

Ozone & Chlorine Dioxide in Pretreatment of Water

In water works operation, classical oxidation agents such as chlorine, chlorine dioxide, ozone, etc are used mainly for destroying germs, algae and migratory shell larvae, and inactivating virus. Further more these agents are used for the oxidation of Ammonia compounds and organic materials, break point chlorination, for elimination of iron and manganese and finally for polishing the water by removing the odor and taste causing substances as well as for micro flocculation.

But during oxidation, undesirable reaction products often develop, example odor and taste active substances such as chloro phenols. Depending on the type of oxidation agents used, toxic substances such as chlorites and chlorates or potentially carcinogenic matter such as THMs are produced. Nutritive substances for bacteria such as aldehydes and ketones can also appear. These are beneficial for biological treatment stage but not desirable in a pipe line network since they can cause re-germination.

Chlorine dioxide is significantly more suitable than chlorine as a network protection agent. While chlorine gives the water the taste and remains in the water, chlorine dioxide degasses through the pressure drop at the water tap. It can be smelled, but most of it disappears from the water. The taste of the water is pleasing. Moreover chlorine dioxide remains in the water over a broad range of pH 6-9 . Its efficiency against waterborne pathogens over this range of pH is indicated by the fact that the Ct value for Giardia and enteric viruses are nearly half that of free chlorine.

Chlorine dioxide does not react with ammonia and only slowly with organic , thus making it more effective than chlorine.

It has been well established that the use of Chlorine dioxide have resulted in the formation of Chlorinated compounds such as Chloroform that are highly toxic to Human and known cancer causing chemicals.

During tests to minimize the problems of chloroform, chlorites and chlorates, it was noticed that a reduction of small dosage of Chlorine dioxide can result in drastic fall in the Chloroform and other THM contents in the water

No doubt diseases which can be transmitted by water can be eliminated by chlorination. This is precisely why when there is a taste of chlorine in water, people feel safe to consume the water and if there is no chlorine smell, the water should be left alone.

With Today's raw water pollution Chlorine cannot be use any more without hesitation. This is due to the unwanted by products formed during ozonation. However there are ways and means to keep these unwanted substances within limits .

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As Early as 1975, an article in EPA Report 906 established potential carcinogenicity of some of the chlorinated compounds. The connections with the toxic substances may be shown in the example of the Water supply of New Orleans . In this drinking water up to 400 micro grams of carbon tetra chloride and tetrachlorethylene were discovered. The blood samples of several persons were also tested and as expected the same substances were found .On the other hand the blood of test persons supplied with drinking water not containing any of these substances , none could be found. The connection is obvious.

THMs in drinking water

THM are molecules produced from reaction of chlorine (Pre-chlorination – Post-chlorination) with some organic matters called Precursors of THM .THM 's Precursors are organic molecules Which may react with chlorine (pre-chlorination - post chlorination) to produce THM. THMs have potential adverse health effects. One out of 1,00,000 people drinking Chlorinated water for a period of more than 10 years develop rectal or colon cancer. In India , incidence of rectal and colon cancers are the highest when compared to other cancers such as lung ,oral and breast cancers . The incidence of rectal and colon cancers are lower in European countries where controls are strictly adhered on the Minimum concentration levels of these disinfection by products. THMs once produced are difficult to remove. We have to therefore destroy the Precursors

Main Precursors of THM are : Humic acids , Resorcinol , Anin , Phenols and poly-phenols Benzoic acid, Salicylic aldehyde.

Main THMs in drinking water are : Chloroform , Bromoform , Bromo-dichloromethane Dibromochloromethane Chloro,di-chloro and tri-chloro acetic acids , Bromo, dibromo and tribromo acetonitrils , Chloro and bromo propanes, chloro and bromo nitromethanes.

Pesticides : The other most common contaminants in drinking water are pesticides. The most frequently encountered pesticides are Triazines, Ureas substituted Insecticides such as Atrazin ,Simazin .Their by products Isopoturon ,Diuron ,inuron ,Lindane ,Parathion ,Malathion Aldrin ,Dieldrin .All these products are toxic for human.

How to remove THM & Pesticides

1. Activated Carbon Filtration – Most widely used today. Efficacy not enough to meet MCL on THMS . Maintenance difficult particularly if pre treatment is ineffective.
2. Combination of Ozone and Chlorine –dioxide – Ideal combination
3. Combination ozone/ Carbon Filtration : Use mainly for the degradation and removal Of organic micro-pollutants
4. Combination ozone/ H₂O₂ plus carbon filtration

Water treatment experts have found that the use of ozone, prior to chlorine dioxide is one sure method, It used all over Europe. Unlike chlorine, ozone during treatment reduces the values of the spectral absorption coefficient (UV-Extinction at 254nm) without forming any THMs . THMs possibly present in the water are also decomposed, and through the development of ketones and aldehydes, the activated carbon filters act as Biological filters .No more aldehydes and Ketones are found after these filtration .

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Hence the use of Ozone along with Activated Carbon is preferred to the use of Activated carbon alone.

Advantages of Ozone along with Activated Carbon (BAC)

1. Removes Ammonia if Nitrification is possible
2. BAC offers contact time of 10- 15 minutes
3. BAC allows Porosity: 10 to 100 μm
4. Bacteria loss: 5% by backwash
5. Removes about 50% of BOC
6. THM concentration reduces at $< 10 \mu\text{g/l}$
7. Chlorine demand decreased by over 50%
8. Free chlorine residual in piping stable

.OZONE !

1. Increases lifetime of BAC . Life of Activated Carbon used, will last for more than four to ten times longer filter runs when ozone is used as a pre oxidant, only because the aldehydes and ketones formed during ozonation make the carbon filters biologically more active.
2. Reduces backwash frequency
3. Colour reduction, Odour reduction, Disinfection

OZONE AS AN OXIDANT: The use of ozone in Drinking water provided the following uses:

1. Predisinfection
2. Preoxidation
3. Oxidation of iron and manganese
4. Improvement of the flocculation step –
5. Algae removal

Use of Ozone as Pre-Oxidant

Ozone Actions: The advantages of ozone used as pretreatment:

Viruses are inactivated in split seconds and bacteria and pathogenic germs are destroyed. The larvae of migratory shellfish are completely annihilated in a very short time. Water is decolorized and become crystal clear. Ozone eliminates odor of algae and other odors and improves tastes of water. Phenolic compounds are destroyed. So are pesticides found in water. Heavy metals such as iron and manganese are reduced improving the taste of the water,. UV values are substantially decreases.

By replacing pre-chlorination by pre-ozonation The following benefits accrue:

Ozone does not produce THMs

Ozone does not react with THMs (except volatilization)

Ozone is more selective than hydroxyl radicals against THM precursors

Ozone destroys precursors.

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Studies have revealed that by the use of Ozone as a pre-oxidant there is a reduction of the potential formation of THM at least 50%.

Ozone is ideal for application prior to biological treatment processes such as slow sand filters and activated carbon filters because their operation time is extended by a factor of four to ten.

Pathogen inactivation with ozone followed by chlorine dioxide.

DISINFECTANT DOSE TO OBTAIN 99% MICRO-ORGANISM INACTIVATION

	DISINFECTANTS				UV 253.7 Nm
	Chloramine	Ozone	Free Chlorine	ClO ₂	
Optimal	pH 8 to 9	pH 6 to 9	pH 6 to 7	pH 6 to 7	-
Dose – Criteria	Ct mg.mn/l	Ctmg.mn/l	Ct mg.mn/l	Ct mg.mn/l	Mj/cm ²
Micron organisms:					
E coli	95- 180	0.02	0.034 – 0.05	0.4 – 0.75	6
Bacillus .S	-	0.1	-	-	16
Polio I	770-3740	0.1 –0.2	1.1 – 2.5	0.2-6.7	48
Rotavirus	3810 – 6480	0.006 –0.06	0.01-0.05	0.2-2.1	-
Phage f2	-	-	0.08-0.18	-	-
Giardia Lambia	-	0.5-0.6	47-150	-	-
Giardia muris	1400	108 – 2.0	30 – 630	7.2 –18.5	-
Cryptosporidium	-	2.5 –3	7200	-	-

From the table, ozone is by far most effective in terms of lower Contact Time(ct) and lower dose per mg .minute. The sequential applications of ozone and chlorine dioxide have resulted in inactivation of Crytosporidium parvum oocysts over and above that afforded by either oxidant used alone. With a correct combination a 3 logs reduction can be obtained.

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