text{ cm/sec}$. Under alkaline conditions pH=9 and above the A_{ss}^0 is less than the equilibrium ozone concentration predicted by Henry's Law due to rapid ozone decomposition. At pH=9, the value of K_1 is 0.43 s^{-1} .

The value of A_{ss}^0 is strongly dependent on pressure in the range of 1 to 3 atm even at alkaline pH-s as indicated by Figure A-1. Above 9 atm the pressure affects A_{ss}^0 only slightly. The effect of interfacial area (a) on A_{ss}^0 is shown in Figure A-2. As the data indicates, the value of A_{ss}^0 is strongly dependent on a' in the range of $a' = 0$ to 1.0 cm^{-1} but has little effect above $a' = 5.0 \text{ cm}^{-1}$. The effect of gas flow to reactor volume G/V is shown in Figure A-3. The data indicates that above the value of $G/V = 4.65 \times 10^{-4} \text{ mol/sec cm}^{-3}$, G/V has little effect on A_{ss}^0 .

These trends should also be indicative for unagitated bubble column, continuous flow, diffusion-type ozone contactors normally used in large scale ozone treatment systems.

The mass transfer of ozone was measured in a 4 ft high counter-current bubble column by Hill and Spencer (3). They determined the overall mass transfer coefficient as $K_L = 7.1 \text{ lb/mol/hr} \times \text{ft}^2$. The liquid was found to be sufficiently agitated to have uniform bulk concentration.

The measured mass transfer coefficients in bubble column and in other devices are listed in Table A1.

The mass transfer coefficients in bubble column, followed Hughmark's proposed correlation fairly well (7), E. -8.

$$N_{sh} = 2 + 0.0187 \left[(N_{Re})^{0.484} (N_{Sc})^{0.339} \frac{(Dp \cdot g)^{1/3}}{D^{2/3}} \right]^{0.072} \quad 1.61$$

E. -8

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FIGURE A-1. Effect of Pressure on the Steady State Ozone Concentration.

FIGURE A-2. Effect of pH and Interfacial Area on the Steady State Ozone Concentration in a Batch Reactor.

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FIGURE A-3. The Effect of G/V on the Steady State Ozone Concentration.

where the velocity in the Reynolds number is represented by the slip velocity between the bubbles and the liquid and where:

- N_{Sh} = Sherwood number
- N_{Re} = Reynolds number
- N_{Sc} = Schmidt number
- D_p = bubble diameter (ft)
- g = gravitational force (ft/hr²)
- D = diffusivity (ft²/hr)
- U_s = slip velocity (ft²/hr)
- V = kinematic viscosity (ft²/hr)
- E = fractional gas hold up
- L = liquid height when bubbling (in.)
- L_o = liquid height when not bubbling (in.)
- V_{sg} = superficial gas velocity (ft/sec)
- V_{sl} = superficial liquid velocity (ft/sec)
- $\bar{\rho}$ = average liquid density
- $\bar{m}$ = average liquid molecular weight

MASS TRANSFER AND SIMULTANEOUS CHEMICAL REACTION

In many practical applications of ozone for water and wastewater treatment, the mass transfer of ozone occurs simultaneously with a chemical reaction. The reaction may effect the solubility of ozone, and in addition, the rate of solution may increase if the reaction is fast enough to compete with diffusion in the region near the interface.

The chemical reaction may be a kinetically first order reaction in dissolved ozone or a second order reaction involving dissolved ozone and another chemical present in the liquid phase. This chemical must diffuse to the interface to meet and react with the arriving ozone molecule. The effect of the reaction on the mass transfer can be very different in these two cases.

The mass transfer in the presence of a simultaneous chemical reaction may not even be proportional to the driving force especially in the case of bi-molecular reactions (6). A fast chemical reaction such as the reaction of ozone with phenol and certain cyanides may increase the

mass transfer rate if the reaction occurs near the interface. The rate of mass transfer may be proportional to the interface and not to the total liquid volume.

Assuming an irreversible first order reaction of ozone, represented by "A", the total rate of solution (R), is expressed by E. -9 and the relative rate of solution (r) by E. -10.

$$R = K_L a V (C_1 - C) = \frac{K_L^0 a \theta \phi (1 + K_I \theta)}{1 + K_I \theta + K_L^0 a \theta \phi} \quad \text{E. -9}$$

$$\frac{1}{r} = \frac{QC_i}{R} = \frac{LC_i}{R} = \frac{1}{K_L^0 a \theta \phi} + \frac{1}{1 + K_I \theta} \quad \text{E. -10}$$

Where

Q = water volumetric rate (cm³/s)

C = concentration ozone in water (mol/cm³)

C_i = C at the interface

V = volume of water in the tank (cm³)

$$\theta = \frac{K_L}{K_L^0}$$

K_L⁰ = coefficient of purely physical mass transfer

s = density of water lb/ft³

$$\phi = \frac{V}{Q}$$

K_I = first order reaction rate constant

L = mass velocity of water

R = rate of absorption of gas (g mol/s)

ρ = density of fluid

The two terms on the right hand side of E. -10 can be considered as resistances to interfacial mass transfer and to chemical reaction rate respectively.

The effect of reactivity (K_I) on the rate of gas absorption in an agitated reactor is shown in Figure A-4.

For irreversible bi-molecular reactions where a gas A, such as ozone reacts with a nonvolatile reagent B, present in the water, the reaction rate (R_{II}) may be represented by E. -12.

$$R_{II} = k_{II} C_A C_B \quad \text{E. -12}$$

The concentration distribution near the interface is shown by Figure 5. Assuming that the initial concentration of B, designated as B_0 is large compared to the concentration of A at the interface (C_{Ai}), then we may write E-13 for the mass transfer coefficient as:

$$K_{LA} = (D_A k_{II} B_0 t)^{1/2} \quad \text{E. -13}$$

When the reaction rate constant k_{II} is large, that is where the reaction is fast. The rate of absorption depends on two concentrations, and is given by E-14.

$$N_A = r^{1/2} (C_{Ai} + \frac{r}{Y} B_0) k_L^0 \quad \text{E. -14}$$

In this case, unlike the first order reaction case, the rate is not proportional to the concentration of A, the gas being absorbed. In fact, C_{Ai} may be nearly zero and the mass transfer rate will be largely due to the effect of B_0 .

The above considerations clearly illustrate the powerful effect of chemical reactions and their rate on mass transfer. Thus, the true understanding of the ozone treatment when simultaneous reactions are involved, means that mass transfer and reaction kinetics must be understood separately. Ultimately, the reaction kinetics (chemical reactivity), is dependent on the structure of the chemical which determines the mechanism and rate of the reaction.

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FIGURE A-4. Effect of Reactivity on Rate of Gas Absorption in Stirred-Tank Reactor.

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FIGURE A-5. Effect of Irreversible Reaction.

REACTION MECHANISM

Ozone is a very powerful oxidizing agent, and is strongly electrophilic. Only fluorine and some transient species such as free radicals and radical ions have higher oxidation potentials.

The reactions of ozone with organic compounds fall into four major groups as follows:

1. The reaction with organic compounds containing double bonds (Olefins) involves the formation of a pi complex between ozone and the olefin which either proceeds into 1, 3 dipolar cyclo-addition and ozonolysis products or forms a sigma complex which loses oxygen to produce an epoxide (9). Steric hindrance favors epoxide formation. Diperoxides and polymeric peroxide may also form. See Figure A-6 (10). The reaction solvent has an important bearing on the final product as shown by Figure A-7. A commercially very important reaction of ozone of this type is the conversion of oleic acid into pelargonic acid and azealic acid as shown in Figure A-8. Some of the other olefin reactions are shown in Figure A-9.
2. The reaction with nucleophiles is fast and produces their oxides as shown in Figure A-10. The compounds of this group frequently encountered in water treatment include cyanide, hydrogen sulfide, mercaptans, and other nitrogen, sulfur, and phosphorous compounds.
3. The reaction with aromatic compounds such as benzene, fragments the ring structure as shown in Figure A-11. A much studied reaction is the oxidation of phenol (11). The reaction proceeds through several intermediates as shown in Figure A-12. The disappearance of phenol and the formation of intermediates is shown as a function of reaction time in Figure A-13.

FIGURE A-6. Mechanism of Ozone-Olefin Reactions.

FIGURE A-7. Reaction of Zwitterion With Participating Solvents.

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FIGURE A-8. Ozonolysis of Oleic Acid.

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FIGURE A-9. Ozonolysis of Cyclic Olefins.

Figure A-10. Ozonation of Nucleophiles.

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FIGURE A-11. Ozonolysis of Benzene.

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FIGURE A-12. Ozonolysis of Phenol in Water.

FIGURE A-13. Variations of all Intermediates as a Function of Time (compounds are given as percentages of TOC).

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FIGURE A-14. TOC Removal as a Function of the Ozone Dosage.

TABLE A-2. Contactor Requirements of Major Ozone Applications.

Application	Water Flow	Special Requirements	Contact Time	Ozone Dosage (mg/L)	Recommended Contactors
Wastewater Disinfection, Municipal	1-200 MGD	Plug flow min reaction with organics	5 min contact and 10 min holding	3-8	Multi-stage in-ground covered diffusion type contactor
Potable Water Treatment, Municipal	1-200 MGD	Plug flow	10 min contact	1-3.5	Multi-stage inground covered diffusion type contactor
Industrial Wastewater Treatment, Mass Transfer Controlled, e.g. cyanides, phenol	0.05-5 MGD	Efficient mass transfer	5-15 min or as required	15-100	Diffusion type contactor, position pressure injector or venturi ejector agitated reactors
Industrial Wastewater Treatment, Reaction Rate Controlled e.g. COD removal	0.05-5 MGD	Sufficient reaction time	15-60 min as required	15-100	Diffusion type contactor
Industrial Process Water Treatment	0.02-5 MGD	Depends on objectives of treatment	5-15 min	1-20	Diffusion type contactor

TABLE A-3. Contactor Characteristics.

Contactor	Recommended Applications	Operating Flexibility		Operating Pressure	
		Water Flow	Ozone Flow	Water	Ozone
Bubble Column	General Purpose, Large Flows	0-100%	10-100%	None	6-12 psig
Positive Pressure Injector	Disinfection	80-100%	10-100%	6-12 psig	8-14 psig
Venturi Ejectors	Low Pressure Ozone	85-100%	10-100%	5-12 psig	None
Stationary Mixers	Specialty, Small Flows	80-100%	10-100%	6-20 psig	8-22 psig
Stirred Reactors	Specialty, Small Flows	0-100%	10-100%	None	2-5 psig

The total organic carbon removal is shown in Figure A14 as the function of ozone dosage. Note the amount of ozone necessary for complete oxidation to carbon dioxide.

4. The reaction with aliphatic alcohols, acids and hydrocarbons is relatively slow, but it becomes substantially faster in the presence of u.v. light as indicated in Figures A15, A16 (12).

The hydroxyl radical produced by the decomposition of ozone is believed to be the key oxidant in these reactions as well as in most reactions of ozone with refractory organics in water (13). The formation of hydroxyl radical is shown in Figure A17.

OZONE CONTACTORS

Most of the gas-liquid contactors have been considered for ozone treatment as indicated by several recent reviews of the subject (14, 15, 16, 17 and 18). The type of ozone application determines the requirements placed on the ozone contactor. The most frequently used device is the bubble column or some variation of it. It is also called a diffusion contactor, sparged tank or water column.

The general requirement for a contactor include:

- Low cost.
- Minimum energy consumption.
- Minimum attention by operator, automatic operation, 1- maintenance.
- Efficient mass transfer.
- Simple design, preferably no moving parts, nothing to clog.
- Flexibility to allow the variation of operating parameters.

Each ozone application has its own specific requirement as outlined in Table 2. In addition, the magnitude of flow and space available has an important bearing on the choice of contactor.

The various contacting devices and their characteristics are summarized in Table 3 and discussed in some detail in this report.

FIGURE A-15. Ozonation of 2-Propanol.

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FIGURE A-16. UV-Ozonation of 2-Propanol.

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FIGURE A-17. The Decomposition of Ozone in Water.

COUNTER CURRENT SPARGED COLUMN

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FIGURE A-18, Ozone Contact Chamber for Large Flows of Water.

BUBBLE COLUMN

The ozone is diffused into the water at the bottom of the 10 to 18 ft water column under the hydrostatic pressure of the water. There, the ozone is dispersed into fine bubbles with diameters less than 1/4 in. by means of ceramic diffusers (20 to 60 permeability), cindered stainless steel tubes (10 to 25 ft micron pore size), or porous ozone resistant, plastic tubes. The bubbles rise to the surface with the approximate velocity of 20 to 25 cm/sec. The placement of diffusers is important for the even distribution of bubbles and for maintaining plug flow conditions.

In a single column design, the water may pass cocurrent or counter-current to the bubbles. The latter is shown in Figure A-18. A typical mass transfer curve for both cases is shown in Figure A-19. The single column design is suitable to treat small flows approximately 1 million gallons per day (MGD) or less.

For large flows, 2 to 20 MGD, the contactor is divided into several chambers to maintain plug flow conditions. Several of these multi-chamber contactors may be used to treat flows up to several hundred MGDs.

These large multi-chamber contactors may have a single counter-current chamber (Chamber 2, Figure A-18) or two, three counter and cocurrent flow chambers for the first introduction of ozone. The main treatment occurs here. These chambers are usually operated to provide a 0.4 mg/L ozone residual or slightly more and maintain this residual for 7 minutes in an average water treatment plant. This residual and contact time is believed to be sufficient to kill essentially all viruses (19) and to achieve most other treatment objectives. However, the ozone dosage, residual and contact time should be designed to meet the treatment objectives at hand.

The off-gas from chamber 2 is normally reintroduced to the incoming water upstream either by a blower diffuser combination or a blower turbine agitator combination in Chamber 1. The objective here is make use of all the ozone generated and to remove most of the ozone from the off gas before it is discharged through the vent. The final off gas still may

FIGURE A-19. Counter-Current Ozone Transfer.

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FIGURE A-20. Parallel-Current Ozone Transfer.

may have to be treated for the complete removal of ozone. The catalytic type ozone decomposers are recommended for this purpose to conserve energy. The 4 to 50 ppm of ozone normally present can effectively be removed by a combination of catalyst and mildly elevated temperature (120° to 160°F).

The final chamber (Chamber 3, Figure A-18) or some other means should be provided to remove entrained bubbles especially if additional water treatment steps follow where air bubbles can interfere.

This bubble column diffusion system uses minimum energy and offers maximum flexibility for the treatment of large flows of water. It is a versatile, efficient, all purpose contactor for large or small flows. It should be considered first for any application of ozone.

A special design of the bubble column contactor is the Torricelli contactor. See Figure A-20. The contactor is operated under the hydrostatic pressure of two water columns to promote mass transfer. Its use is justified when space or other limitations prevent the use of atmospheric bubble columns.

STIRRED TANK CONTACTOR

The mechanically agitated reactors (Figure A-21) have been studied in great detail for chemical processing applications.(8) They have also been shown to be effective as ozone contactors (7,20) and have been used successfully for laboratory and pilot plant scale specialty ozone applications (21).

Although the stirred tank contactors are effective and flexible ozone contactors, they are not recommended for most ozone applications due to the relatively high energy required for the agitator. However, they might be used to an advantage in small specialized applications when agitation is required for an independent reason such as bringing the solution in the proximity of a light source.

Mechanical agitation may also be used in combination with bubble column, venturi ejector or other gas injection devices.

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FIGURE A-21. Toricelli Contactor
for Ozonation.

FIGURE A-22. Stirred Tank Reactor.

VENTURI EJECTORS

These contactors were used frequently in combination with the large, flat plate type ozone generators which could only operate at atmospheric or close to atmospheric pressures. The water moving under gravity or pump pressure acts as an aspirator sucking the ozone into the water.

Additional mixing was often provided by a turbine mixer for large scale installations as shown in Figure A22.

The gas to liquid ratio is relatively small limiting the ozone dosage per each pass through the ejector. This problem may be resolved by using several contactors in series. (22) This approach however, requires the repumping of the water each time, as shown in Figure A23.

Although ejectors or eductors are reliable and effective ozone contactors, they are energy intensive and have limited ozone water operating range.

Their use in combination with modern pressurized ozone generators cannot be justified for most applications.

POSITIVE PRESSURE INJECTOR

The positive pressure injectors, as their name implies, operate by the injection of ozone under pressure into a stream of water. The ozone pressure must exceed the water pressure, which is in the range of 6 to 12 psig. The mixing of gas and water occurs at a turbulent zone at the point of ozone introduction. The turbulence is generated by the pressure of the water. Then the mixed flow is passed through a baffled chamber to provide sufficient contact time as indicated by Figure A24.

The disinfection of treated wastewater effluents was considered a special application for positive pressure injectors (23,17). The objective of this treatment is to disinfect with minimum ozone dosage, that is to avoid as far as possible the competing side reactions, the oxidation of refractory organics present in the water. This system was used successfully in several pilot plant studies (23) and a 6 MGD plant is currently under construction at Meander, Ohio.

FIGURE A-23. Otto Type Aspirator/Injector.

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FIGURE A-24. Blue Plains Tertiary Treatment Pilot Plant.

FIGURE A-25. Positive Pressure Injector.

The positive pressure injectors require the repumping of the water unless it is already pressurized for another reason. The repumping represents a significant energy expenditure. Other less energy intensive systems such as the bubble column, have proven to be equally effective (24). The application of the positive pressure injector should only be considered when the water is available under pressure.

There is insufficient information available on plant scale experiences operating parameters, and scaling up the system for large flows. The use of several injectors in a series might be necessary for flows above 1 MGD.

MISCELLANEOUS OTHER CONTACTORS

Static mixers, such as the Kenics mixer (Figure A-25) have been used successfully to dissolve ozone in water (6,18). These devices divide the ozone bubble carried by a stream of water repeatedly into smaller bubbles thereby enlarging the surface area available for mass transfer. The number of the mixer elements used will have a strong effect on the final bubble size. These static mixer devices are suitable for the introduction of small dosages of ozone and only provide for very short contact times. They might be considered for special applications such as the disinfection of water with very low ozone demand and uniform flow.

Spray towers and spray scrubbers (see Figure A-26), have been considered for cyanide treatment by ozone (25). This type of ozone contacting is suitable for the treatment of wastewater containing highly reactive contaminants. However, they have not found wide application due to their relatively large size and large energy requirement for repumping of the water.

There are other contact chambers as shown on Figure A-27, which are either modifications or hybrids of the two to three designs mentioned above. They have not been studied in detail nor have they been used in many installations. A pilot unit of the total injector shown by Figure A28, was studied in some detail (14). This variation of the bubble column was found to be an efficient but inflexible mass transfer device. The variation of water flow seriously affected its operation.

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FIGURE A-26. Possible Use of Spray Towers and/or Cyclonic Scrubbers for the Removal of Reactive Contaminants From Wastewater.

FIGURE A-27. Schematic Flow Diagram for Surface Agitators.

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FIGURE A-28. Pilot Constriction of the Total Injector System for Ozone Dispersing of Water.

ENERGY REQUIREMENT OF OZONE CONTACTORS

Ozone treatment is a relatively energy intensive process. A significant portion of the energy consumption is used for the operation of the ozone contactor and for the additional amount of ozone necessary due to the less than 100% mass transfer. The capital cost and operating cost, that is the energy requirement, of ozone contactors, is shown in Table A-4 in terms of percent of the total ozone system.

TABLE A-4. Ozone Contactor Cost.

	% of Ozone System
Capital cost	10 - 20%
Operating cost	5 - 20%

The operating energy and overall energy requirements of various ozone contactors is shown in Table A-5. The data indicates that the bubble column contactor is the most energy efficient device. The use of the other contactors can only be justified if the necessary water pressure is available on the account of a preceding process, or when space or special process considerations render the additional energy expenditures necessary.

TABLE A-5. Energy Requirement of Ozone Contactors.

Contactor	Mass Transfer Efficiency	Operating Energy Required Per MG (kWh)	Overall Energy Per MG (kWh)
Bubble Column	80-95% single pass	0-50	14-95
	90% double pass	25-75	28-78
Positive Pressure Injector	80-95%	0-153	14-208
Venturi Ejectors	40-85%	0-103	41-265
Stationary Mixer	40-90%	0-300	28-365
Stirred Reactor	70-90%	500	528

The operating energy may be provided by the pressure of ozone gas for the bubble column or by the water pressure for positive pressure injector, venturi and stationary mixer, and by the electrical power for the agitator of the stirred reactor. The ozone may be available under pressure because of the operating characteristics of the ozone generating equipment and no additional energy is necessary for the contactor. Similarly, the water may also be available under pressure.

The overall energy requirement includes the operating energy and ozone loss of the off gas. These data are based on 3 mg/L ozone dosage, and 1% ozone generated from air and a 24 hr/day operation.

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