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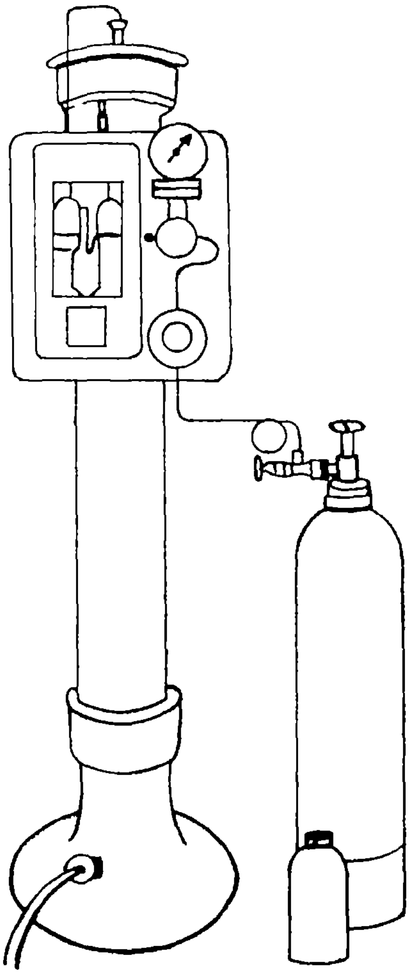

CHLORINATION

and use of

CHLORINATORS

Indian Water Works Association

Manual of Water Supply Practices

With best Compliments
from. 11 11/92

CHLORINATION
and use of
CHLORINATORS

Indian Water Works Association
Bombay

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Foreword

This Manual has been prepared to supplement the IWWA Workshop on CHLORINATION AND USE OF CHLORINATORS. This Workshop is a part of a comprehensive Operators' and Engineers' Training Programme developed by IWWA about 15 years back. Years of intensive development efforts have been made by leading chlorination experts to produce this course and this manual.

The objectives of this manual are to acquaint the experienced operator and engineer with the theory, application, use and safety factors pertaining to chlorine; to help prepare the operator and engineer for advancement of his skill and knowledge in newer, more modern and applicable methods of chlorination; all of which lead to promote awareness amongst the Water Supply Water-quality fraternity.

The Council of Management of IWWA expresses its sincere appreciation to all persons and companies who contributed to the preparation, review and final editing of this handbook. In particular, it wishes to acknowledge the work put in by the Principal Author, Dr. A. D. Patwardhan. Acknowledgement has also to be given to those members — past and present — of the Scientific and Technical Committee of IWWA, not forgetting, of course once again the dedication, interest and personal involvement of Dr. A. D. Patwardhan.

This manual promises to be an extremely useful guide to chlorination plant operators, engineers, students, not to belittle the utility of this publication to manufacturers of chlorine, chlorine containers and chlorinators.

S. P. Unvala
Hon. Director
INDIAN WATER WORKS ASSOCIATION

BOMBAY
March 1989

Indian Water Works Association

Other Manuals

Manual-I

DESIGN OF LARGE DIAMETER STEEL PIPELINES

Compiled by . Shri L. G. Dhayagude, Shri J. W. Pednekar
Price : Rs. 100/- (in India) or U.S.$ 20 (Overseas)
Members of IWWA will get a discount of 25%.

The manual is the first amongst the series which Indian Water Works Association (IWWA) has published in 1987 for the benefit of not only its members but also the fellow engineers working in the field of water supply in all developing countries of the world.

The objective of this manual is to acquaint the Water Works Engineers with the theory, application, uses and design factors pertaining to large Diameter Steel Pipelines. The manual gives information about the design of both underground and above-ground pipes, types of supports commonly used, anchorages for pipelines and different types of specials required to be used along the pipelines' alignment. A separate Chapter has also been given with solved examples to show the use of the design formulae, factors and charts. Basic information about surge pressures developed due to water hammer has also been given.

The manual has been compiled by the authors, who have a long standing experience in the Municipal Corporation of Greater Bombay, in the design, fabrication and laying of such pipelines. Large diameter steel trunk mains are the order of the day and are almost invariably being used in the rapidly exploding cities in the third world. This manual will therefore become a very useful guide to the planners and designers of water supplies of these cities.

Preface

The subject of chlorination of water, more appropriately called 'Disinfection' is one of a great importance from the view-point of protecting public health. Chlorination of wastewater, on the other hand, aims at protecting the receiving waters from microbial contamination. The element 'Chlorine' has proved its versatility in dealing with certain impurities in water and waste-water. Other substances like ozone, chlorine dioxide, etc. have been effective as disinfectants, but none of them has been able to replace chlorine ; rather, they have been used to supplement the action of chlorine. It is, therefore, necessary that persons concerned with water and wastewater treatment should know more about this useful substance, its properties, its uses and limitations, methods of determining its concentration in water and waste-water, equipment used to handle it and safety measures to be taken in case of an emergency.

The author has drawn freely upon information available in the literature and has acknowledged the sources of information at the end of every chapter. A list of useful Indian Standard Specifications, names and addresses of suppilers of chlorine and its compounds, chlorination equipment suppliers and safety equipment suppliers has also been included with the hope that the usefulness of the book will be enhanced.

The author wishes to acknowledge with thanks the help given by Shri I. C. Gandhi, Chief Engineer (Mech. & Elec.), Municipal Corporation of Greater Bombay, in permitting free use of the literature available with him and to Shri S. R. Kshir-sagar, Hon. Editor of the Journal of IWWA for offering valuable suggestions towards improvement of the contents by going through the entire manuscript of this manual. Thanks are also due to Shri Sunil Rane and Shri Anil Karkhanis for preparing neat drawings for this book.

— A. D. Patwardhan

Indian Water Works Association

Other Manuals

Manual-II

LEAK DETECTION AND WASTE PREVENTION IN WATER DISTRIBUTION SYSTEMS

Compiled by : Shri V. M. Shidhaye
Price : Rs. 100/- (in India) or U.S.$ 20 (Overseas).
Members of IWWA will get a discount of 25%.

Large volumes of water brought, treated and distributed at high cost are being lost through leakages in the distribution systems in most of the public water supply schemes. Such leakage and wastage of water may amount to even 40 to 50% of the actual water demand and which results in loss of revenue and lesser availability of water and deterioration in its quality (especially when the supply is intermittent). The problem could be solved by prompt detection of these leaks and immediate repairs of the systems. This manual compiled by Shri V. M. Shidhaye, who has a long experience of doing such works while serving in Municipal Corporation of Greater Bombay and published by IWWA in 1988 is giving a very useful guidance to the water supply engineers, in-charges of management of public water supply systems on the various causes of leakages and wastages, the methods of their measurement, techniques and instruments used for detection. A few case studies of such leak detection surveys and their cost details have also been given. The manual includes guidance on formation of leak detection cells and the training of personnel for such work in the Municipal and other such organisations. It will certainly be very useful therefore in improving the water supply service level of civic bodies in the country and removing the cause of public complaints thereby winning its goodwill.

CHAPTER 1

Introduction to Water and Wastewater Chlorination

The aim of water treatment is to convert raw water from its contaminant-laden stage to an aesthetically acceptable and hygienically safe end product. Water acquires many impurities during its passage through the hydrologic cycle. In addition, its use for domestic, industrial, commercial, agricultural and recreational purposes adds greatly to these impurities. Various combinations of unit operations and processes are used in practice for the removal of impurities. The nature and impurities in raw water and the end use of treated water determine the degree of required treatment.

Among the unit processes, the one most important process from the point of view of the consumer's health is that of disinfection. The term 'Disinfection' denotes that process which aims at destroying disease-producing organisms in water. There are many agents of disinfection ranging from such physical means as heating, use of ultraviolet rays or of ultrasonic waves, to chemicals like oxidizing agents, metal ions, acids, alkalis, and surface-active agents. The most commonly used agents in the field of water and wastewater treatment, are the halogens — chlorine, bromine and iodine. Of these, chlorine has been the most popular agent, due to its ease of application, measurement and control, its reasonable persistence in treated water and its low cost compared with bromine and iodine. Other disinfectants may be found more effective than chlorine, but only under special conditions. But none of them has been a serious competitor of chlorine so far. It appears, therefore, that chlorine will continue to remain the disinfectant of choice for some more time to come.

HISTORY OF DISINFECTION:

Chlorine has been in use as a disinfectant for well over 170 years De Morveau and Cruickshank used it as a general disinfectant around 1800 A.D. Jewell and Fuller employed it for experimental purposes in 1896. A year later, it was used for temporary sterilization of potable water distribution mains by

Woodhead and Maidstone at Kent in the U.K., following a typhoid epidemic. The first continuous application of chlorine to raw water on a municipal scale was started in England in 1904-05 A.D. by Sir Alexander Houston and Dr. McGowan. In 1908, Johnson disinfected water supplied from the Bubbly Creek treatment plant in the USA. Jewell used chlorine gas, and later, chlorinated lime for the temporary treatment of filter effluents at Adrian, Michigan, USA. Till then, the sources of chlorine were either bleaching powder or sodium hypochlorite. In 1910, liquid chlorine became available on a commercial scale and was used by Maj. Darnall of the U.S. Army Medical Corps for disinfecting water. Wallace and Tiernan improved upon the then available equipment for dispensing liquid chlorine in 1913. Since then, liquid chlorine has been the chief source of chlorine for disinfection.[1]

Palin[2] summarizes the history of water chlorination thus:

A.D. 1905-1915 — Period of hypochlorite disinfection, with some scepticism and prejudice against chlorination.

A.D. 1915-1925 — Evolution of gaseous chlorination and continued education of the public.

A.D. 1925-1935 — Very great interest shown in chlorination. Bacterial and taste-removal problems were very much to the fore and the use of chlorine-ammonia treatment was much advocated.

A.D. 1935-1945 — Period of greater flexibility in chlorination methods and an increased use of semiautomatic feeding apparatus.

A.D. 1945-1955 — Advances in the understanding of basic principles coupled with much fundamental research. Greatly improved methods for the control of chlorination.

In the field of wastewater treatment, chlorination has been used as an effective means of controlling the spread of diseases. Until late in the 19th Century, odours were believed to be responsible for the spread of diseases, thereby leading to the conclusion that control of odours would control the spread of diseases. As early as 1832 A.D., an American Professor published a review titled 'Facts Regarding the Disinfecting Power of Chlorine' which contained more than 25 references for preventing the spread of infection in hospitals and mortuaries. The earliest recorded practice of large-scale wastewater chlorination is the use of chlorinated lime by the Royal Sewage Commission in 1854 to deodorize London's wastewater. During the next 40 years, many British patents were issued to control the use of chlorine and chlorine compounds for treating wastewaters. The application of chlorine for disinfection of wastewaters was first described in 1879 A.D. when faeces of typhoid patients were treated with bleaching powder before disposal into sewers.

Around 1880 A.D., the role of bacteria in the spread of diseases was realized. Thereafter the use of chlorine was aimed at destruction of bacteria rather than destruction of odours (which were assumed hitherto to be responsible for spreading diseases). Upto this time, the chief source of chlorine was bleaching powder. In 1887, a patent was granted in the USA for use of chlorine generated from the reaction between manganese dioxide, sulphuric acid and sodium chloride. Six years later, another patent involving electrolysis of brine, or of the wastewaters themselves, for producing sodium hypochlorite was granted.

Wide use of chlorination as an integral process of wastewater treatment came about with the production of liquid elemental chlorine around the end of the 19th century. Between 1925 and 1937 chlorine was employed for uses other than disinfection of wastewaters, notable among these being control of trickling filter flies, reducing foaming in Imhoff tanks, reduction of BOD, control of odours in treatment plants and in sewers, aiding activated sludge thickening, reducing activated sludge bulking and removal of oil and grease.[3]

The possibility of using chlorination as a means of treating industrial effluents was recognized in 1916 A.D. with the treatment of tannery wastes. In 1928, chlorine was applied to the treatment of dairy wastes. A year later, it was used for BOD reduction of cannery wastes Coagulation and colour reduction of textile wastes was achieved with chlorine in 1933. Oxidation of cyanides was done with chlorine in 1942. Beet sugar wastes were treated with chlorine in 1949 and phenol-bearing wastes in 1950.[3]

In recent years, superchlorination followed by dechlorination has come into vogue, mainly because of the deteriorating quality of raw water sources. With further improvements in dosing and measuring chlorine, closed-loop chlorination and automatic recording of residuals have been developed. Thus it is now possible to effectively disinfect a raw water source of rapidly changing quality.

In addition to the above uses, chlorine has been found useful at treatment plants which have to convey their treated effluents over long distances to the receiving bodies of water. Here it helps to minimize aftergrowths of slimes in the conveying pipelines, and of microorganisms in the receiving waters. Dissolved oxygen depletion in these waters is also reduced thereby. Chlorination can act as a stop-gap arrangement at an overloaded wastewater treatment plant till adequate facilities are built for handling the extra load. It is also used to meet the seasonal demands of high quality treated effluents.

At this stage, it is essential to note a few of the unfavourable aspects of chlorination. An excess of chlorine can cause toxicity to the biological life in the receiving waters. Production of odorous and harmful compounds due to reactions between chlorine and other impurities in water and interference with the performance of the BOD test are two other factors which need careful consideration when chlorination of wastewaters is contemplated.

PRESENT AND FUTURE TRENDS :

Today chlorine continues to be the favourite disinfecting agent in water treatment. Due to increased pollution of our natural resources, chlorination after filtration of water has proved to be inadequate. Therefore prechlorination of raw water is becoming common. However, this practice and the presence of certain organic substances in raw water has given rise to the formation of halogenated organics such as chloroform and other trihalomethanes.[4 5] Even some of the water works in India are reported to have produced waters showing the presence of trihalomethanes.[6] These compounds are known for their cancercausing properties. The present WHO guideline limits the concentration of trihalomethanes to 30 micrograms per litre as chloroform.[7] A solution to this problem appears to be to combine ozone and chlorine treatment of water. Activated carbon treatment or air-stripping of treated water is also found to help.[8]

The formation of haloforms in water is highly pH-dependent. Prechlorination of water following recarbonation has reduced chloroform concentration in treated water by 75 per cent.[9]

A new disinfectant proposed for treating water for drinking purposes and destroying, though partly, the precursors of organohalides is the ferrate ion (FeO_4^{--}). But it does not provide a stable residual in the treated water. Therefore moderate chlorination is required to maintain residual germicidal properties.[10]

Newer methods of determining residual chlorine in water are also being developed. The well-known orthotolidine (OT) and the orthotolidine-arsenite (OTA) tests are being largely replaced by the Diethyl-p-phenylene diamine (DPD) test,[11] stabilized neutral orthotolidine (SNORT) test[12] and Free Available Chlorine Test with Syringaldazine (FACTS).[13] These new tests are more sensitive, more specific and are unaffected by commonly interfering substances in water.

From the above discussion, it is apparent that chlorine alone is unable to contain pollution and produce water of acceptable quality. But other agents of disinfection must be used, their role being more by way of supplementing the action of chlorine, rather than replacing it as a disinfectant.

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CHAPTER 2

Properties of Chlorine

INTRODUCTION :

Chlorine, fluorine, bromine and iodine form a remarkable family of elements called 'halogens' which means 'sea-salt producers'. This name was given because the sodium salts of these elements resemble sea salt, i.e. sodium chloride. These elements have strong resemblances among themselves and they exhibit a gradation in their properties with increasing molecular weights.[1]

This chapter describes various properties of chlorine, its reactions in water and wastewater, its effects on other properties of water and its effect on microorganisms normally present in water. Factors which affect the usefulness of chlorine as a disinfectant are also described.

PROPERTIES OF CHLORINE :

First discovered by a Swedish Chemist, C. W. Scheele, in 1774 A.D., chlorine was considered to be a compound containing oxygen. Sir Humphrey Davy identified it correctly as an element in 1810 A.D. and gave it the name 'CHLORINE', derived from the Greek word 'CHLOROS' meaning green. Some of the important physical and chemical properties of chlorine are given below in Table 1.[1 2 3 4 5]

The degree of solubility of chlorine in pure water is indicated in Table 2. It is seen from this table that water can hold a decreasing percentage of chlorine in solution with increasing temperature. In practice, the solubility of the gas is found to be about half of the values indicated in the table. Thus at 30 deg C, a solution containing about 0.285 %, i.e. 2850 mg/l of chlorine can be prepared. This value is worked out on the basis that a 1% solution contains 10,000 milligrams of the substance in 1 litre. (1% is equal to 1 gram per 100 grams or 10 grams

Table 1

Physical and Chemical Properties of Chlorine

1.	Symbol	Cl
2.	Atomic weight	35.453
3.	Freezing (or melting) point	—101°C
4.	Boiling point	—34°C
5.	Colour	Pale greenish yellow
6.	Odour	Pungent
7.	Specific gravity at 0°C	2.482
8.	Vapour pressure at 25°C	5300 mm.
9.	Solubility in water	See table 2.
10.	Chemical activity	Displaces bromine and iodine from Br^- and I^-.
11.	Bleaching action	Readily bleaches vegetable colouring matter

Table 2

Theoretical Solubility of Chlorine in Water

Temperature, °C	Per cent chlorine	Temperature, °C	Per cent chlorine
10	0.98	60	0.33
20	0.71	70	0.28
30	0.57	80	0.22
40	0.46	90	0.127
50	0.39	100	Zero

per 1000 grams. This is 10 grams in 1000 millilitres of water, or 10,000 mg/l, assuming that the density of water does not change from 1 gram per millilitre due to this substance.

Chlorine, when in a dry condition, is not corrosive, but its solution is extremely corrosive. Suitable materials for handling chlorine gas are copper, iron and steel, while for handling chlorine solution, glass, hard rubber, lead and silver are useful. Since chlorine dissolves in water to form a corrosive solution, it is absolutely essential to prevent leaks of the gas and to provide adequate ventilation in the chlorine room to minimize accumulation of water vapours.

The effect of chlorine on human beings needs to be considered from two angles, viz. (i) effect on consumers and (ii) effect on the operating personnel. Both of these have been considered in the subsequent chapters.

REACTIONS OF CHLORINE :

Chlorine reacts with many substances in water, sewage and industrial wastes. Its action is mainly by way of oxidation, bleaching and disinfection (i.e. killing of disease-producing organisms), and depends on the type and amount of reacting substances present. It can also render water sterile when added in sufficient amounts. For ease of understanding, the reactions of chlorine are grouped under the following headings:

(a) Reactions with water,

(b) Reactions with sewage and

(c) Reactions with certain industrial wastes.

(a) Reactions with water:

When chlorine is added to pure water, it reacts with the water in two steps, viz (i) hydrolysis and (ii) ionization.

Hydrolysis: $Cl_2 + H_2O \rightleftharpoons HCl + HOCl$. This reaction gives rise to hydrochloric acid and hypochlorous acid. The hypochlorous acid ionizes (or breaks down) into its component ions, viz. H^+ ion and hypochlorous ion, i.e. OCl^-. $HOCl \rightleftharpoons H^+ + OCl^-$.

From the two above reactions it is seen that when chlorine reacts with water, the H^+ ion concentration in the water increases, i.e. the pH value of the water decreases. In other words, addition of chlorine reduces the alkalinity of the water to some extent.

It should be noted that the hypochlorous acid and the hypochlorous ion have the ability to kill microorganisms. Therefore, their concentration in water should be as large as possible. It is apparent from the two above reactions that the pH value of water undergoing treatment is significant in this regard.

Thus if laboratory experiments indicate that a dose of 0.1 mg/l produces the desired degree of disinfection at pH 5.0, a change in pH of water will necessitate a change in the dose of chlorine to achieve the same degree of disinfection (See table 3 below).

Table 3

Effect of pH value of water

pH value	Content of residual, per cent			Chlorine dose, mg/l for the same degree of disinfection
	Cl_2	HOCl	OCl^-	
4.0	0.5	99.5	0	—
5.0	0	99.5	0.5	0.1
6.0	0	96.5	3.5	0.1027
7.0	0	72.5	21.5	1.27
8.0	0	21.5	72.5	3.70
9.0	0	1.0	99.0	28.0

Reaction with water containing ammonia nitrogen —

When water being treated contains ammonia, the chlorine reacts with the ammonia, forming chloramines, their proportion in water depending upon the pH value of the water. The reactions are as follows:

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

$$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O$$

$$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O$$

$$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O.$$

Compounds formed in the above reactions are respectively monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and nitrogen trichloride (NCl_3). Monochloramine exists in water at pH values above 8.5, dichloramine at pH values between 5.5 and 8.5, while nitrogen trichloride exists at pH less than 4.5. The disinfecting power of these substances in their decreasing order is — dichloramine, monochloramine and nitrogen trichloride.[2] Although the chloramines are far less effective as disinfectants than hypochlorous acid and hypochlorous ion, they persist in the water for a long time.

Reactions with phenolic compounds —

Phenols and phenolic compounds react with chlorine to form taste-producing chlorophenols. Even very low concentrations of chlorophenols are sufficient to impart undesirable taste to water; e.g. orthochlorophenol (1 in 20,000 million parts), parachlorophenol (1 in 5000 million parts) and trichlorophenol (1 in 1000 million parts).[6]

(b) Reactions with sewage :

Domestic sewage contains a large and complex variety of suspended, colloidal and dissolved organic and inorganic substances in addition to large numbers of bacteria, protozoa and other organisms. Some of the reactions of these substances are very rapid while others are slow. Among the variable components of wastewater which affect chlorination practices are : (i) inorganic reducing materials such as hydrogen sulphide, sulphite, nitrite, ferrous and manganous ions, (b) ammonia and amines, (c) other organic substances, particularly unsaturated compounds and (d) bacterial and other organisms.[7] The main purpose of chlorination of sewage is the destruction of pathogens and can be achieved only if the dose of chlorine is large enough to meet the demands due to substances other than bacteria and viruses. Obviously, therefore, chlorination cannot be considered the sole method of sewage treatment, since very large doses would be required. This is uneconomical. Therefore, sewage must be adequately treated before it can be subjected to chlorination at a reasonable cost.

Chlorine is used in a sewage treatment plant for overcoming odours in pipes and channels, controlling fly nuisance in trickling filters, bulking of sludge in aeration tanks of activated sludge process, and for aiding in oil and grease removal. Treated effluents are chlorinated to minimize aftergrowths of microorganisms in the conveying pipes. Here chlorine also helps to reduce oxygen depletion in the receiving bodies of water. Approximate doses required to achieve the above objectives are given in Chapter 4. Points of addition of chlorine in sewage treatment are shown in Fig. 1.

(c) Reactions with industrial wastes:

Industrial wastes are extremely variable in their strength and composition, even from two different plants manufacturing identical products. Some industrial wastewaters teem with biological life while others are discharged in a sterile condition. Therefore, no general formula for the required dose of disinfectant can be given. However, wastes which have been successfully treated with chlorine include cyanide-bearing effluents, phenols, textile mill wastes, paper mill wastes, tannery effluents, oil refinery discharges and food processing wastes. Wastewaters which can be successfully reused after treatment have also been chlorinated.

In the above cases, chlorine acts either as a disinfectant or as an oxidizing agent, or as both, depending on the nature and composition of the wastewater and the degree of treatment it has received before chlorination. The dose of chlorine can be determined only by laboratory experiments.

Chlorine reacts with most of the organic and some inorganic compounds present in water, sewage and industrial wastes, but does not react with carbohydrates (with the exception of laevulose), methyl and ethyl alcohols, glycerol, starch, and oleate, palmitate and acetate of sodium.[10] As newer compounds make their appearance in the waste-waters, this list is likely to be extended further.

EFFECT OF CHLORINE ON MICROORGANISMS:

Water contains bacteria, protozoa, algae, viruses, spores, cysts etc. depending upon its degree of pollution. In order to render the water hygienically acceptable, the addition of the disinfectant must be large enough to kill all disease-producing organisms in water. The action of a disinfectant depends on its ability to diffuse through the cell wall of the organism. The

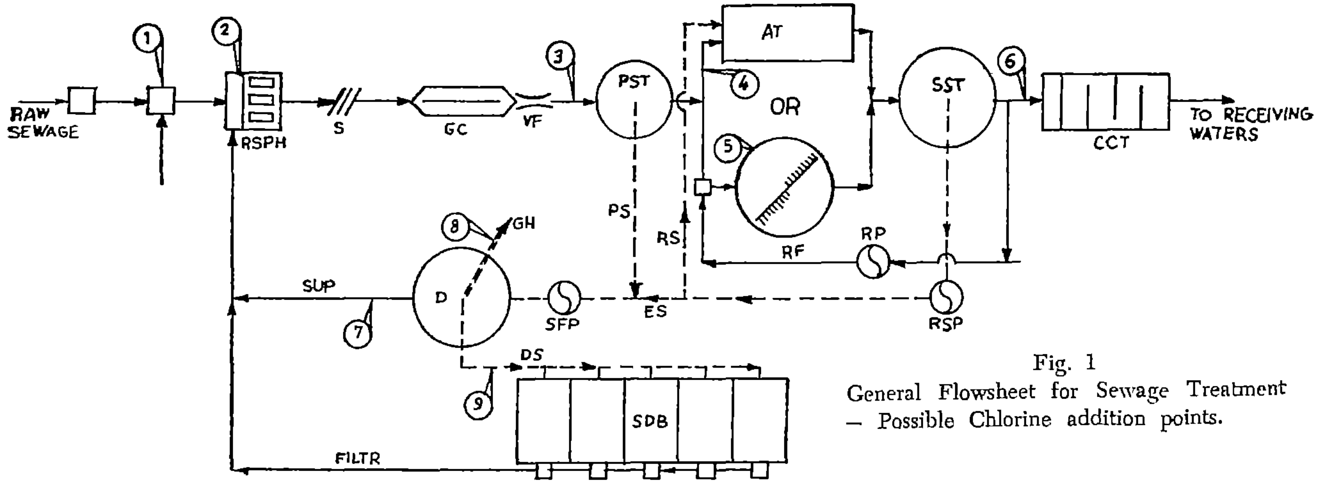

Fig. 1
General Flowsheet for Sewage Treatment
– Possible Chlorine addition points.

LEGEND –

1-2	Odour Control Corrosion Control	6	Bacteria Control, Bod Satisfaction
3	Aid to Settling Grease Removal.	7	Odour Control.
4	Sludge Bulking.	8	Wet Scrubbing of Gas.
5	Filter Ponding, Fly Nuisance.	9	Odour Control.

RSPH	Raw Sewage Pump House.	ES	Excess Sludge
S	Screens	PS	Primary Sludge
GC	Grit Channel	D	Digester
VF	Venturi Flume	GH	Gas Holder
PST	Primary Sett Tank	DS	Digested Sludge
AT	Aeration Tank	SDB	Sludge Drying Beds
SST	Sec Sett Tank	SUP	Supernatant
CCT	Cl_2 Contact Tank	FILTR	Filtrate
TF	Trickling Filter	RSP	Return Sludge Pumps
RF	Recirc-flow	RP	Recirc-Pumps
RS	Return Sludge	SFP	Sludge Feed Pumps

resistance offered by the organism to such diffusion determines the ease with which it can be destroyed. The most susceptible organisms to the action of a disinfectant are the young, vegetative, bacterial cells while the most resistant ones are the spores and the cysts. Green and Stumpf[11] suggest that the death of the organisms is due to a chemical reaction of HOCl with an enzyme system which is essential as a catalyst for glucose utilization and the enzyme affected is triosephosphate dehydrogenase. In addition to its ability to react with the enzyme, the HOCl molecule, on account of its small size and electrical neutrality, can easily pass through the cell membrane and kill the microorganism. The hypochlorite (OCl^-) ion, due to its negative charge, is unable to penetrate through the cell membrane and hence is a poor disinfectant.

Venkobachar **et al**[12] observed that zeta potential, permeability and oxidative phosphorylation are the important properties of a cell membrane affected by exposure to chlorine. Knox **et al**[13] reported that chlorine in bactericidal doses inhibited the sulphhydryl enzymes. Fryberg[14] found a leakage of cellular components after chlorine treatment and considered it to be the reason for the death of the cells.

As stated above, microorganisms in their growing, or 'vegetative' state are most susceptible to the action of the disinfectant. Cysts and spores of the organisms are more easily removed from water by settling and filtration on account of their larger size. It is difficult to destroy them by disinfection because they have a tough chitinous cover around them which resists the action of the disinfectant.

In order to inactivate viruses in water, the usual conditions viz. free residual chlorine of 0.2 mg/l at pH 7.0 are not enough. Viruses are classified as (i) plant viruses, (ii) animal viruses and (iii) bacterial viruses, depending upon the cells they infect. Animal and bacterial viruses are commonly present in wastewaters. Of primary concern in wastewater treatment is the enteric virus group. Contact times required to inactivate 99.99% of various human enteric viruses range from about 3 minutes for Reo 1 virus to more than 60 minutes for Echo 3 virus, when a free residual chlorine of 0.5 mg/l is maintained at pH 7.8 and a water temperature of 2°C.[9]

FACTORS AFFECTING EFFICIENCY OF CHLORINE AS A DISINFECTANT :

A number of factors have an effect on the efficiency of chlorine as a disinfectant. They are :

1. **Nature, concentration, distribution and condition of organisms to be destroyed;**
2. **Nature, concentration and distribution of chlorine and its reaction products in water;**
3. **Nature and condition of water to be treated :**
4. **Temperature of water and**
5. **Time of contact between the water and the disinfectant.**

These factors are described below :

1. Nature, concentration, distribution and condition of organisms :

The effect of chlorine on microorganisms is already mentioned above. Concentration of organisms as such enters into the problem of disinfection only when the number of organisms is large enough to compete for the disinfectant. Other substances with which chlorine reacts are also usually present in water harbouring such large numbers of organisms. Therefore a part, or all, of the chlorine added may be used up in such side-reactions and very little is available for killing the pathogens. Clumps of bacteria, such as staphylococci, protect the organisms from the action of chlorine.

2. Nature, concentration and distribution of chlorine and its reaction products in water :

From the reactions of hydrolysis and ionization of chlorine in water, already described above, it is possible to determine the ionization constant of hypochlorous acid. This constant, k_i, is temperature-dependent. Its values at temperatures of water from 0°C to 35°C are given below (See table 4).

Table 4

Ionization Constants k_I-of hypochlorous acid[15]

Temperature, °C.	Value of k_I
0	1.496×10^{-8}
5	1.762×10^{-8}
10	2.040×10^{-8}
15	2.328×10^{-8}
20	2.618×10^{-8}
25	2.904×10^{-8}
30	3.180×10^{-8}
35	3.443×10^{-8}

From the ionization reaction, the ionization constant for hypochlorous acid can be written as:

$$k_I = \frac{[H^+]\ [OCl^-]}{[HOCl]},$$ where the bracketted quantities indicate molar concentrations of hydrogen ions, hypochlorous ions and unionised hypochlorous acid.

The above equation is modified further thus:

$$\frac{[OCl^-]}{[HOCl]} = \frac{k_I}{[H^+]} \qquad \text{or}$$

$$\frac{[HOCl] + [OCl^-]}{[HOCl]} = \frac{k_I}{[H^+]} + 1.$$

Here the numerator on the left hand side of the equation indicates the total quantity of water added to the water while the denominator shows the concentration of hypochlorous acid, which is the major disinfectant. If we indicate the sum of HOCl and OCl^- by R and the concentration of HOCl by C, the above equation becomes $\frac{R}{C} = \frac{k_1}{[H^+]} + 1$. This equation shows that for a given temperature of water and total dose of chlorine, i.e. R, the concentration of C depends upon the H^+ ion concentration of the water. Table 3 shows that lower the pH value, higher the concentration of HOCl and hence more complete is the disinfection. The values of chlorine dose shown in table 3 are of significance when waters naturally high in pH value, or those softened by lime-soda softening process, or those requiring raising pH value to control corrosion are to be disinfected.

3. Nature and condition of water to be treated:

Water contains impurities which can (a) consume chlorine by reacting with it, or (b) offer shelter to microorganisms or (c) form compounds which have little or no disinfecting power. It is, therefore, essential that water should receive adequate treatment before it is subjected to chlorination, so that the added chlorine is available for destruction of pathogenic organisms.

Reactions with chlorine can occur due to reducing substances like ferrous and manganous ions, hydrogen sulphide, sulphite, nitrites etc. Chlorine oxidizes these substances and is consumed in the process. Therefore the treatment of water and wastewaters prior to chlorination must aim at removal of, or oxidation of, such substances.

Suspended matter in water and wastewater can protect microorganisms from the action of chlorine because of their small size. Hence removal of suspended matter by sedimentation and filtration, and by sedimentation and biological treatment in sewage and industrial wastes treatment is essential if the added chlorine is to act as a disinfectant. It has been shown that much larger doses of chlorine are required to be lethal to viruses in the presence of organic matter than in its absence. This also explains the greater success in the destruction of viruses when water has undergone full treatment, and also when breakpoint chlorination is practised.[16]

Ammonia nitrogen and nitrogen-bearing compounds in water combine with chlorine to form respectively weak disinfectants like taste and odour producing chlorophenolic compounds. For complete removal of the above impurities, the use of chlorine alone is certainly uneconomical. Therefore they must be eliminated from water and wastewater before chlorination is done.

The pH value of water undergoing treatment by chlorine is one very important factor which determines its effectiveness. This is so because the concentration of hypochlorous acid (which is the main disinfectant), is pH-dependent. (See table 3).

4. Temperature of water :

The rates of most chemical reactions increase with temperature. Disinfection involves diffusion and penetration of chlorine through the cell wall and its reactions with the cell's enzyme/s. Both these steps are temperature-dependent. Generally, a lowering in temperature of about 6°C of the water requires increasing the time of contact 1.5 to 3.5 times that required at the higher temperature, in order to achieve the same degree of microbial kill. If contact time cannot be increased (as is usually the case in actual practice), the dose of chlorine has to be increased for lower temperatures by the same proportion as above.[17]

5. Time of contact :

The time for which a disinfectant remains in contact with the organism to be inactivated is important from the point of view of its disinfecting efficiency. This is because the biocidal action is due to diffusion and penetration followed by reaction of the disinfectant with the cell's enzyme/s. During its reaction with organic matter the concentration of the disinfectant decreases, thereby requiring greater time for the action to be complete than if the organic matter were absent. In water distribution systems, where the first consumer is located near the point of addition of the disinfectant to the water, or in swimming pools, where the time for which the disinfectant remains in contact with the contaminating matter is small, time of contact becomes a significant factor. The reaction of chlorine with ammonia takes about a minute to go to completion, depending upon the pH and temperature of the water. During this time, the free residual chlorine concentration decreases rapidly but its bactericidal power is retained. So there is a short period of time in chlorine-ammonia treatment when the rate of kill of the microorganisms is quite high. When the formation of chloramines is completed, the rate falls to a very low value.[18]

The concentration of the disinfectant, together with the time of contact, is expressed mathematically as: $C^n x t$ = constant, where C is the disinfectant concentration, t is the time of contact and n is the dilution factor. The value of n varies between 0.75 and 2.0 and has to be determined experimentally. Values of n more than 1 indicate that the efficiency of the disinfectant increases rapidly as its concentration increases. Values of n less than 1 indicate that time of contact is more important than disinfectant concentration. When n is equal to 1, time of contact and concentration are of equal importance. The importance of these values is illustrated by the following example:

In a water at pH 7.0, a dose of 0.5 mg/l of total chlorine produces satisfactory disinfection in a contact time of 5 minutes. It is decided to raise the pH of the water to 8.5 to control corrosion of the distribution system. Experiments show that n has a value of 1.25 in the expression $C^n t$ = Constant, Assuming that only HOCl has any killing ability, and the ionization constant for HOCl is 2.7×10^{-8} mols/l at 20°C, what will be the increased time of contact if the dose is not to be changed? Alternatively, what will be the dose if the contact time is not to be changed?

Solution:

From the equation $\frac{R}{C} = 1 + \frac{k_i}{[H]^+_i}$ R is 0.5 mg/l, $H^+ = 10^{-7}$ mols/l and k_i is 2.7×10^{-8} mols/l. Substituting these values, we have C = 0.39 mg/l. Next, $C^n t$ = Constant. Here n is 1.25 and t is 5 minutes. Therefore, the product $C^n t$ is 1.55, a value obtained by substituting the values of C, n and t.

Now if the dose is to be kept constant, i.e. R is 0.5, at a pH of 8.5, the value of C will be 0.052. This is much smaller than the value of 0.39 mg/l. So the time of contact will have to be increased and its new value will be given by $0.52^{1.25} x t = 1.55$. This gives t = 62 minutes. Alternatively, if the time of contact is to be kept constant, the dose will have to be increased. Using the equation for $\frac{R}{C}$ given above, and solving for R, we get R = 3.74 mg/l.

It will be seen from the above example that a change in pH of water by 1.5 units has a significant effect on the time of contact and the dose of chlorine.

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CHAPTER 3

Forms of Chlorine

Chlorine is present as a gas at normal temperature and pressure, but can be converted into solid or liquid form by suitably changing the pressure on the gas. Compounds of chlorine can also be manufactured and are offered as sources of chlorine. These are described briefly below.

Compounds of chlorine commonly used in water treatment and wastewater treatment are bleaching powder, calcium hypochlorite and sodium hypochlorite.

Bleaching powder :

$CaO.2CaOcl_2.3H_2O$.

The method of passing chlorine gas over finely divided lime for making bleaching powder is used even today, although patented by Tennant in 1799. In producing bleaching powder, the temperature of the reacting substances is maintained below 35°C to minimize formation of chlorates. If the above reaction is carried to completion, the theoretical chlorine content of bleaching powder would be 49%. However, at chlorine levels of 37% and above, the powder tends to absorb moisture from the air and melts, thereby losing its stability.[1]

Calcium Hypochlorite :

(also called HTH, or Perchloron or Pittchlor)
$Ca(OCl)_2.4H_2O$.

When a slurry of lime and sodium hydroxide is chlorinated and cooled to minus 23°C, crystals which form are centrifuged to remove the mother liquor and insolubles. These crystals are then added to a slurry of chlorinated lime. When this mixture is warmed, it precipitates calcium hypochlorite dihydrate and sodium chloride remains in solution. The slurry is then filtered and the resulting cake is granulated, dried and sized. The product contains 70% available chlorine and less than 3% lime.[1]

Sodium hypochlorite NaOCl :

Unlike bleaching powder or calcium hypochlorite, sodium hypochlorite is a liquid containing from 3% to 15% available chlorine and is reasonably stable on account of its high alkalinity. It may be prepared by reacting gaseous chlorine with a solution of sodium hydroxide, in accordance with the patented Laval Process. It can also be prepared by adding bleaching powder to sodium carbonate, allowing the calcium carbonte formed during the reaction to settle and decanting the clear supernatant liquor.[2,3] Another way to prepare sodium hypochlorite is by the electrolysis of brine.

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CHAPTER 4

Dose of Chlorine

INTRODUCTION :

The main aim of chlorination of water supplies is to render the water safe for human consumption. As already mentioned in Chapter 2, sewage and a number of industrial wastes are also subjected to treatment with chlorine for improving their quality and assisting in a more efficient operation of the wastewater purification plants.

DETERMINATION OF CHLORINE DOSE :

The amount of chlorine to be added in order to achieve the desired objective is determined by conducting a 'chlorine demand' test in the laboratory. It consists of adding different doses of chlorine to equal volumes of samples of water being tested, giving equal time of contact to all samples for reaction between chlorine and contaminants and determining the residual chlorine in the samples at the end of the contact period. The difference between the amount of chlorine added and that remaining at the end of the test is the chlorine demand of the sample.

The term 'chlorine demand' is of little significance when one considers the objectives of wastewater chlorination; instead 'chlorination requirement' is a more appropriate term.[1] It can be defined as the amount of chlorine that must be added per unit volume of wastewater to achieve the desired results under stated conditions such as pH value of the wastewater, its temperature, time of contact etc.

As a result of the study of chlorine demand for waters of different quality, and from experience gained by treatment of sewage and industrial wastes with chlorine, it is possible to give approximate dosages to achieve specific goals. The following tables give these values.

Table 1 pertains to application of chlorine in raw water storage reservoirs.

Table 2 gives values of dosages to be used during water treatment.

Table 3 gives the minimum bactericidal and cysticidal concentrations of chlorine in treated water required at various temperatures and pH values.

Table 4 gives chlorination requirements for various purposes in sewerage and sewage treatment.

Table 5 gives desirable doses for miscellaneous purposes such as cyanide removal, cooling water chlorination, ammonia removal, outdoor swimming pool disinfection etc.

Table 1

Approximate Values of Lethal Doses of Chlorine for Various Organisms[2]

Name of organism		Lethal dose, mg/l
1	**Diatoms :**	
	Achnantes	0.25
	Asterionella	0.5 to 1.6
	Cyclotella	1.0
	Melosira	2.0
	Synedra	1.0
	Tabellaria	0.5 to 1.0
2.	**Chlorophyceae (Green algae) :**	
	Coelastrum	1.0
	Dictyosphaerium	0.5 to 1.0
	Protococcus	1.0
	Spirogyra	0.7 to 1.5
	Tetrastrum	1.0
	Volvox	0.3 to 1.0
3.	**Cyanophyceae (Blue-green algae) :**	
	Anabena	0.5 to 1.0
	Aphanizomenon	0.5 to 1.0
	Clathrocystis	0.5 to 1.0
	Coelosphaerium	0.5 to 1.0
	Oscillatoria	1.1

Name of organism	Lethal dose, mg/l
4. **Protozoa :**	
Ceratium	0.3 to 1.0
Dinobryon	0.3 to 1.0
Endamoeba histolytica	3 to 100
Synura	0.3 to 1.0
Uroglenopsis	0.3 to 1.0
5 **Crustaceans :**	
Cyclops	1 to 3
Daphnia	1 to 3
6. **Fungi :**	
Achlya	0.6
Crenothrix	0.5
Didymohelix	0.25
7. **Miscellaneous organisms :**	
Chironomus (Bloodworm)	15 to 50
Chironomus (Midges)	3.0
Nais	1.0

[a] These doses must be adjusted according to alkalinity and temperature of water.

Table 2

Approximate Chlorine Doses for Specific Purposes[3]

Purpose of addition	Dose, mg/l
1. Colour removal	5 to 100
2. Iron bacteria control	2 to 10
3. Iron precipitation	0.63 times iron content
4. Manganese precipitation	1.3 times manganese content
5. Hydrogen sulphide odour removal	2.1 times H_2S content
6. Ammonia removal	10 times the ammonia content

Table 3

Bactericidal and Cysticidal Concentrations of Free Residual Chlorine[3]

PH value	Free residual chlorine, mg/l	
	Bactericidal 0 to 25°C	Cysticidal 22° to 25°C
6.0	0.2	2.0
7.0	0.2	2.5
8.0	0.2	5.0
9.0	0.6	20

Table 4

Chlorination of Sewage in Sewers and in Sewage Treatment Plant[4,5]

Sr. No.	(A) Purpose of chlorination	Dose, mg/l
1.	Upsewer odour control	1.5 to 10
2.	BOD reduction	5 to 12
3.	Slime growth prevention	1 to 10
4.	Grease removal	2 to 5
5.	Aid in sludge thickening	3 to 5
6.	Control of activated sludge bulking	2 to 8
7.	Control of trickling filter ponding	2 to 10*
8.	Control of trickling filter flies	3 to 10
9.	Digester supernatant oxygen demand reduction	20 to 80

Sr. No.	(B) Quality of sewage	Dose, mg/l**
1.	Raw sewage	6 to 24
2.	Primary settled sewage	3 to 18
3.	Chemically precipitated sewage	3 to 12
4.	Trickling filter plant effluent	3 to 9
5.	Activated sludge plant effluent	3 to 9

* Combined residual at the distributor nozzle

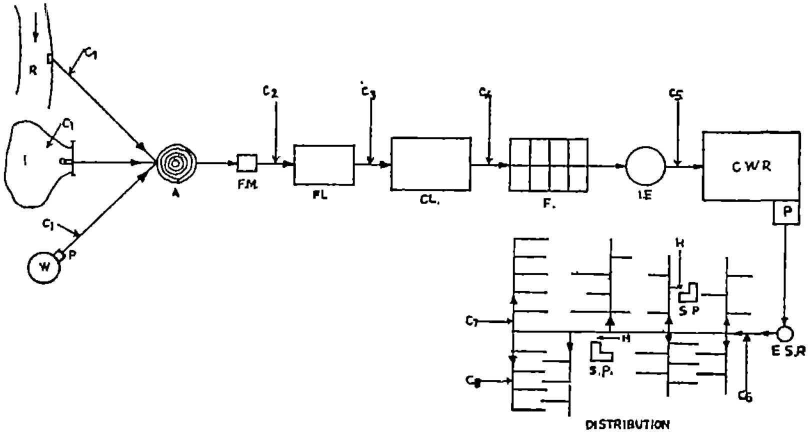
** 0.5 mg/l residual after 15 minutes of contact time.

Table 5
Chlorination for miscellaneous purposes

Sr. No.	Purpose of chlorination	Dose, mg/l
1.	Converting cyanides to cyanate	2.7 times cyanide content as CN
2.	Converting cyanides to nitrogen and carbon dioxide	6.8 times cyanide content as CN
3.	Cooling towers — once through systems	5 to 15, intermittently
4.	Cooling towers — open recirculation systems	3 to 5
5.	Swimming pools with water circulation in 6 to 16 hours	
	outdoor pools	8 to 10
	indoor pools	2 to 5
6.	Disinfection of treated water reservoirs	200 mg/l at 30 min. contact time
7.	Disinfection of new and repaired mains	10 mg/l at 24 hour contact time

CHLORINATION PRACTICES:

Chlorine may be added to water (i) at source, (ii) at one or more points within the treatment plant, and (iii) at one or more points in the distribution system. Addition of chlorine before filtration is termed 'prechlorination', while that after filtration, 'postchlorination'. Boosting the dose of chlorine in large distribution systems to maintain the desired residual in the water is done by rechlorination. The quality of water may be such as to require large doses of chlorine, resulting in 'break-point' chlorination or 'superchlorination'. This results in producing hygienically acceptable, but aesthetically unacceptable water, due to the odour and taste imparted to it by the large chlorine residual. This condition is corrected by dechlorination, done with the help of reducing agents like sodium bisulphite, $NaHSO_3$, or Sodium sulphite, Na_2SO_3, or by use of sulphur dioxide, SO_2. Passing the chlorine-bearing water through a carbon bed also helps to reduce the chlorine concentration in the water. Chlorine may also be employed to control algal and other undesirable growths of organisms in the raw water and treated water reservoirs. It is highly desirable to disinfect water supply pipes, whether they are newly laid or are being put back into service after repairs In areas where piped water supplies are not available, water is drawn from dug wells and tube wells. Maintaining water from such sources in a hygienically safe condition can be done with the use of chlorine. A brief description of each of the above processes is given below. A diagrammatic representation of the points where chlorine can be profitably added to water is given in fig. 1.



NOTATION –

R	River.
I	Impounded Reservoir.
W	Well.
A	Aeration Fountain.
FM	Flash Mixer.
FL	Flocculator.
CL	Clarifier.
F	Filters.
IE	Ion Exchanger.
CWR	Clear Water Reservoir.
P	Pump House.
ESR	Elevated Service Reservoir.
SP	Swimming Pool.
H	Halogen Addition Point (Cl_2, Br_2, I_2).
C_1, C_2 etc.	Possible Points of Halogen Addition. (mostly Cl_2).

Fig. 1

Collection, Treatment and Distribution of Water possible Chlorine addition points.

CHLORINATION OF DISTRIBUTION MAINS & RESERVOIRS :

The chlorination of new mains and mains after repairs is a must to supply bacteriologically safe water.

The mains are classified into two types from the operation point of view. (1) Small mains having diameter less than 250 mm (2) Large mains having more than 250 mm diameter. The smaller mains are chlorinated using 'injector' which provides continuous flow of heavily chlorinated water. The large mains should be chlorinated by chlorine gas obtained from mobile chlorinator.

The chlorination of either small or large mains can be proceeded as follows:

1. Isolate carefully the zone of main to be chlorinated.
2. Empty the main as completely as possible.
3. Flush it to remove grit or dirt accumulated in the zone.
4. Apply the chlorine dose continuously either in the form of strong solution or gas as near as possible to the end of isolated zone. Continue the dosing till water is clear of dirt and grit or sediment. Allow to flush for another 3-5 minutes. About 20 ppm dose is applied to the water in mains.
5. Check periodically for chlorine concentration to ensure that the correct dose of chlorine is being maintained (20ppm).
6. Shut down both the ends and allow the main to remain full of chlorinated water for a specified contact period. Generally 2 hour period is advised.
7. Flush the main properly by clean water from both ends till all the chlorinated water has been expelled.

The chlorination of reservoirs is generally done when the reservoir is return/put to service after a long period.

The reservoirs, specially walls and floors are washed using hose pipe. Chlorinated water is injected through inlet till the water level rises to 30 cm from the bottom. Ensure that the chlorine in the water is not less than 20 ppm. Allow to stand for about an hour. Drain the water and refill the reservoir to a depth of 1 to 1.3 m. Test for bacteriological analysis. If the results are satisfactory, fill the reservoir completely and put to service.

Prechlorination:

This is done (i) at source, or (ii) in the flocculation basin, or (iii) at the filter inlet. When chlorine is added at source, the purpose is to remove colour-, odour- and taste-producing substances. This helps to meet a part of the chlorine demand and reduces the 'postchlorination' requirements. Prechlorination aids coagulation by oxidizing the organic matter in the raw water. It controls slime and mudball formation in filter beds. In addition it provides a safety factor in disinfecting heavily contaminated waters, while keeping residuals in the distribution system to a minimum.[7]

Approximate chlorine dose requirements for the above purposes are given in tables 1 and 2.

Postchlorination:

The most significant single point of application of chlorine in a water treatment plant is after filtration, before the water is stored in the clear water reservoir. It is added here principally to destroy pathogenic organisms including the virus. From this point of view, 0.5 mg/l of free chlorine residual after a contact time of 1 hour is considered sufficient to inactivate virus, even in waters which were originally polluted. This free residual should be insisted upon in distribution areas suspected of endemicity of jaundice. For other areas, 0.2 mg/l of free residual after a contact time of 30 minutes is considered sufficient.[6]

Rechlorination:

This involves addition of chlorine to water after it has left the water treatment plant. The addition may be done at the service reservoirs, or directly into the distribution mains, or at the booster pumping stations. Presence of chlorine serves the purpose of maintaining the desired residual in the water at the consumer's tap. It also minimizes slime growth in the pipe lines. A free residual of 0.2 to 0.4 mg/l is sufficient. An initial period of adjustment is necessary for attaining this chlorine residual before the free chlorine in the filter effluent reacts with the slime or deposit in the pipe till it is oxidized. Generally three transition periods are encountered: (i) chlorine demand of the organic matter in the pipes removes all the chlorine; (ii) combined residual chlorine is present in the water due to reaction with the free ammonia; (iii) free residual chlorine remains in the system as desired, after having oxidized the slimes and the deposits. These periods may range from 1 to 6 months, during which continuous tastes may be produced in the water. These periods can be greatly reduced by prior flushing of the mains and practising free residual chlorination with gradual increment in doses. This is illustrated in table 6 below. It is assumed here that the previous practice in this system was to maintain 0.2 mg/l combined residual in the treated water, without controlling residuals in the distribution system.

Table 6

Transition periods in disinfection.[2]

Period	Residual at treatment plant, mg/l		Residual at centre of distribution	
	Free	Combined	Free	Combined
Previous to start	—	0.2	—	—
Start	0.1	0.1	—	—
End of 1st week	0.2	—	—	Traces
End of 2nd week	0.3	—	—	0.1
End of 3rd week	0.4	—	—	0.2
End of 4th week	0.4	—	0.1	0.2
End of 5th week	0.4	—	0.2	0.1
End of 6th week	0.4	—	0.3	—

Another way to maintain adequate residuals in the distribution system is to practise chlorine-ammonia treatment. This process was developed to provide a persistent residual without creating chlorinous tastes. In water supply systems handling waters with low pH, and where technical control for the maintenance of free residual throughout the distribution system is not feasible, chlorine-ammonia treatment is practised. For waters with pH not exceeding 8.5 to 9.0, a ratio of ammonia to chlorine of 1:3 is found to be suitable. But if the water contains phenolic compounds, the dose of ammonia must be such as to force the chlorine to react with ammonia rather than with phenols. In extreme cases the ammonia dose may be twice the chlorine dose. If the water has a high pH, high organic content or is at a low temperature and can be contacted with the chlorine for only a short time, the ammonia content is kept at ¼th the residual concentration of chlorine after ammonia is added. When adequate taste-control cannot be achieved, even by this procedure, the chlorine dose is increased to yield a free residual in the treated water and is then followed by dechlorination. In any case, the dose of ammonia must be kept at a minimum.[2]

Chlorine-ammonia treatment has certain shortcomings. The chloramines are far weaker than free chlorine as disinfectants. They cannot destroy quickly any secondary pollution which may be introduced into a supply system. Moreover, it is costlier to apply two chemicals through two separate units of dosing equipment than to apply larger doses of chlorine alone. Therefore, free residual chlorination is preferred to chlorine-ammonia treatment.

Superchlorination and Breakpoint chlorination:

Superchlorination consists of adding high doses of chlorine to obtain free residuals. The method is useful for waters with a doubtful quality and those subjected to rapid fluctuations in quality. Short contact periods of 5 to 20 minutes are combined with high chlorine doses to achieve disinfection. But this may necessitate dechlorination of the treated water before use. Superchlorination is useful for emergency water supplies, for temporary installations and in cases where economic considerations are secondary.

Results obtained by superchlorination can also be got by breakpoint chlorination. It has been successfully used in waters having ammonia and organic amines. In breakpoint chlorination, enough chlorine is added till the ammonia and amines are destroyed and free residual chlorine is present. Waters containing ammonia may also contain oxidizable organic matter which consumes the added chlorine. Therefore, it is necessary to know from laboratory tests the total dose of chlorine for oxidation of organic matter and for achieving breakpoint. A chlorine to ammonia ratio of 10:1 is considered sufficient if the water is free from other organic matter. Long times of contact, of the order of 2 hours, are required to obtain the desired microbial destruction in the water under treatment. Skilled supervision and regular chemical analysis of water are required to adjust the chlorine dose according to the changing quality of water. Breakpoint chlorination is, therefore, also called 'controlled superchlorination'.

Dechlorination :

It consists of removal of excess chlorine from the water. It can be done by simply exposing the water to air and sunshine, but is not employed for treated waters. Instead, chemicals like sodium bisulphite, sulphur dioxide, or sodium thiosulphate are used. An activated carbon bed is also used for dechlorinating small volumes of water. The theoretical reactions in dechlorination with these substances are as follows :

Sulphur dioxide : $SO_2+Cl_2+2H_2O \longrightarrow H2SO_4+2HCl$.

Sodium thiosulphate : $2Na_2S_2O_3 + Cl_2 \longrightarrow Na_2S_4O_6 + 2NaCl$.

Sodium bisulphite : $NaHSO_3+Cl_2+H_2O \longrightarrow NaHSO_4+HCl$.

Sodium sulphite : $Na_2SO_3+Cl_2+H_2O \longrightarrow Na_2SO_4+2HCl$.

Activated carbon : $C+2Cl_2+2H_2O \longrightarrow CO_2+4HCl$.

Sulphur dioxide is handled and fed in the same way as chlorine. The sodium compounds are used in a dry form. Activated carbon is used in the form of a packed bed of granules through which water is passed. Whichever dechlorinating agent is used, its dose is kept such as to leave a little residual chlorine in the water.

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CHAPTER 5

Determination of Chlorine Residuals

INTRODUCTION :

Addition of chlorine in one or the other form to water and wastewater has been practised for a number of reasons already described in the previous chapters. However its concentration in the waters and wastewaters so treated must be determined in order to know whether the disinfectant is added in the right amounts. Such determinations constitute an important step in the control of treatment processes.

In the case of water treatment and distribution, the presence of residual chlorine in a sample indicates that chlorine is available for overcoming chance contamination and aftergrowths in the distribution system. But its absence must alert the treatment plant operator to the possibility that either the treatment is not adequate, or the dose is insufficient, or there is a large enough contamination of the treated water which has wiped out the residual chlorine and rendered the water unsafe for consumption.

In sewage and industrial wastes treatment, the presence of residual chlorine in large concentrations is usually not expected due to the reactions of the added chlorine with a number of compounds present. However it is necessary to know how much chlorine is added to achieve the desired effect.

METHODS OF DETERMINATION :

All methods of determining residual halogens, i.e. chlorine, bromine, iodine, in a sample depend on their oxidizing power. Therefore, any other oxidizing agent present in the sample may interfere with the determination. The following methods are commonly used : (i) Orthotolidine test, (ii) Orthotolidine-arsenite test, (iii) Stabilized neutral orthotolidine test, (SNORT test), (iv) Starch-iodide test, (v) Drop-dilution test, (vi) Diethyl-p-Phenylene Diamine (DPD) test, (vii) Free available chlorine test with Syringaldazine (FACTS), (viii) Methyl orange test and (ix) Amperometric titration test.

Phelps proposed in 1909 the use of orthotolidine as a colorimetric indicator for chlorine residuals. Elms and Hauser made the test quantitative by incorporating colour standards This made it possible to determine chlorine in the field as well as in the laboratory. About 1940, the difference in disinfecting powers between free chlorine and combined chlorine was demonstrated[1] Thereafter analytical methods for differentiating between free and combined chlorine residuals were developed. The DPD test was introduced in 1957[2] and the FACTS test around 1975.[3]

(i) Orthotolidine test:

Orthotolidine, an organic compound, is oxidized in acid solution by chlorine, chloramines and other oxidizing agents to produce a yellow-coloured compound. The intensity of colour produced is proportional to the amount of the above substances present.[1] Interferences in the test include nitrite, ferric and manganic compounds. These substances increase the colour intensity and give a high reading. If the sample under test contains no more than 0.3 mg/l iron, 0.01 mg/l manganic manganese or 0.1 mg/l nitrite nitrogen, the development of colour may be taken as that due to chlorine.[4] If the sample under test is at a temperature of less than 20°C, it should be gently warmed to this temperature and a contact period of 3 to 5 minutes should be given before reading the residual chlorine.[1]

(ii) Orthotolidine-arsenite test:

This test permits measurement of the relative amounts of free available chlorine, combined available chlorine and colour due to interfering substances. Free chlorine reacts instantaneously with orthotolidine while combined chlorine reacts much more slowly. Therefore, total residual chlorine is measured first, giving a contact time of 5 minutes. Then a second test is made using sodium arsenite as a reducing agent stronger than orthotolidine. In this test, sodium arsenite is added within 5 seconds of adding orthotolidine. The yellow colour developed is mainly due to free residual chlorine. The difference in readings between the first and the second test gives the combined residual.

The precision of the test depends upon the time intervals recommended for the addition of the reagents and on the temperature of the sample. For very precise results, the sample should be chilled as quickly as possible to 1°C before adding the reagents.[1 4]

A detailed procedure for the orthotolidine and OTA tests is given at the end of this chapter.

(iii) Stabilized Neutral Orthotolidine (SNORT) Test :

This test is used only for the determination of free residual chlorine. It is based on the development of the blue meriquinone colours of orthotolidine in the neutral pH range of sample-reagent mixture. The colour developed is measured with a photometer. If a sample has manganic compounds, natural colour or turbidity in it, 5 ml of arsenite solution (5 gm sodium arsenite in a litre of distilled water) is added to 100 ml of the sample and this blank is used to set 100% transmittance on the photometer. All samples are then measured relative to this blank[5]

(iv) Starch iodide test :

This test is useful in measuring residual chlorine concentrations greater than 1 mg/l. It was the test in use upto 1913 A.D for controlling chlorination. It is based on the principle that free and combined chlorine residuals oxidize iodide ions to free iodine in a solution of pH equal to or less than 8.0. The liberated iodine produces blue colour in the presence of starch. Titration of this solution to a colourless endpoint with a reducing agent like sodium thiosulphate gives a quantitative indication of the amount of chlorine present.

The test is useful in determining residuals in disinfection of water mains, reservoirs etc. where chlorine concentrations are much above 1 mg/l. It is also useful in determining available chlorine in bleaching powder.

A field method for combined residuals upto 0.5 mg/l is proposed by Thorsell et al.[6] It consists of adding to 7 ml of water sample a reagent containing 25 mg each of potassium iodide, soluble starch and potassium hydrogen tartarate. The chlorine reacts with potassium iodide and liberates iodine, which reacts with starch to form blue colour.

Another field method is the drop-dilution method for measuring residuals greater than 10 mg/l. This method is not accurate enough to replace either the starch-iodide method or the orthotolidine method. It consists of adding 0.5 ml orthotolidine to 10 ml of distilled water in a colour comparator cell, mixing thoroughly and then adding a drop of the sample to this distilled water. The colour develops rapidly and is compared against chromate-dichromate standards. If the addition of 1 drop fails to produce colour, the contents of the cell are discarded and the above procedure is repeated, but two drops of sample are added for colour development.[4]

(vi) Diethyl-P-Phenylene Diamine (DPD) Test :

Developed by A. T. Palin in England, this method, useful for determining free residual, combined residual and for differentiating between monochloramine, dichloramine and nitrogen trichloride, is preferred to the OT or the SNORT test. It uses an indicator solution of diethyl-p-phenylene diamine. It can be used quantitatively either by the ferrous titrimetric method (ferrous ammonium sulphate), or colourimetrically using a colour comparator and reagents in tablet form.

As compared with the neutral OT method (SNORT), the colours produced are more stable, fewer reagents are required, and a full response in a neutral solution is obtained from dichloramine. Since dichloramine imparts an acrid taste while nitrogen trichloride gives an obnoxious smell to water, it is important to know the concentrations of these substances in water. The DPD test serves this purpose very ably.[5]

(vii) Free available Chlorine Test with Syringaldazine :

This procedure, originally reported by Bauer and Rupe, was modified by Cooper et al.[3] It consists of adding different volumes of syringaldazine, phosphate buffer and the sample to a test tube and allowing the colour to develop. This colour is measured on a spectro-photometer at a wavelength of 530 nM. The test has a lower detection limit of 0.1 mg/l and gives a linear response upto 5 mg/l. By adding a dilution step, the range can be extended to 10 mg/l of free available chlorine.

(viii) Methyl Orange Test :[5], [7]

This test depends on the almost instantaneous decolourization of methyl orange by chlorine on a quantitative basis, whereas chloramines are much slower in their bleaching effect. It is claimed that the method is not seriously affected by interference from nitrite, iron and chlorine-ammonia compounds. However the accuracy of the final result depends upon the addition of exact volumes of the reagents. Absorbance of methyl orange is temperature-dependent. So it is difficult to get accurate results by this test.

(ix) Amperometric Titration Method :

This is a method in which the current passing through the titration cell between an indicator electrode and an appropriate depolarized reference electrode is measured as a function of the volume of a suitable titrating solution. In general, the end-point in this titration can appear as (a) cessation of current at equivalence point, or (b) a sudden increase in current or (c) an abrupt change in current.[5]

In this method, free available chlorine is determined by titration between pH 6.0 and 7.5, while combined available chlorine by titration between pH 3.5 and 4.5. Phenylarsine oxide (PAO) is used as the titrating agent because its reaction with chlorine is independent of pH. Interference due to nitrogen trichloride, chlorine dioxide, bromine, iodine, copper, silver and high colour is experienced but none due to manganese, nitrite and iron ions. The method is suitable for use in the laboratory and as a reference against which to check other methods of chlorine determination.[4]

CHLORINE DETERMINATION IN WASTEWATER :

Generally speaking, it is very difficult to produce free residual chlorine in a wastewater sample, on account of the presence of ammonia nitrogen in the case of sewage and the presence of a number of competing substances in the case of both, sewage and industrial wastes.

Two methods for measuring total residual chlorine in wastewater are : (i) back-titration procedure of the amperometric method and (ii) modified starch-iodide method which uses phenylarsine oxide (PAO) as a reducing agent in place of sodium thiosulphate. Both these methods are detailed out in reference No. 5 'Handbook of Chlorination' by C. G. White.

ORTHOTOLIDINE METHOD :

Principle :

Orthotolidine is an aromatic compound. It gets oxidised by chlorine and produces a yellow coloured compound.

This method measures a relative amount of free and combined available chlorine even in the presence of reducing inorganic substances with suitable modification as against Iodometry. The method is more sensitive to lower concentration and gets affected by temperature and contact period. To obtain a proper colour, (a) the solution should be at a pH 1.3 or lower during contact period; (b) the ratio of orthotolidine to chlorine must be at least 3 : 1 and (c) concentration of chlorine should not exceed 10 mg/l.

Procedure :

Addition of sample to reagent — Use 0.5 ml orthotolidine reagent in 10 ml cells, 0.75 ml in 15 ml cells, 5 ml in 100 ml, and the same ratio for other volumes. Place the orthotolidine reagent in the Nessler tube, colorimeter cell or other container; add the sample to the proper mark or volume and mix.

Colour Development and Comparison :

Compare the colours of the sample and standards at the time of maximum colour development (If the potable sample contains predominantly free chlorine the maximum colour appears almost instantly and begins to fade. Samples containing combined chlorine develop their maximum colour at a rate that is largely dependent on temperature, although the nitrogenous compounds present may influence this rate. Usually at 20°C, maximum colour develops in about 3 min; at 25°C, in about 2.5 min; and at 0°C, in about 6 min. About 5 min. after maximum colour develops, a slight fading begins. Therefore, samples containing combined chlorine should be read within 5 min. and should, preferably, be allowed to develop colour in the dark); when colour comparison is made against chromates-dichromate standards, use the same cell depth for both samples and standards.

Compensation for Interference :

Compensate for the interference due to the presence of natural colour or turbidity in one of two ways : (1) View the sample and standard horizontally after placing an untreated sample of the same thickness of clean water behind the sample under comparison; or (2) add 1 or 2 drops (0.05 to 0.1 ml) of decolourising solution to the developed chlorine-orthotolidine colour and mix until the yellow colour disappears (within a minute). Read the values from the calibration curve as 'apparent chlorine' and interferences as chlorine and then subtract. Alternatively, decolourise a portion of the developed sample and use to null the photometer whereupon the chlorine value is obtained directly from the curve. In the presence of excessive turbidity, centrifuge the sample for a brief period to bring it within the nulling range of the photometer.

As the methods described above are not commonly used (so far) in our country the Orthotolidine Method used at most of the waterworks is described in detail below :

ORTHOTOLIDINE-ARSENITE (OTA) METHOD :

Procedure :

Sample and reagent volumes — Label three comparator cells or French square bottles 'A' 'B' and 'C'. Use 0.5 ml orthotolidine reagent in 10 ml cells, 0.75 ml in 15 ml cells and the same ratio for other volumes of sample. Use the same volume of arsenite solution as orthotolidine.

Free available chlorine :

To cell A, containing orthotolidine reagent, add a measured volume of water sample. Mix quickly, and immediately (within 5 sec) add arsenite solution. Mix quickly again and compare with colour standards as rapidly as possible. Record the result (A) as free available chlorine and interfering colours.

Estimation of interference :

To cell B, containing arsenite solution add a measured volume of water sample. Mix quickly, and immediately add orthotolidine reagent. Mix quickly again and compare with colour standards as rapidly as possible. Record the result(B). Compare with colour standards again in exactly 5 min. and record the result (B). The values obtained represent the intefering colours present in the immediate reading (B) and in the 5 min. reading (B).

Total available chlorine :

To cell C, containing orthotolidine reagent, add a measured volume of water sample. Mix quickly and compare with colour standards in exactly 5 min. Record the result (C) as the total amount of residual chlorine present and the total amount of interfering colours.

Measure photometrically the colours developed by following the four directions above and convert the readings to the proper chlorine values by referring to a calibration curve prepared by treating known chlorine concentrations in the same manner as the unknown samples.

Calculation :

Total available residual chlorine =

C—B2

Free available residual chlorine =

A—B1

Combined available residual chlorine =

Total available residual Cl — free available residual Cl.

DROP DILUTION METHOD FOR FIELD USE :

General discussion :

The drop dilution method is designed for field measurements of free residual chlorine where concentrations are greater than 10 ml/l and where speed of estimation is of importance. It is particularly useful in connection with the disinfection of mains or tanks where laboratory apparatus is not available. The test is not intended to displace titration methods and should not be used where accuracy is desired. This test must not be made in direct sunlight.

Procedure :

If the comparator cell holds 10 or 15 ml, place 0.5 ml orthotolidine reagent in the cell. If a 100 ml Nessler tube is used, place 5.0 ml orthotolidine reagent in the tube. Fill the cell or tube to the mark with distilled water and mix thoroughly. Add to the cell or tube 1 drop of the water under test. Mix thoroughly.

A sample of water with such concentrations of chlorine as may be estimated by this method usually contains only free available chlorine, although traces of combined available chlorine are occasionally found. In view of the rapid colour devlopment, compare the colour at once against chromate-dichromate standards with the same cell depth for samples and standards.

If the addition of 1 drop of the water under test produces no colour, dicard the contents of the cell. Refill with orthotolidine and distilled water as before and add 2 drops of the water under test. Continue this procedure with increasing amounts of sample until an easily readable colour, equivalent to not less than 0.1 mg/l, is produced.

Calculation :

$$\text{Free available residual chlorine-mg/l cl} = \frac{\text{ml cell volume x reading x 20}}{\text{drops of sample}}$$

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CHAPTER 6

Equipment for Chlorination

INTRODUCTION

Addition of chlorine to water and wastewaters is made in the form of chlorine solution.Therefore, chlorine feeding devices work on the principle of (a) making a chlorine solution of the required strength and (b) discharging it into the water or wastewater at a controlled rate.

For treating small volumes of water, where the total requirement of chlorine is small, bleaching powder is usually employed as the source of chlorine. For ease of handling and feeding, sodium hypochlorite or calcium hypochlorite is better than bleaching powder. But for disinfecting larger volumes of water supplies and treating wastewaters with high doses, chlorine gas in cylinders is the preferred source.

A brief description of some of the chlorine feeding devices follows :

Bleaching powder feeding devices :

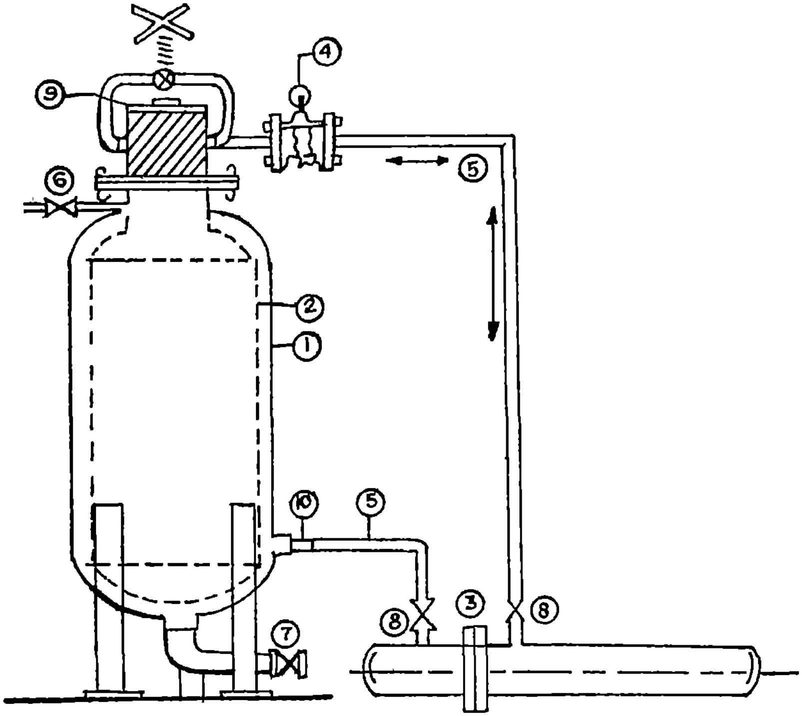
(a) *Differential pressure type :*

This type of chlorinating device is commercially available for use with piped water supplies. It works on the principle of differential pressure generated by flowing water across a venturimeter or an orifice plate. A strong mild steel vessel, containing a rubber bag filled with a mixture of bleaching powder and soda ash in proper proportion (usually 5 : 1) is connected to the water supply line such that the upstream tapping of the venturi or orifice plate sends water into steel vessel for exerting pressure on the rubber bag. The outlet from the rubber bag is connected, in turn, to the throat of the venturi or just downstream of the orifice plate. An amount of bleaching powder solution, proportional to the pressure difference between the upstream and throat (in the case of a venturimeter) or between the upstream and downstream tappings (in the case of an orifice plate) is squeezed out of the rubber bag and is drawn into the supply pipe line. The rate of outflow of the bleaching powder solution can be controlled with a needle valve.

Advantages of this device are : (i) It is simple in construction ; (ii) It has no moving parts in it ; (iii) It does not require an external source of power to operate.

Among the disadvantages are : (i) Its use is limited to small water supplies ; (ii) The rubber bag needs replacement once every 4 to 6 months, or when the water contained in the mild steel vessel shows presence of chlorine, whichever is earlier.

These devices are available in sizes for treating water from 300 m³ per day to 2000 m³ per day. A schematic of the device is shown in Fig. 1.



1. M.S. Pressure Vessel
2. Rubber Bag for Bleaching Powder
3. Orifice Plate or Venturimeter
4. Control Valve
5. Pipe with Clamps
6. Air Valve
7. Drain Valve
8. Outlet & Inlet Valves
9. Chlorine Feeding Valve
10. Nozzles

Fig. 1
Bleaching Powder Dosing Equipment

(b) *Drip Chlorinator* :

This device is useful for treating well waters or water flowing in an open channel It consists of a chlorine solution tank-fitted with a float connected to a delivery tube and a constant flow feeding device. A 1% solution of chlorine, enough to last for about 5 days is prepared and filled in the chlorine solution tank. The solution drips out and its flowrate is adjusted with a stopcock.

The float, tubing and the tank holding the chlorine solution are made out of corrosion-resistant material. A schematic of the drip chlorinator is shown in Fig. 2. This device can also be used to feed sodium hypochlorite solution. In that case, use of corrosion-resistant material for storage and feeding is not as critical as when bleaching powder is used as a source of chlorine.

For chlorination using chlorine gas, the most commonly used devices are : (i) Gravity feed type, (ii) Pressure feed type and (iii) Vacuum feed type.

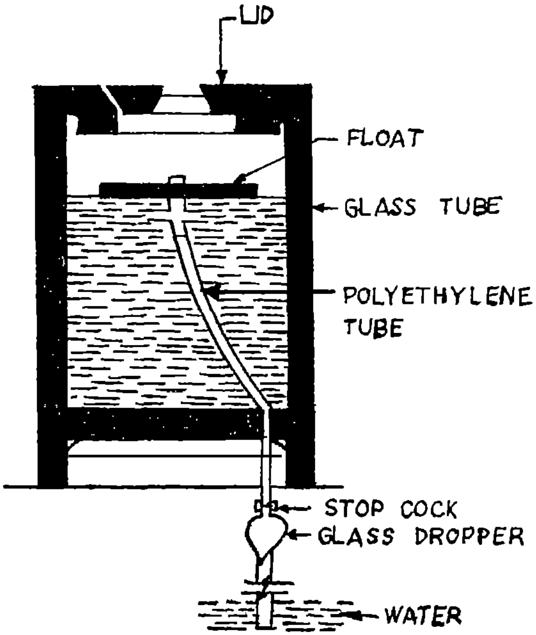


Fig. 2
Drip Chlorinator

(i) *Gravity feed type chlorinator* :

This chlorinator works on the principle of withdrawal of the gas from the cylinder, stepwise reduction of its pressure and dissolution of the gas into a small volume of water to form a strong solution of chlorine, which is then added to the water to be treated, to give the necessary residual concentration. The components of this chlorinator are (a) a chlorine cylinder of 46, 68 or 907 kg, (b) a control panel consisting of a dry gas filter, pressure gauge, stop valve, flow regulating valve, pressure reduction valve/s, manometer for gas flow measuring and a calcium chloride tube through which the gas passes, (c) Solutionizer, consisting of a source of water, a vertically placed earthenware tower filled with coarse gravel, a perforated tray at its top for

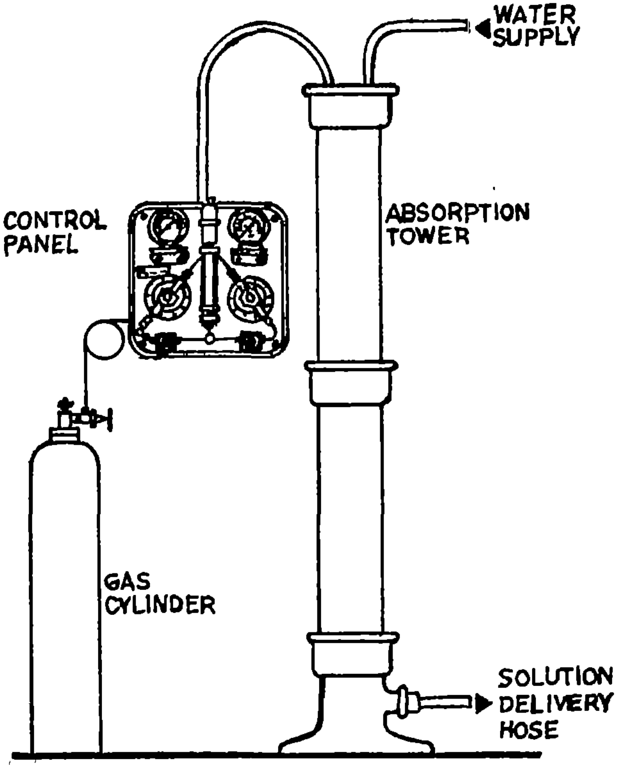


Fig. 3
Gravity Type Chlorinator Schematic.

distributing the water, a corrosion-resistant perforated pipe for admitting chlorine gas to the solutionizer, a bottom tray to collect the chlorine solution and a chlorine solution outlet. The arrangement of cylinder, panel and solutionizer is shown in Fig. 3.

(ii) *Pressure feed type chlorinator* :

When chlorine solution must be delivered under pressure as in a pipe, the gravity solutionizer is replaced by an injection solutionizer. The gas, as it leaves the control panel, is introduced into a water-sealed cavity surrounding the injector. Water emerging from the jet of the injector with a high velocity absorbs the chlorine gas. The resulting solution is passed through a recovery zone to regain the pressure and is subsequently injected into the pipe. The arrangement is shown in Fig. 4.

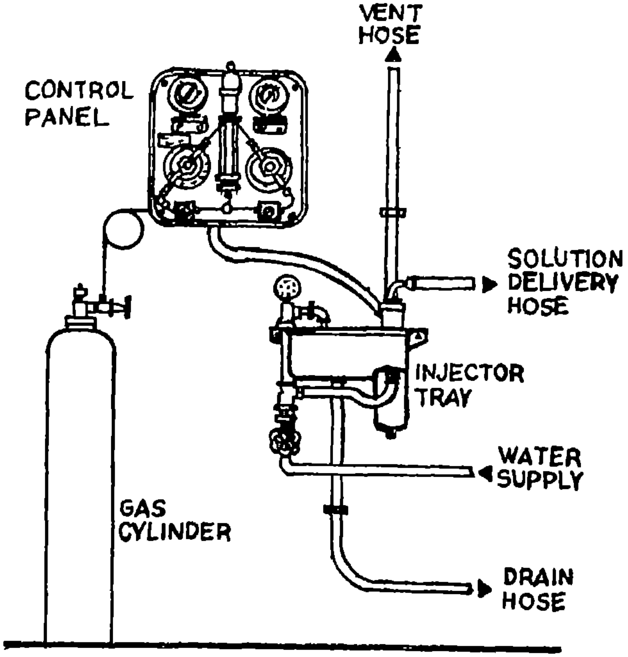


Fig. 4
Pressure Type Chlorinator Schematic.

(iii) *Vacuum type chlorinator* :

It consists of a gas filter, a variable vacuum controller, variable area flow meter, constant vacuum chlorinator and injector assembly. Chlorine gas, till it dissolves in water, is at a pressure below atmospheric. This avoids leakage of gas into the atmosphere. Instead, in the event of a leakage, atmospheric air gets into the chlorinator. Usually such chlorinators are also provided with automatic shutoff arrangements in case of failure of water supply to the chlorinators.

The rate of flow of chlorine is adjusted and maintained by operating the variable vacuum control. Metered gas is delivered to an aspirator type of injector where it is entrained into the operating water supply and delivers chlorine solution to the point of application. This equipment requires the pressure of water to be three times that in the water main. Hence the system is suitable for use with large water mains. A schematic arrangement of a typical vacuum type chlorinator is shown in Fig. 5.

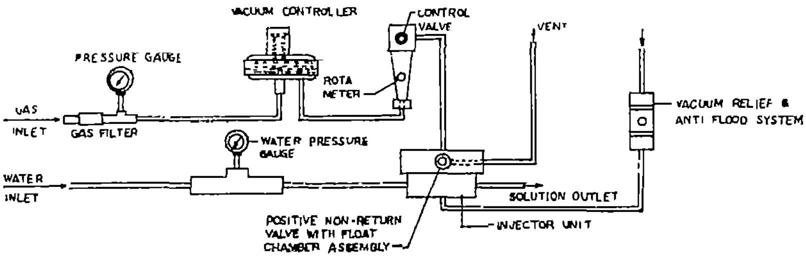


Fig. 5
Vacuum Type Chlorinator Schematic.

(iv) *Electrolytic chlorination type* :

This equipment works on the principle that when direct current is passed through a brine solution, chlorine gas and hydrogen are produced. The chlorine dissolves in the water and in the presence of sodium chloride, forms sodium hypochlorite solution which can then be fed to the water to be treated.

$$NaCl + H_2O - 2e^- \longrightarrow \underset{\text{Sodium hypochlorite.}}{NaClO_2} + H_2\nearrow$$

The equipment used consists of a salt saturation tank, an electrolysis cell, DC power supply and a booster pump or an orifice assembly. Saturated brine is diluted with water and is passed through the electrolysis cell, where sodium hypochlorite solution is formed. This solution is then fed to the water to be treated through a booster pump or through an orifice assembly. These units are available for treating water upto about 5000 m^3/day.

Chlorine Cylinders :

Liquid chlorine is usually stored in vertical cylinders made of seamless mild steel or in welded steel horizontal 'tanks', nearly 80% of the contents being in a liquid form, the rest in gaseous form. The maximum filling density of all containers is 125%, the filling density being the per cent ratio of the weight of gas in the cylinder to the weight of the water the cylinder can hold at 15.5°C. The vertical cylinders contain 32, 45 or 68 kg chlorine and are about 125 to 250 mm dia and 460 to 1980 mm long. The horizontal tank holds 909 kg and is 710 to 760 mm dia and 2100 mm long. The cylinders are tested for a pressure of 56 kg/cm^2 and the tanks to 35 kg/cm^2.[1]

For each of the chlorine cylinders or tanks, there is a maximum rate of withdrawal of the gas which must not be exceeded in order to avoid withdrawal of liquid chlorine from the containers. These rates are generally taken as 0.9 kg per hour from cylinders and 6.5 to 7.5 kg/hour for tonne containers. For withdrawals in excess of the above figures, two or more cylinders (but not more than 4) are connected to a common manifold. When discharging through a manifold, care must be taken to ensure that all the connected cylinders are at the same temperature, For even higher withdrawals, chlorine evaporators are used.[2]

Chlorine evaporators :

In general, when the daily requirement of chlorine exceeds 900 kg per day, chlorine evaporators are used. They consist of a sealed chlorine pressure chamber immersed in hot water, the temperature of which is thermostatically controlled. Liquid chlorine enters this chamber, absorbs heat and is converted into gas. It is standard practice to provide a manual or automatic pressure reducing valve in the chlorine gas outlet line adjacent to the evaporator to prevent liquid chlorine from passing through the evaporator into the chlorine gas supply line.[3]

Cylinder-mounted pressure type feed regulator:

This device is an alternative to the pressure type chlorinator. It requires the pressure at Chlorine feed point to be less than 1 kg/cm². It can feed the gas directly into low-pressure water mains, reaction vessels etc. where a concentrated dose of chlorine is required. It consists of a pressure regulator, usually with a gas flow meter which is mounted directly on the cylinder. The outlet of the pressure regulator is connected to the gas diffuser through plastic tubing. A pressure gauge indicates the pressure of gas after regulation. These assemblies are available in feed range from 100 gm/hour to 75 kg/hour. Assemblies upto 10 kg/hour are mounted on the gas cylinder or tonner, while those with a higher capacity are wall-mounted. It is claimed by the manufacturers of these assemblies that chlorine feeding is not affected by changes in temperature of the air leading to cooling of the gas and subsequent reliquefaction. The mounting of the regulator is quite simple since it is done directly on the cylinder.[4]

Materials suitable for handling chlorine:

Cylinders and tonne containers are made out of solid forged (seamless) mild steel. They must comply with the requirements for cylinders for liquid gases (given in the Gas Cylinder Rules, 1940, of the Government of India), with such modifications as ordered from time to time by the Chief Inspector of Explosives, Government of India. [1,2]

Dry chlorine reacts with aluminium, arsenic, gold, mercury, selenium, tellurium, tin and titanium. At certain temperatures, potassium and sodium burn in dry chlorine. Carbon steel ignites at temperatures above 250°C. Dry chlorine, both gaseous and liquid, may be handled safely in equipment fabricated from iron, steel, O4Cr19Ni9 and O7Cr19Ni9Mo2Ti28 stainless steels, Hastelloy C, Monel, nickel, copper, brass, silver, lead and platinum below 110°C. (At temperatures above 65°C, chlorine reacts with steel at an accelerated rate.). However, this temperature is considerably lower if the metal or alloy is in finely divided, sponge or wire form.

Titanium, platinum, gold and silver are resistant to wet chlorine. This fact is to be borne in mind when preparing specifications for parts of chlorinators which will come in contact with chlorine. At low pressure, wet chlorine may be handled in equipment made of glass, porcelain and glazed stoneware. Gaseous chlorine, wet or dry, may be handled by hard rubber equipment at normal temperature and pressure. Wet gas is corrosive to steel; special material such as PVC, FRP etc. should be used to handle it.[1]

Pipes and conduits used for conveying chlorine are made from special materials. Low carbon steel pipes upto 12 mm dia. are suitable for handling dry chlorine upto 175°C. Stainless steels are recommended for handling dry chlorine upto 315°C. Copper and copper alloy materials can withstand temperatures upto about 600°C. Other metals such as bronze, lead and nickel and nonmetals such as ceramics, glass, rubber, plastics etc. are also used but are subject to specific limitations.[2]

Safety measures in storing chlorine and its compounds:

Chlorine containers should be stored in a cool, dry, well-ventilated place away from boilers, open flames, steam pipes or any other potential sources of heat. They must never be left in the open, exposed to the sun. All cylinders should be stored in an upright position while all tonne containers should be stored on their sides. Chlorine containers should never be stored with acids and articles of corrosive and inflammable nature. They should never be stored near elevators or gangways, where heavy objects may fall and strike them. All empty containers should be stored separately and should be marked with a tag bearing the word 'EMPTY' clearly written on it. No unauthorised person should be allowed to enter the chlorine storage area. ONE SET OF SAFETY KIT AND EMERGENCY KIT WITH ALL COMPONENTS IN GOOD WORKING ORDER SHOULD BE AVAILABLE IN THE IMMEDIATE VICINITY OF THE STORAGE AREA. When they are stored, the valves on all cylinders and tonne-containers must be protected by a stout metallic cap securely attached to the cylinder body. This cap should be kept in position on all containers in storage (whether full or empty) and at all times except when the container is in use.

Any abnormality or defect such as a dent, a faulty valve etc. on a container should be immediately noted and brought to the notice of the supplier. No attempt should be made by the user to repair defective valves.[5]

When the cylinders are to be moved, they should never be lifted by means of the metal caps, nor should rope slings, chains or other magnetic devices be used. Loaded cylinders should be moved on a balanced hand truck with a clamp support at least 2/3 of the way up the cylinder. Tonne-containers should be handled with a suitable cradle with chain slings in combination with a hoist or crane having at least 2 tonne capacity.[5]

Cylinders and tonne containers being trucked should be carefully checked, clamped, or otherwise suitably supported to prevent their shifting or rolling. They should not project beyond the sides or ends of the vehicles in which they are transported. All valves on the cylinders and tonne containers should be tightly closed during transportation and storage. This will avoid leakage of chlorine from filled cylinders and entry of moisture into empty cylinders.[2]

Bleaching powder and sodium hypochlorite should be stored in airtight containers. They should be stored in a cool, dry place, away from wet areas within the plant. All bleaching powder containers in use should be invariably closed tightly after withdrawal of bleaching powder from them. Sodium hypochlorite loses its strength singificantly if it is stored at temperatures exceeding 25°C, for more than 100 days. Therefore, only that quantity of sodium hypochlorite which will last for 8 weeks should be stored in the treatment plant.

It is absolutely essential to mention here that where bleaching powder or sodium hypochlorite is used, frequent determination of available chlorine is the only way to tell the operator how much of the above compounds should be fed so that the right amount of treatment is given to the water.

Handling the equipment for chlorine feeding:

All equipment for this purpose needs careful, routine maintenance, the most significant step being that which prevents leaks and their attendant problems. It is necessary to understand the working of the equipment, its components, requirements of preventive maintenance and steps to be taken to avert serious breadkdowns in the process of chlorination. Chlorine feeding equipment should never be in the hands of untrained persons. All instructions given by the suppliers of the equipment must be strictly followed in order to get the best performance from the equipment. Adequate spares must be available to the plant personnel to enable them carry out repairs and replacement. The instruction manual supplied with the equipment (which is normally conspicuous by its absence in the plant) must be readily available to the operator.

All equipment for chlorination must be kept in a scrupulously clean condition. Maintaing the equipment dry by frequent wiping with a piece of clean cloth ensures that corrosion is minimized. Routine checks for leakage of chlorine can be done with a piece of cloth soaked in liquor ammonia, held near the point of suspected leak. Presence of white fumes of ammonium chloride indicate a leak. Such leaks never stop by themselves but invariably get worse. Therefore they must be attended to immediately.

A preferred cleaning fluid for cleaning internal parts of a chlorinator is carbon tetrachloride. However it must be ensured that all the cleaned parts of the chlorinator are thoroughly dry before it is reassembled.[6] All repairs, replacements and routine cleanup works done on a chlorinator should be recorded in a separate register.

Chlorination room specifications:

Proper construction and placement of chlorination equipment inside the chlorination room can eliminate a number of maintenance problems. There should be adequate light available in the room. It should be properly ventilated. Since chlorine is a gas heavier than air, it tends to settle near the floor of the room. Therefore, large openings in the walls of the room near the floor should be provided. In fact, a room with walls made from RCC grillwork for the first meter or so from the floor should normally ensure adequate natural ventilation. Where large quantities of chlorine are to be handled, forced ventilation using exhaust fans located near the floor of the room should be provided. The electric switches for these fans should be invariably located outside the room. In cold weather, when the ambient temperature falls below 8°C, interference with the supply of chlorine from the cylinder may occur. At such times, provision should be made to heat the air in the room rather than applying direct heat to the cylinder.

All the water piping entering and leaving the chlorination room must be checked frequently for leaks. Any damp condition in the room can lead to corrosion of the metallic parts of the chlorinator and other articles of metal in the room.

When repairs to the chlorinator are to be carried out, appropriate tools should be available inside the room. A safety measure at such times is to run a fan BEHIND the operator, so that any gas which can emanate from the panel will be carried away from the operator.

Chlorine leak detectors are a desirable feature in a large chlorination facility. There are two types of these detectors. One type brings air to be detected in direct contact with orthotolidine impregnated paper. A photoelectric cell analyzes the discoloration and this information is transmitted to an alarm circuit. Another type passes air through a water solution and detects the change in conductivity due to the presence of small amounts of chlorine.[3]

Emergencies and emergency management:

One of the most common emergencies which can arise in a water or wastewater treatment plant is leakage of chlorine either through the cylinder or through the piping which carries the gas. UNDER NO CIRCUMSTANCES SHOULD WATER BE APPLIED TO A LEAK SINCE A CHLORINE LEAK INVARIABLY GETS WORSE WITH TIME. The measures to to be taken to avert serious mishaps are aimed at protecting the personnel from the ill-effects of chlorine and to prevent the spread of chlorine into the surroundings.

The effect of chlorine on human beings is shown below in table 1.

Table 1

Effect of chlorine at various concentrations[2]

Sr. No.	Effect	PPM of chlorine by volume
1.	Least amount required to produce slight symptoms after several hours' exposure	1.0
2.	Least detectable odour	3.5
3.	Maximum amount that may be inhaled for 1 hour without serious consequences	4.0
4.	Noxiousness, difficulty in breathing	5.0
5.	Amount required to cause throat irritation	15.0
6.	Amount causing coughing	30.0
7.	Amount dangerous in 1/2 to 1 hour	40 to 60
8.	Fatal in a very short time	1000

Exposure of the skin to high concentrations of chlorine for a short time is not much irritating or corrosive. But splashes of liquid chlorine on the eyes, skin and clothing may cause immediate irritation and chemical burns and severe damage to body tissue. Chlorine is not known to produce any chronic systemic effects.[2]

Fire hazards due to chlorine are moderate, but chlorine may react to cause fires or explosions upon contact with turpentine, ether, hydrocarbons, hydrogen, powdered metals, swadust and phosphorus. Therefore, particular care should be taken in operation of processes in which these substances may come in contact with chlorine.[2]

Liquid chlorine increases considerably in volume when it evaporates, 1 volume of the liquid being equal to 457.6 volumes of gas at 0°C and 1 atmosphere. Danger due to pressure buildup inside a heated container, leading to hydrostatic ruptures with explosive violence is to be guarded against. It is imperative to keep chlorine containers away from direct sources of heat.[5]

As a regular part of chlorine storage and use, provision should be made for emergency disposal of chlorine from leaking tonne-containers and cylinders. Chlorine may be absorbed in solutions of caustic soda(NaOH), or soda ash (Na_2CO_3) or agitated lime slurry [$Ca(OH)_2$]. Proportions of above alkalis and water are given in Table 2.

Table 2

Proportion of alkali and water

Chlorine container capacity kg	Caustic soda & water		Soda ash and water		Hydrated lime and water	
	Weight kg.	Volume lit.	Weight kg.	Volume lit.	Weight kg.	Volume lit.
45	58	182	136	450	58	566
68	90	270	220	680	82	815
900	1160	3680	2720	9050	1160	11350

A suitable tank should be provided to hold the above volumes. Chlorine should be led to the tank through a piping weighted at the open end to hold it under water. The chlorine cylinder or container should not be dumped into water, since it can float and the gas can still escape into air.[2]

In the event of a person in the treatment plant getting exposed to high concentrations of chlorine, and becoming unconscious, the person should be immediately moved to uncontaminated area. If breathing has not ceased, the person should be placed on his back and should be kept warm, using blankets. If breathing has apparently ceased, artificial respiration should be started immediately. If oxygen inhalation apparatus is available, it should be used by a person authorised for such duty or by a physician. Stimulants are rarely necessary if adequate oxygenation is maintained. Milk may be given to the person to soothe throat irritation but nothing should be given to an unconscious person by mouth. If the skin is exposed to chlorine, it should be thoroughly cleaned with a lot of soap and water. No ointments should be applied to the affected skin for 24-hours. Contaminated clothing should be removed immediately. If eyes are affected, they should be thoroughly washed with water for at least 15 minutes. If a person has swallowed liquid chlorine, he should be made to drink fresh water, or milk of magnesia or lime water.

All employees should be given thorough training in the use of first-aid equipment. They should also be trained in carrying out minor repairs to chlorination equipment. Most importantly, they must be made to appreciate correct use of tools, preventive maintenance of the equipment and keeping chlorine storage areas free from conditions which will lead to gas leaks.

GENERAL SAFETY PRECAUTIONS:

1. Permit only trained and responsible personnel to handle chlorine.
2. Keep valve protection hoods in place except when containers are emptied.
3. Never tamper with fusible plugs or expose these to heat.
4. Never expose cylinders or ton containers to heat or immerse in hot water.
5. Use only suitable and safe means to handle and move containers.
6. Store containers away from flammable materials and in a clean ventilated fire resistant area.
7. Never mix other gas cylinders while storing or transporting
8. Moisture should not be allowed to enter containers.
9. Suck back of liquid be avoided.
10. Never force connections that do not fit. Never use hammer to open valve but only use approved equipment.
11. Take special care for manifold systems. Do not use manifold for liquid phase transfer.
12. Open valves completely for unloading operations.
13. Keep tools free of oil, dirt or grit.
14. Proper tools to be used for servicing.
15. Never load a leaking container.
16. Report leak conditions at once to suppliers.

MATERIALS OF CONSTRUCTION:

At increased temperatures chlorine corrodes almost all materials, especially with the presence of moisture. Ordinary low carbon steel (½% minimum) pipes are preferred for handling dry chlorine upto 177°C. Stainless steels are recommended for handling dry chlorine at higher temperatures upto 316°C. Common steel constructions stand upto 150°C. Copper and copper alloy materials stand upto 590°C. Other metals such as bronze, lead, nickel and non-metals such as ceramics, glass, rubber, plastics, etc. are also used but under specific conditions.

Wet chlorine is very corrosive. Gold, lead, nickel, molybdenum alloys, platinum, silver tantalum and titanium are resistant. At low pressures, ceramics, glass, hard rubber, certain types of plastics can be employed. For high pressures, common metals lined with resistant materials are most suitable.

GAS MASKS:

It will not be out of place to mention here about the use of gas masks. Persons handling chlorine are likely to expose themselves to the effects of chlorine and should, therefore, be provided with suitable gas masks.

Two types of gas masks are in use: (1) Canister type and (2) Breathing type. The Canister type is not to be used when the chlorine content in the air is more than 1% and oxygen content is less than 16%. Canisters merely remove contaminants during inhalation. They do not supply oxygen. They can be used safely only when sufficient oxygen is present.

The life of a canister depends on concentration of chlorine in the atmosphere. Effective service life may be several hours when exposesd to very low concentrations, but at high concentrations a canister may last for only a very short time. A record of its service should be kept, and the canister replaced after two hours of use in mild concentrations of chlorine. In higher concentrations, the canister should be replaced after each use. A slight taste of chlorine is a warning that replacement is necessary.

Canisters with broken seals do not retain their chlorine absorptive capacity indefinitely. If the seal has been broken for a year, the canister should be replaced even though not used. Spare canisters with seals unbroken should be readily available at all times.

The breathing type gas mask has either compressed air or oxygen and can be used for a sufficiently long time in atmosphere where chlorine concentration is heavy.

The gas masks should be kept at a place outside the location of the probable leaks. They should be routinely inspected and kept in order..

In order that the staff is able to make use of these gas masks, they should have enough practice, and drills at regular intervals may be arranged for this purpose.

PIPING SYSTEM:

1. Chlorine piping arrangement should be as simple as possible
2. There should be minimum number of screwed or flanged joints and minimum number of loops and traps.
3. Residual stresses in pipes should be eliminated by bending pipes while it is hot where such connections are required.
4. Chlorine pipes should be located above ground for easy detection of leaks.
5. The pipes should be well supported, protected against temperature variations, sloped to allow drainage and set at an elevation to leave some clearance.
6. Shutoff valves at ends and valves at intermediate points provide a means of isolating leaks.
7. Expansion chambers have to be provided in chlorine pipe line systems to avoid excessive hydrostatic pressures.
8. Liquid chlorine should never be trapped between two shut off valves unless there is an expansion chamber.
9. Sometimes in cold temperature conditions, condensations of gaseous chlorine may occur in pipe lines. This can be overcome by reducing the pressure or by the use of non-combustible pipe line insulation.

PIPE PREPARATION:

1. New pipes should be cleaned and dried thoroughly and checked for leaks before laying.
2. Cutting oil, grease and other foreign material inside pipes and fittings should be completely removed by flushing or

pulling a piece of cloth saturated with trichloroethylene or chlorinated solvent through the pipe length.

3. No hydrocarbon (Benzene etc.) or alcohol should be used for cleansing.

4. New valves or flanges, etc. with grease or in oily conditions should be dismantled and cleaned before use.

5. Valves should be tested for seat tightness with 10 kg/cm^2 air pressure.

6. Entire pipe system should be hydrostatically tested to 20 kg/cm^2 pressure.

7. Pipe system should be dry. Steam is passed through lines from the high end for the condensate and foreign matter to drain out. Steaming should be done till line becomes fairly hot and dry air blown through pipes until the dew point of discharge air equals that of entering air. After this the pipes are filled with dry air and tested for leaks. Leaks are tested with soapy water at the outside of joints. Then small quantities of chlorine gas are sent in and pressure built up by dry air and leakage tested.

OPERATIONAL CARE :

While starting a chlorinator, operating water should be opened into the chlorinator first. Chlorine supply is thereafter to be opened starting from the chlorinator and ending up on the drum or cylinder valve.

The operations are reversed while shutting down. Chlorine supply should be stopped first, starting from the drum or cylinder valves and ending up on the chlorinator stop valve. Thereafter shut off operating water. This ensures complete removal of chlorine gas from the equipment as well as piping system.

While disconnecting any line or removing any component from the chlorinator, care should be taken to plug the open ends to prevent moist air entry which would otherwise form oxide encrustations inside, causing obstruction to free flow.

Though in modern trend of manufacture there is extensive use of non-corrosive materials such as PVC, fibreglass, etc. but wherever metal parts are used, they have to be lined from outside.

Exposed surfaces could also be protected by applying petroleum jelly mixed with gasoline.

Operational care also demands careful handling of the equipment. The components are accurate and precision made. They are to be soft handled. Hard and fast operation will overstrain the component and spoil their settings. Maintenance will be incomplete if there are no proper tools to attend. The repair works will not be prompt if essential spares are not kept in stock. Special care on these aspects needs particular attention.

REFERENCES:

1. Course Manual on 'Chlorination and Use of Chlorinators'. Course conducted by Indian Water Works Association Bombay Centre, Victoria Jubilee Technical Institute, Bombay and Candy Filters (India) Ltd..,
2. IS : 646-1970. Liquid chlorine, Technical. (First revision) (with amendment no. 1) (Reaffirmed 1978).
3. White, Geo. Clifford. Handbook of Chlorination. Van Nostrand Reinhold Co. New York (1972).
4. Information pamphlet no. CCE/12 of M/s Chloro Control Equipment.
5. Safe Handling of Chlorine – A Guide for Consumers. Published by Alkali Manufacturers' Association of India. (1986).
6. Kavanagh, J. P. Chlorinator Maintenance and Operation. Sewage and Industrial Wastes. Nov. 1953.

APPENDIX A :

List of useful Indian Standard Specifications in connection with chlorination.

IS : 10553-1983. Requirements for chlorination equipment.

Part 1. General guidelines for chlorination plants including handling, storage and safety of chlorine cylinders and drums.

Part 2. Vacuum feed type chlorinators.

Part 3. Pressure feed type chlorinators.

Part 4. Gravity feed type gaseous chlorinators.

IS : 646-1970. Liquid chlorine, Technical. (First revision) (with amendment no. 1) (Reaffirmed 1978).

IS : 7681-1975. Welded low-carbon steel gas cylinders for chlorine gas (with amendments nos. 1 to 6).

IS : 4263-1967. Code of safety for chlorine (Reaffirmed 1976).

IS : 1065-1971. Bleaching powder, stable (first revision) (Reaffirmed 1978).

IS : 9825-1981. Chlorine tablets.

IS : 9189-1979. Method for determination of free chlorine in chlorinated organic liquid compounds (colorimetric).

APPENDIX B :

List of manufacturers of chlorine, its compounds, chlorination equipment and safety kits

(1) *Manufacturers of chlorine and its compounds* :

Andhra Sugars Ltd.,
P.O. Tanuku, 534211,
Venkatarayapuram,
Andhra Pradesh.

Atul Products Ltd.,
P.O. Atul 396 001.
Dist. Valasad (Gujarat)

Ballarpur Industries Ltd.,
Thapar House, 124, Janpath,
New Delhi 110 001.

Bihar Caustic and Chem. Ltd.,
Garhwa Road, P.O. Rehla 822 124,
Dist. Palmau (Bihar).

Ilac Ltd.,
Anik Chembur,
Bombay 400 074.

Jayashree Chemicals Ltd.,
14, Netaji Subhash Road,
Calcutta 700 001.

Kanoria Chemicals & Ind. Ltd.,
Park Plaza, 71, Park Street,
Calcutta 700 016.

Kothari Industrial Corp. Ltd.,
Kothari Building,
Nungabakkam Road,
Madras 600 034.

Century Chemicals,
Industry House,
Churchgate Reclamation,
Bombay 400 020.

Chemfab Alkalies Ltd.,
Taem House, G.S.T. Road,
Vandalur, Madras 600 048.

Dhrangadhra Chem. Works Ltd.,
Nirmal, 3rd Floor,
Nariman Point, Bombay 400 021.

Durgapur Chemicals Ltd.,
Durgapur 713 215,
Dist. Burdwan (W.B).

Grasim Industries Ltd.,
Industry House,
Churchgate Reclamation,
Bombay 400 020.

Gujarat Alkalies and Chem. Ltd.,
P.O. Petrochemicals 391346,
Vadodara (Gujarat State).

Hari Fertilizers,
B-45/47, Shiv Mahal,
Connaught Place,
New Delhi 110 001.

Hukamchand Lute and Ind. Ltd.,
15, India Exchange Place,
Calcutta 700 001.

Titaghur Paper Mills Co. Ltd.,
95, Park Street,
Calcutta 700 016.

Travancore Cochin Chem. Ltd.,
P.O. Udyogmandal 683 501,
Via Alwaye (Kerala).

Gujarat Heavy Chemicals Ltd ,
Prakash Complex,
Rajmahal Road,
Veraval 362 265 (Gujarat).

Sree Rayalaseema Alkalis and
Allied Chemical Ltd.,
48/18/1, Parkash Nagar,
Kurnool 518 004 (A.P.).

Mettur Chemical and Ind.
Corporation Ltd.,
Mettur Dam, R. S., 636 401,
Salem Dist. (Tamilnadu).

Modi Alkalis & Chem. Ltd.,
New Friends' Colony,
18, Community Centre,
New Delhi 110 065.

National Rayon Corp. Ltd.,
Ewart House, Homi Mody St ,
Bombay 400 023.

Punjab Alkalis & Chemicals Ltd.,
SCO 119-120, Sector 17B.,
Chandigarh 160 017.

Saurashtra Chemicals,
Porbandar 360 576,
Gujarat.

Shriram Fertilizers and Chemicals,
Kanchenjunga Building,
18, Barakhamba Road,
New Delhi 110 001.

Standard Alkali Chem. Div.,
Mafatlal Centre,
Nariman Point,
Bombay 400 021.

Tata Chemicals Ltd.,
Bombay House, Homi Mody Street,
Bombay 400 023.

Hindustan Heavy Chemicals Ltd.,
7E, Lindsay Street,
Globe Building,
Calcutta 700 087.

Hindustan Paper Corpn. Ltd.,
75-C, Park Street,
Calcutta 700 016.

Note :— The above addresses were obtained from Alkali Manufacturers Association of India, 105, Bajaj Bhavan, Nariman Point, Bombay 400 021.

(2) *For chlorine tablets* :

Goodmans Rural Water Systems,
403, Saraswati House,
27, Nehru Place,
New Delhi 110 019.

(3) *For Manufacturers of Chlorinators* :

Aquas Engineering Corporation,
P.O. Box 262, Lucknow (U P.).

Babubhai Narottamdas & Co.,
Walbhat Road, Goregaon East,
Bombay 400 063.

Bird & Co,
(Process Engg. Division),
Dakhindari,
Calcutta 700 048.

Candy Filters (India) Ltd.,
Mahalaxmi Chambers,
22, Bhulabhai Desai Road,
Bombay 400 026.

Chloro Control Equipment Co,
13/M-E, Laxmi Industrial Estate,
Off Veera Desai Road,
Andheri East, Bombay 400 058.

IAEC (Bombay) Pvt. Ltd.,
43, Dr. V. B. Gandhi Marg,
Bombay 400 023.

National Hydraulics,
5, Modern Industrial Estate,
Bahadurgarh (Haryana).

Overseas Engineering Co.,
37A, Bentinck Street,
Calcutta 700 069.

Pearl Filter Enterprises,
87, Chowringhee Road,
Calcutta 700 071.

Paterson Engineering Co. (India) Ltd.,
28, Chittaranjan Avenue,
Calcutta 700 072.

Indian Engineering (Works) Corporation,
361. North Phase, SIDCO Industrial Estate,
Ambattur, Madras 600 098.

(4) *For Manufacturers of bleaching powder dosing equipment* :

Ambica and Co.,
Kamlekar Building,
Opp. Shantadevi Talkies,
Vadodara (Gujarat).

Candy Filters (India) Ltd.,
Mahalaxmi Chambers,
22, Bhulabhai Desai Road,
Bombay 400 026.

For electrolytic chlorination units :

Chloro Control Equipment Co.,
13/M-E, Laxmi Industrial Estate,
Off Veera Desai Road,
Andheri East, Bombay 400 058.

Ion Exchange (India) Ltd.,
P. O. Box No. 6273,
Tiecicon House,
Dr. E. Moses Road,
Bombay 400 011.

(5) *For suppliers of valves for cylinders and tin-containers* :

M/s. Kesan Metal Products Pvt. Ltd., Surat.

Technovalves, Chitpur Ghat, Calcutta.

(6) *For safety apparatus and emergency kits* :

M/s. Industrial Medical Engineers, P. O. Box No. 5206, New Delhi 110 053.

M/s. Pradeep Safety Private Ltd., Raja Bahadur Motilal Mansions,
1st floor, Mamsin Road, Fort, Bombay 400 023.

M/s. Precision Control Products, P. O. Box 8053, Bombay 400 056.

M/s. Dalal and Dalal Co, 567/3, M. G. Road, Opp. High Court, Indore
(M.P.).

Agents for foreign suppliers of safety equipment :

M/s. Joseph Leslie Agencies Pvt. Ltd., Safety Engineers' Medical Dept.,
11, 712, APEEJAY House, 130, Apollo Street, Fort, Bombay 400 001.