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Ozonation at the Stander Water Reclamation Plant

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Abstract

The results achieved by ozonation at the Stander Water Reclamation Plant, Pretoria, are discussed. A packed column together with an injector mixing device gave ozone utilization levels higher than 95 % at dosages of about 10 mg/dm³. Redistribution plates in the packing proved necessary to prevent poor adsorption due to backmixing in the gas phase. Disinfection is satisfactory if total oxidant residuals can be maintained at more than 0,2 mg/dm³ for 15 min. The results indicated that ozonation also lowered the chemical oxygen demand and total organic carbon concentration in the water. In spite of the fact that it appears to be necessary to always supplement ozone with other disinfectants, ozone leads to a reduction in water reclamation cost by extending the useful life of the activated carbon unit process.

Introduction

Among the various pollutants in wastewater, bacteria, viruses and other micro-organisms are potentially the most harmful. A single pathogenic virus is sufficient to start a disease in man, as it is capable of rapid multiplication. Conventional secondary treatment does not make wastewater safe from a microbiological point of view.

As advanced wastewater treatment is usually practised to protect the environment it is necessary to inactivate micro-organisms. For most direct reuse applications, it is necessary to also inactivate pathogens, but for the production of potable water it is imperative to inactivate all pathogens and to reduce the total plate count to below 100 per cm³ (Grabow & Isaacs, 1978).

These aims can only be achieved in a well designed and properly operated disinfection unit process. Clarification, particularly at high pH, also leads to a high reduction in bacterial counts, but cannot be relied upon for effective disinfection. Advanced treatment is a costly operation, therefore disinfection of the reclaimed water must be integrated in the process in such a way that the consumption of chemicals is minimized and control is simple but effective.

In conventional drinking water treatment there are various options for disinfection (Van Leeuwen, 1978a). Chlorination and ozonation are the most popular methods with ultraviolet irradiation and the use of certain oxidants like bromine, iodine, peroxides, permanganates and chlorine dioxide lagging behind. In advanced wastewater treatment, chlorination and ozonation are about the only disinfection unit processes employed (Van Leeuwen, 1978a), although chlorine dioxide also shows promise.

Usually the main application of ozone in water and wastewater treatment is for disinfection purposes. Owing to the fact

that ozone is such a powerful oxidant, many oxidation reactions take place parallel to the disinfection process. The more substances in water that can be oxidized by ozone, the higher the ozone demand, therefore more ozone is required for disinfection. At the same time the chemical oxygen demand (COD) and total organic carbon (TOC) concentration are lowered and the oxidation of organic substances may become an important secondary function or even a primary function of ozonation.

Ozonation is uneconomical for the removal of large concentrations or large fractions of organic substances encountered in wastewater. Chian, Smith and De Walle (1975) found that an ozone resistant fraction develops after 60 to 80 % TOC removal. For more efficient removal of organic material and lowering of chemical oxygen demand, other unit operations are required. Process design can be adapted to accommodate one of two possible additional units that can operate during ozonation. Ozonation products in water are often polar and these products can lead to the formation of microflocs which can be removed by filtration or flotation. Wachs, Narkis, Schneider and Wasserstrom (1978) described a laboratory reactor in which surface active substances can be removed by foam separation during ozonation. Ozonation can also promote biodegradability of dissolved organic matter which can subsequently be removed biologically on filters or active carbon beds (Wachs *et al.*, 1978; Nebel and Stuber, 1975; Nebel *et al.*, 1973; Melnyk and Netzer, 1975; Gilbert, 1975; and Eberhardt *et al.*, 1974).

This paper deals with the results achieved by ozonation at the Stander Water Reclamation Plant, Pretoria (Prinsloo *et al.*, (1978)). The main aspects that will be discussed are disinfection, interaction with active carbon and the effect on reclamation costs.

Description of Ozonation System

Ozone Production

Ozone is produced *in situ* at the Stander Water Reclamation Plant in a Degremont MB 110 ozone generator with a maximum production rate of 2 kg ozone per hour from air. This production rate is sufficient to introduce 10 mg ozone per dm³ of water at the nominal flow rate of 4 500 m³/d and a utilization efficiency of 95 %. With a water flow rate of 3 500 m³/d, it is possible to dose 12,5 mg/dm³ at a reduced efficiency of 91 %. The ozone generator can operate safely at 85 % of its nominal capacity so that the ozone dosage is limited to 8,5 mg/dm³ at 4 500 m³/d or 10,5 mg/dm³ at 3 500 m³/d.

Ozone Absorption

The ozone absorption system at the Stander plant consists of a packed column (with redistributors) placed on top of a baffled

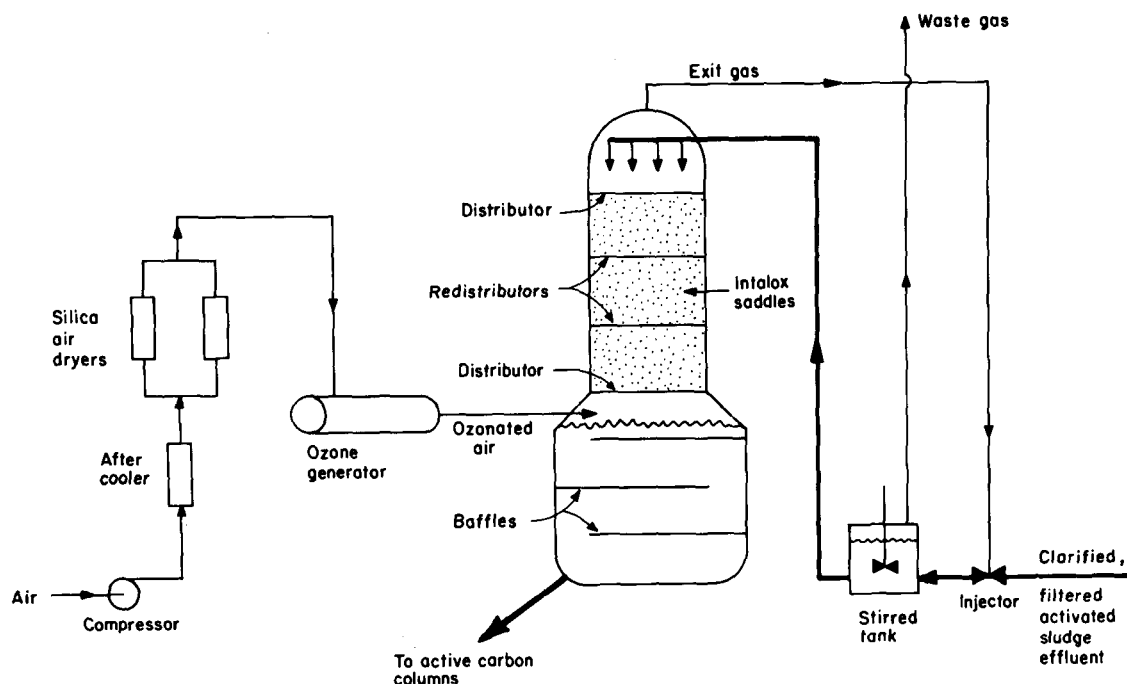


Figure 1
Ozonation process unit at the Stander Water Reclamation Plant

reactor and a prestage contacting system in which the exit gas from the column is contacted with water prior to the packed column (See Fig. 1). Additional contacting and phase separation are achieved in a small stirred vessel from which the waste gas is discharged to the atmosphere and the water pumped to the top of the packed column.

Ozonation Control

The specification of an adequate residual for ozonation control proved to be a difficult assignment. The question arose whether the primary function of ozonation was disinfection or the removal of dissolved pollutants. It has been proved by amongst others, Boucher *et al.* (1968) and Roan *et al.* (1973) that disinfection ability can be linked to ozone residual, but the difficulty in differentiating between ozone and its oxidative derivatives in the ozonated water poses a problem in correlating disinfection results with measured residuals. Ozone concentrations can be determined from the strong absorption of ultraviolet radiation at 254 nm by the ozone molecule. Methods based on a colour development also measure other less powerful oxidants present in the water.

It was found on the Stander plant that ozone residuals could not be directly measured by ultraviolet absorption. The main reason for this was some substance in the water which ab-

sorbed the irradiation more strongly than ozone, but which was itself affected by ozone so that its effect diminished gradually throughout the ozonation process. As it was not possible to measure this background effect, it was also not possible to correlate UV absorption to ozone concentration.

Oxidants were measured on the Stander plant by an iodometric procedure. For accuracy, buffered N,N-diethyl-p-phenylenediamine (DPD) (Palin, 1967) was used as an indicator, while backtitration was effected with a standard ferrous ammonium sulphate solution. Weaker oxidants, like chloramines and peroxides, were also measured by this method. The method developed by Masschelein and Fransolet (1977) to measure ozone in the presence of other oxidants (e.g. chlorine) using acid chrome violet K (ACVK) as an indicator, was also used on the Stander plant. It could be shown that this determination was not affected by chlorine or chloramines, but it was not certain whether it was influenced by other (weaker) oxidants formed as intermediate reaction products from ozone with other dissolved products in water. The correlation of this method with the iodometric method was reasonable. As the iodometric method is simpler for plant control, it remained the most suitable analytical tool.

Ozone concentration in air was measured by absorbing the ozone from a measured sample of air in a potassium iodide solution and then measuring the amount of iodine formed by

titrating with a standard sodium thiosulphate solution (APHA, 1971). In the water phase, total oxidant concentration was measured by developing a colour with DPD after addition of potassium iodide and a buffer solution. The coloured DPD was then backtitrated with a standard ferrous ammonium sulphate solution (Palin, 1967).

The chemical oxygen demand, ammonia, nitrate and total Kjeldahl nitrogen analyses were performed by autoanalytic methods. Total organic carbon was measured on a Beckman carbon analyser (Van Steenderen, 1976).

Operational Results of Ozonation Unit Process

Mass Transfer and Ozone Demand

The efficiency of the mass transfer equipment proved to be more than adequate in terms of (conservative) design expectancies. The absorption of ozone in the column alone amounted to between 88 and 95 % with ozone dosages ranging from 12,5 mg/dm³ to 8 mg/dm³. Together with the off gas re-utilization

system the efficiency varied from 91 to 98 %. (Van Leeuwen, 1979)

Clarified, filtered activated sludge effluent had an unexpectedly high ozone demand, higher than that of biofilter humus tank effluent. The reason for this was not clear and could not be coupled to a high chemical oxygen demand, nor was it in line with pilot plant tests on similarly treated biofilter humus tank effluent. The ozone demand to establish a measurable residual after 15 min contacting was on the average about 9 mg/dm³ but peak demands of more than 13 mg/dm³ have been encountered. Apart from relatively high treatment costs, another implication was underdosage during peak demand periods.

Interaction between Chlorine and Ozone

Primary chlorination after primary clarification (see Fig. 2) was necessary because:

ferric chloride coagulation was not effective in the removal of micro-organisms, thereby not providing the extra safety barrier provided by lime clarification (Van Vuuren, Van

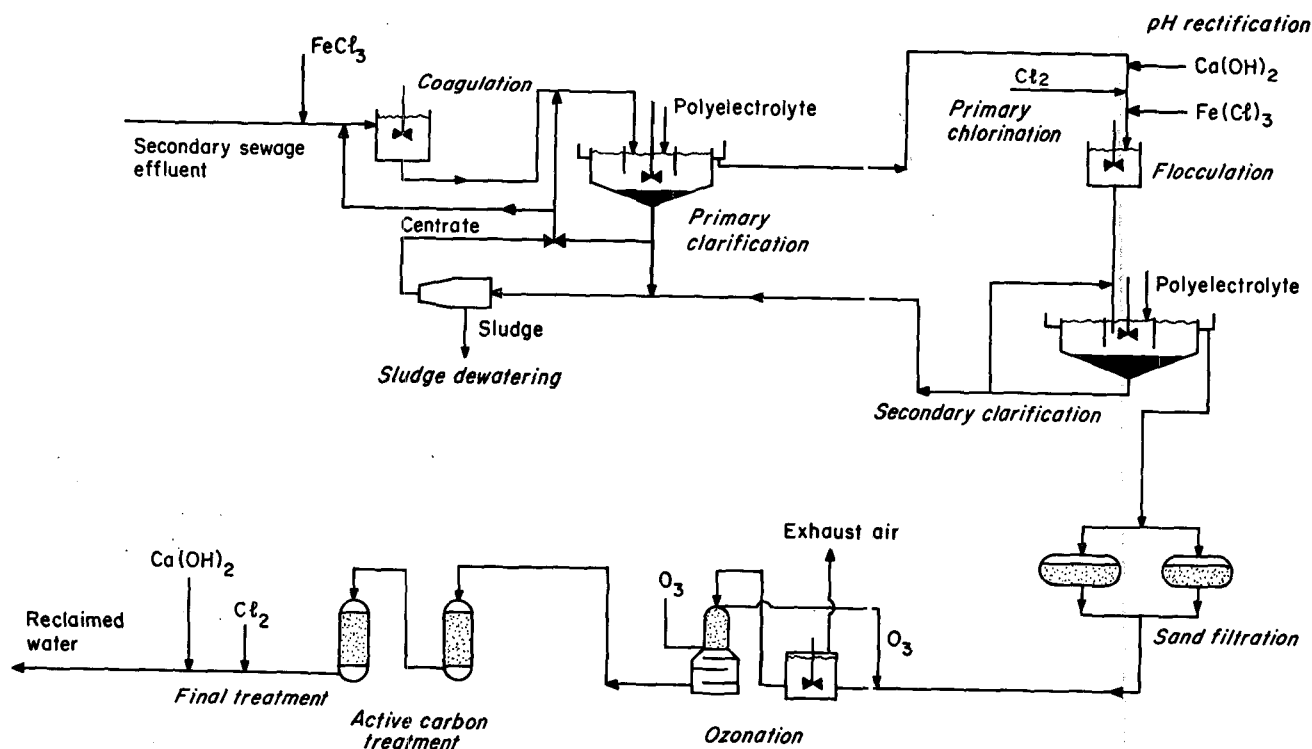


Figure 2
Flow diagram of the 4 000 m³/d Stander Water Reclamation Plant

Leeuwen and Prinsloo, 1980); and

ozonation could not be relied on entirely to act as the major disinfection unit process. Six order reductions in enteric viruses and coliphages could be achieved, but poorer bacterial results with incomplete activation of *Pseudomonas aeruginosa* and coliform organisms indicated some shortcomings.

Primary chlorination proved to provide a more efficient safety barrier against micro-organisms than lime treatment, and also led to better clarification during secondary settling. Without primary chlorination, faecal streptococci often remained after ozonation. Primary chlorination could always inactivate all faecal streptococci. Interactions between ozone and chlorine and chloramines did take place. It was found that small ozone dosages (c. 5 mg/dm³) lowered the total oxidant concentration while free chlorine could not be found after ozonation. Larger dosages of ozone increased total oxidants temporarily, but after 20 minutes' retention time the total oxidant residual was smaller than the original combined chlorine residual. The final residual was a weak oxidant that showed no response on ACVK and could be residual chloramine or weak oxidants formed by ozone. The only way to differentiate might be by the method developed by Richard (1977) using syringaldazine, an indicator specific for chlorine and chloramines, but the possibility has not yet been investigated. Interaction between chlorine and ozone would imply reduced oxidation and disinfection capacity.

Disinfection

Due to the high ozone demand, dosages of up to 12 mg/dm³ were not always sufficient to establish a sufficient residual for effective disinfection (Grabow *et al.*, 1979). The inactivation of viruses and bacteriophages did not present a problem. Coliphages on *E. coli* B and *E. coli* Hfr were reduced by almost six order of magnitude (99, 9997 %) and no enteric viruses could be found in 18 samples of 10 dm³ each. Whenever the total oxidants residual exceeded 0,2 mg/dm³ after 12 min retention, the bacterial counts were acceptably low. However, since the total oxidants residual was often less than 0,05 mg/dm³, the average reduction in population of certain bacterial species was rather low. The total plate count was on the average decreased by only 40 % and faecal coliforms by between 80 and 100 %. The reduction in *Pseudomonas aeruginosa* and *Candida albicans* varied from 50 to 80 %. Faecal streptococci and acid-fast bacteria were less resistant to ozone and their numbers were reduced by between 94 and 100 %. In contrast, breakpoint chlorination between the two settlers on the plant always resulted in bacterial count reductions of at least three orders of magnitude. No faecal streptococci, *C. albicans*, faecal coliforms, coliphages or enteric viruses could be found after the secondary clarifier. Due to equipment malfunctioning breakpoint was not always achieved but after final chlorination, the water was always free from pathogens, with only occasional detection of indicator organisms. The total plate count could also be maintained well below 100/cm³ after breakpoint chlorination.

The Effect of Ozone on Active Carbon and Water Properties

During the period May 1978 to May 1979 intensive analyses were performed in order to evaluate the chemical effects of ozonation in water reclamation. It was found that the average decrease in

chemical oxygen demand during ozonation was 3,5 mg/dm³, from 14 mg/dm³ to 10,5 mg/dm³, or about 20 % over the unit process. A further decrease of 3,5 mg/dm³ or 25 % occurred over the primary active carbon. Secondary active carbon removed about 1,5 mg/dm³ or 15 % of the remaining applied load. The simultaneous removal of total organic carbon amounted to 1,9; 1,1 and more than 0,3 mg/dm³ by ozonation, and primary and secondary active carbon treatment respectively (Van Leeuwen & Prinsloo, 1978). After secondary active carbon treatment the total organic carbon concentration was less than 1 mg/dm³ which made accurate determination difficult.

The influence of ozonation on the effectiveness of active carbon for COD lowering is demonstrated in Figure 3. Curve C₁ demonstrates the removal of chemical oxygen demand by primary active carbon (once regenerated) over a period of three months. The water influent was biofilter humus tank effluent after lime clarification, filtration and chlorination. Curve C₂ depicts the removal of COD by the same carbon (after regeneration) from activated sludge effluent after lime clarification, filtration and chlorination, occasionally supplemented by ozonation. Curve C₃ depicts COD removal by the same carbon (again regenerated) from activated sludge effluent after lime clarification, filtration and ozonation alternated with chlorination during the first three months and then lime clarification, filtration and ozonation only. The dotted curve shows the combined effect of ozonation and primary active carbon the last four months of operation.

The rate of COD and TOC removal by active carbon remained virtually unchanged during the last six months of operation. The iodine number of the active carbon samples from the columns changed gradually during the last six months from about 550 to 450 (primary columns) and 650 to 550 (secondary columns).

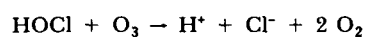
After 10 months of operation with ozone of the Stander plant it could be observed that chemical oxygen demand and dissolved organic substances could be removed very effectively by the combination ozonation/active carbon (see Fig. 3). With chlorine instead of ozone, active carbon had to be regenerated every three months after reaching iodine numbers of below 500. Only after 8½ months the iodine number of the active carbon dropped below 500 — the value reached normally after 3 months of operation without ozone.

A slight decrease in total Kjeldahl nitrogen was evident throughout the ozonation unit process — from 1,8 mg/dm³ to 1,6 mg/dm³ (10 %). Of the remainder, 75 % was removed during the two stages of active carbon treatment. Simultaneously an increase in nitrate-nitrogen of 0,6 mg/dm³ was observed after the active carbon columns and a drop in dissolved oxygen level from 12 mg/dm³ to 8 mg/dm³.

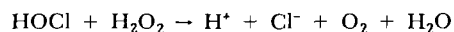
The efficiency of ozone adsorption at an average of 95 % is high when compared with most commercial units in operation in Europe where 75—90 % is considered acceptable. It is probably an improvement on conventional units, but not necessarily an optimal design. Future research will be aimed at optimizing packed columns or utilizing plate columns.

Iodometric titrations may not be the most accurate parameter for ozonation control but the simple analytical procedures have proved satisfactory for the present studies.

At least part of the chlorine and/or chloramines reacted with the ozone. A possible reaction between chlorine and ozone could be the following:



in which chlorine is reduced to chloride. A similar reaction involving peroxides is also possible:



The effect of ozone on the lowering of chemical oxygen demand and oxidation of organic carbon follows two pathways. Firstly, direct oxidation of organic substances, resulting in a diminished load on the active carbon. Secondly, biological activity is probably enhanced by either improving the biodegradability of certain organic substances by ozone oxidation or by increasing the oxygen concentration in the water or both. Further proof of the biological activity on the active carbon was the decrease in total Kjeldahl nitrogen and the concomitant increase in nitrates and decrease in dissolved oxygen. Exhaustion of the active carbon from an adsorption point of view did not result in a significant deterioration of results in terms of chemical oxygen demand lowering, indicating that a mechanism different from adsorption was responsible for the improvement in water quality.

The Effect of Process Configuration on Treatment Costs

Continuous operation of the Stander plant using various configurations and options of clarification, chlorination, ozonation, stabilization and active carbon provided data for calculating the production cost of reclaimed water. The capital costs were calculated by amortization at an interest rate of 11 % over 20 years. Maintenance and supervision were adequately provided for. Only the important unit processes are mentioned in Table 1 which summarizes the costs involved using various configurations. The inclusion of the ozonation unit process costs 1,5 to 2,8 c/m³. A decrease in active carbon treatment costs of 2 to 4 c due to extended life, more than offsets the cost of ozonation, leading to a small overall cost benefit particularly on large-scale operation. The use of ferric chloride for clarification also leads to a cost reduction due to reduced chemical, maintenance and sludge handling costs and does not influence ozonation or active carbon treatment costs.

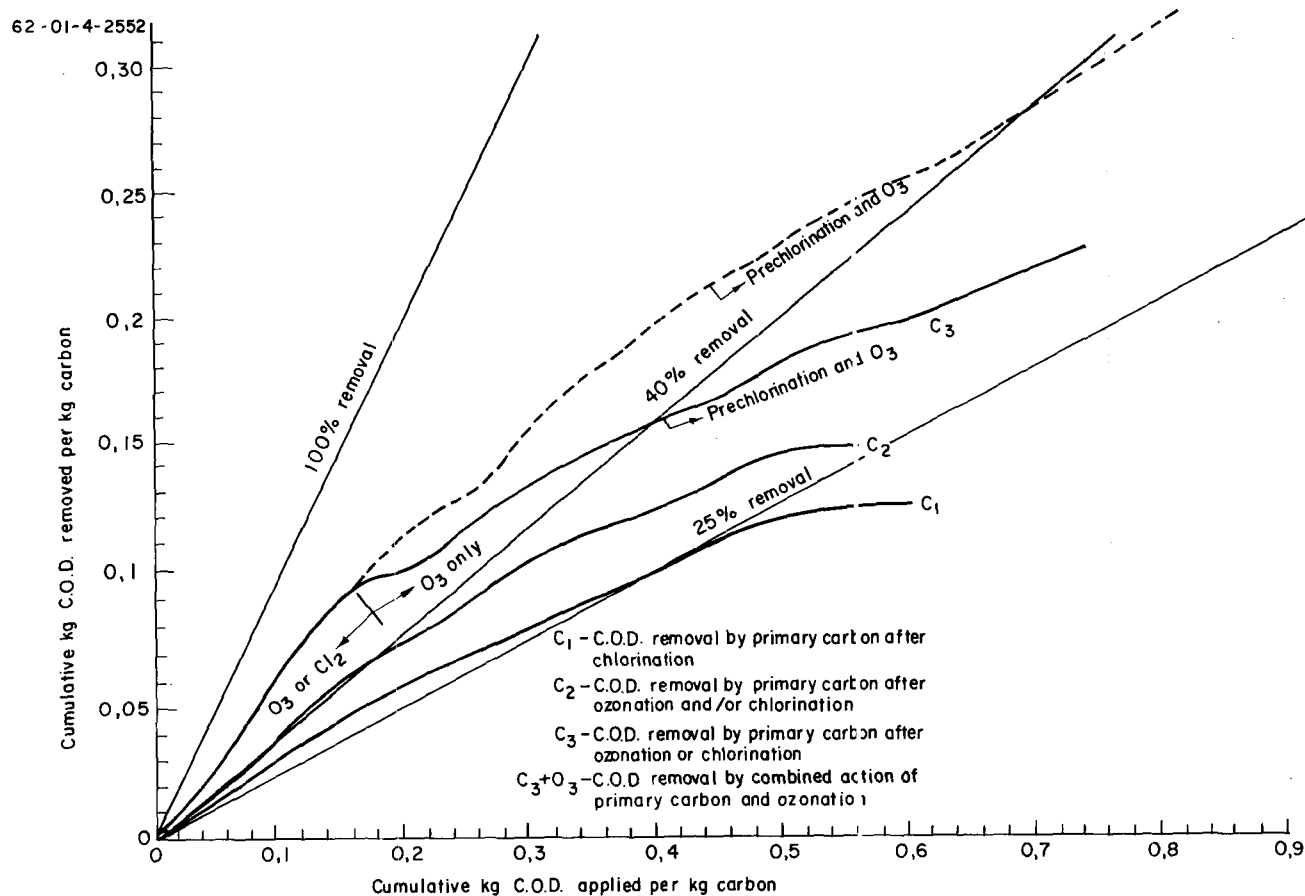


Figure 3
Removal of chemical oxygen demand by ozone and/or chlorine and active carbon

TABLE 1
A COMPARISON BETWEEN THE TOTAL COSTS
OF VARIOUS RECLAMATION PROCESS CONFIGU-
RATIONS (IN c/m³)

Process configuration	Scale (m ³ /d)	
	4 000	40 000*
Lime clarification, chlorination and active carbon (regenerated 3-monthly)	30	13
Lime clarification, ozonation and active carbon (regenerated 12-monthly)	29	12
Ferric chloride clarification, ozonation and active carbon regenerated 12-monthly)	27	10

*Scale-up according to the method of Guthrie, 1969.

Discussion and Conclusions

Multistage mass transfer equipment operates efficiently in the ozonation of treated wastewater. Whether a packed column (with redistributors) is an optimal choice is not certain. The main aspect of further research should be to compare various multistage operations for their applicability to ozone transfer, both for use in water and wastewater treatment.

Ozonation cannot fully replace chlorination for disinfection purposes. For final disinfection prior to distribution, it is not possible to establish a lasting residual with ozone and it is therefore still necessary to chlorinate. In order to provide the safety barrier lost when lime clarification is replaced by ferric chloride clarification, it is preferable to aid ozonation with pre-chlorination.

Ozonation lowers the chemical oxygen demand and total organic carbon concentration of water. It also enhances their removal by active carbon. Ozonation significantly extends the capability of active carbon to reduce COD. It does so, firstly, by lowering the load applied to the carbon and, secondly, by enhancing biological growths on the carbon. This can be demonstrated by electronmicroscope photos and chemically by the decrease in total organic carbon and total nitrogen concomitant with a decrease in dissolved oxygen and an increase in nitrates.

The effect of ozone on dissolved substances in water seems to be an enhancement in the biodegradability of these substances. This aspect should be studied further, from a physical, biological and chemical point of view. Monitoring ozonation and active carbon over a long period parallel to active carbon without pre-ozonation is presently being carried out on pilot plant scale to provide physical and biological results. In-depth studies into the mechanisms of ozone oxidation of pollutants should provide more information about transformation to a more biodegradable state.

The use of ozonation in water reclamation lowers the total

cost of the product by reducing the cost of active carbon treatment.

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