are windblown to the shore where they decompose producing malodours. Decaying algae also settle to the bottom, reducing dissolved oxygen.

Even a relatively mild algal bloom can result in accumulation of substantial decaying scum along the windward shoreline because of the lake's vast surface area. The most devastating aspect of eutrophication is that the process appears to be difficult to retard. Once a lake has become eutrophic it remains so, at any rate for a very long time, even if nutrients from point sources are reduced.

9.2.2.4 Sunlight

Algae require sunlight for their life processes and hence the growths are profuse in seasons of intense sunlight. Clear waters favour the growth of algae because they permit the penetration of sunlight to greater depths.

9.2.2.5 Characteristics of Reservoirs

Shallow reservoirs offer more favourable conditions than deep reservoirs because their dissolved nutrients closer to the surface may stimulate algal growth. Irregular margins and shallow areas encourage the growth of aquatic weeds which offer anchorage for the epithetic algae.

9.2.2.6 Temperature Effects

Temperature has a considerable influence on algal growth. The blue-green and the green algae make their presence when the water temperatures reach $20\text{-}30^0$ C.

9.2.3 REMEDIAL MEASURES

9.2.3.1 Preventive Measures

Preventive measures should, therefore, be based on control of those factors such as reduction of the food supply, change of the environment or exclusion of sunlight though they are not always practicable. Clear water reservoirs, service reservoirs and wells may be covered to exclude sunlight, but such a remedy is obviously inapplicable in the case of large reservoirs of raw waters. Turbid water prevents light penetration and thereby reduces algal population. Activated carbon (10.5 to 24.5 kg/hectare) reduces algal population by excluding sunlight but the disappearance of activated carbon in the water may support algal growth again. To a limited extent, the environmental conditions for the growth of algae may be made unfavourable by proper care in the construction and operation of reservoirs, as explained in 5.2.7.2 (f) and (g).

9.2.3.2 Control Measures-Algicidal Treatment

Algicidal measures may be adopted to control algae in reservoirs. As has been explained earlier, it is preferable to initiate the treatment in the early stages of algal growth.

(a) Microscopic Examination

To decide on the best time at which the water should be treated, it would obviously be necessary to have a regular programme of microscopic examination of the water. Such

examination is especially necessary during the season in which algal invasions may be expected.

(b) Time for Treatment

Generally, the practice has been to apply algicides when the total count reaches or exceeds 300 areal units. Algae which are known to be particularly troublesome should be eradicated even though the total count is much less than 300 areal units. For example, algcidal treatment is indicated as soon as Synura, a type that causes severe smell troubles is encountered, irrespective of the total count.

(c) Types of Algicide

A large variety of algicides are available and a number of new algicides are being synthesized. Many of these are complex organic compounds and are credited with specific action against particular species. Chemicals such as ketones, aldehydes, organic acids, quaternary ammonium compounds, silver nitrate, ClO_2 and rosin amines have also been tried as algicides. However, these are costly and have not come into general use. The most widely used algicides are copper salts and chlorine and potassium permanganate in small scale water supplies. The chemical to be used as an algicide should be species selective, non-toxic to aquatic life particularly fish, harmless to human beings, have no adverse effect on water quality and inexpensive and easy to apply.

(1) Copper Salts

The most common algicide is copper sulphate. Its action is due to the copper ion which acts as a direct protoplasmic poison. The reaction is a function of the concentration of the chemical and the time of exposure of the algal cells to the action of the copper.

(i) Copper Sulphate

The copper sulphate reacts with the bicarbonates in the water to form a basic copper carbonate which further decomposes to form copper hydrate. The basic copper carbonate is somewhat soluble especially if the water is not very hard and if it contains carbon dioxide. The copper hydrate is almost insoluble in water. It remains in a colloidal form for sometime before it precipitates out. This reaction is retarded by low temperature and organic matter in the water, while temperature and suspended matter accelerate it. It, thus, follows that the efficacy of copper sulphate as an algicide is influenced by the temperature of the water, its hardness, its content of organic matter and suspended matter.

The added copper sulphate is rendered inactive in a short while. This is both an advantage and a disadvantage. It is an advantage because the content of the copper in the water rapidly gets reduced to levels below those at which copper is toxic to human beings by mere efflux of time and without the need for any elaborate treatment for removal of the excess copper. Tendency of copper to get out of the solution is a disadvantage because the algicidal effect is rendered purely temporary. With the disappearance of the copper from the field of action, another crop of algae can come up necessitating a repetition of the treatment.

(a) Dosage

Doses of copper sulphate required to kill algae are generally expressed in terms of concentration in mg/l of the salt $CuSO_4.5H_2O$. Some authorities express the doses in terms

of the equivalent of copper. The values may be inter-converted on the basis of the following reaction :

$$100 \text{ parts of copper sulphate } (CuSO_4.5H_2O) = 22.32 \text{ parts of copper}$$

The quantity of copper sulphate required has to be calculated on the basis of the volume of water in the reservoir. A knowledge of the types of the algae present, quantity, period of multiplication and seasonal succession is necessary to decide on the dose to be applied. The lethal dose for different types of algae are given in Table 9.1. These apply for a temperature of 15^0C and may be decreased by about 2.5 percent for each degree rise of temperature above 15^0C.

TABLE 9.1
COPPER SULPHATE REQUIRED FOR CONTROL OF DIFFERENT ALGAE

Algae	Copper Sulphate concentration, mg/l
I. Cyanophyceae	
1. Anabaena	0.12 – 0.48
2. Aphanizomenon	0.12 – 0.50
3. Clathrocystis	0.12 – 0.25
4. Coelosphaerium	0.20 – 0.33
5. Microcystis	0.20
6. Oscillatoria	0.20 – 0.50
II. Chlorophyceae	
1. Cladophora	– 0.50
2. Clostrium	– 0.17
3. Coelastrum	0.05 – 0.33
4. Drapamaldia	– 0.33
5. Enteromorpha	– 0.50
6. Volvox	– 0.25
7. Hydrodictyon	– 0.10
8. Microspora	– 0.40
9. Scenedesmus	– 1.00
10. Spirogyra	– 0.12
11. Ulothrix	– 0.20
12. Zygnema	– 0.50
III Diatomaceae	
1. Asterionella	0.12 – 0.20
2. Fragilaria	– 0.25
3. Melosira	– 0.20
4. Tablellaria	0.12 – 0.50
5. Navicula	– 0.07
6. Synedra	0.36 – 0.50
7. Stephanodiscus	– 0.33

IV. Flagellates	
1. Cryptomonas	0.50
2. Dinobryon	0.10
3. Euglena	0.50
4. Mallomonas	0.50
5. Synura	0.12 – 0.25
IV. Miscellaneous	
1. Chara	0.10 – 0.50
2. Nitella	0.10 – 0.18

(b) Method of Application

Copper sulphate is generally applied by towing gunny bags containing the crystals tied to the bows of a motor-boat which is plied on the water. The crystals dissolve readily and mix with the body of the water. The rate of dissolution may be varied either by varying the speed of the motorboat or by varying the opening of the bags containing copper sulphate. The boat should traverse a predetermined zigzag path so as to get the best distribution of the chemicals.

It is generally preferable to choose a moderately windy day for the application of copper sulphate and also to ply the motorboat against the direction of the wind. Application of copper sulphate on a bright morning would be preferable as a large proportion of the algae would be at the top. If the algae are a type which remain scattered in the water, the application of copper sulphate in the evening may be preferable. To reach shallow bays, the finely powdered crystals may be scattered by hand or may be sprayed in the solution form with the aid of a suitable pump mounted on the boat.

Copper sulphate can also be applied on the basin walls, weir of settling tanks or filter troughs when the algae become a nuisance.

(c) Effects of Copper Sulphate

Copper sulphate is poisonous to fish. The doses, which are lethal to fish, are given in Table 9.2

TABLE 9.2
CONCENTRATION OF COPPER SULPHATE LETHAL TO FISH

Fish	mg/l
Tout	0.14
Carp	0.30
Suckers	0.30
Catfish	0.40
Pickerel	0.40
Goldfish	0.50

Fish	mg/l
Perch	0.75
Sunfish	1.20
Black bass	2.10

Comparison of these figures with those for the algae shows that the lethal doses for algae are very near the lethal doses for fish. Hence very careful control over the dose and the method of application is necessary to avoid large-scale mortalities of fish.

Despite care, it may be not be possible to avoid the death of a few fish which may have got into the regions of heavy local concentrations of copper sulphate. When a water which is heavily laden with algae is treated with copper sulphate, the dead and decaying algae may reduce the dissolved oxygen in the water to levels at which fish life cannot be sustained. The dead algae may also accumulate on the gills of the fish and smother them. Such death of fish due to smothering usually occurs on the second or third day following treatment by copper sulphate.

(d) Increase of Organic Matter and Bacteria

As a result of the death and decay of the algae, the organic matter in the water is increased and ample supplies of food become available for the saprophytic bacteria which begin to multiply at a very rapid rate with the consequent uptake of oxygen. A point is finally reached when the water cannot support this rapid growth of bacteria and then these gradually get reduced in number.

The decay of the algae also causes a temporary increase in the odour of the water. For these reasons it is necessary to close the supply for several days after treatment with copper sulphate. To permit such closure of supply, it is desirable that every reservoir consists of at least two separate compartments. Generally, the reservoir is ready for service after about two or three days after application of copper sulphate. Good practice requires that laboratory tests for water quality should be made before the water is allowed to pass on to the consumers. Such tests should also include the determination of copper to ensure that it is within the permissible limits given in Table 2.1.

(e) After Growths

The algicidal treatment of a reservoir with copper sulphate may be followed by a secondary growth of algae. This is particularly to be expected when conditions favourable for algal growth are present, viz., water rich in algal nutrients and plenty of sunshine. The secondary growth is generally more profuse than the first and consist of types which are more resistant to the action of copper sulphate than the original forms. Hence it would be necessary to repeat the treatment at intervals and also to employ higher doses of algicides or use more powerful algicides during the subsequent treatments.

(ii) Other Compounds

Attempts have been made to develop compounds of copper which can persist for longer periods. Treatment with copper citrate which can stay in solution for longer periods has been

practiced but this chemical is much costlier than copper sulphate. By using a complex of copper with ammonia in conjunction with chlorine-cupri-chloramine process, the algicidal effect of copper is reinforced. The use of more persistent compounds of copper necessitate, however, a more rigid control over the treatment so as to ensure that the water is not supplied to the public until the copper content gets well below toxic limits.

(2) Chlorine

Chlorine is normally a bactericide but also used as an algicide. Whereas copper sulphate is more commonly applied to water in reservoirs, chlorine is generally added to the water as it passes the control point.

Chlorine has specific toxic effect and causes death and disintegration of some species of algae. The essential oils present in the algae are thus liberated and may cause tastes and odours. Occasionally these essential oils as well as the organic matter of the dead algae may combine with chlorine to form new or intensified odours and tastes. Such intensification of odours makes the control of algae by chlorine a problem which challenges the ingenuity of the operator.

(i) Dosage

The lethal doses of chlorine for the more common types of algae are given in Table 9.3

TABLE 9.3

AMOUNT OF CHLORINE REQUIRED TO DESTROY MICROSCOPIC ALGAE

Algae	Chlorine Dose mg/l
Aphanizomenon	0.85
Cyclotella	1.00
Melosira	2.00
Dinobryon	0.5
Uroglenopsis	0.5
Synura	0.3

(ii) Methods of Application

Chlorine may be applied either as a slurry of bleaching powder or as a strong solution of chlorine from a chlorinator. The latter is preferable.

Small reservoirs may be treated by applying a slurry of bleaching powder at the influent end or by towing bags containing the bleaching powder in the water. Chlorination for algal growth is more commonly adopted in the pretreatment part of the water works. The point of application is generally at the point of entry of raw water into the treatment plant or just ahead of the coagulant feed. Algal growths in raw water conduits can be got rid of by heavy doses of chlorine. Addition of chlorine along with coagulant is sometimes practiced, but this

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is to be discouraged since the turbulence would result in the dissipation and wastage of chlorine.

(iii) Microstrainer

A special process known as microstraining is being used in some water treatment plants. The microstrainer is an open drum. The water is passed through a finely woven fabric of stainless steel. The size of the openings in the mesh determines the size of the plankton removed from the water.

9.2.3.3 Relative Merits of Chlorine and Copper Sulphate Treatment

Each plant should conduct experiments and decide on the type and dose of the algicide on the basis of local conditions. To a certain extent the method will depend on the facilities available for dosing the water with chemicals, the general arrangements of the system as well on the costs. There are, however, certain special conditions where the use of copper sulphate is not possible and chlorination has to be preferred. For example, when the point of application is too near the point of entry into a pipe, copper sulphate cannot be used as the copper will plate out on the metal and become inactive. Similarly when the problem is to prevent algal growth in a coagulant basin, copper sulphate cannot be used as it will be thrown out of solution almost immediately. In cases where the supply cannot be shut off for periods sufficient to cause a reduction of the copper content to permissible limits, chlorination has to be preferred.

When chlorination causes an intensification of the algal tastes and odours, application of heavy doses of chlorine followed by removal of the excess usually overcomes the difficulty.

The growth of plankton in reservoirs may be controlled by copper sulphate treatment. Generally satisfactory results have been secured, but this chemical has not always been effective as an algicide. The doses required for this purpose differ with each organism, so, economy in the use of copper sulphate and its distribution in reservoirs warrants microscopic examination of appropriate samples collected at significant locations, to determine the types of organisms and their relative numbers. The recommended doses are 0.3 mg/l or less, so this dose may be used in the absence of laboratory control. On the other hand, many troublesome organisms may be killed with doses of 0.12 mg/l, indicating the economy possible when microscopic examinations can be made.

The required dose is influenced by temperature, alkalinity and carbon dioxide content of waters.

Effective control of microorganisms throughout the year is facilitated by the continuous application of copper sulphate to the water entering reservoirs, the microorganisms are thus controlled before heavy growths occur, avoiding the necessity of periodic treatment. Furthermore, the prevention of growths obviates the subsequent destruction of large quantities of organisms, which would result in the reduction of the dissolved oxygen content of the water, and hence protects fish life because the lowering of the oxygen content is frequently responsible for fish-kills, erroneously blamed on copper sulphate. The continuous application of copper sulphate, however, reduces the available supply of food for fish, so

continuous treatment should be restricted to those reservoirs used exclusively as sources of public water supply.

Copper sulphate may be continuously applied with either commercial chemical feeders or homemade equipment of a solution tank and a constant-head tank with an orifice or control valve. Another simple device consists of a perforated box so supported in the water of the entering stream that the depth of submergence may be varied at will. Lumps of copper sulphate are placed in the box, to be dissolved by the water flowing through the box. The rate of solution may be controlled by raising or lowering the box, which should be kept filled to a point above the water level. Doses of 0.12 mg/l have been found effective in raw-water reservoirs, and doses as low as 0.03 mg/l have been used to treat filtered water before it enters open storage reservoirs.

Algae in water treatment plant may be removed by the application of chlorination, ozone, chlorine dioxide or activated carbon. Prechlorination will kill many of the algae and facilitate their settling. Prechlorination will prevent the growth of algae in basin walls and will aid in the removal of algae by coagulation and sedimentation, because the dead cells of these organisms are more readily coagulated. The chlorine in the settled waters will also destroy slim organisms on the filter sand and thus prolong filter runs and facilitate filter washing. Doses required for this purpose may have to be over 5.0 mg/l to meet the chlorine demand of water, oxidize free ammonia, etc. and leave 0.2 to 0.5 mg/l free residual chlorine in the settled water.

Most economical results are secured with the use of prechlorination for initial disinfection by free residual chlorine and post chlorination with chlorine dioxide. Chlorine dioxide doses sufficient to give an apparent content of 0.2 to 0.3 mg/l free residual chlorine in the filtered water are adequate, this amount of chlorine dioxide being equivalent in oxidizing power to 0.5 to 0.75 mg/l free residual chlorine.

Ozone is very effective in the destruction and gives more uniform, predictable results and is a very active oxidizing agent. Ozone is only slightly soluble in water and hence persists in the treated water for periods upto about 30 minutes. Control is through the use of special equipment indicating the concentration of ozone in the treated water, or by the orthotolidine test. The latter indicates the presence of 0.1 mg/l ozone when the reagent colour is equivalent to 0.15 mg/l of residual chlorine.

9.3 CONTROL OF TASTE AND ODOUR IN WATER

9.3.1 GENERAL

Taste and odour in water are subjective phenomena and are difficult to quantify exactly. The problems of taste and odour (one co-exists with the other) are more intensive and more frequent in surface water sources as these are more subject to contamination by natural and man made wastes. Taste and odour are caused by dissolved gases like hydrogen sulphide, mercaptans, methane, organic matter derived from certain dead or living micro-organisms (blue and green algae), decomposing organic matter, industrial liquid wastes containing phenols, cresols, ammonia, agricultural chemicals, high residual chlorine and chloro-phenols. It is possible that some of the dissolved gases may be found in well water also. Odour can be classified as aromatic, earthy, swampy, septic or chemical.

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Biological organisms are one of the most common causes of taste and odour in water. Diatomaceae with Asterionella and Synedra, actinomycetes and free swimming nematodes are the principal offenders causing earthy or musty odour. Apart from algae, decomposing leaves, weeds or grasses also cause odour. Vegetation that grow in the low-water areas in the reservoir subsequently get submerged and decompose resulting in odour. Chemical and refinery effluents have the greatest potential for odour, followed by domestic sewage. Odour tests indicate that only a few mg/l of these materials are needed to produce a detectable odour.

In short, taste and odour producing materials in water are chemical compounds of many varieties with different physical and chemical characteristics, present in water because of direct pollution or biological activity. Most of these compounds are in solution and some exist in the form of particulate and colloidal compounds. Those in solution are comparatively more difficult to remove.

9.3.2 CONTROL OF TASTE AND ODOUR

Preventive and corrective treatment of raw and processed water is necessary for control and elimination of taste and odour problems. Wherever possible, preventive steps like control of microorganisms are to be undertaken where the source of raw water supply is from rivers, reservoirs or lakes and control of effluent discharges. Special treatment is given to water in the treatment plant for the removal of odours, by aeration, oxidation by chemicals or adsorption by activated carbon.

9.3.2.1 Preventive Measures

Reservoir preparation and management are fundamental for an effective tackling of the problem. For construction and management of reservoirs, 5.2.7.2 (f) and (g) may be consulted. Control of algae for the mitigation of this problem has been discussed in detail in 9.2.

9.3.2.2 Corrective Measures

Odours can be removed by mechanical aeration, oxidation by chemicals like chlorine or its compounds or ozone or permanganate and adsorption of odour by agents such as activated carbon, floc or clays.

For removing dissolved gases like hydrogen sulphide and volatile matter, aeration can be practised at the start of water treatment. Free available residual chlorination at prechlorination or postchlorination stage can bring about complete elimination of taste and odour. Inadequate chlorination will only intensify the odour of water containing phenolic compounds and tannin and lignin imparting a medical taste. Even with breakpoint chlorination it may not be possible to remove taste and odour from water in certain cases. Such compounds can be removed by super-chlorination. Super-chlorination is normally done at the lake outlet or the plant inlet in order to bring the maximum chlorine concentration and the maximum contact time together to effect oxidation. This should invariably be followed by dechlorination using sulphur dioxide or sodium sulphate to reduce the residual chlorine to

acceptable limits. Using ammonia with chlorine in combined residual chlorination can partly mask or delay chlorophenol tastes in water.

Chlorine Dioxide which is 2.5 times more powerful than chlorine as an oxidizing agent has been found extensively efficient and the general dosage values range from 0.2 to 2.0 mg/l. This is a specialized form of chlorine treatment used for taste and odour control where large doses of chlorine are to be avoided. Chlorine dioxide gas is released in water on site by the inter-action of a solution of sodium chlorite ($NaClO_2$) with a strong chlorine solution of 6000-7500 mg/l

$$2NaClO_2 + Cl_2 \longrightarrow 2ClO_2 + 2NaCl$$

Through the theoretical ratio of chlorine to sodium chlorite is 1 : 2.6, values between 1:2 and 1:1 are employed in practice. Chlorine dioxide is more expensive and is used for taste and odour control only. It is applied at the first stages of the treatment plant. Thereafter, the final desirable residual chlorine may be adjusted by simple chlorination after filtration. Ozone at dosages of 1.0 mg/l has also produced good results. Chloramination is useful in the removal of phenol tastes.

Preferred method of treatment for taste and odour removal is activated carbon. Activated carbon is made from hydrocarbon or carbohydrate sources, the principal requirement being that the carbon residue left after destructive distillation has a porous structure. Odour producing substances which cannot be removed by oxidation are physically adsorbed on to the surface. This treatment is usually applied before filtration. The contact time varies from 10 to 60 minutes. Activated carbon performs well at lower pH values. A bed of carbon or suspension kept in circulation could be used. The active surface must be preserved from coating by other chemicals. Application of carbon can be before sedimentation if taste and odour is severe and frequent and in certain cases after sedimentation. The approximate dosage for routine, continuous application as suspension is 2 to 8 mg/l, for emergency treatment 20 to 100 mg/l. Carbon beds are generally 1.5 to 3 m deep with the sizes 0.2-0.4 mm with loadings of about 4.8 $m^3/hr/m^3$ of bed. Filtration rates range from 7.2 to 15 $m^3/m^2/hr$ with expected efficiencies of about 90%. As many variables are involved, pilot plant tests are indicated. Carbon can also be used as a polishing agent to remove residual odours after other treatment.

Variables such as pH, temperature, quantity and type of organic matter in the influent water and detention time have a marked effect on the efficiency of removal of odorous materials.

9.4 REMOVAL OF COLOUR

9.4.1 CAUSES OF COLOUR

Colour in water may be due to natural causes or as a result of human activity. Waters occurring in peaty soils acquire colour because of the presence of colloidal organic matter. Colour is also due to mineral matter in solutions, as a colloid or in suspensions as in the case of ground water in certain areas. Waters containing oxidized iron and manganese impart characteristic reddish or black colour. Heavy growths of algae may also impart colour to the water. Discharge of industrial wastes or heavy sewage pollution may also bring in colour.

9.4.2 COLOUR REMOVAL

The appropriate treatment for the removal of colour from a water has to be determined for each individual case on a consideration of the causative factors and on the basis of local trials.

9.4.2.1 Colour due to Iron and Manganese

Colour due to iron and manganese may be removed by specific treatment for the removal of these constituents as discussed in 9.6.

9.4.2.2 Colour due to Algae

A water which is coloured because of the growth of algae, has to be treated to eliminate the source by control of the algae as discussed in 9.2 or to remove them by processes such as micro-straining. Microstrainers are cylindrical drums 3 m diameter x 3 m long with stainless steel screens having openings of 0.025 mm. The proprietary units have sizes varying from 0.75 m dia x 0.6 m long to 3 m dia x 3 m long. The latter size will handle 10-30 lpm of water with a power consumption of about 3 kW. The headloss is only about 150 mm with unit capacities of 7.2 to 12 m^3/hr per m^2 of strainer, the capacity depending upon the concentration of microorganisms in the raw water. The coatings of microorganisms are continuously washed down by a jet of water, with the volume of wash water varying from 1 to 3% of the volume of water strained.

9.4.2.3 Colour due to Colloidal Organic Matter

Coagulation at low pH range by chemicals such as alum or ferric salts is used for removing colour due to colloidal organic matter. Ferric coagulants are generally superior to alum. After removal of the colour colloids the pH of the water will have to be corrected by treatment with lime. The colour colloids are often stabilized at high pH value and hence the addition of lime to aid coagulation is fraught with danger in the case of waters which are coloured. It is essential that laboratory tests should be conducted to determine the most suitable chemical and its optimum dosage in the given conditions.

9.4.2.4 Colour due to Industrial Wastes

Colour due to industrial wastes may be removed by the use of bleaching powder or chlorine or by activated carbon. Since removals are more efficient when the concentrations are high, it is advisable to treat the effluents for colour at the factory site itself before discharge into the water bodies.

9.4.2.5 Oxidation of Colour

In some cases, colour is not removed by coagulants and it will be necessary to oxidize the coloring matter. Application of heavy doses of chlorine is one of the methods commonly adopted. When the colour is not destroyed by such treatment, the water may have to be treated with strong oxidizing agents like chlorine dioxide. Refer 9.3.2.2.

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9.4.2.6 Treatment by Activated Carbon

Treatment with activated carbon is effective against most problems of colour in waters. Carbon removes the coloring matter by adsorption. Application has already been discussed in 9.3.2.2.

9.5 SOFTENING

9.5.1 GENERAL

Water is said to be hard when it does not form lather readily with soap. The hardness of water is due to the presence of calcium and magnesium ions in most cases.

Bicarbonates, sulphates and chlorides are the anions associated with the hardness. The purpose of softening is to remove these salts from the hard water, to reduce the soap consuming properties and to ensure longer life to washed fabrics, mitigate its scale forming tendencies, and improve palatability.

Usually a total hardness of 75 to 100 mg/l (as $CaCO_3$), would meet these requirements. The magnesium hardness should not exceed 40 mg/l to minimize the possibility of magnesium hydroxide scale in domestic hot water heaters. Calcium and magnesium associated with bicarbonates are responsible for carbonate hardness and that with the sulphates, chlorides and nitrates contribute to non-carbonate hardness.

Normally, the alkalinity measures the carbonate hardness unless it contains sodium alkalinity. The non-carbonate hardness is measured by the difference between the total hardness and the carbonate hardness. Carbonates and bicarbonates of sodium are described as negative carbonate hardness.

A summary of the more common salts and the problems they cause in water are presented below:

Alkaline causing		Saline (neutral causing)		Acidity causing
Na and K Alkalinity only	CO_3 Hardness	Non CO_3 Hardness	Salinity only	
$KHCO_3$	$Ca(HCO_3)_2$	$CaSO_4$	K_2SO_4	Mineral acids and
K_2CO_3	$CaCO_3$	$CaCl_2$	KCl	acid salts are
$NaHCO_3$	$Mg(HCO_3)_2$	$MgSO_4$	KNO_3	restricted to acid
Na_2CO_3	$MgCO_3$	$MgCl_2$	Na_2SO_4	mine wastes and
				rare mineral water
			$NaCl$	
			$NaNO_3$	$FeSO_4$

Water is classified with regard to its hardness as follows :

Classification	Total hardness as mg/l of $CaCO_3$
Soft	50
Moderately Hard	50-150
Hard	150-300
Very hard	300

When hardness is less than 150 mg/l, softening for domestic purposes is not usually justified.

9.5.2 METHOD OF SOFTENING

The two methods ordinarily used are lime and lime-soda softening and ion-exchange softening.

9.5.2.1 Lime and Lime-Soda Softening

Softening with these chemicals is used particularly for water with high initial hardness (greater than 500 mg/l) and suitable for waters containing turbidity, colour and iron salts because these have a tendency to inactivate the ion-exchange bed, by a coating on the granules. Lime-soda softening cannot, however, reduce the hardness to values less than 40 mg/l while ion-exchange softening can produce a zero-hardness water.
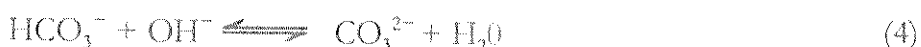
(a) Lime Soda

(i) Chemical Reactions

When lime and soda are added to water containing calcium and magnesium salts, the following reactions take place.
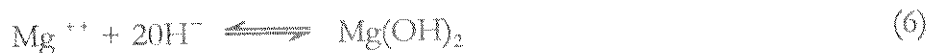
$$CaO + H_2O \longrightarrow Ca(OH)_2 \tag{1}$$

(Quicklime Slaking)

$$Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH^- \tag{2}$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \tag{3}$$

(Removal of CO_2)

$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O \tag{4}$$

$$Ca^{++} + CO_3^- \rightleftharpoons CaCO_3 \tag{5}$$

Solid (Removal of Calcium hardness)

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$$Mg^{++} + 20H^- \rightleftharpoons Mg(OH)_2 \qquad (6)$$

Solid (Removal of Magnesium hardness)

Reaction (3), (4) and (5) indicate that carbon dioxide, which is present in water, is converted by hydroxyl ions in lime to CO_3^{2-} which combines with Ca^{++} to form relatively insoluble $CaCO_3$. The alkalinity present as bicarbonate furnishes the necessary CO_3^{2-} by reaction with added OH^- (equation 4) for equation (5) to be completed. Magnesium ions will have to be removed as $Mg(OH)_2$, according to equation (6) since $MgCO_3$ is fairly soluble. The removal of Mg^{++} is effective around pH ranges of 10 to 10.5 for which additional OH^- ions in the form of lime have to be made available. No reduction of hardness takes place by removal of magnesium by the addition of lime since an equivalent amount of Ca^{++} ion is put back into the solution from the lime added. When all the alkalinity is used by OH^- to form CO_3^{2-} any further CO_3^{2-} needed, has to be added to the water. This is the case when non-carbonate hardness is present in the water and the needed CO_3^{2-}; can be added in the form Na_2CO_3 (Soda ash).

For calculating the theoretical amount of lime and soda required for softening an analysis of the following constituents is necessary, viz., free CO_2, bicarbonate (usually the total) alkalinity, total hardness and magnesium. Appendix 9.1 gives illustrative example to compute chemical dosage required in water softening using lime-soda process. Chemical requirements (mg/l) are computed by the sum of the following factors.

On a 100% purity basis, the dosage of lime as CaO required for softening as obtained from the chemical equations is as follows :

1. For every gram of CO_2 to be removed   1.27 g

2. For every gram of CO_3 hardness as $CaCO_3$
   to be removed   0.56 g

3. For every gram of Mg as Mg to be removed   2.33 g

4. Additional lime required for raising the pH
   to the range of 10 to 10.5 for
   precipitation of Mg $(OH)_2$ 30-50 mg/l

5. Soda ash requirements as Na_2CO_3 to remove
   one gram of non-carbonate hardness as $CaCO_3$ 1.06 g

6. Additional soda required to neutralize
   every gm of excess lime   1.89 g

Plant conditions like temperature, time of detention and agitation influence the completion of reactions and the dosages of chemicals may have to be increased to provide for the inadequacies.

Alternatively caustic soda can be used instead of lime. The reactions are:

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$OH^- + HCO_3 \rightleftharpoons CO_3^{2-} + H_2O$$

$$Ca^{++} + CO_3^{2-} \rightleftharpoons CaCO_3$$

$$Mg^{++} + 2OH^- \rightleftharpoons Mg(OH)_2$$

Liquid caustic soda can be used since it can be handled and fed easily. The amount of calcium carbonate sludge formed in this case is theoretically half that formed by the use of lime. However, caustic soda is costlier than soda ash which is more expensive than lime.

Waters higher in carbonate than in noncarbonate hardness will require relatively more lime than soda ash for their treatment. The sludge settling out carries with it a large portion of the turbidity, iron, manganese, silica, colour producing matter and bacteria in the water. The softened water may have a higher pH due to neutralization of CO_2 with lime, thus reducing its corrosive nature.

(2) Process Equipment

Lime soda softening plants include chemical feeders, rapid mix, flocculation and sedimentation basins and rapid sand filters. The process design must ensure the promotion of the chemical reactions necessary to remove the hardness from water by converting them into insoluble precipitates and then settle these precipitates and filter the partially clarified water.

(i) Chemical Feeders

The solubility of calcium hydroxide (slaked lime) is low being of the order of 1600 to 1800 mg/l in cold water. It is common practice, therefore, to feed a 5% slurry of lime so that unusually large solution tanks are avoided. Soda ash is added in solution form. Types of chemical feeders used are discussed in 7.3.

(ii) Rapid Mix and Flocculating Basins

Rapid mixing ensures a thorough mixing of the slaked lime (lime slurry) and soda ash with the water. A mixing period of 5 to 10 minutes is necessary due to the low solubility of lime. Peripheral speeds of paddles for rapid mixing basins should be 45 to 60 cm/ sec with water velocities of 15 to 30 cm/sec. The addition of lime and soda ash results in a supersaturated solution of calcium carbonate and magnesium hydroxide after which some precipitation of the two compounds starts immediately. These are kept in suspension to further the growth of these precipitates. Some of the settled sludge deposited, from the settling basin is often recirculated to the rapid mix basin for aiding in flocculation. This may ensure promotion of chemical reactions with the previously precipitated solids and the formation of more readily settleable precipitates. The flocculation basin promotes precipitation and floc growth after the chemical reactions have been completed.

The removal of the reaction products takes place by precipitation on the surface of the previously formed particles which enhances the reaction rate. The flocculation time required varies from 40 to 60 minutes. Mechanical flocculators are preferred to baffled ones. Tapered

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flocculation is generally preferable. The precipitates are formed on the paddles in rapid mixing and flocculation basins, which may require periodic cleaning.

(iii) Sedimentation Basins

They may be circular or rectangular and the detention time varies from 2 to 3 hours depending on the character of the flocs. The limiting horizontal velocity is usually about 0.3 m/min. A large volume of sludge is produced since every mg/l of hardness produces approximately 2 mg/l of dry sludge and therefore an extra basin capacity must be provided. Continuous mechanical sludge collection and removal is almost always used.

Another type of softener is the sludge blanket type which is used for flows larger than 2 MLD and where compactness is an essential requirement. The treated water is passed and sieved upward through a suspended sludge blanket composed of previously formed precipitates. Some of the hydrated lime in suspension may be carried down by sludge. In this type, the upward flow or sieving through the blanket offers full scope for a complete solution and utilization of the added lime. The intimate contact of the treated water with a large mass of solids which serve as nuclei prevents supersaturation and hence overcome problems of after precipitation. The need for separate filtration can also be dispensed with. The upflow velocity at the sludge blanket zone should be equal to one half the settling velocity of the floc in order to have a good blanket of flocs. Overflow rates of 50 to 100 $m^3/d/m^2$ could be used. Experience has shown that use of precipitated calcium carbonate granules or other suitable catalysts of 0.3 to 0.6 mm grain size in these sludge blanket units could reduce the detention times to one quarter that of the regular units without loss of efficiency.

(3) Sludge Disposal

The disposal of sludge is usually carried out by lagooning it. Plenty of land area is required as the sludge does not dry up rapidly. Lime can be reclaimed from the sludge and it has to be free from magnesium if it is to be reused. One of the common methods (Hoover Process) is to precipitate the calcium sludge in the first stage by adding just enough chemicals and then precipitating the magnesium sludge in the second stage. The sludge from the first stage, which is devoid of magnesium, is dried and calcined. The resulting calcium oxide is reused for softening and the carbon dioxide utilized for recarbonation. Another method (Lykken-Estabrook Process) is to apply the total chemicals required for the precipitation of calcium of about 12% of the water and precipitating the calcium and magnesium sludge which is wasted. The water from this portion carrying excess chemicals is then mixed with the rest precipitating only calcium sludge which can be calcined and reused. The reclamation processes also reduce the quantity of sludge to be handled.

(4)   Filters

(a)   Conventional softening units are followed by rapid sand filters but incrustation of filter sand due to precipitation of super-saturated calcium carbonate has to be guarded against. The application of 0.5 mg/l or more of polyphosphate or metal phosphate has been found to prevent effectively not only the sand incrustation but also coatings of calcium carbonate on the filter walls and wash water troughs. Surface wash devices are used to remove loose deposits. Another method of checking after

precipitation is to adjust the pH value of the softened water to about 8.3 by recarbonation. Carbon Dioxide is applied to the effluent from the settling tank. The gas can be obtained by burning coke, oil or gas in excess of air and then scrubbed to remove the other gases. In small plants, dry ice or liquid CO_2 can be used. The carbonation tank must provide 15 to 30 minutes retention time with a depth of water equal to 3 to 4.5 m and the whole plant should be well ventilated.

(b) Excess Lime Treatment

Plain lime or lime soda treatment is used when the bulk of hardness is due to calcium and magnesium is not significant. However, when the water contains more than 40 mg/l of magnesium warranting its removal, excess lime treatment has to be resorted to since magnesium has to be removed as magnesium hydroxide whose solubility decreases with increasing pH values. The water treated thus is highly caustic and has to be neutralized following precipitation. This is done either by recarbonation or by split treatment. In the latter case, the total flow is divided into two parts, one part being treated with excess lime and the settled effluent mixed with unsoftened water. The final residual hardness in the water will depend upon the percentage flow bypassed and the levels of hardness in both the portions.

(c) Hot Lime Soda Process

The hot lime-soda process is used for boiler feed water treatment. This is similar to cold process except that the raw water is heated to about 95° to 100° C before it is taken to the reaction tank. The reactions take place rapidly, the decreased viscosity hastening the settling of the precipitates. A greater degree of softening is accomplished than that in the conventional cold processes.

9.5.2.2 Ion Exchange Softening

The ion exchange process is the reversible inter-change of ions between a exchange medium and a solution and this process is used extensively in water softening. The hardness producing ions preferentially replace the cations in the exchangers and hence this process is also known as base exchange softening. The ion exchange can produce a water of zero hardness. There is only a temporary change in the structure of the exchange material which can be restored by regeneration. The ion exchanger can work on the hydrogen or sodium cycle, the hydrogen ions being released into the water in the former case and the sodium ions in the latter. The regenerants are an acid and sodium chloride respectively. In general the ion exchange materials used in softening, also called zeolites, are hydrated silicates of sodium and aluminium having the formula $xNa_2O.yAl_2O_3.zSiO_2$. The reaction can be depicted as follows.

$$Na_2Z + \frac{Ca^{++}}{Mg^{++}} + 2A^- \longleftrightarrow \frac{Ca}{MgZ} + 2Na^+ + 2A^-$$

Where A^- represents the relevant anions of bicarbonates, sulphates or chlorides and Z represents anionic part of the zeolite.

Treatment with zeolite thus increases the dissolved solids in the ratio of 46 : 40 of the hardness removed. The reverse equation operates during the regeneration resulting in a strong solution of calcium and magnesium salts, which is run to waste.

(a) Inorganic Zeolites

The two common inorganic zeolites are the natural and synthetic types. The natural zeolite is available as green sand while the synthetic or gel type is obtained by the reaction of either sodium aluminate or aluminium sulphate with sodium silicate which after, drying is graded to suitable sizes by screening. A cubic metre of green sand weighs 1600 kg with a specific gravity of 2.1 to 2.4 and for regeneration it requires 3.5 to 7 kg of salt for every kg of hardness removed. The synthetic inorganic zeolite weights 900 to 1100 kg per cubic metre. The relevant exchange capacities and regenerant requirements are given in 9.5.2.2 (d).

(b) Organic Zeolites

They are lighter than the inorganic zeolites weighing 500 to 800 kg/m^3. These consist of sulphonated carbonaceous material and sulphonated styrene type resins which have excellent cation exchange properties, requiring for regeneration 2-4 kg of salt for every kg of hardness removed. These are resistant to attack by acid solutions and hence can be regenerated with acid also. They can be used for waters with a wide pH range. The loss due to attrition is negligible compared to the synthetic inorganic zeolites.

(c) Raw Water characteristics

For application to ion exchangers, the raw water should be relatively free from turbidity, as otherwise the exchange material gets a coating which affects the exchange capacity of the bed. The desirability of using filters prior to zeolite beds or resorting to more frequent regeneration would depend upon the level of turbidity. Metal ions like iron and manganese, if present are likely to be oxidized and can coat the zeolites, thus deteriorating the exchange capacity steadily since the regenerant cannot remove these coatings. Oxidizing chemicals like chlorine and carbon dioxide as well as low pH in the water will have a tendency to attack the exchange material particularly the inorganic types, the effect being more pronounced on the synthetic inorganic zeolites. Waters low in silica content are likely to pick up silica from synthetic inorganic zeolites, which has to be avoided in boiler feed water. The organic zeolites operating on brine regeneration cycle do not add any silica to the water and consequently are ideally suited for boiler feed water.

(d) Design Criteria

The design criteria for a softening system is based upon (i) the required flow rate, (ii) the influent water quality, (iii) desired effluent water quality, (iv) exchange capacity and hydraulic characteristics of the exchanger, (v) period between regenerations, (vi) type of operation, (vii) number of units required, (viii) rate, time of contact, uniformity and concentration of brine application, (ix) rate and volume of rinse and (x) quality of regenerant. A softening unit is similar to a rapid sand filter unit regarding the hydraulics and equipment.

Volume of exchange material to be used in cubic metres (E) is calculated by the formula :

$$E = \frac{QH}{1000G}$$

Where,

Q = Volume of water to be treated between regeneration, in m^3

H = Hardness of water in mg/l

G = Exchange capacity of the material kg/m^3

Generally, ion exchange beds are encased in shells, shell diameter and bed depth being adjusted to maintain a rinse rate of flow in the range of 0.15 to 0.30 m/min. The vertical units are 0.2 m to 3 metres in diameter while the horizontal ones are 3 m in diameter and 8 to 9 m long. The ion exchange bed has a depth of 0.6 m usually and is placed over supporting gravel (size depending upon composition of the exchange material but with similar specification as those for rapid gravity sand filters) of 0.30 to 0.45 m depth with an underdrain system at the bottom for collecting softened water. After the softening cycle, the softener should be backwashed for 3 to 5 minutes to loosen the exchange resin and remove particulate matter. The rate of backwash should ensure atleast 50% bed expansion. Then regeneration of the bed is carried out with brine solution. The brine distribution manifold is placed immediately above the softener bed.

Exchange capacities and the common salt requirements of Cation exchangers are presented in Table 9.4

TABLE 9.4
EXCHANGE CAPACITIES AND COMMON SALT REQUIREMENTS OF CATION EXCHANGERS

Cation Exchanger	Capacity Kg/m^3	Common Salt kg/kg exchanged
Green sand	7 - 14	3.5 – 7
Synthetic Siliceous Zeolite (inorganic)	14-37	2.5 – 3.5
Synthetic Organic	------	------
Sulphonated Coal	12-70	2 – 4
Resin, Polystyrene	25 – 100	2 – 4

The optimum concentration of brine for restoration of maximum exchange capacity in any resin is about 10 to 15% and the contact time for regeneration varies from 20 to 45 minutes. A dosage of salt of 15 kg/ min/m^3 of resin using 10% brine solution is usually applied at a rate of about 150 lpm/m^3 of exchanger. For sea water, about 200 to 400 lpm/m^3 of exchanger is necessary.

The total rinse water requirement is 3 to 10 m^3/m^3 of material and applied at a rate of 9 to 18 $m^3/h/m^3$ in the slow and 30 $m^3/h/m^3$ in the fast types. The rinse water is introduced through the brine distribution network or by simply flooding the unit through a hose.

The salt or brine storage tank should provide for a capacity of 24 hours or 3 successive regenerations, whichever is greater.

(e) Disposal of Spent Brine

The total waste flow from a softening unit may vary depending upon the capacity of the exchanger and the hardness removed in each cycle. The waste flow consists of a mixture of salts of sodium, calcium and magnesium with concentration as high as 9000 to 12,000 mg/l. The disposal of spent salt or spent brine poses a problem. Methods like controlled dilution, evaporation ponds, disposal at sea or brine wells can be adopted.

9.5.2.3 Combination of Lime and Zeolite Softening

For waters which contain a large carbonate hardness, a combination of lime and zeolite softening can be practised. The lime treatment, which is applied first, removes by precipitation a large part of the carbonate hardness, simultaneously decreasing the amount of dissolved solids in the water. After leaving the lime reaction tank, the water is settled and filtered and then passed through the zeolite softeners which by base-exchange remove the residual carbonate hardness and all the non-carbonate hardness.

The combination of lime and zeolite offers the following advantages :

(a)   It gives a water with a lower hardness than can be obtained by lime and soda ash treatment.

(b)   It reduces the amount of total dissolved solids which the zeolite treatment alone would not do.

(c)   It gives a lower cost of chemicals than with lime and soda ash and possibly lower than with zeolite alone, depending on the relative costs of salt and lime.

Surveys carried out in other countries have clearly brought out the fact that the benefits of savings of soap alone justify the expenses of softening on municipal scale. There are other benefits like good public relations that add to the attractiveness of the proposition. The practice has not, however, caught up with this trend even in those countries. With greater demands of higher quality water, water softening may have to be carried out on a municipal scale also.

9.6 REMOVAL OF IRON AND MANGANESE

Appreciable amounts of iron and manganese in water impart a bitter characteristic, metallic taste and the oxidized precipitates can cause. Coloration of water which may be yellowish brown to black and renders the water objectionable or unsuitable for domestic and many industrial processes. In addition, staining of plumbing fixtures and laundered materials can also result. Carrying capacity of pipelines in the distribution system is reduced due to the deposition of iron oxide and bacterial slimes as a result of the growth of microorganisms (iron bacteria) in iron bearing water. Concentration of iron in excess of 0.2 to 0.3 mg/l may cause nuisance, even though its presence does not affect the hygienic quality of water.