

A SIMPLE GUIDE TO THE CHEMISTRY, SELECTION AND USE OF CHEMICALS FOR WATER AND WASTEWATER TREATMENT

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EXECUTIVE SUMMARY

Introduction

Every year in South Africa an estimated R500m is spent on chemicals used in the treatment of drinking and waste water. Most of this money is allocated on the basis of tenders issued and contracts awarded.

The evaluation of tenders is generally undertaken by a team of people from various disciplines within the awarding organisation and the decisions they make can have a significant effect on the quality of water or waste that is produced and also on the finances of the organisation for which they work.

It is obvious therefore that these decisions – which chemicals to use, how much to use, how much should be paid, who is the most professional supplier – are important ones and ones that should be taken whilst in possession of the most factual and impartial information.

This guide aims to provide those decision-makers, and other users of water treatment chemicals, with specific and useful information about water treatment chemicals. It is a chemistry text book aimed specifically at those people who have to make informed decisions but who have not had a formal education in chemistry or whose chemistry education has not been specific in detail relevant to water treatment chemicals.

It does not, however, aim to be a comprehensive chemistry textbook and chemicals not used in water treatment are not discussed; nor are properties that are irrelevant to the water treatment application of the chemical.

The guide is designed to serve as a reference book with each chapter being self contained and specific. It will be easily understood by those readers that do not have a formal chemistry education and hopefully will provide some useful additional insight and information to those that do. The guide is divided into ten chapters and includes an appendix at the end that contains various useful equations. The contents of each chapter are listed below.

Chapter 1

Introduction to chemical elements

Those relevant to water treatment

Basic valency theory

Molecular weight calculations and simple reactions and calculations

References on this topic are extensive, but since the aim of this guide is to produce an 'easy-to-use' manual, the chemical elements are discussed only in as far as they are relevant to the concept of the guide. No attempt is made to discuss properties of atoms or elements in any greater detail than is necessary to provide a basic understanding of valency and the balancing

of chemical reactions. In all cases examples are drawn from water treatment to illustrate the concepts in simple and relevant ways.

The categorisation of chemical substances into organic and inorganic compounds is discussed with relevance to chemicals used in water and wastewater treatment.

Chapter 2

Acids and bases, pH and alkalinity

Chapter 2 deals with acids, bases, pH and alkalinity which are core topics in understanding water treatment chemistry. The chapter starts with a simple explanation of pH, again relating it to everyday experiences.

Water hardness and alkalinity are described and the relationship between pH, hardness and alkalinity explained together with water stabilisation. The importance of water stabilisation in water treatment is discussed with respect to aggressive, scaling and corrosive conditions. The Langelier and Ryznar indices are also discussed.

Various acids and bases commonly used in water and wastewater treatment are discussed.

Chapter 3

Coagulation and flocculation

In this chapter, coagulation and flocculation, two of the important processes used in water and wastewater treatment, are described.

A description of the different types of compounds that occur in water, both dissolved and suspended, is provided as this is important in understanding the function of coagulation and flocculation. The causes of some water treatment problems due to some of these particles are also described.

Particles suspended in water can be categorised into three classes based on their origin:

- Inorganic materials, such as silt or minerals
- Organic matter
- Biotic material including algae, viruses and bacteria

Coagulation and flocculation are essential steps in the process towards removing these particles.

Chapter 4

Iron salts – formulae, chemical and physical properties, applications and reactions

From Chapter 4 onwards, the guide becomes more specific in terms of the various chemicals used in water treatment. The range of chemicals used is extensive, as can be deduced from the list of chemicals that have been approved in terms of a recent WRC project (WRC Report No. 1600/1/09), 'National Standards for Water and Wastewater Treatment Chemicals' which lists 46 chemicals, excluding proprietary brands and formulations (John and Trollip, 2009). Each chemical is discussed in terms of its manufacture, chemical and physical properties, applications and relevant chemical reactions. Due to the high number of chemicals, the most logical system was to group them into broad categories based on chemical structure and or function.

A coagulant is any chemical that is used to bring about the agglomeration of particles suspended in water and a wide range of such chemicals exists. They can be classified as inorganic or mineral compounds such as aluminium and ferric salts or as organic, such as polyelectrolytes.

Iron salts are discussed both for their application in drinking and wastewater treatment and also in the removal of phosphates. The company web sites of the various producers provide a good deal of non confidential and public domain information. Production processes are based on the reaction of an acid (sulphuric or hydrochloric) with an iron source such as iron ore or scrap iron with some variation in the process depending on the source used.

The application of iron salts is either as a particle coagulant relying largely on 'sweep coagulation' for particle removal or for the control of phosphates by precipitation. The use of ferric salts results in a reduction in the alkalinity of the water and in order to maintain the pH of the water at a level ideal for ferric salt coagulation and to prevent the water becoming corrosive, the addition of lime or soda ash may be required.

Chapter 5

Aluminium salts – formulae, chemical and physical properties, applications and reactions

Aluminium salts are produced by several South African and International companies. Unlike iron salts, aluminium-based water treatment chemicals are produced in a wide variety of chemical and physical forms. This is due to the more soluble hydroxide forms of aluminium (Gregory and Duan, 2001). Aluminium-based chemicals include sulphates and chlorides as is the case with iron salts, but in addition, a wider range of polymerised chlorides known collectively as polyaluminium chlorides (PAC) are also manufactured for use in water treatment.

Aluminium salts are prepared by reacting bauxite or certain clays with sulphuric acid. If the transportation distance is not too great the reacted solution can be taken to the waterworks and used directly. Alternatively the solution can be concentrated by evaporation and crystallised to

the solid form and delivered as lumps (kibbles) or ground and delivered in granular or powder form. Aluminium sulphate is often known as alum, even though it is not in fact a true alum.

The reaction mechanisms that occur during aluminium sulphate treatment are similar to those found when using ferric salts, and as was found with ferric salts, aluminium salts result in a reduction in the pH, since for every 1 mg/l of aluminium sulphate that reacts to produce a precipitate of aluminium hydroxide, 0.5 mg/l of alkalinity (as CaCO₃) is consumed (Water Quality and Treatment, 1990). This is discussed in more detail in Chapter 7.

Chapter 6

pH correction chemicals – types, sources, advantages and disadvantages

Following the description and discussion of coagulants, the book looks at the wide range of pH correction chemicals, of which lime is the most widely used. 'Lime' is technically hydrated calcium oxide, but is mined as limestone (CaCO₃) and then heated in kilns to produce quicklime (CaO). It can then be slaked, or hydrated, to produce slaked/hydrated lime (Ca(OH)₂). It is in the form of quicklime or slaked lime that lime is most commonly used in water and wastewater treatment applications (Water Quality and Treatment, 1990). Hydration of quicklime is either carried out *in situ* at a water treatment plant or more commonly at a central production site close to the source. Two broad categories of lime are described, these being 'white' and 'brown' depending on impurity levels and calcium oxide content. Other chemicals used in pH correction and covered in the text include soda ash and caustic soda.

Chapter 7

Polyelectrolytes

Introduction to the concept of polymers

Polyamines and polyDADMACs, polyacrylamides – properties and differences, applications, safety and health issues

Inorganic or mineral coagulants, such as aluminium sulphate and ferric chloride have been used for the coagulation of colloidal suspension in water for centuries, while in comparison polyelectrolytes are a relatively new innovation in water treatment. Polyelectrolytes are used in water treatment both for coagulation and as coagulant/flocculant aids to strengthen flocs and improve their settleability (Van Duuren, 1997). Polyelectrolytes, often generically referred to in the industry as 'polymers' are the next large group of flocculants discussed.

The polyelectrolytes used in water treatment are high molecular weight, synthetic organic polymers, produced by the polymerisation of one (homopolymer) or more (copolymer) types of monomer units. Since the type and number of monomer units can be varied during the manufacture of polyelectrolytes, a wide variety of polymers can be produced. In addition to this the polymer chains can be linear, branched or cross-linked, adding to their complexity

(Letterman and Pero, 1990). They can contain both negatively and positively charged sites and this characteristic is used to classify them as:

- *Cationic*, having an overall positive charge
- *Anionic*, having an overall negative charge
- *Non-ionic*, being neutral
- *Amphoteric*, having both positive and negative sites (Letterman and Pero, 1990; Hamilton *et al.*, 1994)

The more highly charged a polymer, the more soluble it is likely to be (Hamilton *et al.*, 1994). Cationic polyelectrolytes are usually referred to as primary coagulants, while non-ionic and anionic are referred to as coagulant aids or flocculants and these have relatively high molecular weights, often in the region of ten times or more that of the typical primary coagulant (Letterman and Pero, 1990).

The polyelectrolytes used in water treatment are derived from petrochemicals and the most common compounds used in water treatment are:

- Polyamines, produced by the reaction of epichlorhydrin with dimethylamine
- Polydiallyldimethyl ammonium chloride produced from allyl chloride and dimethylamine

Cationic polymeric coagulants, unlike their inorganic counterparts, are not affected by the pH of the water and on account of their much higher charge density, can be applied in much lower doses than aluminium and iron salts (Lind, 1994a and 1994b). Another benefit of these chemicals is that they tend to produce stronger, larger and better settling flocs (Ghosh *et al.*, 1985). Furthermore, for surface waters low in suspended solids, like many of those used as a raw water source in Southern Africa, polyelectrolytes can be used in conjunction with direct filtration, which can allow for significant savings in water treatment plant construction (Ghosh *et al.*, 1985).

Chapter 8

Disinfectants and oxidants

Chemicals used – properties, application, comparison

Description of demand, residual, etc.

Disinfection and oxidation are wide ranging topics. The most commonly used disinfectants and oxidants used in water and wastewater treatment are discussed. By far the most common are those derived from chlorine, with liquid chlorine gas still the single most common means of disinfecting drinking water. More than 90% of the potable water produced worldwide is disinfected using chlorine.

Whilst chlorine based chemicals dominate water disinfection and oxidation, other chemicals are commercially viable. These include ozone, chlorine dioxide, chloramines and bromine.

Oxidation is generally carried out early on in the treatment process, whilst disinfection usually takes place in the final stage of treatment before the drinking water is distributed or the wastewater effluent discharged.

Many disinfectants also perform the function of oxidants and this important aspect of their use is also described. For example, chlorine dioxide and ozone are often used for manganese oxidation. Manganese oxidation with chlorine is very slow and as a result manganese generally precipitates only after filtration, resulting in problems in the reservoir and distribution system, whereas the oxidation reaction rate with chlorine dioxide and ozone is rapid, allowing for removal of the precipitated manganese in the clarifiers and filters. Disinfectants can also oxidise taste and odour compounds, reduce colour through oxidation of highly coloured organic compounds and improve the overall quality of the water.

Chapter 9

Activated carbon – types and sources

Important properties – iodine number, pore size, etc.

Evaluation methods

Activated carbon was initially used in water treatment essentially for the removal of taste and odour compounds, but is also becoming widely used for the removal of other organic contaminants, especially those with potentially harmful health effects.

In Southern Africa, powdered activated carbon (PAC) is used primarily for the removal of two algal taste and odour compounds, namely geosmin and 2-methylisoborneol (2-MIB). These occur mainly due to the presence of two *cyanobacteria* or blue-green alga genera, *Microcystis* and *Anabaena* (Wnorowski and Scott, 1992).

Activated carbon is produced from a variety of raw materials, although coal, wood and coconut are most commonly used in the manufacture of PAC for potable water treatment applications. The physical properties of the carbon are dependent upon the raw material, as well as both the method and extent of activation used. In general, coconut tends to give rise to a dense structure containing only a few larger pores, while wood-based activated carbon has an open structure with many larger pores. The coal-based carbon usually has a structure somewhere between that of coconut- and wood-based carbons (Greenbank, 1992). Experience has shown that coal-based and wood-based carbons are usually more effective for water treatment applications.

Granular activated carbon (GAC) can be used instead of PAC, but whereas PAC is generally used only once and then discarded with the sludge, GAC can be used until it is saturated (i.e. no longer able to absorb the contaminant(s) for which it is being used) and it can then be regenerated and reused. Biologically Activated Carbon (BAC) is also discussed.

Chapter 10

*Miscellaneous chemicals used in special applications
Potassium permanganate, copper sulphate, etc.*

A number of chemicals are not routinely used at water and wastewater plants, but can provide cost effective treatment options, and the more commonly used of these are described. For example, potassium permanganate is used as an oxidant in certain specialised cases, particularly where manganese is present. The addition of permanganate converts the manganese that is in a reduced and soluble form to insoluble manganese dioxide, which can be removed by coagulation at the sedimentation stages.

Copper sulphate can be used to control algae, but unfortunately it is toxic to fish (Degremont, 1991). The dose also has to be carefully controlled, since the maximum allowable limit for copper in potable water is 1.0 mg/l (SANS 241).

Appendix

Calculations – solution strength, dose rates, tank capacities, etc.

Calculations are provided to assist in calculating the amount of chemical required in making up a solution of a particular concentration, how to convert flow rates and dosage rates, determine tank sizes, pumping rates and pump sizes and other relevant calculations.

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GLOSSARY

ACH	Aluminium chlorhydrate
BAC	Biologically activated carbon
BNR	Biological nutrient removal
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
Ct	Product of the concentration and time (used for disinfection)
d	Day(s)
DAF	Dissolved air flotation
DMA	Dimethylamine
DO	Dissolved oxygen
DWAF	Department of Water Affairs and Forestry
<i>E. coli</i>	<i>Escherichia coli</i>
EIA	Environmental impact assessment
GAC	Granular activated carbon
ISO	International Standards Organisation
kg	Kilograms
Kℓ	Kilolitre
Kℓ/d	Kilolitre per day
KW	Kilowatts
KW/kg/d	Kilowatts per kilogram per day
ℓ	litre
m ³	Cubic metres
m ³ /d	Cubic metres per day
mg/ℓ	Milligrams per litre
m/h	Metres per hour
Mℓ	Megalitres
Mℓ/d	Megalitres per day
mℓ/ℓ	Millilitres per litre
mm	Millimetres
m/m	mass per mass
m/s	Metres per second
m/v	Mass per volume
NSF	National Sanitation Federation
NTU	Nephelometric turbidity units
O&M	Operation and maintenance
PAC	Polyaluminium chloride or Powdered Activated Carbon
PST	Primary settling tank
PVC	Polyvinyl chloride
PVA	Polyvinyl acetate
SABS	South African Bureau of Standards
SS	Suspended solids
TDS	Total dissolved solids

TOC	Total organic carbon
µm	Micrometre
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
WAS	Waste activated sludge
WWTP	Wastewater treatment plant

CHAPTER 1

THEORY AND NOMENCLATURE

Chemistry can be a complicated and confusing subject to the non-chemist. However, a basic knowledge of the subject is required if one is to understand how to select and use water and wastewater treatment chemicals. This guide attempts to provide the basic chemical knowledge necessary to make the correct decisions regarding the choice and application of these chemicals, without burdening the reader with unnecessary information and detail. The guide is intended to provide a quick and easy reference to the information needed and in order to do this we need to start with the fundamental theory of chemistry.

1.1 Atoms, Molecules and Compounds

All known chemicals are categorised in a table called the periodic table and the latest version of the periodic table lists 103 different chemicals, referred to as elements. The periodic table arranges all the elements in a logical sequence, based on similarities in chemical properties. In 1869 Mendeleev originally arranged the elements based on atomic weight, in rows known as periods or series, in such a way that the columns of the table contained elements with similar chemical and physical properties (Cotton and Wilkinson, 1976; Brown, 1974). It was only later that it was realised that the correct sequence relationship was actually due to atomic number and not atomic weight, but since these are in most cases the same, this did not have a significant impact on the periodic table. A version of the periodic table is shown in Figure 1.

Obviously not all elements have an application in water treatment and the table in Figure 2 shows the periodic table with everything removed except those elements that have some role to play in water treatment, and which will feature in the subsequent chapters of this guide.

Elements in their simplest form consist of atoms. Until the atomic bomb was invented it was thought that nothing could be further subdivided than an atom and the power of the atomic bomb is a representation of the energy that binds the parts of an atom together.

An atom is the simplest form of an element, but few elements exist in pure form, since they are not stable in this state and are therefore often found associated with another element or elements, known as molecules. A good example of this is oxygen. The chemical symbol for oxygen is O, but oxygen atoms are unstable in this form and cannot exist in this state under normal conditions of temperature and pressure. However, if an oxygen atom combines with another atom of oxygen, a stable O₂ molecule is formed and is in fact the form of oxygen contained in air (air contains 21% oxygen). It is also the form of oxygen supplied in oxygen gas cylinders.

The oxygen atom is a fairly unstable one and will therefore combine, or react, with a large number of other chemicals, the most important one in terms of this guide, being H₂O or water, in which two hydrogen atoms combine with an atom of oxygen.

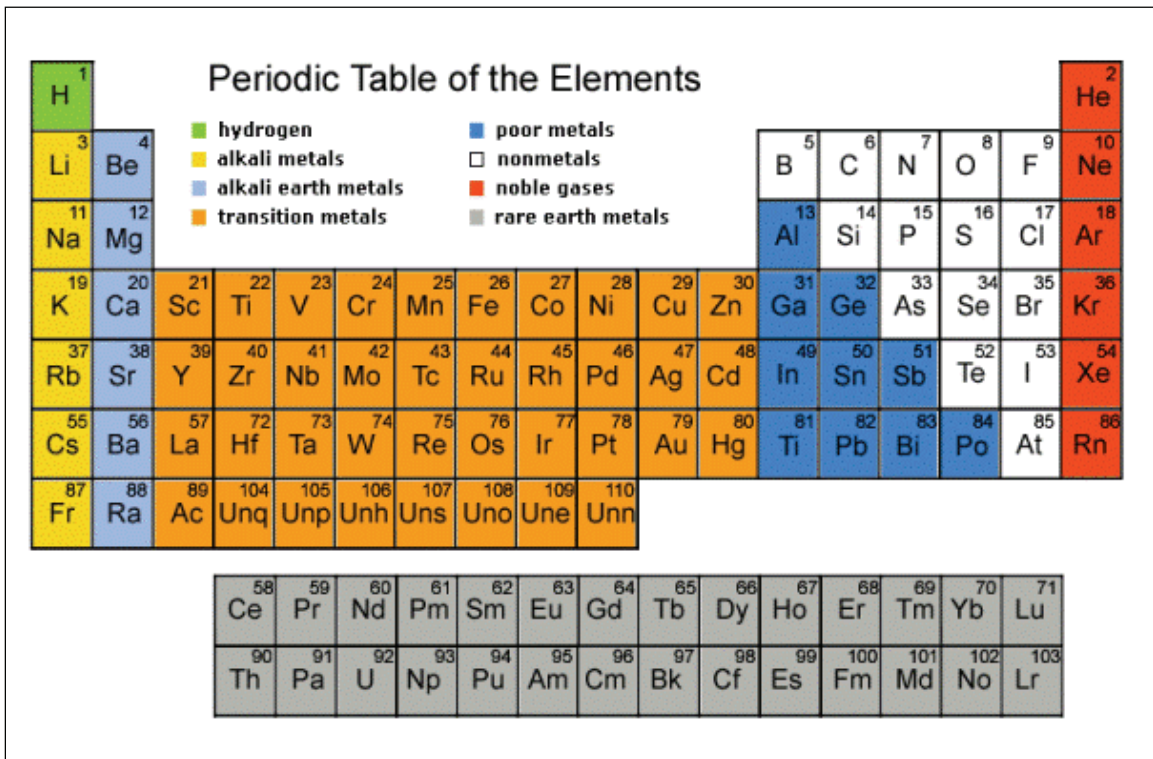


FIGURE 1: Periodic Table of the Elements

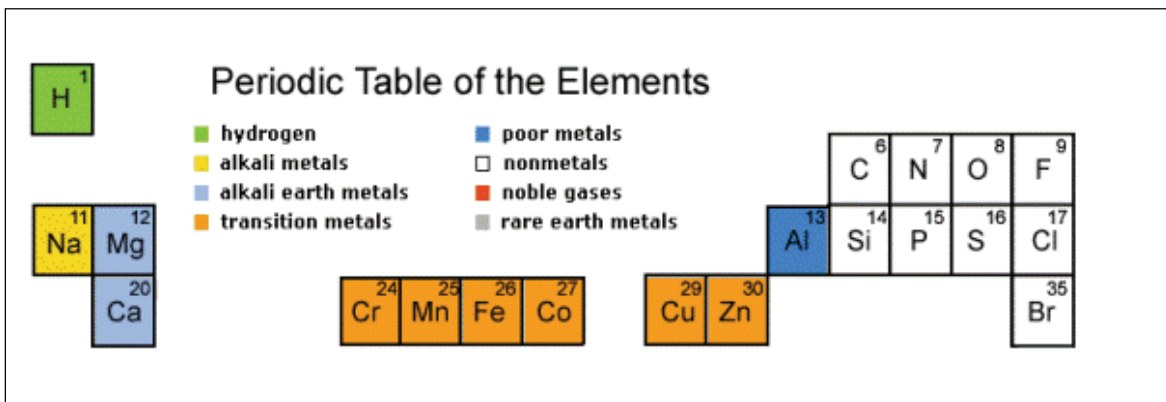


FIGURE 2: Periodic Table of the Elements that are especially important in water and wastewater treatment

1.2 Valency

All water treatment processes involve chemical or biochemical reactions and many of the chemicals used in water treatment are manufactured using chemical reactions. It is therefore essential in the understanding of the chemicals we use, and the processes in which we apply them, to have some understanding of how chemical compounds are made and what reactions may occur when they are used. In order to do this we have to discuss valency.

The theory of valency is fairly complex and depends on the number of electrons that an element possesses. Atoms strive to have stable arrangements of electrons in their outer energy levels. To understand this fully, one needs to study valency chemistry and this information can be obtained from any basic chemistry book, but for the purposes of this explanation, it is sufficient to know the general valencies of an atom. In the example of water (H₂O), hydrogen generally has a valency of one (actually +1), while that of oxygen is generally two (actually -2) and therefore two atoms of hydrogen will react with one atom of oxygen. In this arrangement, both the hydrogen atoms and the atom of oxygen achieve an energetically stable state.

It is possible to alter the valency of atoms using energy and in this way ozone (O₃) is formed. Molecular oxygen (O₂) is transformed into O₃ using electrical energy (usually by passing O₂ over a sparkless discharge). However ozone is highly unstable and quickly reverts to the more stable O₂ form, at the same time releasing energy. Ozone is therefore highly reactive and is also a very effective disinfectant.

Knowing the valency of an atom can help in predicting how it will combine with other atoms, so calcium, which has a valency of two (Ca²⁺) would be expected to form CaO with oxygen, and carbon, with a valency of four (C⁴⁺) would be expected to form CO₂ (carbon dioxide) with oxygen. However valency is only one of many factors influencing reactions and the type of bond (covalent, ionic, Van der Waals, etc.), the bond energy of the compound, free energy changes during a reaction, and electronegativity, are just some of the factors which influence reactions. To complicate matters still further, many atoms have more than one valency. A good example is sulphur, which can exist in a number of different states. Hence we can form H₂S (S²⁻), SO₂ (S⁴⁺), H₂SO₄ (S⁶⁺) and many more. This multitude of valencies arises due to the number of possible stable arrangements of the electrons in the outer energy levels of sulphur.

Iron is another example of an atom with multiple valencies and is relevant here since it is an important chemical in water and wastewater treatment. Iron can exist in both a bivalent (ferrous or Fe²⁺) and trivalent (ferric or Fe³⁺) state.

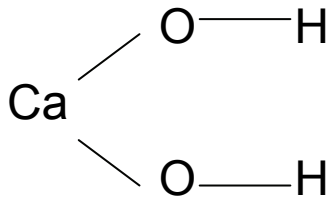
It should be clear then that although valency can be useful in predicting how different atoms will combine (or in predicting that they will not combine), it only addresses one aspect of reaction chemistry, so must be used cautiously. However, in many cases valency can be used to predict how atoms will combine, for example:

NaCl: sodium chloride or table salt where sodium is represented as Na⁺ and chloride as Cl⁻.

HCl: hydrochloric acid, also known as swimming pool acid, where hydrogen is represented as H⁺ and chloride as Cl⁻.

Ca(OH)₂: Calcium hydroxide or slaked lime. This is the form of lime commonly used for pH correction, where calcium is represented as Ca²⁺ and hydroxide as OH⁻. The respective valencies are: Calcium 2+, Hydrogen 1+ and Oxygen 2-.

So we have:



1.3 Classification of Chemicals

Classification of chemicals in the periodic table into groups with similar physical and chemical properties has already been discussed. However chemicals are broadly divided into two groups, namely organic and inorganic chemicals. This has relevance for this guide book, especially when discussing the various coagulants that are used in water and wastewater treatment (see Chapters 5 and 7). Organic chemicals are classified as chemicals that contain carbon and inorganic chemicals are classified as those that don't contain carbon.

1.3.1 Organic Chemicals

Obvious examples of organic chemicals are those found in living organisms, such as proteins, lipids, enzymes and lignins. Other examples are petroleum, oil, plastics, rubber, solvents, greases, activated carbon and organic polyelectrolyte coagulants. Activated carbon is used in water treatment to remove organic contaminants, such as taste and odour compounds, colour and pesticides and is discussed more fully in Chapter 9. Organic polyelectrolyte coagulants have become widely used in water and wastewater treatment over the past few decades, finding application as primary coagulants, floc aids to strengthen the formation of flocs and to assist in the thickening of sludges. These chemicals are described more fully in Chapter 7. Other organic compounds with relevance to water treatment are humic and fulvic acids. These naturally occurring organics are typically found in natural waters in the Cape, which as a result are highly coloured and difficult to treat. Treatment options for these waters are also discussed in Chapter 7.

1.3.2 Inorganic Chemicals

Simply put, inorganic chemistry is the study of chemicals other than carbon compounds, although some 'carbon compounds', for example CaCO_3 (limestone or agricultural lime), are generally included as inorganic compounds. Inorganic chemistry encompasses an enormous number of compounds, since there are over a hundred elements capable of producing an almost endless number of compounds. However, chemicals relevant to water and wastewater treatment include a relatively small number of chemicals, mainly lime, soda ash, sodium bicarbonate, sodium hydroxide, ferric and aluminium salts (e.g. ferric chloride, aluminium sulphate), bentonite, sodium aluminate, activated silica, ammonia, sodium chloride, sodium

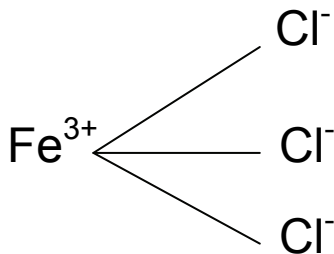
chlorite and most disinfectants, such as chlorine, sodium hypochlorite, calcium hypochlorite, chlorine dioxide and ozone.

1.4 Estimating Chemical Reactions

Some of the most common chemical processes that occur in water treatment do not lend themselves to calculation. It would be very convenient for example if there were some chemical or physical property of water that could be used to calculate exactly how much coagulant needed to be added to the water to achieve an acceptable water quality, or how much carbon needed to be added to the water to remove taste and odour compounds to a level where they would no longer pose a nuisance. Unfortunately this is not possible under normal working circumstances and in such cases it is necessary to establish the correct dosages by conducting laboratory or full scale tests (for detailed information on conducting such tests refer to Freese *et al.*, 2004).

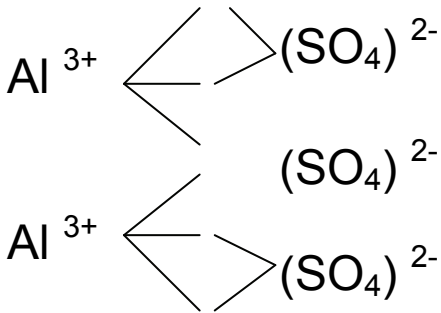
However, there are many chemical reactions that can be reduced to calculation and this has some useful applications in water treatment. Knowing the valency assists in determining how the chemicals will combine, but we also need to know the molecular masses. These can be calculated by obtaining the atomic weights for the individual elements from a periodic table. For example, if ferric chloride and aluminium sulphate (often incorrectly called 'alum'¹), both commonly used chemicals in both water and wastewater treatment, are considered.

The chemical formula for ferric chloride is:



and the formula for aluminium sulphate is:

¹ Although the term 'alum' is used for aluminium sulphate, the word refers to a whole class of chemical compounds. The specific compound is the hydrated aluminium potassium sulphate with the formula $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The alums have the related stoichiometry, $\text{AB}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The properties of aluminium sulphate are quite different from those of the $\text{AB}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ alums and therefore the more accurate term 'aluminium sulphate' is used in this guide to identify the compound.



Both iron (Fe^{3+}) and aluminium (Al^{3+}) are trivalent under these conditions (both iron and aluminium can exist in other valency states), chloride is univalent (Cl^-) and sulphate is bivalent (SO_4^{2-}).

In the case of the formula for aluminium sulphate, the lowest common denominator is applied, which is 6, therefore:

$2 \times 3 = 6$ (i.e. two Al atoms are required) and $3 \times 2 = 6$ (i.e. three SO_4 molecules are required).

It is now possible to calculate the molecular mass of each compound. The atomic masses for the relevant elements are:

Iron	56
Chlorine	35.5
Aluminium	27
Sulphur	32
Oxygen	16

Therefore:

The molecular mass of ferric chloride is $56 + (3 \times 35.5) = 162.5$

And the molecular mass of aluminium sulphate is: $(2 \times 27) + ((3 \times (32 + [16 \times 4])) = 342$

The active ingredients in ferric chloride and aluminium sulphate are iron and aluminium respectively and therefore we can calculate the iron content of ferric chloride as:

$$\left(\frac{56}{162.5}\right) \times 100 = 34.5\% \quad [1]$$

and aluminium content of aluminium sulphate as:

$$\left(\frac{54}{342}\right) \times 100 = 15.8\% \quad [2]$$

Based on this, it appears that a ton of ferric chloride to contain more active ingredient than a ton of aluminium sulphate.

However, a knowledge of the basic chemistry is needed here in order to make a proper comparison. Firstly, ferric chloride is not available commercially in South Africa in pure crystalline form, but rather as a 42% solution. This means that the iron content of that solution will be 34.5% of 42% which is 14.5% – about the same as the aluminium concentration we calculated above for solid aluminium sulphate (alum) kibble.

Furthermore, aluminium sulphate is never produced as pure $\text{Al}_2(\text{SO}_4)_3$, but always contains waters of crystallisation. Therefore, the correct chemical formula for aluminium sulphate (solid or liquid) is $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (Degremont, 1991). This means that the aluminium content (i.e. the active ingredient) of pure aluminium sulphate kibble is in fact only around half that calculated above in Equation [2] as determined in Equation [3].

$$\left(\frac{54}{666}\right) \times 100 = 8.1\% \quad [3]$$

Some manufacturers specify the activity of aluminium sulphate kibble in terms of Al_2O_3 , the concentration usually being in the order of 15 to 16% as Al_2O_3 . In this case, the Al content of the kibble is calculated as being 52.9% of Al_2O_3 , by Equation [4]:

$$\left(\frac{54}{102}\right) \times 100 = 52.9\% \quad [4]$$

The Al content of the kibble is therefore 52.9% of 15 to 16% or between 7.9 to 8.5%.

To complicate matters further, aluminium sulphate is also often supplied commercially as a solution of between 46 and 48%. For accurate determination of the dose, the actual concentration of active compound can be determined from the specific gravity (SG) of the solution (see Chapter 5), but it is important that the chemical formula is known. This should be provided by the supplier.

The above example serves to illustrate the danger of using valency alone to determine a reaction and highlights the importance of knowing the fundamental chemistry in order to correctly calculate dosages and chemical usage.

CHAPTER 2

ACIDS AND BASES, pH AND ALKALINITY

2.1 The pH Scale

The pH scale runs from 0 to 14 with 0 being the strongest acid value and 14 being the strongest alkali (also referred to as a 'base') value. This scale is simply a means of measuring acidity or alkalinity and is an easy and convenient way of expressing the activity of hydrogen ions in solution, since the numbers involved are very large. For example, it has been found that in pure water at 22°C the concentration of hydrogen ions is 10^{-7} moles per litre (Water Research Centre (WRc) Handbooks, pH, 1994), but in strongly acidic solutions, the hydrogen ion concentration can be in the region of 100 000 times greater. The pH scale expresses pH as the negative log of the hydrogen ion concentration or $-\log [H]$. Therefore the pH of pure water at 22°C is 7 (i.e. $-(7)$ or 7). This is an important concept to understand, because a difference of 1 in pH is in fact a difference of ten times in terms of the hydrogen ion concentration. In other words, the difference between pH 2 and pH 12 represents a change in hydrogen ion concentration from 0.1 moles per litre to 0.00000000001 moles per litre. A mole is defined as the number of gram molecular weights (moles) of a substance per litre of solution. For example the molecular weight of sodium hydroxide is 40, so a 1 mole per litre (i.e. 1 M solution) of sodium hydroxide contains 40 g of sodium hydroxide in 1 litre of solution (Peters *et al.*, 1974).

The pH scale is in fact used as a measure of both acidity and alkalinity; pH 0 to 7 indicates acidity and pH 7 to 14 indicates alkalinity (pH 7 is neutral, neither acidic nor alkaline).

The prevailing pH is a very important factor in water and wastewater treatment, both in terms of treatment and manufacturing processes, since pH affects many of the chemical reactions. For example the reaction of an inorganic coagulant, such as aluminium sulphate, is dependent on pH. The optimum pH for turbidity removal is around 6.8, while precipitation of the organic matter present is best at a pH of around 5. The addition of aluminium sulphate also results in a reduction in the alkalinity and the pH, a factor which can have serious consequences in wastewater treatment if not rectified. This is discussed more fully in this chapter under the section on 'lime' and in Chapter 5.

The pH is also important in disinfection reactions. For example pH affects the proportion in which the various species of chlorine occur and therefore affects both the disinfection efficiency and the residual concentration of chlorine (White, 1999). See Chapter 8 for more information on this.

2.2 The Relationship between pH, Alkalinity and Hardness

The relationship between pH, alkalinity and hardness is not always clearly understood because each measures a different aspect of water quality, although each of these is related in some

way. As described above, pH is a measure of the acidity or alkalinity of water or a solution. Hardness and alkalinity are described in more detail below.

2.2.1 Hardness

Hardness was originally intended to be a measure of the ability of a water to precipitate soap and since soap is predominantly precipitated by calcium and magnesium ions, hardness is now defined as the sum of the calcium and magnesium ions. These are both expressed in mg/l calcium carbonate (CaCO₃). Hardness can consist of both carbonate and non-carbonate hardness and simply stated, if the hardness (expressed in mg/l CaCO₃) is equal to or less than the alkalinity (also expressed in mg/l CaCO₃) then all the hardness is referred to as 'carbonate' hardness. If the hardness is greater than the alkalinity, the difference between the hardness value and alkalinity value is referred to as non-carbonate hardness (method number 2340-A, Standard Methods, 1998). Carbonate hardness, as the name suggests, is due to the presence of carbonate and bicarbonate salts of magnesium and calcium, while non-carbonate hardness arises from various alkaline salts of calcium and magnesium (e.g. CaSO₄). Since carbonates, bicarbonates and many compounds that contribute to non-carbonate hardness are alkaline in nature, it is obvious that a hard water will generally also be one that is alkaline in nature and therefore has a pH of more than 7. Borehole waters are typically very hard due to the dissolution of calcium and magnesium into the water from the soil. The classification of water according to the hardness content is listed in Table 1.

Hard waters cause scaling of pipes and eventual blockage of the pipe. Chemical precipitation processes can be used to soften hard waters and these processes are described in more detail in Chapter 6.

**Table 1: Classification of water according to hardness content
(from Van Duuren, 1997)**

Hardness range (mg/l CaCO ₃)	Hardness description
0-50	Soft
50-100	Moderately soft
100-150	Slightly hard
150-200	Moderately hard
200-300	Hard
>300	Very hard

2.2.2 Alkalinity

Alkalinity, in its simplest definition is the sum of all the titratable bases, and in fact is measured by titrating a water sample with an acid to a particular end-point (i.e. pH value). Therefore, reference is made to phenolphthalein alkalinity (phenolphthalein is an indicator that changes colour at a pH of around 8.3) and total alkalinity (titration to a pH of 4.5). It is in fact a measure of a combination of properties of water and is usually used in conjunction with other measurements, such as pH and hardness, when assessing a water sample.

Generally, the alkalinity of surface water, such as that from an impoundment or a river, is a function of the carbonates, bicarbonates and hydroxides, although other compounds, such as borates, phosphates and silicates can also contribute to the alkalinity. Measurement of the alkalinity is used in the interpretation and control of many water and wastewater treatment works processes and this will become evident in some of the subsequent chapters in this guide.

As mentioned above, alkalinity is predominantly due to carbonates, bicarbonates and hydroxides. The most predominant water soluble carbonates and bicarbonates are those of calcium and magnesium. Therefore hard waters are generally also high in alkalinity and of course, since these are alkaline compounds, the pH of water high in hardness and alkalinity is therefore generally high.

2.3 Water Stabilisation

In order to protect the infrastructure of water and wastewater works, as well as the associated distribution systems, it is essential to ensure that a water is stable. A stable water is one which will neither scale nor corrode the surfaces and pipes in treatment works and distribution systems. Essentially there are three processes that can occur due to a water that is unstable (Van Duuren, 1997), namely:

Precipitation (resulting in scaling): The precipitation of calcium and iron minerals on the inside walls of pipes can seriously restrict the carrying capacity of the pipes.

Aggression: This term is used when the water contained in concrete lined structures attacks the cement. It is due to one of two processes:

1. Soft waters, also called undersaturated waters (meaning undersaturated in terms of calcium carbonate) dissolve some of the minerals from the concrete surfaces of tanks and pipes.
2. Water containing high concentrations of sulphate species (>350 mg/l) will react with some of the minerals contained in concrete, causing it to deteriorate.

Corrosion: The term 'corrosion' has a very specific meaning in water treatment, but it is often confused with the process of 'aggression', so it is important to be aware of what each term is actually referring to. Corrosion occurs when electrochemical reactions occur between water and metal components in the system. These electrochemical reactions can result in dissolution of the metal and lead to pitting or nodule formation on the metal surfaces, 'red water' and eventually destruction of the pipes.

Stabilisation of water involves conditioning it by adjusting the pH, alkalinity and/or acidity, the hardness and the calcium carbonate (CaCO_3) saturation state or potential. It now becomes clear why parameters such as pH, hardness and alkalinity are so important in water and wastewater treatment. Calculations to determine which chemicals and what dosages need to be used in order to stabilise the water are done using equilibrium chemistry. Langelier (1936) developed a saturation index that establishes whether water is over- or undersaturated with respect to calcium carbonate (CaCO_3). The calculations are fairly complex and also involve the use of

complicated diagrams, but Friend and Loewenthal (1992) produced an easy-to-use software programme called Stasoft that can be used to compute these equations. One needs to determine the alkalinity, hardness, TDS and temperature of the water. These figures are entered into the programme and the state of the water is determined and the required treatment and dosages calculated. Stasoft is available from the Water Research Commission.

Another index used for water stabilisation is the Ryzner index (Degremont, 1991), but this is more often used in the conditioning of cooling systems. The Ryzner Index makes use of the Langelier Saturation Index to determine the tendency of oxygenated water to either corrode or scale surfaces, especially those of cooling towers.

Water stabilisation chemistry is complex, but the costs of ignoring this important aspect of water treatment can be huge. Fortunately Stasoft simplifies the process and can be used by anyone, not only professional water chemists.

2.4 Acids

We all have contact with acidic material on a daily basis. Common drinks such as wine, Coca Cola, beer, lemon juice and vinegar are all acidic. 'Stronger' acids that are commonly encountered include 'pool acid' and battery acid. The terminology can be confusing when acids and bases are discussed in chemical manuals. The terms 'strong' or 'weak' when used to describe acids and bases refer to the types of bonds involved, which determine the degree of dissociation that a molecule undergoes. For example, hydrochloric acid (HCl), or pool acid, has strong ionic bonds and therefore almost completely dissociates in water. Hydrochloric acid is therefore referred to as a strong acid. Glacial acetic acid (CH_3COOH , the type of acid found in vinegar) has weaker, non-ionic bonds and therefore only partially dissociates in water. This is therefore referred to as a 'weak acid'. A study of the types of bonds that can form is required to properly understand these concepts, but the point being made here is that the terms 'strong' and 'weak' do not refer to the apparent 'corrosivity' of an acid or base. A weak acid, such as glacial acetic acid, is particularly dangerous in concentrated form, being capable of congealing proteins and causing permanent blindness if splashed into the eye.

It is also possible to obtain concentrated or diluted solutions of strong or weak acids, so one must avoid confusing the terms 'strong' and 'weak' with concentrated and diluted.

The problem is further complicated by the fact that there are a number of different ways of defining acids and bases in chemistry. Acids and bases can be defined in terms of their ability to donate protons (acids) or accept protons (bases) known as Brønsted-Lowry Definition, or in terms of their ability to accept electrons (acids) or donate electrons (bases) known as the Lewis Definition (Cotton and Wilkinson, 1976). In certain solutions, based on the above definitions, a compound that is generally accepted as being an acid, in fact behaves as a base and vice versa (Cotton and Wilkinson 1976). However, for the purposes of this guide, an acid refers to chemicals such as hydrochloric or sulphuric acids.

Acids are not widely used in water and wastewater treatment, but they are an essential part of the manufacturing process of a wide range of the chemicals that have water and wastewater treatment applications. Hydrochloric acid for example remains a major component of many water treatment chemicals such as ferric chloride and aluminium chloride. Hydrochloric acid is unusually corrosive to stainless steel, which as its name implies, is unaffected by most chemicals. Thus you will find that chemicals containing hydrochloric acid are never transported or stored in stainless steel tanks.

Sulphuric acid is used in the manufacture of chemicals such as aluminium sulphate and ferric sulphate. Concentrated sulphuric acid, like concentrated hydrochloric acid, is an extremely dangerous chemical and all necessary safety precautions must be employed when handling these chemicals.

2.5 Alkalis

Alkalis, for the purpose of this guide, are chemicals used for pH adjustment and which have pH values greater than 7. As was explained for acids, the term 'strong' and 'weak' when used for alkalis refers to the dissociation of an alkali in water. An alkali, such as sodium hydroxide which almost completely dissociates in water is called a 'strong' alkali or base, while sodium bicarbonate, which dissociates only partially in water, is referred to as a 'weak' alkali or base.

Alkalis commonly encountered in our day to day environment include baking soda (sodium bicarbonate), antacid powders and tablets (calcium and magnesium carbonates), and laundry powders and in the industrial environment, lime and caustic lye (sodium hydroxide).

Various alkalis are used in water and wastewater treatment, such as sodium hydroxide (caustic lye or caustic soda), various types of lime (limestone, quicklime and slaked lime), sodium carbonate (soda ash) and sodium bicarbonate. These are discussed in more detail in Chapter 6, but because of their wide application in water and wastewater treatment, references to these chemicals appear in other chapters of the guide as well.

CHAPTER 3

FLOCCULATION AND COAGULATION

3.1 Dissolved and Particulate Matter

The primary aim of coagulation and flocculation is to remove the suspended particles from water and if possible any dissolved particles that may be undesirable in the final water or effluent. Basically the matter present in water can be divided into two categories – dissolved solids and suspended, or colloidal, particles. Before coagulation and flocculation can be properly described, it is necessary to have some understanding of how these two types of matter impact on water treatment.

3.1.1 Total Dissolved Solids

Some dissolved salts, namely those that contribute to pH, hardness and alkalinity were discussed in the previous chapter, but there are obviously far more that need to be considered in water and wastewater treatment.

The total amount of dissolved material in water is referred to as the Total Dissolved Solids (TDS). The unit of measure is milligrams per litre (mg/l) and the TDS is obtained by filtering a known volume of water into a pre-dried and weighed crucible to remove all suspended material and then evaporating the filtered water to dryness (method number 2540-C, Standard Methods, 2000). The weighed residue is adjusted to an mg/l value and is referred to as TDS.

These dissolved materials cannot be seen and don't contribute to the clarity of the water but they can result in colour in the water and their presence can cause problems later in the water treatment process. For example the waters of the Eastern Cape can contain such a high concentration of dissolved humic and fulvic acids, that they resemble the colour of black tea. In spite of this the water is quite clear and is low in turbidity. However it is obvious that such water would be unacceptable as a purified drinking water. Treatment options for these difficult, low pH, low alkalinity, highly coloured waters are discussed in Chapters 4, 5 and 9.

Other dissolved chemicals that can cause problems in water treatment are iron and manganese. Both these chemicals do not impart colour to the water when they are in their soluble forms (ferrous, Fe^{2+} and manganous, Mn^{2+}), but once they become oxidised, as can happen when the water is exposed to air or laundry powders, or disinfected, they convert to insoluble forms (ferric, Fe^{3+} and manganese IV, Mn^{4+}) and precipitate out of solution. When this happens, unsightly brown or black staining of bath and toilet surfaces, pool surfaces and clothing can occur.

Ferrous iron or soluble iron compounds are easily oxidised in the presence of air. The rapidity with which dissolved iron is oxidised is often observed with borehole water. When the borehole water is initially pumped out of the ground, it is generally very clear, but within an hour or so of being exposed to the air, the water starts to turn cloudy and sometimes become highly turbid

after only a few hours. This is because the dissolved ferrous iron (Fe^{2+}) has been oxidised to insoluble ferric iron (Fe^{3+}) by exposure to the air. Many water treatment works add chlorine at the head of the works and this is generally adequate for iron oxidation and to ensure that the iron precipitates out of solution before reaching the filters.

Conversely, the oxidation of manganese from soluble Mn^{2+} to insoluble Mn^{4+} is relatively slow and can result in problems if not treated in the water works as it can come out of solution in the reservoir or distribution system. There are a number of ways of oxidising manganese, namely:

- Chlorine used at the head of the works can aid in the oxidation of manganese, but even with the addition of chlorine, this reaction is still fairly slow and it is also important that the chlorine be added as early in the treatment process as possible if the manganese is to be removed on the filters. If there is insufficient time for adequate oxidation to occur, there may still be soluble manganese present which will pass through the filters and precipitate out of solution once the water is in the reservoir or distribution system.
- Raising the pH also assists the oxidation of manganese. Again, it is important to allow adequate time for complete oxidation to occur.
- Potassium permanganate may be used if relatively high manganese concentrations are an ongoing problem. It was mentioned in Chapter 1 that manganese can have multiple valency states and it is this factor that is employed when using potassium permanganate for the oxidation of manganese. Soluble manganese is in an oxidation state of Mn^{2+} or, in other words has a valency of 2+, while insoluble manganese is in an oxidation state of Mn^{4+} . The chemical formula for potassium permanganate is KMnO_4 and in this compound manganese has a valency of 7+ or is in the oxidation state of Mn^{7+} . By adding the correct amount of KMnO_4 to the water, the Mn^{7+} reacts with Mn^{2+} to produce Mn^{4+} . However it is critical that the potassium permanganate dose is carefully controlled otherwise excess Mn^{7+} remains and the water turns pink. Once this has occurred the reaction cannot be reversed, certainly not under full scale plant conditions.
- Chlorine dioxide is a very effective oxidant and can also be used for oxidation of soluble manganese. It can also be used as a disinfectant (see Chapter 8 for more information on its disinfectant properties).
- Ozone is one of the most powerful oxidants used in water and wastewater treatment, but the dose needs to be carefully controlled in order to prevent over-oxidation of the manganese to permanganate. The generation of ozone has to take place on site and it entails relatively high capital cost. Ozone, like chlorine dioxide, is also used for disinfection and more information is provided in Chapter 8.

3.1.2 Total Suspended Solids

Particles suspended in water can be categorised into three classes based on their origin:

- Inorganic materials, such as silt or minerals.

- Organic matter.
- Biotic material including algae, viruses and bacteria.

The total amount of suspended materials is measured as Total Suspended Solids (TSS) in units of milligrams per litre (mg/l), and in this case a water sample of known volume is filtered through a pre-dried and weighed glass-fibre filter which is then redried to constant weight at 103-105°C and reweighed so that the mass of suspended solids filtered out can be calculated (method number 2540-D, Standard Methods, 2000). However, suspended matter results in 'cloudiness' of the water and a very common measurement used to determine 'clarity' or 'cloudiness' of water (or any other liquid) is turbidity. Turbidity is defined as a 'reduction of transparency caused by the presence of undissolved matter' (WRc, Turbidity, 1994) and provides an indication of the amount of suspended matter present in a liquid. Essentially turbidity is a measurement of the light scatter due to suspended particulates, the size and number of the particles affecting the amount of scatter. Turbidity is most commonly used in the measurement of suspended matter in water and is particularly useful for monitoring of especially potable water treatment, but also wastewater treatment processes as it encompasses a large number of different factors that can affect the treatment processes. Turbidity can easily be measured in NTU using a laboratory turbidity meter.

Suspended particles, also often referred to as colloidal particles, are negatively charged and therefore continually repel each other. This forces the particles to travel minute distances in constantly changing direction so that they don't settle out, but remain in suspension.

3.2 Coagulation

Coagulation is the process in which the negatively charged suspended particles that are present in water in a stable suspension are destabilised. This is done by the addition of a positively charged coagulant which then neutralises the negative charges present (i.e. destabilises them). Once the particles have been destabilised or neutralised, the process of flocculation occurs in which the destabilised particles combine into larger and larger particles until they are heavy enough to settle out by sedimentation, or large enough to entrap air bubbles and be floated using dissolved air flotation

The terms 'coagulant' and 'flocculant' are often used interchangeably, although coagulation and flocculation have been identified as two mechanisms in a two-step operation. Coagulation is the destabilisation (or charge-neutralisation) reaction, while flocculation is the bridging of the destabilised particles to form larger particles (Tambo, 1990). However, the term 'coagulant' is often used for any chemical that is used to bring about both these reactions and a wide range of such chemicals exists. They can be classified as inorganic (or mineral) compounds such as aluminium sulphate and ferric chloride, or as organic, such as polyelectrolytes.

Coagulation is a process that requires rapid dispersion of the coagulant and for this reason high mixing energy is generally provided at the point of coagulant addition. In contrast, flocculation requires a gentle mixing energy which will allow floc formation to occur without damaging or

breaking up the floc. For this reason flocculation generally occurs in baffled flocculation chambers or in the floc blanket of a clarifier or pulsating clarifier where sufficient energy is provided for inter-particle collisions to occur, but not to break up the floc.

As a general rule for coagulation, especially with polyelectrolytes, the more energy the better and this is provided on plants in a number of ways depending on the plant design and the design engineer's preference. This is referred to as the rapid mixing stage and is the stage where the colloid particles first come into contact with the coagulant chemical. It is obviously important that all the colloid particles come into contact with a coagulant molecule and that this occurs as quickly as possible, hence the need for high energy.

Inorganic or mineral coagulants, such as aluminium sulphate, have been used for water treatment for centuries, while in comparison polyelectrolytes are a relatively new innovation in water treatment. Polyelectrolytes are used in water treatment both for coagulation and as coagulant/flocculant aids to strengthen flocs and improve their settleability (Van Duuren, 1997).

The choice of coagulant is dependent on the treatment process and treatment objective. For example, in waters containing a high concentration of organic humic and fulvic acids (e.g. highly coloured waters described above) as well as clay particles, inorganic coagulants generally perform better (Van Duuren, 1997), while positively charged organic polyelectrolytes, which are of much higher molecular weights (around 10^5) than the inorganic coagulants, are effective on many types of raw water where they both destabilise and act as bridging agents at the same time. However, they are not effective for the coagulation of colour particles (Tambo, 1990). Weakly charged anionic or non-ionic polyelectrolytes of even higher molecular weights (10^6 to 10^7) are used as coagulant aids to strengthen and improve the settleability of flocs formed using inorganic coagulants (Tambo, 1990).

There is an enormous amount of literature dealing with the fundamental theory of coagulation, and a number of different coagulation reactions are described in the literature (Amirtharajah and Mills, 1982; Amirtharajah and O'Melia, 1990; Dempsey, 1984; Dempsey, 1989; Johnson and Amirtharajah, 1983). However, the two most important reactions are 'charge neutralisation' and 'sweep coagulation', which will be discussed in more detail.

3.2.1 Charge Neutralisation

As described above, particles suspended in water have tiny negative electrical charges on their surfaces and as a result they are constantly in motion as they drift towards each other and get forced away by repulsive forces. This process can in fact quite easily be seen with a low power microscope and is called Brownian Motion after the scientist who first discovered it. The discovery of the surface charge and the forces that they create was made by a scientist called Van der Waal and so these forces are called Van der Waal's forces.

Most material suspended in water consists of clay or silica particles from the soil and these particles are always negatively charged. Thus they can be said to be anionic because they will

be attracted to an anion or a positively charged particle or point. In simple terms that is what a coagulant is, a chemical with a positive charge, although the chemistry of coagulation is a specialised subject and the resultant chemicals are rather more complicated than the simple statement above implies.

Both inorganic and organic polyelectrolyte coagulants destabilise suspended particles through the process of charge neutralisation, but the organic polyelectrolytes are particularly effective in this process as they are very large molecules with many positively charged groups attached to them and so they will be used to describe the process of charge neutralisation.

The polyelectrolyte coagulants are in fact polymers, chemical compounds in which one or more smaller chemicals (called monomers) are polymerised to form very large, high molecular weight compounds in which the monomer or monomer units occur in a pattern that is repeated over and over again. These polyelectrolyte coagulants can be extremely large, with molecular weights in the order of tens of millions (compare that to water which you may recall has a molecular weight of 18). Not only is the polymer a very large molecule but it contains within each repeating unit a positively charged chemical group. Figure 3 shows a simplified diagram of such a polyelectrolyte coagulant.

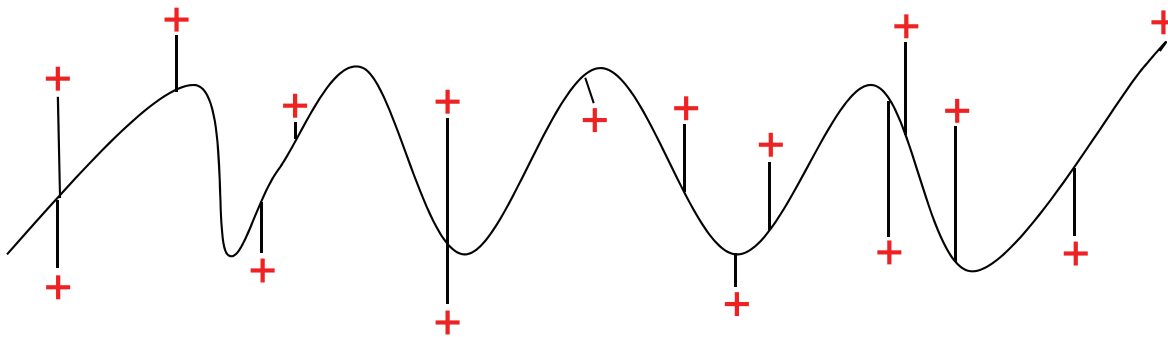


FIGURE 3: Schematic representation of a polyelectrolyte compound

However, just to provide some idea of the true complexity of these compounds, Figure 4 depicts the chemical reaction and resultant polyelectrolyte formed. Now each one of the positively charged sites on the molecule chain is capable, by electrostatic forces, of attracting and binding a negatively charged particle, creating a neutralised structure, such as that schematically represented in Figure 5.

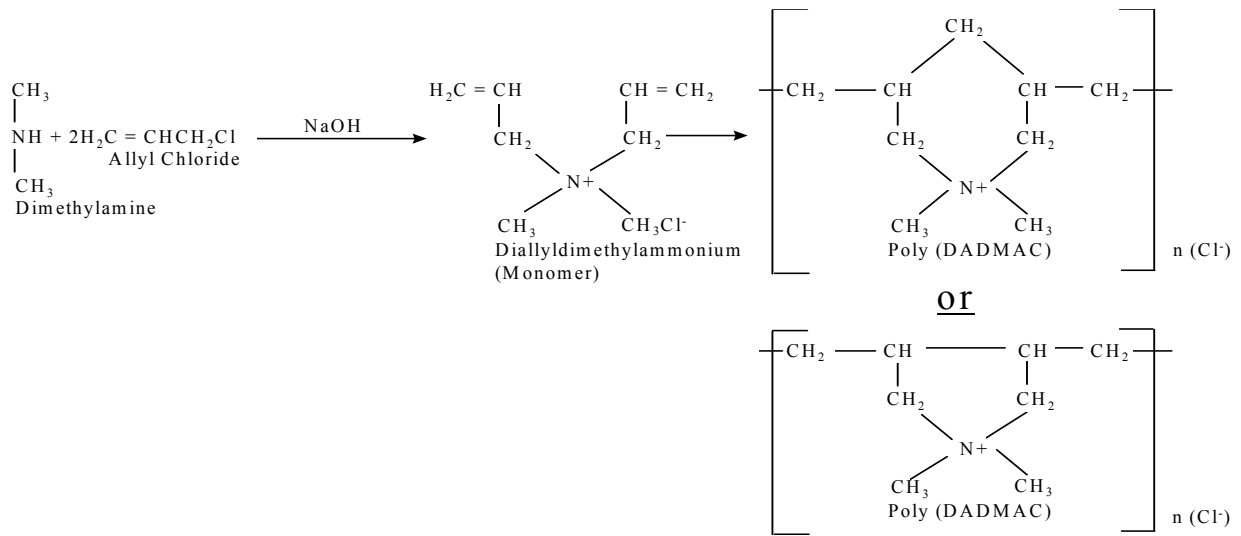


FIGURE 4: Polymerisation of dimethylamine to form polyDADMAC

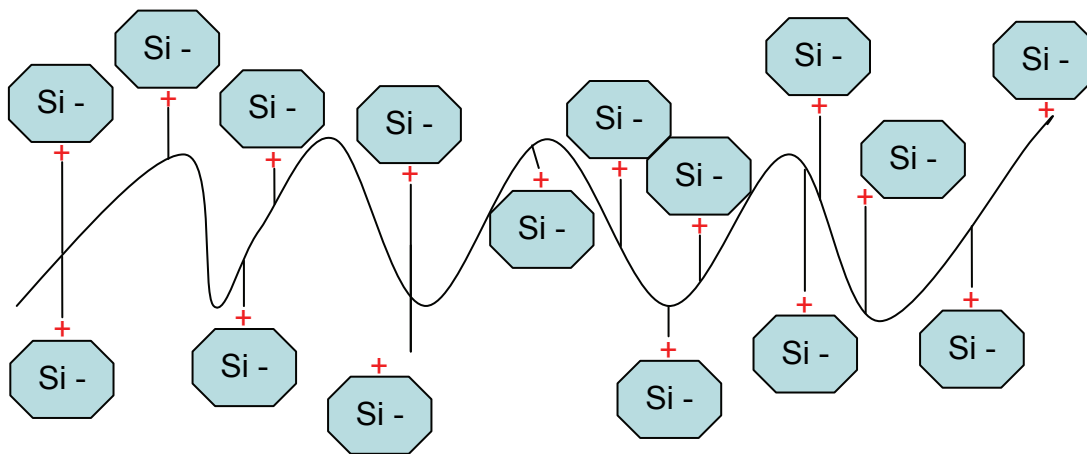


FIGURE 5: Schematic representation of a neutralised compound

It is important to remember that up to this point, the particles are generally not visible to the naked eye, but after charge neutralisation flocculation, or agglomeration of the particles can start to occur and within a few minutes the particles will have usually have grown to a size that can be clearly seen.

An important factor to remember regarding 'destabilisation' is that if too much coagulant is added, that is more than is required to neutralise the negatively charged suspended particles, then 'restabilisation' can occur. This is when all the particles become positively charged and therefore once again form a stable suspension. Once this happens, it is very difficult to rectify the situation.

3.2.2 'Sweep' Flocculation

Polyelectrolyte flocculants were only developed in the late 1960s and prior to that the industry relied almost exclusively on salts of aluminium and iron for the clarification process in water treatment. The most commonly used metal salts were aluminium sulphate, ferric (iron) sulphate and ferric chloride. Both aluminium and iron, when added to water, produce hydroxides which are insoluble and form what are called gelatinous precipitates. Other metals also do this, but in the case of iron and aluminium, their hydroxide precipitates are insoluble at the pH levels that normally occur in water treatment. The precipitate of iron hydroxide is insoluble over a wider range of pH than that of aluminium and this will be dealt with more thoroughly in Chapter 4.

The formation of hydroxides by iron and aluminium is a field of study in its own right, because the reactions are very complex. The result though is that when aluminium or iron salts are added to water in high enough concentrations to form insoluble metal hydroxides (e.g. $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$), large molecules are formed consisting of iron or aluminium molecules linked together by hydroxide (OH^-) ions. These large molecules tend to behave like a finely meshed net and are therefore able to enmesh suspended colloidal particles, which are then 'swept' out of suspension and settled along with the sinking iron or aluminium. This is known as 'sweep-floc' coagulation (Packham, 1965). The process is basically a combination of destabilisation (charge neutralisation) and transport (physical entrainment) (Amirtharajah, 1990).

Polymeric organic coagulants (polymers) do not form these large insoluble precipitates like the metal salts, when used in water treatment, and so 'sweep' or 'sweep-floc' coagulation is not possible using these chemicals. This is important in understanding when and how to use the various coagulants, and is the reason why polymeric organic coagulants are not used for the treatment of waters with high concentrations of colour and other organic contaminants.

The details of how these metal salts and polymeric organic coagulants behave will be discussed in more detail in the chapters devoted to each of them.

3.3 Flocculation

Flocculation forms the second stage of the coagulation and flocculation process and is referred to as the conditioning stage. It is this stage in which the particles which are already in contact with molecules of coagulant start to grow. Flocculation occurs after coagulation has destabilised the suspended colloidal particles in water. Microflocs then start to form and flocculation occurs through the collision of particles and microflocs to form macroflocs. This is an essential process in phase separation (separation of water and particles, since the formation of macroflocs leads to particles that become too heavy to remain in suspension and will settle out (Van Duuren, 1997).

It has been shown that the movement which allows particle collisions to occur is critical and that without it, particles will remain in suspension indefinitely, despite the addition of an effective coagulant (Stamberger, 1962). Therefore flocculation is an important part of water and

wastewater treatment and plants are generally designed with a view to achieving good flocculation. As mentioned above, flocculation can take place in:

1. Specially designed flocculation chambers with baffles.
2. Solids-contact flocculators such as a floc blanket clarifier or pulsating clarifier.
3. Mechanical flocculators, which include a wide variety of paddle systems, propellers and turbines.
4. Air diffusers and inducers can also be used to create agitation.

Phase separation, or the separation of the flocculated particles from the water, can be achieved in two ways:

- The particles can be settled out in some sort of clarifier (remember that many clarifiers found at water works are floc-bed clarifiers so are acting as both flocculating chambers and settling or sedimentation tanks), or
- the particles can be floated using dissolved air flotation.

In a dissolved air floatation tank compressed air is released at the bottom of the tank and results in a stream of tiny bubbles that entrain the flocculated particles and carry them to the surface of the tank where they are mechanically removed.

3.4 Coagulant Aids

The term 'coagulant aid' is often found in water and wastewater treatment handbooks. The use of coagulants to destabilise the colloidal material in water and form a settleable floc is not always successful and additional chemicals or compounds need to be added to assist the coagulation process. These may be added for a number of purposes which will become apparent when the chemicals listed below are discussed. Two of the most commonly used coagulant aids are bentonite and activated silica. These chemicals are described more fully in Chapter 10, which deals with miscellaneous water and wastewater treatment chemicals.

Sodium silicate is supplied as a viscous solution with a SG of between 1.35 and 1.4 at a concentration of 24 to 28%. Preparation of activated silica involves several stages, these being acidification of the concentrated sodium silicate solution, ageing for a definite time and dilution of the resulting solution. Suitable acids for acidification and neutralization of part of the alkalinity are sulphuric acid, hydrochloric acid, aluminium sulphate, sodium bicarbonate and carbonic acid (carbon dioxide). Suppliers of sodium silicate solution frequently state the conditions for acidification, ageing and dilution. For laboratory purposes, approximately 31 ml of 29% sodium silicate solution can be diluted to 1 l to yield a 1.25% SiO₂ solution. Eighty ml of this solution, when added to a 100 ml volumetric flask and acidified with HCl to lower the pH to 5 and diluted to 100 ml gives a 1.0% SiO₂ solution which should be aged or activated for 30 minutes before being used directly as a coagulant aid. The dosage of activated silica, when used under normal practice as a coagulant aid on a plant, is usually within the range of 0.5 to 4 mg/l as SiO₂.

3.5 Coagulant and Dose Selection

It should be obvious by now that to ensure a good quality water or effluent, it is essential that the correct coagulant and the correct coagulant dose be selected. It should also be obvious that there are so many factors influencing coagulation and flocculation that predicting the correct coagulant and dose will be very difficult, if not impossible. Therefore, the most effective way to do this is through a laboratory assessment using what is known as the jar test. The jar test is a batch process and not continuous as is generally the case at full-scale plant operation, but it is a very versatile test that can be used for the following tasks (Water Quality and Treatment, 1990):

1. Coagulant selection.
2. Dosage selection.
3. Coagulant aid type and dosage selection.
4. Determination of optimum pH (only a factor with inorganic coagulants, which are pH sensitive).
5. Determination of best settlement and/or filtration methods.

If possible, tests should be conducted on a number of samples and preferably under different conditions to establish the most reliable product. Having selected a suitable product, the use of routine jar tests remains necessary for a number of reasons:

- The nature and quality of the raw water may change, which may affect the coagulant dose.
- It is necessary to check that the plant dosage matches the demand established in the laboratory.
- Different batches of coagulant may vary and the use of comparative jar tests using some of the original product sample is a useful quality check. This is particularly the case with polyelectrolytes, but inorganic coagulants such as aluminium sulphate and ferric salt solutions sometimes also vary in strength and can also be assessed using a jar test.

For more information on jar test procedures, coagulant and coagulant dose selection and other relevant information refer to the Manual for Testing of Water and Wastewater Treatment Chemicals, WRC Report No. 1184/1/04, by Freese, Trollip and Nozaic (Freese *et al.*, 2004).

CHAPTER 4

IRON SALTS

Various iron salts are used in water treatment, although ferric chloride and ferric sulphate are the most commonly used. The following iron salts will be discussed in this chapter:

1. Ferric chloride
2. Ferric sulphate
3. Ferrous chloride
4. Ferrous sulphate
5. Ferric chlorosulphate

One of the reasons that ferric salts find wide application in water treatment, is that ferric hydroxide is insoluble over a wide pH range (Water Quality and Treatment, 1990).

4.1 Ferric Chloride

Ferric chloride, like many other iron salt compounds, was originally a waste product derived from spent pickling solution. In recent years the demand for ferric chloride has increased and the chemical is purpose made. It is often prepared from reacting scrap iron with hydrochloric acid and since it tends to absorb moisture from the air when in crystalline form, it is usually supplied as a solution.

Ferric chloride is highly acidic and the solution contains free hydrochloric acid. The solution is highly corrosive to nearly all normally used metals including all grades of stainless steel and needs to be stored, pumped and conveyed in synthetic corrosion-resistant materials. The chemical is normally supplied as a solution of about 40% strength as FeCl_3 with a SG of about 1.4 and a pH of less than 1.

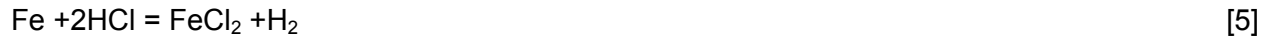
4.1.1 General description

Ferric chloride is sold commercially in solution form and the solution is a characteristic red-brown colour. The solution is acidic and corrosive to most metals. It is regarded as hazardous in terms of handling and transport.

4.1.2 Manufacture

Ferric chloride is manufactured by different processes depending on the locally available raw materials. In South Africa it is produced either in a two stage process starting with scrap iron or in a one stage process starting with ferrous chloride.

The one stage process is actually the same reaction as that of the second stage of the two stage process. The reactions below show both the first stage (Equation [5]) and second stage (Equation [6]) reactions:



The two stage process involves firstly dissolving scrap iron in hydrochloric acid. This process produces ferrous chloride, which has the chemical formula FeCl_2 and which is discussed more detail later.

At this point though, it is convenient to note that ferrous and ferric are two different molecular forms of iron. Ferrous is bivalent and reacts with two chloride atoms to form FeCl_2 and ferric is trivalent reacting with three chlorine atoms to form FeCl_3 . It so happens that when metallic iron such as scrap iron is dissolved in hydrochloric acid it always forms the ferrous chloride and not the ferric since under the very acidic conditions of the acid, only the soluble ferrous form of iron can form.

The ferrous chloride produced from the scrap iron in the first stage is often available as the by-product of the galvanising industry and in cases where ferrous chloride is thus in plentiful supply this can be used as a source. In these cases however the levels of contaminant zinc have to be monitored. The structure of ferrous chloride and ferric chloride are schematically depicted in Figure 6.

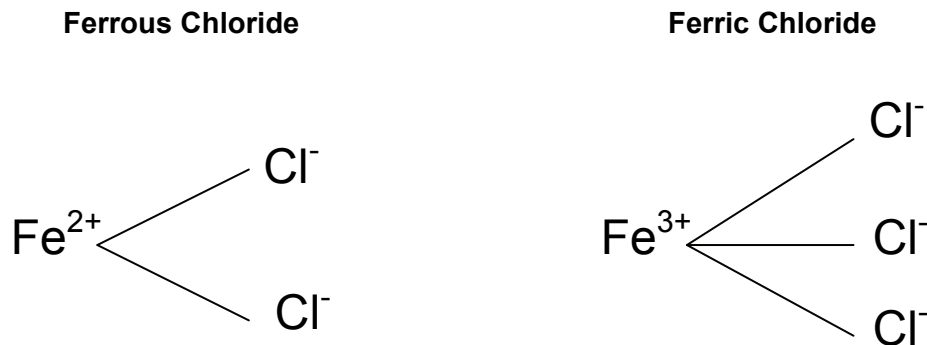


FIGURE 6: Schematic representations of ferrous chloride and ferric chloride

Once the ferrous chloride is produced in stage one of the reaction, it is necessary to oxidise ferrous chloride to ferric chloride (i.e. Fe II to Fe III) by adding chlorine to ferrous chloride.

Although not practised in South Africa it should be mentioned that it is also possible to produce ferric chloride by the reaction of hydrochloric acid with iron ore (Fe_3O_4).

All of the above involve the use of highly corrosive chemicals at high temperatures and the control of corrosion through the use of specialised materials of construction is a crucial aspect of ferric chloride production. This means that the design construction and maintenance of such plants is costly and requires specialist knowledge. There is in fact only one factory in South Africa that produces ferric chloride on a commercial scale for water treatment.

The main direct cost component of ferric chloride is the cost of iron and in particular of scrap iron. This cost is determined by the price obtainable in other markets such as the export market or the recycle market. Indirectly the cost is also affected by the electricity price since the chlorine used to form the chloride part of the molecule is affected primarily by the price of electricity used in its electrolytic generation.

4.1.3 The Characteristics of the Product

Ferric chloride is sold commercially, for use in water treatment, as a dark red-brown solution containing about 14% iron or 42% ferric chloride. A solution containing 14% as iron (Fe) has the same concentration as a solution containing 42% as ferric chloride (FeCl₃) and this is explained as follows:

The atomic weight of iron is 56 and that of chlorine is 35.5.

The molecular weight of ferric chloride (FeCl₃) therefore is $56 + 35.5 + 35.5 + 35.5 = 162.5$.

The percentage of iron in the molecule is $56 \div 162.5 = 34.5\%$

So if we manufacture the product such that it ends up as a 42% solution then the ferric iron content will be 34.5% of 42% which is 14.5%.

The decision to manufacture the product at 42% is based on factors such as the freezing point of the solution and the tendency in more concentrated solutions for ferric chloride to crystallise out of solution. This concentration has been found to be the most practical and is the accepted standard for commercially produced solutions for water treatment applications.

Ferric chloride solutions often contain impurities, the most common being carbon, manganese and other metals derived from the raw materials used in the manufacturing process. Of course the manufacturer takes steps to control the product's quality and these include limiting the amounts of impurities. Table 2 lists the typical chemical and physical properties of commercially available ferric chloride.

TABLE 2: Typical chemical and physical properties of commercially available ferric chloride

Solution strength	42.5-44% m/m
Ferric iron content	14.5-15.4% m/m
Ferrous iron content	Maximum 0.5% m/m
Specific Gravity (at 20°C)	1.3
Free acid	Maximum 1%

4.1.4 Transportation and Storage

As mentioned above ferric chloride solution is corrosive and in particular it should be noted that it is corrosive to stainless steel. As a result it is commonly transported in road tankers that have a special rubber lining and which are dedicated to the transportation of ferric chloride. It will be appreciated that once a rubber lined tank has been used for ferric chloride it is hard, if not impossible, to remove traces to the point where it may be used to transport another product.

Drivers and vehicles need to comply with Hazchem regulations and therefore transportation of ferric chloride is a specialised undertaking for which only a limited number of transport companies possess suitable tankers.

When considering storage, the high SG of the product must be taken into account. Specific gravity is a measure of the density of a chemical, with the standard of 1 being the SG of pure water at a temperature of 25°C. Any solution with a SG of less than 1 will be lighter than water, and if the SG is greater than 1, the solution will be heavier than water. The SG of a ferric chloride solution varies with the concentration of ferric chloride (see Table 3), but is around 1.45 at a concentration of around 42% FeCl₃. This means that 1 000 ℓ of ferric chloride solution will in fact weigh 1.45 tons. It is important therefore to take this into account when constructing ferric chloride storage tanks and their foundations. High density polyethylene (HDPE) is frequently used for storage and is quite suitable as are rubber-lined or fibreglass tanks.

4.1.5 Application of Ferric Chloride in Potable Water Treatment

Ferric chloride is used in both drinking water and waste water treatment although the application technology is completely different in each. In drinking water, ferric chloride can be used as a coagulant both for turbidity removal and for the removal of colour or other organic contaminants. When carrying out turbidity removal only, ferric chloride is usually used at pH values of around neutral pH where sweep coagulation tends to be the predominant reaction (Amirtharajah and O'Melia, 1990).

One of the main advantages of ferric chloride as a drinking water coagulant is the fact that it is a relatively inexpensive chemical, although this advantage is offset to some extent by the following:

- Ferric chloride consumes alkalinity and therefore lime addition is often required in order to ensure that the treated water remains stable (See Chapter 2, Section 2.4 on Water Stabilisation).
- Handling problems, since ferric chloride is highly acidic and corrosive and tends to stain all surfaces with which it comes into contact.

When using ferric chloride for the removal of colour and other organic contaminants, the coagulation reaction is most efficient at a pH of around 5 (Amirtharajah and O'Melia, 1990). In fact optimal colour and organics removal is achieved using elevated dosages of ferric chloride to achieve a pH of around 5 simply through the effect of the ferric chloride itself (i.e. the reduction

in alkalinity caused by ferric chloride will cause the pH to drop), or ferric chloride can be used together with an acid such as hydrochloric acid, to reduce the pH (Freese and Pryor, 1998). In fact in such applications the dose selection is based on the amount of ferric chloride required to reduce the pH to around 5. Ferric chloride is generally a very cost effective option for colour and organics removal, especially at smaller plants. Using elevated inorganic coagulants in this way to remove organic contaminants is commonly referred to as 'enhanced coagulation'.

In South Africa many of the Cape waters are high in colour due to the presence of humic and fulvic acids, which arise from decaying vegetation and enhanced coagulation using ferric chloride (or other iron or aluminium salts) is an effective way of removing the colour from these waters, which are traditionally difficult to treat. However, fairly accurate control of pH is critical, since if the pH is allowed to drop too low, the insoluble ferric iron (Fe^{3+}) will convert to the soluble ferrous iron (Fe^{2+}) form, resulting in brown water.

TABLE 3: Specific Gravity of commercial ferric chloride solution (Freese *et al.*, 2004)

Specific Gravity	Ferric chloride (%)
1.0025	0.5
1.0068	1.0
1.0153	2.0
1.0238	3.0
1.0323	4.0
1.0408	5.0
1.0493	6.0
1.0580	7.0
1.0668	8.0
1.0760	9.0
1.0853	10.0
1.1040	12.0
1.1228	14.0
1.1420	16.0
1.1615	18.0
1.1816	20.0
1.2234	24.0
1.2679	28.0
1.3153	32.0
1.3654	36.0
1.4176	40.0
1.4400	42.0

4.1.6 Application of Ferric Chloride in Wastewater Treatment

The primary reason for removing phosphate from wastewater is because phosphate is a nutrient and if released into surface waters, it can result in nutrient enrichment of the water body (especially when released into a river flowing into a dam (reservoir)). This in turn can lead to excessive growth of algae and aquatic plants, eventually causing oxygen depletion in the water, fish kills and poor water quality. This condition is known as 'eutrophication'. Excessive growth of algae is of course a major aesthetic and environmental problem in many of the dams in South Africa and in some sensitive catchment areas specific regulations exist regarding the discharge of phosphates with the intention of controlling algae growth. Of course if we could eliminate phosphates from our water courses it would be effective in controlling the growth of algae. Unfortunately however, phosphorus has a wide range of unique uses such as in laundry detergents and fertilisers. There have been regulations in some countries to limit or prevent the use of phosphates in laundry detergents but unfortunately the alternative products are expensive and not as effective. Furthermore, phosphates are essential to fertilisers and therefore agricultural run-off would still account for phosphate loadings. Natural sources of phosphate also occur in domestic wastewaters, so limiting phosphates in detergents and fertilisers would not necessarily solve the problem.

Fortunately for water treatment chemists, the phosphate salts of ferric (Fe^{3+}) iron are quite insoluble and this is the key to the most common chemical means of phosphate removal. The reaction is one of precipitation of insoluble ferric phosphate according to the reaction (Metcalf and Eddy, 1999):



We can ignore the parts of the reaction we are not interested in and note that 56 g (or kg or tons) of iron will react exactly with $(31 + 16 + 16 + 16 + 16) = 75$ g (or kg or tons) of phosphate. So 56 g of iron will, in theory remove 75 g of phosphate. It can now be seen that if you know how many g (or kg) of phosphate are flowing into a plant over a period of time, the quantity of iron required to remove the phosphate can be calculated, and therefore the quantity of ferric chloride required can be determined.

However it is not as simple as that. Although in theory the above is correct, these reactions do not account for all the competing reactions that also occur as well as the effects of alkalinity, pH, trace elements, etc. that are found in wastewater. The result is that in practice the theoretical calculated amount provides nothing more than a rough estimation, but hopefully this provides some understanding of how chemical reactions occur and how calculations can be used to at least provide an approximation of dosage rates, etc.

Theory would suggest that we need $75 \div 56 = 1.34$ times as much iron as there is phosphate. This is the stoichiometric amount. In practice though, because of the competing reactions, it is usually found that 1.5-2.5 times the stoichiometric amount of Fe:P is required.

There are many different designs of wastewater plant and as a result the best place to add the ferric chloride also varies. In some plants it is added near the beginning of the works, right before the primary settling tanks, while in others, it is added to the activated sludge plant. A third option is add it near the end of the process into the secondary setting tanks.

Finally, before leaving the subject of ferric chloride we should mention its use as part of a process called 'Chemically Enhanced Primary Treatment' or 'CEPT'. As its name implies this process involves adding ferric chloride (or other metal salts) to the first, or primary settling tanks in a wastewater works. Primary settling tanks rely on gravity and natural flocculation to remove some of the suspended solids from the raw sewage before the settled sewage overflows into the secondary stage. By adding an iron salt to the primary settling tanks, the flocculation process becomes much more efficient and a significant proportion of the phosphate can be removed in the sludge. This reduces the solids that normally flow into the second stage allowing the plant to cope with a higher flow rate. Of course the result is that the amount of solids produced in the primary stage is much greater and this is only acceptable on plants that have enough solids handling capacity, (e.g. digester capacity) to cope with this extra load. Under these circumstances however, CEPT can provide a cost effective means of increasing the effective capacity of a treatment works without having to spend capital expenditure on plant extensions.

4.2 Ferric Sulphate

Ferric sulphate is also extensively used for water treatment, particularly in the Cape area of South Africa. It has been used in wastewater treatment in this country where it has been prepared from waste chemicals. It is also corrosive and has a low pH although it is more comparable in this regard to aluminium sulphate solutions. Although it can be obtained in solid form (e.g. crystals, as a source of iron in animal feeds) it is usually supplied as a solution. The strength of solution supplied is not fixed by convention as much as for the other chemicals.

4.2.1 General description

Ferric sulphate is sold commercially for water treatment in solution form. It is also sold as crystals for example, as a source of iron in animal feeds. The cost is generally based on its iron content as Fe. Depending on solution strength the iron content may range from about 8% up to 14%.

The solution is very similar in appearance to ferric chloride, having a characteristic red-brown colour and like ferric chloride the solution is acidic and corrosive, but not specifically corrosive to stainless steel as it does not contain chloride. It is regarded as hazardous in terms of handling and transport.

4.2.2 Manufacture

There are two processes that are used commercially in South Africa for the manufacture of ferric sulphate. The first of these involves the reaction of iron oxide with concentrated sulphuric

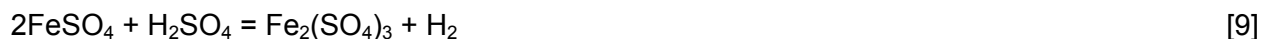
acid. There are many forms of iron oxide but the one required for this reaction is haematite, the type of oxide that we know as rust and this reaction is depicted in Equation [8]. There are large volumes of haematite available wherever there are steel works involved in cleaning oxide from iron.



The process requires heat, which can be generated by the exothermic (heat releasing) reaction of sulphuric acid with water that is first used to make a slurry of the iron oxide. Thereafter, the reaction is self sustaining. This is a problematic reaction process due to the corrosive nature of the acid and the high temperatures involved. In most cases the reaction is pressurised as well. It is also important to ensure that the iron oxide source does not contain any impurities such as other metals that may be harmful in drinking water.

The second process involves the oxidation of ferrous sulphate with the addition of sulphuric acid. Nitric acid is often used as the oxidising agent, although processes exist that use liquid oxygen or aeration. A widely used source of ferrous sulphate internationally is the titanium dioxide industry. The production of titanium dioxide can occur using either sulphate or chloride and when using sulphate, large quantities of ferrous sulphate are produced as a by-product. Other sources include the steel pickling industry and the galvanising industry, but these sources may contain impurities, notably zinc, and obviously levels of such impurities have to be measured and controlled.

The reaction that occurs in production is a simple oxidation:



Nitric acid acts as a catalyst and does not take part in the reaction.

Finally it is also possible to source ferric sulphate as a dry crystalline material and dissolve it in water.

All the sources of iron used in the production of ferric sulphate are by-products of other processes and as a result are generally relatively cheap. (Although alternate uses in cement production have increased demand in recent years). Sulphuric acid is therefore the main determinant of the cost and worldwide shortages have caused significant cost increases.

4.2.3 The Characteristics of the Product

Ferric sulphate is sold commercially, for use in water treatment, as a dark red-brown solution, generally containing about 10% iron, or 37% ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$). These two figures are connected as follows.

The atomic weight of iron is 56 and that of sulphate, 96 (32 + 16 + 16 + 16 + 16).

The molecular weight of ferric sulphate is therefore $(2 \times 56) + (3 \times 96) = 400$.

The percentage of iron in the molecule is $(2 \times 56) \div 400 = 28\%$.

So if the product is manufactured so that it ends up as a 37% solution then the ferric iron content will be 28% of 37% which is 10.3%.

The solution contains 10% iron and therefore the percentage $\text{Fe}_2(\text{SO}_4)_3$ in this solution is:

$$10\% \times 400 \div 112 = 35.7\%$$

As with ferric chloride the strength at which the solution is sold is not determined so much by chemistry as by practical considerations like freezing point, stability, production economics, etc.

Ferric sulphate solution is very acidic, having a pH of less than two, and as a result is corrosive, although not as corrosive as ferric chloride. Like ferric chloride we have to be aware of the levels of impurities because this product is also generally made from by-products and waste products. As mentioned the main potential impurity in this case will be the possibility of finding zinc in the product. Of course manufacturers take steps to control the product's quality and these include limiting the amounts of impurities. Typical properties of ferric sulphate are listed in Table 4.

TABLE 4: Typical chemical and physical properties of commercially available ferric sulphate

Solution strength	36-42% m/m
Ferric iron content	10-12% m/m
Ferrous iron content	Maximum 0.2% m/m
Specific Gravity (20°C)	1.46
Free acid	Maximum 1%

4.2.4 Transportation and storage

Ferric sulphate solution is corrosive, but unlike ferric chloride it is not corrosive to stainless steel and can therefore be transported and stored in stainless steel tanks. Other suitable materials are HDPE, rubber lining and suitable grades of fibre glass. The product has a high SG and this needs to be remembered when specifying tanks. Drivers and vehicles need to comply with Hazchem regulations.

4.2.5 Applications of Ferric Sulphate in Water Treatment

The applications of ferric sulphate in potable and waste water treatment are the same as those of ferric chloride. However, it is a particular characteristic of the South African situation that the majority of ferric sulphate is produced in the Cape, while most ferric chloride is produced in Gauteng.

Transport costs are obviously an important consideration, and since both the iron content and the performance of each product is similar it is the geographic location, and therefore the transport costs, that determine which the most suitable product to use is. As a result, ferric sulphate is extensively used in the Cape region and ferric chloride in Gauteng.

4.3 Ferrous Salts

Ferrous sulphate and ferrous chloride are seldom used in water treatment as they need to be used in conjunction with lime or chlorine to precipitate the iron hydroxide in ferric form. There is however no theoretical reason why it should not be used provided the chemical is cost competitive on the basis of iron content and it does not contain other heavy metals in appreciable quantities.

4.3.1 General Description

Whilst ferric salt solutions are characterised by their typical red-brown colour, these ferrous salts are both green in solution. As mentioned above, ferrous salts are generally available as by-products of the steel pickling, galvanising and titanium dioxide processes. Ferrous chloride is also produced by dissolving scrap iron in hydrochloric acid, either with the objective of producing ferrous chloride, or as part of the process of producing ferric chloride.

The chemical formula for ferrous chloride is FeCl_2 and so the molecular weight is:

$$56 + 35.5 + 35.5 = 127$$

Therefore the percentage ferrous iron in ferrous chloride is:

$$56 \div 127 = 44\%$$

Commercially available ferrous chloride and ferrous sulphate are available in a wide range of concentrations, depending mainly on the source, but Table 5 shows typical specifications for commercially available ferrous chloride and ferrous sulphate.

4.3.2 Transportation and Storage

Ferrous chloride is an acidic solution and being chloride based it is important to remember that it will corrode stainless steel so rubber lined road tankers are generally used and storage is in rubber lined, HDPE or fibre glass tanks. Transport requirements of ferrous sulphate are similar to those for ferrous chloride, although ferrous sulphate is not corrosive to stainless steel.

TABLE 5: Typical chemical and physical properties of commercially available ferrous chloride and ferrous sulphate

	Ferrous chloride	Ferrous sulphate
Solution strength	18-28%	28-30%
Ferrous iron content	8-13% m/m	5-7% m/m
Specific Gravity (20°C)	1.25	1.15
Free acid	Maximum 3%	Maximum 0.25%
pH	<2	1.5-3

4.3.3 Applications of Ferrous Salts in Water Treatment

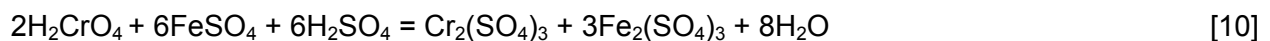
The use of ferrous salts in potable water can create problems if not carefully controlled, since ferrous iron can be oxidised to ferric iron. This oxidation is accelerated by aeration, high pH or the presence of chlorine or other oxidising agents and provided oxidation occurs before the filters, the ferric iron will be filtered out of the water. However, if oxidation only occurs after the water has passed through the filters, then there is the danger that the iron will precipitate out of solution in the reservoir or distribution systems, resulting in red-brown coloured water. It is for this reason that the level of ferrous impurity in commercially available ferric salts is so important.

One process in which ferrous sulphate has long been used in water treatment involves adding ferrous sulphate at the beginning of the treatment process and immediately thereafter, liquid chlorine is introduced, which oxidises the ferrous iron to ferric iron. This effectively provides an *in situ* source of ferric iron, which as described above, is an excellent coagulant. This is called the Copperas process.

4.3.4 Ferrous Salts in Wastewater Treatment

Ferrous salts can be used as an alternative to ferric salts for phosphate removal. Based on the chemistry and the fact that ferrous salts are soluble in water, ferrous iron would not be expected to precipitate phosphate. However, ferrous salts have been found to be quite efficient in the removal of phosphate, although they are usually used in conjunction with lime and not on their own for this application (Metcalf and Eddy, 1999). The process involves two reactions, namely the oxidation of ferrous iron to ferric iron and the precipitation of ferric phosphate. Interestingly, the ferrous iron itself does not act as a coagulant and so the competing reactions that detract from the efficiency of ferric salts do not seem to play a role in the use of ferrous salts for phosphate removal.

Ferrous salts can also be used to reduce toxic chrome 6 (Cr^{6+}) to the non toxic chrome 3 (Cr^{3+}) (Metcalf and Eddy, 1999). Chrome can exist in two valency states, the highly toxic hexavalent state and the non-toxic trivalent state. The reaction is shown in Equation [10]:



The trivalent chrome, now as chrome sulphate, can be precipitated as chromium hydroxide with the addition of lime.

This reaction works equally efficiently with ferrous chloride. This application is found in chrome mine effluent streams, tannery effluents and cement production.

CHAPTER 5

ALUMINIUM SALTS

5.1 Aluminium Sulphate

Aluminium sulphate has been used for several centuries in water treatment and is probably the most well known and commonly used coagulant. The chemical is prepared by reacting bauxite, aluminium trihydrate or certain clays with sulphuric acid.

Aluminium sulphate is often known as alum. The name 'alum' is not an accurate description because chemically alum is actually a much more complex salt of aluminium, hydrated aluminium potassium sulphate ($KAl(SO_4)_2 \cdot 12H_2O$). Although the term 'alum' is used for aluminium sulphate, aluminium sulphate is not one of the alums. Alums are compounds with the general formula $AB(SO_4)_2 \cdot 12H_2O$ and some of them do not contain any aluminium at all (e.g. chrome alum, $K_2Cr(SO_4)_2 \cdot 12H_2O$). Other forms of alum also exist and are manufactured as complex salts with ammonia or iron, for example. The properties of aluminium sulphate are different from those of the true alums and therefore the more accurate term 'aluminium sulphate' is used in this guide to identify the compound without confusion.

Aluminium sulphate is acidic in nature. Its storage and handling requires corrosion-proof tanks, pumps and pipework. Aluminium sulphate when delivered in solution form is usually about 46-48% strength as $Al_2(SO_4)_3 \cdot 18H_2O$ (including by convention the waters of hydration) (Degremont, 1991) and has a SG of about 1.33 at normal temperatures. Stronger solutions tend to crystallise at low temperatures. The measurement of the SG of an aluminium sulphate solution is a rapid check on its strength and is often used to check consignments before conducting a full analysis.

Aluminium sulphate, when prepared from virgin chemicals, does not normally contain any impurities of concern. Pure aluminium sulphate is white and gives a water-white solution. However the presence of iron as an impurity is common which gives the chemical or the solution a yellow or even an orange colour. Iron is not a problem as an impurity as it is a coagulant in its own right and tends to assist the coagulation process. Aluminium sulphate is sometimes prepared from low-grade clays and from waste acid. This in some cases leads to the presence of undesirable concentrations of heavy (toxic) metals in the solution. Although the aluminium sulphate is usually much cheaper in such cases care should be taken when approving its use and it is probably better to confine the use of low grade aluminium sulphate to wastewater treatment.

5.1.1 General description

Aluminium sulphate is available commercially as a solution or as a solid material. Aluminium sulphate in solid form is referred to as kibble, which is available either in granular or powder form. Aluminium sulphate is also available in a variety of levels of purity, depending primarily on the raw materials used for manufacture. The paper industry is a major user of aluminium sulphate and demands an iron free grade which is not an essential in normal water treatment

applications (Austin, 1984), where the iron component can actually aid coagulation. In solution aluminium sulphate is acidic.

5.1.2 Manufacture

There are two main commercial processes in use for the manufacture of aluminium sulphate. The first and most commonly used process worldwide involves the reaction of aluminium trihydrate and sulphuric acid in a heated, pressurised reactor (Austin, 1984):



Some salts, aluminium sulphate being one, incorporate various amounts of water into the crystalline structure as they crystallise and these are known as 'waters of crystallisation'. Solid forms of aluminium sulphate always include some molecules of water as it is not possible to obtain commercial grades of anhydrous aluminium sulphate due to the fact that these would not be economically viable to produce.

The purity of the resulting aluminium sulphate depends on the purity of the aluminium trihydrate used. Aluminium trihydrate is itself produced by refining the mineral bauxite. Bauxite is a mineral consisting of aluminium trihydrate with various other aluminium hydroxides together with, most importantly, haematite or iron oxide. The haematite gives bauxite a reddish colouration whereas refined aluminium trihydrate is white. Aluminium sulphate is produced for commercial purposes using bauxite and sulphuric acid, but unless the process is designed to remove the iron, the resultant aluminium sulphate will not be acceptable to the paper industry, although still quite acceptable to the water industry where the iron impurity may actually add benefit in the coagulation and flocculation processes.

The second most commonly used process, particularly in South Africa, involves the production of aluminium sulphate by leaching aluminium out of mineral compounds that contain sufficiently high aluminium content. By boiling the clay with concentrated sulphuric acid, it is possible to produce an aluminium sulphate solution of commercially viable concentration. These clays generally contain iron as well, so it is not possible to produce a 'paper grade' product by this process, but very large volumes of product which are quite suitable for water treatment are made using this process.

The process involves making a slurry of the clay with water to which sulphuric acid is then added. The reaction of the acid with the slurry water is vigorously exothermic and generates enough heat to start the leaching of the clay, which then continues at elevated temperature and pressure. Once the final product has been formed, the high temperatures still present in the reactor enable the product to be crystallised. The crystallised product is then ground into a variety of specified mesh sizes.

Unfortunately there is no source of aluminium trihydrate in South Africa and this means that all iron free grades have to be produced from imported raw materials. As a result the raw material is purchased in foreign currency and is subject to exchange rate fluctuations. This situation has been made worse in recent times by escalating costs and shortages of sulphuric acid.

The iron containing grades are manufactured in South Africa from locally mined clays and so the import portion is not applicable to this process but the rising cost of sulphuric acid obviously affects this process in the same way as the first process described.

5.1.3 The Characteristics of the Product

Aluminium sulphate is sold commercially, for use in water treatment, as

- An iron free grade, 50% solution in water.
- An iron containing 50% solution in water.
- A solid material of various particle sizes that contains iron as an impurity in various quantities.

As explained above, there is no production of an iron free solid material in South Africa.

Aluminium, like iron, is a trivalent metal element and sulphate is a divalent molecule, and so in order for the valencies to balance the aluminium sulphate molecule has a structure as in Figure 7 below:

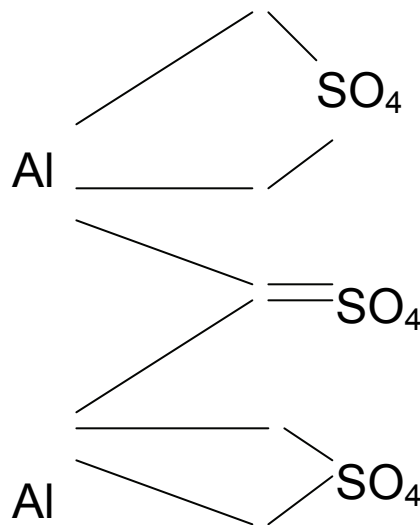


FIGURE 7: Schematic representation of aluminium sulphate

The atomic weight of aluminium is 27 and as previously shown, the sulphate molecule has a molecular weight of 96, giving a total of $2 \times 27 + 3 \times 96 = 342$.

The waters of crystallisation also have to be accounted for and this adds a further 324 to the weight giving a total of 666.

The percentage of aluminium in the molecule is not calculated as $54 \div 342$, but as:

$$54 \div 666 = 8.1\%$$

The aluminium content of aluminium salts is often referred to in terms of aluminium oxide (Al_2O_3) that is present.

The molecular weight of aluminium oxide is $54 + 48 = 102$.

The percentage aluminium in the oxide is therefore $54 \div 102 = 52.9\%$.

So as the aluminium sulphate contains is 8.1% aluminium, the Al_2O_3 content must be:

$$8.1 \div 0.529 = 15.3\%$$

Alternatively, a commercially available aluminium sulphate solution with an Al_2O_3 content of 15.3% would have an Al content that is 52.9% of this, i.e. $52.9 \div 100 \times 15.3 = 8.1\%$ Al.

So far only the strength of the solid forms of aluminium sulphate have been considered, but aluminium oxide is widely supplied and used as a solution of just under 50% as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. Since Al constitutes 8.1% of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, a solution of approximately 50% would contain approximately 4% Al and approximately 7.6% Al_2O_3 .

TABLE 6: Typical chemical and physical properties of commercially available aluminium sulphate

Appearance	Clear to slightly hazy liquid
Al_2O_3	17-18% m/m
Iron	0.03% m/m
Specific Gravity (20°C)	2.7
pH	2.7-3.7

This is typically an aluminium sulphate that would be used in water treatment whereas aluminium sulphate supplied to the paper making trade would have a much lower iron content (typically less than 50 mg/l of iron).

The typical chemical results for solid aluminium sulphate would be close to double the above figures for aluminium sulphate, Al_2O_3 and iron content and the typical particle sizes of the product would be specified.

The SG of a solution can be used to determine its concentration and Table 7 lists the SG values for aluminium sulphate solutions of different concentrations. For more information on how to assess aluminium sulphate and to determine its suitability for a treatment application as well as estimate the dose, refer to the Manual for Testing of Water and Wastewater Treatment Chemicals, WRC Report No. 1184/1/04 (Freese *et al.*, 2004).

TABLE 7: Specific Gravity of commercial aluminium sulphate solutions at 15°C

Specific Gravity	Aluminium sulphate % m/m		Specific Gravity	Aluminium sulphate % m/m	
	Al ₂ (SO ₄) ₃ .18H ₂ O	Al ₂ O ₃		Al ₂ (SO ₄) ₃ .18H ₂ O	Al ₂ O ₃
1.01	1.88	0.29	1.19	30.2	4.63
1.02	3.68	0.56	1.20	31.6	4.84
1.03	5.44	0.83	1.21	32.9	5.04
1.04	7.18	1.10	1.22	34.2	5.24
1.05	8.94	1.37	1.23	35.6	5.45
1.06	10.6	1.62	1.24	37.0	5.67
1.07	12.3	1.88	1.25	38.4	5.88
1.08	13.9	2.13	1.26	39.7	6.08
1.09	15.4	2.36	1.27	41.0	6.28
1.10	17.0	2.60	1.28	42.3	6.48
1.11	18.5	2.83	1.29	43.7	6.69
1.12	20.1	3.08	1.30	45.0	6.89
1.13	21.5	3.29	1.31	46.2	7.08
1.14	23.0	3.52	1.32	47.5	7.28
1.15	24.4	3.74	1.33	48.8	7.48
1.16	25.9	3.97	1.34	50.1	7.68
1.17	27.4	4.20	1.35	51.3	7.86
1.18	28.8	4.41			

5.1.4 Transportation and Storage

Aluminium sulphate is considerably more 'user friendly' in terms of transport and storage than the ferric salts. Firstly, unlike ferric chloride it is not corrosive to stainless steel and so can safely be transported and stored in stainless steel tanks. Secondly because it is colourless and easily rinsed, it does not cause staining of equipment, so dedicated tankers, pumps and hoses are not required. Tanks made from HDPE or fibreglass are acceptable and widely used.

5.1.5 Application of Aluminium sulphate in Water Treatment

Aluminium sulphate is perhaps the most well known of all water treatment chemicals and it was one of the first chemicals to be used for coagulating and flocculating water. Aluminium sulphate is widely used in the treatment of potable water and behaves in a similar way to ferric salts in that the primary behaviour is sweep flocculation following the formation of hydroxides such as Al(OH)₃.

As previously mentioned, aluminium hydroxides have a limited span of pH over which they are insoluble and it is therefore important that the operating pH be carefully controlled to maintain it in the range of 5.8-8.5. Because aluminium hydroxide redissolves at high pH (i.e. pH values over 8.5), it is important that there is sufficient alkalinity in the water during flocculation to ensure complete formation and settling of the insoluble hydroxide. It is not uncommon for hydroxide to be carried over to the point of lime addition resulting in redissolution of the aluminium hydroxide. The dissolved (or residual) aluminium sulphate then passes through the filters and later re-

precipitates in the reservoir or distribution system. A deep layer of aluminium hydroxide precipitate is often found at the bottom of reservoirs where aluminium sulphate is used for treatment of the water. It is therefore important to ensure good pH control throughout the process when using aluminium sulphate.

The other situation in which aluminium sulphate is often the product of choice is for the removal of colour. This is generally applied in drinking water applications although aluminium sulphate does find use in the treatment of coloured effluents such as those emanating from the textile industry. In both cases, the efficiency relies on reducing the pH to a value that allows for optimal colour removal. As was the case when using enhanced coagulation with ferric salts, the pH reduction can be achieved using aluminium sulphate alone, or aluminium sulphate in conjunction with an acid. In any case, the optimum pH for colour removal when using aluminium sulphate has been found to be between 5 and 5.5 (Freese and Pryor, 1998), which is in agreement with the findings of Randtke (1988). However, it was found that if the pH dropped below 4, solubilisation of aluminium occurred and removal of iron and manganese was impaired (Freese and Pryor, 1998).

5.1.6 Application of Aluminium Salts in Wastewater Treatment

Aluminium salts precipitate phosphate in a similar way to the ferric iron salts. Aluminium, like ferric iron, is trivalent and so forms $AlPO_4$ in the same way as ferric ion forms $FePO_4$. The atomic weight of iron is 56 and that of aluminium 27, so 27 grams of aluminium will theoretically remove the same amount of phosphate as 56 grams of ferric iron. It has already been shown that liquid aluminium sulphate when containing approximately 50% as $Al_2(SO_4)_3 \cdot 18H_2O$ only contains around 4% of aluminium (i.e. 40 kg Al per ton) whereas ferric chloride solution contains about 14% iron or 140kg Fe per ton. It would appear therefore that ferric solution is thus more than three times as effective as the aluminium sulphate solution. However, if we consider the reaction of aluminium and iron with phosphate, it is seen that 40 kg Al would react with approximately 141 kg PO_4 , while 140 kg iron would react with approximately 238 kg PO_4 . In other words, iron is more effective than aluminium by a factor of only around 1.7 and not three. If granular aluminium sulphate is used instead of aluminium sulphate solution, then the aluminium content is nearly double (i.e. around 8%) and would then provide a greater phosphate removal effect than ferric chloride solution. This means that transporting granular aluminium sulphate over long distances can provide a very cost effective means of phosphate removal.

5.1.7 Effect on Micro-organisms

Some work has been done that suggests that aluminium is an effective chemical for the control of sludge bulking in a sewage works. Sludge bulking and foaming is caused by the proliferation of filamentous bacteria in the activated sludge section and this can lead to severe operational problems (Metcalf and Eddy, 1999). Research indicates that aluminium interferes with the enzymes responsible for the growth of the filamentous bacteria. There is much research published on this topic but for the purposes of this book it is sufficient to know that aluminium does probably offer a means of control.

5.2 ALUMINIUM CHLORIDE

5.2.1 General Description

Aluminium Chloride exists as a solid and as a solution but only the solution is produced and marketed for water treatment in South Africa. In fact it is similar in many aspects to aluminium sulphate, although it is much less widely used than any ferric salt or aluminium sulphate.

5.2.2 Manufacture

Aluminium Chloride can easily be produced by either passing chlorine gas over molten aluminium (Equation [12]) (Austin, 1984) or by dissolving aluminium or aluminium oxide in hydrochloric acid (Equations [13] and [14] respectively):



Note that the use of the first reaction (Equation [12]) results in the evolution of large quantities of hydrogen and so production processes have to be strictly engineered to cope with this potential hazard. The process can however be conducted at atmospheric pressure whereas the use of aluminium trihydrate requires a pressurised reactor and an external source of heat. Equation [14] is used in the production of hydrated forms of aluminium chloride.

The main cost in the production of aluminium chloride is the metal itself whether in the metal form or the trihydrate form. Hydrochloric acid is relatively cheap and is locally produced so it is not a major contributor to the overall cost.

5.2.3 Characteristics of Aluminium Chloride

Aluminium chloride is produced as a solution and it has a strong acidic fuming smell and a yellowish colour.

It has the following structure:

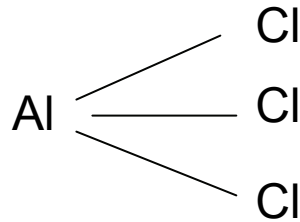


FIGURE 8: Schematic representation of aluminium chloride

The molecular weight is $27 + (3 \times 35.5) = 133.5$.

Therefore the percentage aluminium is $27 \div 133.5 = 20.2\%$ in the 100% active solid material.

However, for water treatment applications it is produced as solution and the commercially available solutions have an aluminium content of about 6% as $AlCl_3$.

TABLE 8: Typical Chemical and Physical Properties of Commercially Available Aluminium Chloride

Appearance	Clear yellowish liquid
Specific Gravity (20°C)	1.15
Aluminium chloride	27-30% m/m
Aluminium	5.8-6.5% m/m
Hydrochloric acid	1.0% m/m maximum

5.2.4 Transport and Storage

Like all chloride based products, aluminium chloride is corrosive to stainless steel and requires plastic, rubber lined or suitable fibreglass tanks for transportation and storage.

5.2.5 Application of Aluminium Chloride in Water Treatment

Very little aluminium chloride is sold for use in potable water, mainly because it has little to recommend it compared to the aluminium sulphate and other aluminium salts in the following sections. It is very acidic and corrosive, is relatively low in activity and has a significant effect on pH. It therefore only finds limited application in water treatment and primarily in circumstances where pH reduction is required in order to optimise colour removal.

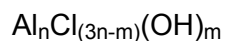
5.2.6 Application of Aluminium Chloride in Waste Water Treatment

As with potable water there is very little aluminium chloride sold for waste water treatment. It generally finds application in situations where colour, such as in textile effluents, requires removal and where a low pH is required in order to break an emulsion.

5.3 Polyaluminium Chloride

5.3.1 General Description

The name polyaluminium chloride, or PAC (not to be confused with Powder Activated Carbon) is a generic name that covers a wide range of complex molecules that can be formed by polymerising aluminium chloride under various conditions. These molecules have the general formula:



These compounds are, however, not as complicated as they seem. For example the most commonly used form of PAC, called aluminium chlorhydrate (ACH) has the formula $\text{Al}_2\text{Cl}(\text{OH})_5$. So in this case $n = 2$ and $m = 5$.

The chemistry of aluminium, as far as forming large polymeric molecules is concerned, is more complex than that of iron salts and there is an almost infinite number of different molecular structures that can be manufactured or that occur as the PAC hydrolyses in water. However the range of chemicals that are widely used commercially in South Africa is quite limited and the descriptions given here will be confined to these compounds.

There are two important factors to consider when selecting a PAC product and these are the amount of active content, measured as the % Al_2O_3 and the basicity. The basicity in this case refers to the ratio of hydroxyl to aluminium ions in the hydrated complex and is usually expressed as a percentage, as will be seen in some of the following specification tables. In general the higher the basicity, the lower will be the consumption of alkalinity in the treatment process and hence the smaller the impact on pH.

5.3.2 Manufacture

The methods used to produce the various types of PAC vary considerably and are also generally closely guarded proprietary knowledge. However they all involve dissolving a source of aluminium in hydrochloric acid. The aluminium source may be aluminium metal in the form of ingots, powder, beads, or more or less any other form, or it may be as the chloride salt or the trihydrate. The reaction may be completed in one stage or in two stages, in a batch or in a continuous process. Some processes are conducted at atmospheric pressure and without external heat whilst others rely on pressure and temperature. In one of the original processes a mixed chloride/sulphate is produced using both hydrochloric and sulphuric acids. By controlling the reaction parameters manufacturers are able to produce the polymer having the active content and basicity they strive for.

The only chemicals involved in the production of aluminium chloride are generally aluminium and hydrochloric acid and therefore, the most influential factor affecting the cost of this chemical is the cost of aluminium. The impact of hydrochloric acid on the overall cost is less significant as it is made locally and is in abundant supply.

5.3.3 Characteristics of Polyaluminium Chlorides

There are as many typical properties as there are grades of product and internationally this would run into dozens. However the variety used in South Africa is limited to two broad types although we will include a third because of its widespread production and use elsewhere.

The three types we will consider are

1. The chloride/sulphate type.
2. An 18% Al_2O_3 product.
3. Aluminium chlorhydrate (ACH).

5.3.3.1 Chloride/Sulphate Products

This type of product is widely used all over the world.

TABLE 9: Typical chemical and physical properties of chloride/sulphate PAC

Appearance	Clear Amber
Al_2O_3	9.9-10
Basicity	50-60%
Chloride	8.5-9.4%
pH	2.5±0.4
Sulphate	2.5-3.3%

This type of product is also often found as a powder, the solution having been spray-dried, which gives rise to a doubling of the activity and salt content. The basicity is around 50%.

5.3.3.2 Products containing 18% Al_2O_3

Although not widely used locally this type of product is very common internationally and is included as the reader may often come across references to such a product. These products are not made by the sulphate process and are simply the product of the controlled reaction of a source of aluminium with hydrochloric acid (Table 10).

5.3.3.3 Aluminium Chlorhydrate

This is by far the most commonly used form of PAC found in water treatment in South Africa. It is also an interesting fact that it is the primary ingredient of personal deodorants. Like the 18% materials, aluminium chlorhydrate (ACH) is made by the reaction of hydrochloric acid and a

source of aluminium. Its popularity stems from its high aluminium content and its very high basicity (Table 10).

The active content of solid aluminium sulphate was explained in Section 5.1.3 and is around 15%. Aluminium chlorhydrate is a liquid and therefore easier to handle than a solid product and yet it is 1.5 times as concentrated as aluminium sulphate solution.

TABLE 10: Typical chemical and physical properties of PAC products containing 18% Al_2O_3 and of ACH

Al_2O_3 content	18-19% m/m	23-24%
Appearance	Amber Liquid	Clear colourless liquid
Basicity	30-40%	80%
Chloride	21-22% m/m	-
pH	0.5-1.8	4-5

5.3.4 Transportation and Storage

Polyaluminium chlorides are not corrosive or hazardous materials and may be transported and stored in stainless steel, plastic or fibreglass tanks.

5.3.5 Application of PAC in Water Treatment

By far the bulk of all PAC produced is used in potable water applications with some also being used in industrial waste treatment; but very little, if any, is used in sewage treatment. The trend has been for PACs to replace aluminium sulphate and the reasons for this are mainly:

- Lower dosage requirement.
- No requirement for any neutralising agent (soda, lime).
- Shorter flocculation time.
- Smaller amount of sludge.
- Reduced number of backwashing steps.

Of these benefits the most important are the reduced amount of sludge produced and the fact that little or no pH correction is required. The use of aluminium sulphate or iron salts leads to large volumes of sludge because of a combination of hydroxide formation and the precipitation of insoluble sulphates. Whilst the practice of returning this sludge to the water sources still occurs in many cases, environmental regulation requires that it be removed from the site. Since this generally involves dewatering and transport by road, anything that can reduce the volume of sludge produced is a contributor to cost savings.

Polyaluminium chlorides, particularly ACH, contain a high ratio of cation (aluminium) to anion (chloride, sulphate, etc.) and therefore can easily be shown to produce significantly less sludge than would aluminium sulphate or an iron salt, in which the cation to anion ratio is lower.

Secondly, because these products are much less acidic than aluminium sulphate, they have little or no effect on the pH of the water to which they are added. The important consequence of this is that little or no lime or other alkali is needed to raise the pH after flocculation. The only lime addition will be that required to produce a stable water where there is insufficient alkalinity. Not only does this save significantly on treatment cost but it also reduces the risk of post-precipitation occurring in the reservoirs and reticulation system.

On the negative side, PACs, particularly those that do not contain sulphate, tend to produce small flocs that are slow to settle and in practice would result in floc carry-over. For this reason PACs are almost always used as a component of a formulated or blended product that contains a coagulant of the polyamine or polyDADMAC (poly diallyldimethylammonium chloride) type. These products offer a 'best of both worlds' scenario with the PAC contributing a high degree of clarity and 'sparkle' and the polyelectrolyte contributing floc size and settling rate.

5.4 Sodium Aluminate

The last of the aluminium salts that needs to be discussed is completely different from the others in that it is a very alkaline product. As has been mentioned previously, aluminium dissolves in both acids and alkalis and sodium aluminate is produced by reaction with sodium hydroxide and is therefore a high pH coagulant. It is this property that makes sodium aluminate unique among inorganic coagulants. There are no iron based high pH flocculants.

5.4.1 Manufacture

Sodium aluminate is produced by dissolving aluminium (usually aluminium trihydrate) in diluted sodium hydroxide (caustic soda). The reaction requires heat and is usually conducted at close to the boiling point of the caustic solution. Sodium aluminate can be produced as a solid material or as a solution. This is achieved through the dilution of the caustic soda. A 25% caustic solution will result in a pulp like product that can be further dehydrated and produced as a solid. In water treatment however it is generally produced and used as a solution and various strengths are commercially available.



5.4.2 Characteristics of the Product

Sodium aluminate is to some extent a difficult material to use, because it has a strong tendency to absorb carbon dioxide from the atmosphere and this results in the formation and precipitation of sodium carbonate and aluminium hydroxide. Some manufacturers have attempted to overcome this problem by the introduction of organic stabilisers such as amines, but the addition of these chemicals tends to make the product uncompetitive in terms of cost.

The strength, or activity, of sodium aluminate is measured in terms of the percentage strength of the solution as $\text{Na}_2\text{Al}_2\text{O}_4$ and as the percentage Al_2O_3 and the percentage sodium oxide, Na_2O .

The formulation and structure of the product, as with so many complex aluminium salts, is not completely understood and various references show different, although similar structures. In its simplest form, taking into account that aluminium is trivalent, the structure can be depicted as follows:

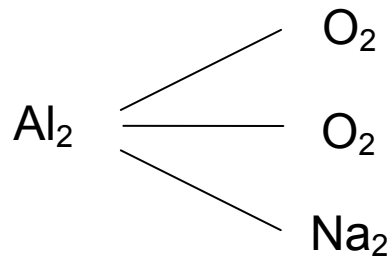


FIGURE 9: Schematic representation of sodium aluminate

Commercial products are normally solutions of approximately 20% sodium aluminate and typical chemical and physical properties of such solutions such as those shown in Table 11.

TABLE 11: Typical chemical and physical properties of sodium aluminate

Appearance	Yellowish-brown liquid
Aluminium (Al)	10.5% m/m
$\text{Na}_2\text{Al}_2\text{O}_4$	20% m/m
Na_2O	18.5% m/m
$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	0.9% m/m
Specific Gravity (25°C)	1.45

Note that the Al_2O_3 content of 10% is relatively high, making it comparable to the 10% PACs and certainly stronger than aluminium sulphate solution.

5.4.3 Transportation and Storage

Although aluminium is not widely used, when transporting or storing caustic soda it should be remembered that it is corrosive to aluminium and so no aluminium fittings can be used. Caustic soda can be transported in mild carbon or stainless steel or in polyethylene, the same materials being suitable for storage as well. Storage and transportation conditions need to be controlled, since as described above, exposure to air results in carbon dioxide absorption and precipitation of the components from solution. Agitation or periods of extended storage in open or partially full tanks can all lead to exposure to air and therefore the tanks should be sealed and agitation kept to a minimum by the correct choice of pumps and pipe layout. Temperature is also important

because low temperatures will quickly cause solidification. Temperatures between 10 and 40°C are therefore recommended.

5.4.4 Application in Water Treatment

Sodium aluminate has, in the past, been a widely used coagulant in water treatment but its use has diminished over the years and today it is employed at very few plants. An advantage of using sodium aluminate is that it allows coagulation/flocculation and pH correction to take place simultaneously in waters that have a naturally low pH. For this reason it is, for example, still used in low pH coastal waters. It can also be used in low alkalinity waters where the use of acidic flocculants would result in the destruction of too much alkalinity and require high dosages of lime to stabilise the water after coagulation and flocculation. Sodium aluminate can also be used for phosphate removal from soft, acidic waters, although it is an expensive option compared to other coagulants such as aluminium sulphate.

In general its relatively high cost and handling difficulties have caused sodium aluminate to be replaced by more 'modern' flocculants.

CHAPTER 6

CHEMICALS USED FOR pH ADJUSTMENT AND STABILISATION

6.1 Introduction

In Chapter 2 the relationship between pH, hardness and alkalinity was discussed as well as the importance of water stabilisation. In this chapter, the different chemicals that are used for pH adjustment and water stabilisation are described.

The chemicals most commonly used for pH adjustment and stabilisation include lime, soda ash, sodium bicarbonate and sodium hydroxide and these are used widely in both water and wastewater treatment. As explained in Chapter 2, the pH of a water is very important in water treatment for a number of reasons. As was explained in the previous two chapters pH affects many of the chemical reactions which occur in the water, in terms of the reactions that occur when using an inorganic coagulant. For example, the addition of aluminium sulphate results in a reduction in the pH, since for every 1 mg/l of aluminium sulphate that reacts to produce a precipitate of aluminium hydroxide, 0.5 mg/l of alkalinity (as CaCO₃) is consumed (Water Quality and Treatment, 1990). This reduction in the alkalinity, and subsequently the pH, may necessitate the addition of lime or soda ash in order to raise the pH to a value that is ideal for a particular application. Inorganic coagulants are often used in wastewater treatment for applications such as phosphate removal, and here too reductions in the pH of the sewage occur depending on the alkalinity content. If the reduced alkalinity is not replaced, the microbes essential for the process will be affected and may even die.

The pH is also important in disinfection reactions. Taking the common example of chlorine or hypochlorite disinfection, the pH affects the proportion in which the various species of chlorine occur. At a pH of around 6.5, HOCl predominates, while at a pH of 9, OCl⁻ is the predominant species (White, 1999). This has very important implications because HOCl is a much more powerful disinfectant than OCl⁻. Adjusting the pH to the correct value allows for better disinfection and more cost effective utilisation of the chlorine.

One of the most important applications for lime, soda ash and sodium bicarbonate is in stabilisation of soft waters or softening of hard waters. Soft waters are low in alkalinity and are therefore corrosive. All waters are corrosive to some extent, but the corrosion due to soft waters can substantially increase water treatment costs due to deterioration in pipes and pumps, which can lead to costly repairs, water losses due to leaks in the pipes and drops in water pressure. Leaching due to corrosion can also result in increased concentrations of metals in the potable water supply and with certain pipe materials, toxic metals such as lead and cadmium can be released into the water. Cement pipes are also very susceptible to corrosion in low alkalinity water. Other problems caused by corrosion include bad tastes, odours and bacterial slimes, which in turn can deplete residual disinfectant concentrations in the water (Water Quality and Treatment, 1990). Adjustment of the pH is the most commonly used method of reducing corrosion and although it does not always eliminate corrosion completely, it can significantly diminish the problem.

Hard waters cause scaling of pipes and eventual blockages. Chemical precipitation using lime, lime-soda ash or caustic soda can be used to soften the water and is usually used in rapid-mix, flocculation and sedimentation process trains like those typically found in conventional water treatment plants, although a solids-contact softener, which combines these processes into one unit, can also be used. The selection of chemical depends on a number of factors including cost, TDS content, the carbonate and non-carbonate hardness and the chemical stability of the water. For example, water that contains little or no non-carbonate hardness can be softened using only lime, but for waters high in non-carbonate hardness, it may be necessary to use both lime and soda ash to reduce the hardness sufficiently (Water Quality and Treatment, 1990; Sanks, 1978). Once a water has been softened, it has high causticity and scale-formation potential and therefore needs to be recarbonated in order to reduce the pH and alleviate scaling in the downstream pipelines (Water Quality and Treatment, 1990). Typically recarbonisation is achieved by adding carbon dioxide.

Lime or lime-soda ash softening tend to be more cost effective than caustic softening, although they often result in a decrease in the TDS content of the water and produce more sludge than the caustic softening process. Caustic soda has the advantage of not deteriorating as rapidly during storage, whereas slaked lime can absorb carbon dioxide and water during storage and quicklime may react with moisture and undergo slaking, resulting in feeding problems (Water Quality and Treatment, 1990).

6.2 Lime

Lime is quarried as limestone (CaCO_3) and then heated in kilns to produce quicklime (CaO). It can then be slaked or hydrated to produce slaked/hydrated lime ($\text{Ca}(\text{OH})_2$). It is in the form of quicklime or slaked lime that lime is most commonly used in water and wastewater treatment applications. Quicklime has a number of advantages over slaked lime, these being (Water Treatment Handbook, 1991):

- Lower costs.
- A higher CaO content.
- A higher bulk density (0.7 to 1.1, compared to 0.3 to 0.6 for slaked lime).

However, if using quicklime, it is necessary to have facilities for slaking the lime, which increases the capital investment. Another disadvantage is that the quality of quicklime tends to be more variable than that of slaked lime.

Lime is often used in very large quantities and in such cases it is usually purchased as quicklime and then slaked in conjunction with the feeding process. Slaking of quicklime is a highly exothermic reaction and requires special safety precautions. Quicklime can be purchased as pebble lime to reduce the problems due to dusting, or in a powder form if using lime from recalcining calcium carbonate sludge. Hydrated lime is generally purchased in powder form and then a slurry is produced for dosing purposes (Sanks, 1978). One disadvantage of quicklime is

that if not properly stored it may slake, and slaked lime can absorb carbon dioxide and water from the air to form CaCO_3 (Water Quality and Treatment, 1990).

It is important when using lime that it contains the correct amount of active ingredient and is of a suitable quality so that it does not result in operational problems. It is also essential that it does not contain contaminants in concentrations high enough to cause either health related problems or affect the treated water aesthetically.

The grit content or sieve analysis of a lime is important in terms of process operation. High grit content can cause mechanical problems with pumps and feed impellers, and in order to prevent damage to equipment the grit content should not exceed 5% (SABS 459-1955). It is recommended that the reader refer to the Manual for Testing of Water and Wastewater Treatment Chemicals, WRC Report No. 1184/1/04, 2004 by Freese, Trollip and Nozaic.

6.3 Sodium Hydroxide

Sodium hydroxide, commonly known as caustic soda, is supplied in a variety of forms; it is available in flakes, pearls or powder as 98.9% NaOH. Solid sodium hydroxide is highly hygroscopic, readily absorbing moisture from the air, which can make storage of this product in humid atmospheres problematic. In addition, it is dangerous to handle and can result in serious alkaline burns to the skin and eyes. It dissolves very readily, solubility increasing significantly as the temperature increases, with large amounts of heat being generated during dissolution. It is therefore often preferable to purchase sodium hydroxide in liquid form as a 50% NaOH solution, which begins to crystallise at temperatures of 12°C (Sanks, 1978).

It is important to ensure that the hydroxide content of the caustic soda is within the range specified by the supplier.

6.4 Soda Ash (Sodium Carbonate)

The chemical formula for soda ash is Na_2CO_3 and it is available as dense granules, as medium granules, as powder and as light powder. Dense soda ash contains a water of crystallisation ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), while light soda ash does not (Na_2CO_3), and in most cases dense soda ash is used, as it is more economical to ship and transport. Soda ash is very soluble (12.5% at 10°C) and is not corrosive, but bulk-handling equipment should include dust collection equipment (Sanks, 1978).

Soda ash is suitable for small plant applications, since it is easier to handle and dose than lime. It is also ideal for post-filter pH stabilisation of aluminium sulphate treated water. Lime must be used prior to filtration, otherwise it will result in an increase in turbidity, but soda ash can be used after the filters and because of its high solubility, it will not affect the turbidity of the water. Soda ash is also used for pH stabilisation of very low alkalinity waters, since the formation of insoluble carbonates, which protect against corrosion, occurs when using this chemical (Water Quality and Treatment, 1990).

6.5 Sodium Bicarbonate

Sodium bicarbonate (Na_2HCO_3) is readily soluble and easy to handle and like soda ash, is used for pH stabilisation of low alkalinity waters (Water Quality and Treatment, 1990).

CHAPTER 7

POLYELECTROLYTES

7.1 Introduction

The term 'polyelectrolyte' is an overall term that covers a number of different chemical types and a wide range of variations within those types. They have come from relative obscurity in the late 1960's to universal acceptance today. During that time, ongoing research has broadened both the range of products and the range of applications.

The products discussed in this chapter will fall into three broad categories, namely

1. Polyacrylamides
2. Polyamines
3. PolyDADMACs

Before discussing these separately and in more detail there are some common characteristics and properties of polyelectrolytes that we can cover under general headings.

7.2 Polymers and Polymerisation

In chemical terms a polymer is formed when a molecular structure is repeated over and over, sometimes millions of times so that the polymer consists of a repeated pattern of 'building blocks' joined together by chemical bonds into one very large molecule. We are all familiar with polymers such as:

- Polyvinyl chloride (PVC) plastic –which, as its name implies, consists of vinyl chloride building blocks.
- Polyvinyl acetate (PVA) – common in such things as adhesives and paint.

The process of polymerisation consists of reactions which result in molecules being joined together in a repetitive manner. There are three main processes by which this is achieved:

7.2.1. Homopolymerisation:

In these reactions the basic building block already exists as a stable chemical molecule and all that is required is a reaction in which the separate molecules are linked into larger ones. Such a reaction is achieved by introducing a chemical agent called a catalyst. The catalyst does not become part of the polymer, but it is responsible for making the polymerisation reaction possible. This type of reaction is referred to as homopolymerisation because only one molecule is used in the polymerisation reaction.

7.2.2. Condensation polymerisation:

In this type of polymerisation two different chemicals are reacted together to form polymer molecules and in the process a small secondary molecule, e.g. water or hydrochloric acid, is eliminated from the structure. Polyamines are an example of this type of polymerisation

7.2.3. Co-polymerisation:

This type of polymerisation takes place when two separate chemical molecules react together to form a polymeric structure without the elimination of other molecules. Anionic and cationic polyacrylamides are examples of co-polymerisation.

Polymer chemistry is an extensive subject in its own right and far beyond the scope of this book, but the purpose of the brief descriptions given above is simply to provide a brief overview of these chemicals and allow the reader a better understanding of how they are produced and how they react. The word 'polyelectrolyte' is often used when referring to these polymerised chemicals, but it should be pointed out that not all polymers are polyelectrolytes. Polyelectrolytes are polymers that have a positive or negative charge on the molecular structure. Thus PVC and PVA are not polyelectrolytes but polyamine and polyDADMACs are.

7.3 Polymer Chains and Charges

Polymers for water treatment tend to be polymers that consist of long chains in which a molecular structure is repeated many times. The length of the chain is determined by the production parameters such as temperature, pH, etc. However it is possible to modify the chain structure and produce what are called cross-linked chains that often have net-like, rather than chain-like structures.

The polyelectrolytes that are used in water treatment are characterised by having positively or negatively charged sites along their chain structure. A cationic polymer such as a polyamine or polyDADMAC will have positively charged sites whereas an anionic product will have negatively charged sites. The diagram in Figure 3 (p18) represents a schematic of a positively charged polymer.

If the production of this polymer was modified by adding other chemicals to promote cross linking we would have a structure that is schematically represented in Figure 10, in which the action of the cross linking is shown in red.

Another important type of structure is the 'branched chain polymer' which, as the name implies, consists of chains with branches. This type of polymer is schematically represented in Figure 11.

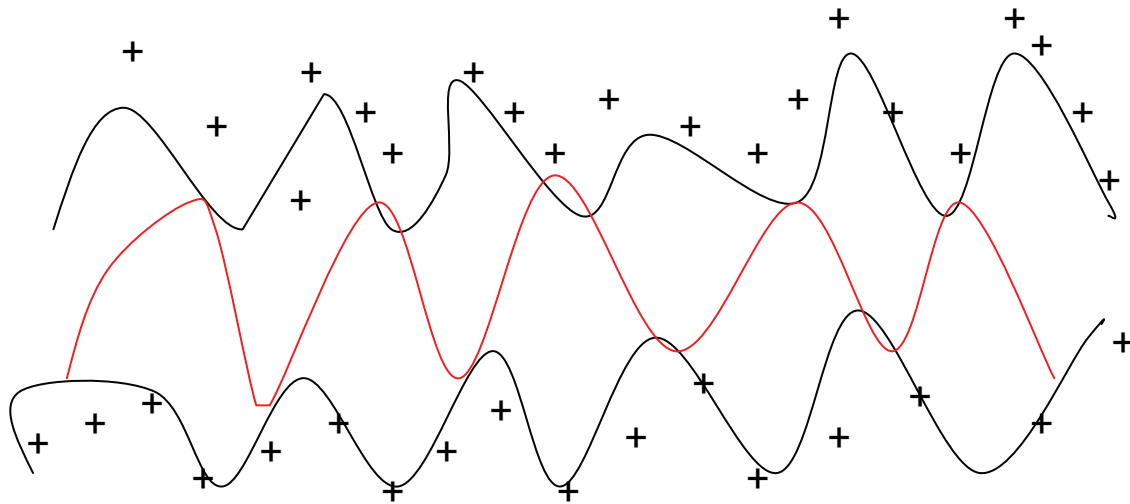


FIGURE 10: Schematic representation of a cross-linked polymer (the red line represents the cross-linkages)

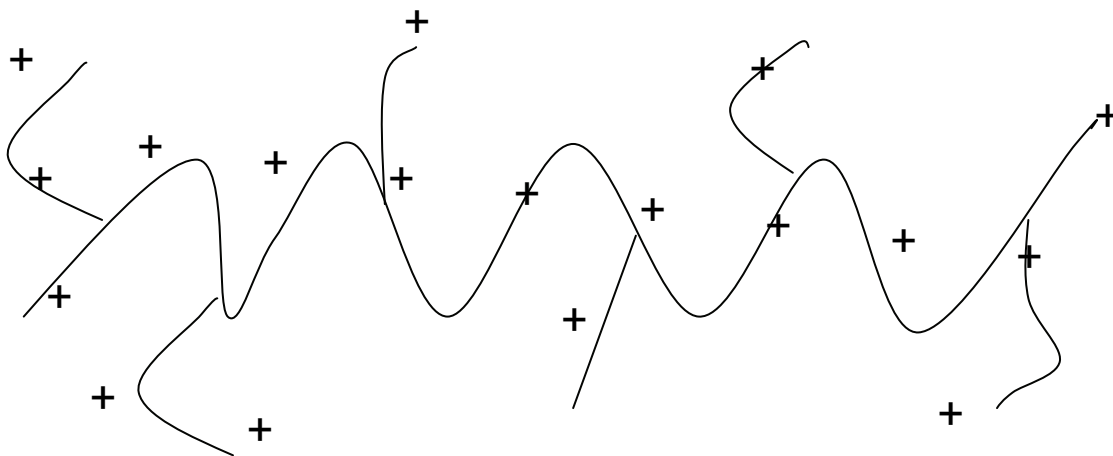


FIGURE 11: Schematic representation of a branched chain polymer

Flocculation is an unpredictable science and it is not possible to predict whether cross-linking or branching will improve or detract from performance in any particular circumstance. This can only be ascertained by repeated testing and evaluation.

7.4 Charge Type and Charge Density

Polyelectrolytes are available as anionic, nonionic or cationic polymers. This terminology describes the charge type, but another important factor is the charge density. Charge density can be measured in the laboratory and is expressed as the percentage of sites carrying charge to the total number of available sites on the polymer structure. Basically though, all this really

indicates is which polymers carry a higher charge density than others. Like the structures above, the effect of charge density can rarely be predicted and only testing will determine if a high or low charge density polymer is most suited to a particular application.

7.5 Molecular Weight

The examples used in Chapters 4 and 5 in which the molecular weights of inorganic salts were determined, the calculations were fairly simple. However, this is not the case with polymeric compounds. The number of monomers ('building block molecules') making up the polymer is unknown and this number can vary in each batch of polymer that is manufactured. Determination of the molecular weight in the manner described in Chapters 4 and 5 is therefore not possible. Of course both the exact structure and the exact molecular weight can be measured with sophisticated analytical equipment but for the purposes of this book that is not necessary. In summary then, there are several variables that exist in polyelectrolyte chemistry and properties, mainly:

- The chain structure.
- The charge type.
- The charge density.
- The molecular weight.
- The physical property – solid or liquid.

Obviously, by changing these variables an extremely wide range of products can be produced. Some of the variables can be specifically controlled within predetermined limits, but other factors during the polymerisation reaction are more random and cannot be controlled easily. The net result is that the selection of a particular polymer for a particular application is rarely achieved by selection based on precise knowledge of properties and is more generally the result of extensive and methodical testing.

7.6 Polyacrylamides

7.6.1 General Description

Polyacrylamides, as the name implies, are polymers of acrylamide. Acrylamide itself is a highly toxic chemical and yet one that occurs in trace amounts in many foodstuffs, especially as a result of frying such things as potatoes. In the polymerised form however, the products are safe to use and to handle. Its structure is described in Figure 12.

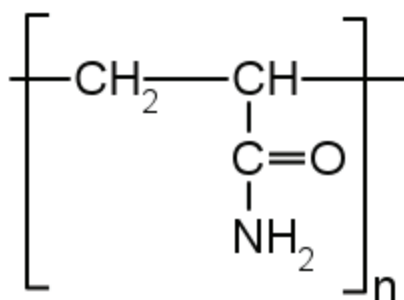


FIGURE 12: Structure of polyacrylamide

Polyacrylamides are produced as granules or beads in the solid form, or as emulsions in the liquid form. These will be discussed in more detail in the following sections. Furthermore, these polymers can be produced as anionic, nonionic or cationic in nature. Combining these three charge types with varying molecular weights and charge densities produces a product range that consists of literally hundreds of products of a wide variety of different specifications.

7.6.2 Manufacture

All manufacturing procedures involve the handling of acrylamide monomer which, as mentioned previously, is a highly dangerous, carcinogenic chemical. As a result all manufacturing procedures have to operate under the strictest conditions of safe practice.

7.6.2.1 Producing Granules

Granular products are most commonly produced in aqueous solution by the addition of a catalyst or initiator. At the same time a salt may be added to produce an anionic or cationic final product. For example the addition of sodium acrylate will produce an acrylamide/acrylate copolymer that is anionic in charge, while the addition of a cationic monomer, usually a compound having an ammonium chloride component (called a quaternary ammonium compound), will result in a cationic polymer being produced.

Once initiated the polymerisation reaction is both rapid and exothermic and careful control of the production parameters is required in order to ensure consistency from batch to batch. Production is usually carried out using a batch process, but a continuous process has been developed using belts resembling conveyor belts onto which the monomer/catalyst mixture is poured. The polymerisation reaction occurs continuously and the solid material is removed from the end of the belt.

Regardless of the method used, the resultant product is a solid, which is first dried and then chopped up, prior to grinding and milling to produce the required particle size of around 20-100 mesh to resemble fine sugar.

7.6.2.2 *Producing Beads*

An alternative production method utilises a suspension of the acrylamide monomer in water, the relevant anionic or nonionic co-monomer and the catalyst. Aqueous solutions of the ingredients are suspended in a hydrocarbon using a dispersing agent. The resultant product consists of discrete beads, with a typical particle size of 100-2000 microns. This process is specialised and not used by many polyacrylamide producers as it is an expensive procedure that requires careful control to ensure the formation of beads of uniform size.

The difference between bead and granular products can be seen in the different particle shapes, the granular material resembling sugar and the bead material resembling ion exchange beads. They can also be differentiated by feel; the beads having a distinctly round, smooth texture.

7.6.2.3 *Producing Emulsions*

The third type of polyacrylamide that is produced is in the form of an emulsion. These products are produced by emulsifying the acrylamide and co-monomers in a hydrocarbon such as paraffin, using an emulsifying agent. The catalyst is then added and the polymerisation reaction takes place while the monomers remain homogenised in the hydrocarbon. This is a common production process and there is a wide range of emulsion products in common commercial use.

7.6.3 A Comparison of Granular, Bead and Emulsion Products

As mentioned above, polymer science comprises an extensive field of chemistry in its own right and manufacturers of polyacrylamides each have a great deal of proprietary information and use various 'tricks of the trade' in manufacturing their products. Different manufacturers use different co-polymers, different catalysts and different processes. As a result, the comparisons made here can only be of a general nature and there are exceptions to all the rules.

The advantage of the liquids is that they are easier to handle and to dose on the plant. Solid materials are notoriously difficult to dissolve in water and require specialised systems in order to achieve efficient dissolution without producing wastage of the product. On the other hand, emulsions generally contain only about 30-40% active material, whereas the solid materials contain 100% active material. Since all polyacrylamides are currently imported into South Africa it follows that the solid materials are more cost effective to import. However, there are products of certain structures and molecular weights that can only be made as emulsions and as a result they remain in wide use despite the additional cost.

The differences between granular and bead materials are less obvious and in most cases of little or no consequence. The beads tend to be less hygroscopic than the granular materials, which may be a consideration in cases where product is stored in dosing hoppers in humid conditions.

There is presently no significant production of polyacrylamide flocculants in South Africa and therefore most polyacrylamides are imported into the country. The raw materials are derived from the petrochemical industry and therefore the main factors affecting the cost are the oil price and the exchange rate. Polyacrylamides are traditionally produced in Europe and the USA but more recently several producers have been established in China, Korea and Japan.

7.6.4 Anionic Polyacrylamide

Anionic polyacrylamides are produced by co-polymerising acrylic acid, or the sodium salt of the acid, with acrylamide monomer. The ratio of the two ingredients will determine the extent of the anionic charge (usually measured as a percentage). Figure 13 shows the structure of a typical anionic polyacrylamide while Table 12 shows the typical properties of an anionic granular polyacrylamide.

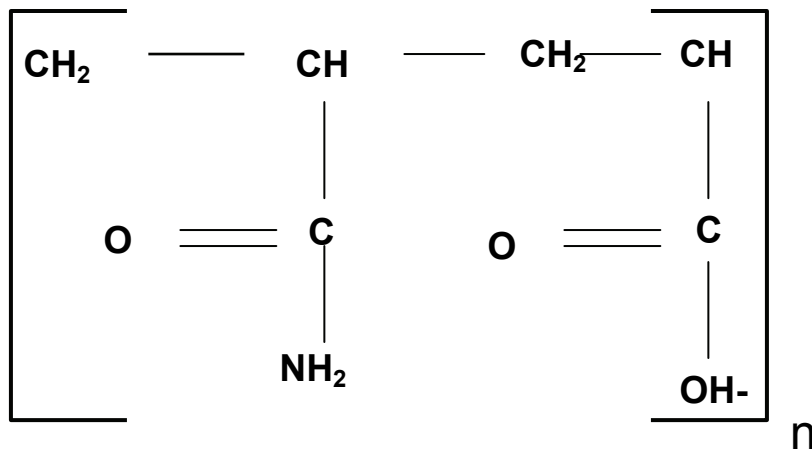


FIGURE 13: Structure of a typical anionic polyacrylamide

The molecular weight is determined by the type and concentration of the reaction initiator and the reaction parameters.

TABLE 12: Typical properties of an anionic granular polyacrylamide

Appearance	White Granule
Molecular weight	5-22 million
Particle size	20-100 mesh
Active content	Minimum 90%
Free monomer	0.05%

Granular and bead polyacrylamides are very difficult to effectively dissolve into water on a plant scale. When added to a tank of water they tend to form into gelatinous clumps, commonly called 'fish eyes' which are very resistant to further dissolution. If a large portion of the added product forms 'fish eyes', this material is effectively unusable and will add to the overall cost of use of the product. It is therefore important when considering the use of polyacrylamides that a suitable system is installed to ensure effective dissolution. There is a wide variety of commercially available systems, ranging from simple manual based systems to fully automatic make-up systems. In all cases though, the common factor is the ability to rapidly disperse the granules into a water stream before the opportunity for 'fish eye' formation occurs. Continued gentle stirring is then required for up to two hours to fully dissolve and hydrate the material. Normally solutions of around 0.5% are prepared. These dissolution systems tend to be quite expensive and this is often considered a negative factor in the use of polyacrylamides.

Emulsion products were developed to overcome this disadvantage and produce a product that could be more easily diluted and dosed. Emulsions need to be 'flipped' or 'inverted' and this involves the addition of the emulsion into a high energy, low shear environment such as the vortex of a stirred tank at a concentration of about 0.5%. This process causes the emulsion to change (or 'flip') from a water in oil emulsion to an oil in water emulsion. Once the polyacrylamide molecules are in the emulsified water particles, they gradually become fully hydrated. Typical properties of an emulsion polyacrylamide are described in Table 14.

TABLE 14: Typical properties of an emulsion polyacrylamide

	Anionic	Cationic
Appearance	Opaque milky white liquid	Opaque milky white liquid
Active solids	30%	40%
Residual Monomer	<1%	<1%

7.6.6 Applications in Drinking Water

The application of polyacrylamides in drinking water needs to be carefully controlled since, as mentioned, the acrylamide monomer is highly carcinogenic. For this reason, manufacturers generally specify the residual monomer content of the final products. Most reputable manufacturers do in fact produce drinking water grades of their products and these are generally found to have a suffix after the name, e.g. LT (low toxicity) indicating that they are of a special drinking water quality. Products not specified as such should not be used in drinking water applications. In spite of the strict control governing the levels of monomer present in polyacrylamides used in drinking water treatment, the maximum allowable dose is restricted to 1 mg/l. However, the dosages of polyacrylamide used in water treatment are generally well below 1 mg/l. Overdosing of polyacrylamides can cause severe blinding of filters, so high doses of polyacrylamides should also be avoided for this reason.

The most commonly used polyacrylamides in water treatment are the anionic polyacrylamides. Generally, polyacrylamides are used in conjunction with other chemicals, since polyacrylamides used on their own are not capable of floc formation. However, when used in conjunction with a

coagulant such as aluminium sulphate, ferric chloride or a polymeric coagulant, they enhance floc formation resulting in larger, stronger flocs. In such applications, the polyacrylamide is added to the water treatment process after the addition of the primary coagulant, typically in a low energy, conditioning environment such as the centre well of a clarifier. The flocs formed tend to be much larger and settle more rapidly than those formed using only a primary coagulant and therefore the use of polyacrylamides as 'floc aids' is confined to settling processes and not to flotation processes. Polyacrylamides are not widely used in South Africa as floc aids, since it is generally possible to achieve adequate settling using primary coagulants alone. Most South African waters respond well to treatment using a single primary organic coagulant such as a polyamine, a polyDADMAC or blended coagulants consisting of an organic polymer and polyaluminium chloride. As a result, these products are extensively used in this country, although in many other countries, the inorganic coagulant and polyacrylamide option is still used.

The other predominant application of polyacrylamides in drinking water is in the dewatering of the sludges produced in the clarification process. In this application, the polyacrylamide is used in conjunction with a mechanical dewatering apparatus, such as a belt press or centrifuge. The polyacrylamide is selected on the basis of its ability to produce large floc particles that readily separate from the water, allowing for the production of a significantly thickened sludge. The nature of the sludge is dependent on both the raw water quality as well as the types of chemicals and dosages used in the treatment process. For example, the sludges formed when using aluminium sulphate for coagulation tend to be colloidal and sticky and are often difficult to thicken or dewater mechanically (Sanks, 1978). In contrast, the sludges produced during lime-soda ash softening treatment are generally dense, stable and inert, and dry well. Laboratory testing and plant scale trials are required in order to find a product that produces a floc with right characteristics of 'separability' and drainage without causing blinding of the belt or filter. The performance of the product is determined by the dryness of the sludge produced and the recovery of solids as a percentage of the total solids. These two factors are inversely related and the only way to determine the most suitable product is through physical testing. For more information on tests to evaluate polyacrylamides for sludge thickening refer to the Manual for Testing of Water and Wastewater Treatment Chemicals, WRC Report No. 1184/1/04, 2004 by Freese, Trollip and Nozaic.

7.6.7 Applications in Sewage Treatment

Whereas the use of polyacrylamides in drinking water treatment applications is almost exclusively confined to the anionic products, sewage treatment applications are almost always restricted to the use of the cationic products. The application in sewage treatment is for the dewatering of sludge which, as in potable water sludge treatment, relies on the combination of chemical and mechanical methods.

Sewage sludges vary considerably, depending on the source of the sludge. For example, the sludges produced in the primary settling tanks are quite different from those derived from the secondary settling tanks. At some wastewater works the sludges are mixed, producing a sludge

that is different from either primary or secondary settled sludge. To complicate matters, the success of dewatering is dependent on a number of factors and therefore a polyacrylamide that is suitable for a particular sludge when used in a centrifuge, may not work for the same sludge when used on a belt press. It is therefore important to select a polyacrylamide based on not only the sludge type, but also taking into account the type of mechanical dewatering device that will be used. For example, some dewatering systems, such as screw presses and centrifuges, result in the flocs being exposed to high shear forces, and if the flocs are not sufficiently strong these shear forces will break up the flocs resulting in a loss of cohesion and poor dewatering performance. Belts can easily blind if the wrong product is selected, preventing the separated water from draining through the belt filter.

There are literally hundreds of polyacrylamides available in an endless range of charge densities, molecular weights, molecular structures, etc. and there are no set rules to simplify selection. Each case must be taken on its merits and test work carried out in order to identify the most cost effective product.

7.7 Polyamines and PolyDADMACs

The second group of polyelectrolytes commonly used in water and wastewater treatment consists of polyamines and polyDADMACs. The term polyDADMAC is an abbreviation for the chemical name of the molecule, namely **diallyldimethylammonium chloride**. The term polyDIMDAC is also often used for these polyelectrolytes, but they are different terms used for the same thing. DIMDAC is an abbreviation of **dimethyldiallylammonium chloride**, which is diallyldimethyl ammonium chloride, with the order of chemicals changed. The ISO standards for naming chemicals states that alphabetical order should be used so the term DADMAC is actually the correct description.

Polyamines and polyDADMACs are both cationic polyelectrolytes that are supplied as aqueous solutions for use in coagulation and flocculation applications. They are similar to each other in many aspects and can often be used interchangeably in a particular application. However, there are also some significant differences and so they are discussed separately in this guide.

7.8 Polyamines

7.8.1 General Description

Polyamines, as their name implies, are polymers that contain repeated amine groups and it is these amine groups that give them their cationic nature. Unlike polyacrylamides, polyamines are only cationic, there being no anionic or nonionic versions. The products exist as aqueous solutions with a typical amine odour and they are clear, slightly yellow in colour and non-hazardous.

7.8.2 Manufacture

Polyamines are produced by polymerising epichlorhydrin with dimethylamine (DMA) and so are sometimes referred to as 'epi-dma' polymers. In simple terms the production process consists of slowly adding the DMA to the epichlorhydrin in a closed reactor. The reaction is very exothermic, and requires careful control of the rate of addition in order to keep the reaction under control. Generally the reactor is cooled with chilled water and the more efficient the cooling, the shorter the production period.

Epichlorhydrin itself is a highly dangerous chemical having a very low flash point and also being carcinogenic. Dimethylamine has a very powerful odour of amine and can be an atmospheric pollutant if the storage and handling facilities are not well designed. The reactor itself must therefore be fitted with scrubbing facilities to control vapour and odour emissions. Obviously then, polyamine production is a fairly complicated process, requiring sophisticated plant design and qualified and experienced staff. The reaction is depicted in Figure 15 below.

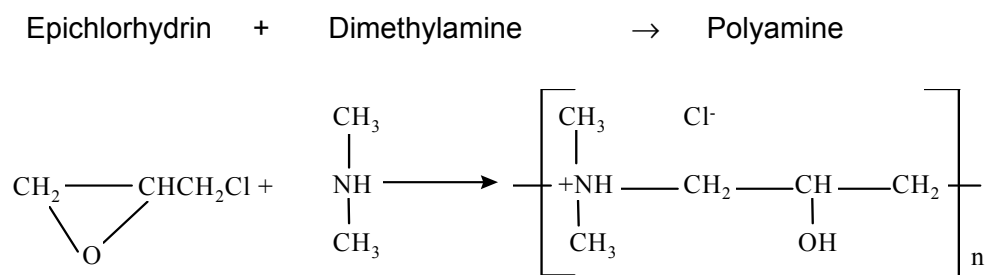


FIGURE 15: Reaction of epichlorhydrin and DMA to produce polyamine

The positively charged NH group provides the polymer with its cationic charge.

In practice manufacturers add other ingredients to modify the polymer structure, and common among these are ammonia and ethylenediamine, both of which modify the extent of cross linking in the structure. The polymer formed has a structure quite different from that of most other polyelectrolytes, possessing cationic charges situated along a backbone chain, as opposed to being on branched side groups.

A problem that often affects polyamine production is that as well as producing the desired polyamine molecule, various other unpredictable side reactions also occur which produce small amounts of other chemicals. One such group of chemicals formed in this way is the propandiols, some of which are highly carcinogenic chemicals. As a result, the specification of these by-products is important, and products manufactured to National Sanitation Foundation (NSF) or similar accreditation schemes, need to conform to strict standards.

Since epichlorhydrin is an imported chemical, it is a major contributor to the cost of polyamines. The typical properties of a polyamine are listed in Table 15.

TABLE 15: Typical properties of a polyamine

Appearance	Clear yellowish liquid
Active solids content	48-52%
Specific Gravity (25°C)	Approximately 1.15
Viscosity cps (25°C)	250-500
pH	4-6

7.8.3 Transport and Storage

Polyamines are not corrosive or hazardous and may be transported and stored in stainless steel, fibreglass or plastic.

7.8.4 Application in Water Treatment

Polyamines have become widely used in drinking water treatment for the coagulation and flocculation of suspended solids. Depending on the circumstance, they may be used alone or in combination with aluminium salts, iron salts or additives such as bentonite. As with all polymeric coagulants and flocculants, the amount of mixing energy that can be created at the point of addition of the chemical will affect the efficiency of coagulation; generally, a greater energy input provides better results.

Once the flocculation process has started and floc particles begin to form, it is important that only gentle agitation, often referred to as 'conditioning', takes place in order to allow development and growth of the floc. Vigorous mixing or energy applied at this stage can cause the floc particles to break up or 'shear' and once this occurs, the flocs will not reform.

Polyamines are particularly useful in the treatment of high turbidity waters where they are generally more cost effective than high doses of aluminium sulphate or ferric chloride. The floc particles formed are generally of a good size for rapid settling and polyamines used alone are often able to cope with water with turbidity measuring hundreds or even thousands of NTU.

In applications where colour removal is important, polyamines can also often give good results. A further advantage of these products is that since they have a pH close to neutral, the use of lime for subsequent pH correction is either not necessary or can be reduced significantly, thereby reducing treatment costs still further.

In recent years a wide range of products has been developed that consists of polyamine blended with polyaluminium chloride and these blended products offer the best of both inorganic and organic properties.

Accreditation bodies, such as NSF, typically specify a maximum allowable dosage of 20 mg/ℓ for polyamines.

7.9 PolyDADMAC

7.9.1 General Description

Like polyamines, polyDADMACs are generally sold as clear, aqueous solutions varying from virtually colourless to yellowish in appearance. They do not possess the typical amine smell of a polyamine and by this means alone an experienced operator will be able to differentiate between the products. They are also nonhazardous.

7.9.2 Manufacture

PolyDADMAC is produced by the homopolymerisation of DADMAC monomer. A catalyst is used to promote the reaction, although unlike polyamines, there is not a combination of two ingredients, but only the polymerisation of one molecule into a polymer chain. The reaction is depicted in Figure 16 below.

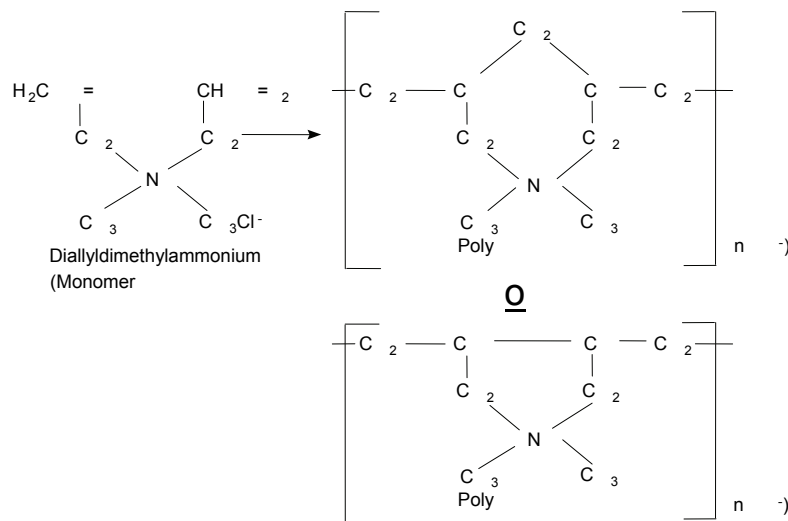


FIGURE 16: Reaction of DADMAC monomer to produce polyDADMAC

The polymer consists of a ring structure that is repeated to form the polymer chain. This ring structure contains positively charged nitrogen, which is the source of the cationic charge.

Manufacturers have developed slight modifications of this process in order to create differing structures. Various other ingredients have been added to the process, but success has been varying and the large majority of production processes still rely on the straightforward process described above in Figure 14. Unlike the polyamine production process, this reaction is not violent or exothermic, but actually requires some heat input.

PolyDADMACs have a higher molecular weight than polyamines and therefore, on an equal solids basis, are much more viscous than polyamines. Whereas polyamines are generally sold at around 50% solids and are easily handled at that strength, a polyDADMAC in excess of 30% solids is so viscous that it becomes very difficult to pump or pour the solution. For this reason

the solids content is usually adjusted down to around 30% in the reactor while the product is still hot, and further to around 25% for commercial use.

Because the production reaction is much less vigorous and because the raw materials are nontoxic and easy to handle, it is much easier to set up a polyDADMAC production facility than a polyamine facility and there is much less risk of producing a product with harmful by-products.

DADMAC monomer is not produced in South Africa; it is produced by a relatively small number of companies throughout the world, although there are well established, major producers in Europe and the USA. The monomer is produced in the petrochemical sector and is therefore linked to the oil price and like all our other polyelectrolytes the cost in South Africa is highly dependent on the exchange rate. A list of the typical properties of a polyDADMAC is shown in Table 16 below.

TABLE 16: Typical Properties of a PolyDADMAC

Appearance	Clear water white to yellowish liquid
Active solids	25-27%
Specific Gravity	1.03-1.05
Viscosity	100-300 mPs @ 25°C
pH	2-4

7.9.3 Transport and Storage

PolyDADMACs are non corrosive, nonhazardous products and may be transported and stored in stainless steel, fibreglass or plastic containers.

7.9.4 Application in Water Treatment

PolyDADMACs are widely used in water treatment and have similar applications to polyamines. In fact, in the large majority of cases either product can be used with equal success and the choice is generally based on treatment cost. It is therefore important to bear in mind that the vastly different solids concentrations of the two products will not correlate to treatment cost.

Whilst it is true to say that polyamines and polyDADMACs are interchangeable in the majority of circumstances, there are applications where one will outperform the other, to a greater or lesser extent, and although the reasons for this are clear in some cases, in others they are not. For example, it has been observed that polyDADMACs are generally more effective than polyamines in plants using floc blanket clarifiers. Measurement of the floc cohesiveness has shown that polyDADMAC flocs tend to be more cohesive than polyamine flocs. However, where colour removal is of importance, polyamines are usually found to provide superior colour removal to polyDADMACs.

As with polyamines, reputable manufacturers will have their products certified by the NSF or similar authority that will stipulate the maximum dosage for use in water treatment. Accreditation bodies such as NSF typically specify a maximum allowable dosage of 35 mg/l for a typical polyDADMAC of around 25% solids.

7.10 Summary

As can be seen from the contents of this chapter, the topic of polyelectrolytes is a large and diverse one. It is also true to say that the range of polyelectrolytes is amongst the most widely used and least understood of all water treatment chemicals and it is useful to summarise some of the important facts surrounding polyelectrolytes:

- Polyacrylamides are available as solids (granules or beads) but polyamines and polyDADMACs are to all intents and purposes only available as aqueous solutions.
- Polyacrylamides are available with anionic, cationic and nonionic charges whereas polyamines and polyDADMACs are always only cationic.
- Polyacrylamides are not widely used in drinking water treatment but are very widely used in dewatering applications both for sewage and potable water sludges.
- Invariably anionic products are used for potable water sludges and cationic products for sewage sludges.
- Polyamines and polyDADMACs are not used for sludge dewatering but are widely used, alone or in combination with inorganic salts, for coagulation and flocculation in drinking water production.
- Many polyelectrolytes are manufactured from hazardous and toxic raw materials and it is therefore important that they conform to international standard specifications.

CHAPTER 8

DISINFECTANTS AND OXIDANTS

8.1 Introduction

The chemicals used in the processes of disinfection, pre-oxidation and the removal of taste and odours will be discussed in this chapter.

Before discussing the disinfectants used in water and wastewater treatment it is important to define the term 'disinfection'. Disinfection can be defined as the inactivation of pathogenic or disease-causing microorganisms. It is important to note that disinfection does not imply the deactivation of all micro-organisms, but only those that are disease causing. Sterilisation on the other hand is the term used to imply complete deactivation of all micro-organisms.

Disinfection is usually carried out in the final stage of treatment before the drinking water is distributed and is intended to remove pathogenic organisms, such as bacteria and viruses, from the water. However, as mentioned previously, water which has been disinfected is not sterile and does contain a number of harmless, non-pathogenic, organisms.

The disinfection of water ideally requires two stages:

1. The first stage involves the removal of the pathogenic organisms from the water by the reactions taking place with the disinfectant.
2. The second stage involves maintaining a residual concentration of the disinfectant in the water in order to protect the reticulation system from re-infection and ensure that the water at the furthest point in the reticulation system remains safe.

Some disinfectants have very strong bactericidal effects and remove pathogenic organisms highly effectively, but do not have a residual effect and therefore cannot protect the reticulation system. For example ozone is highly effective in removing bacteria and viruses, but to protect the disinfection system with a residual requires the secondary addition of chlorine, chlorine dioxide or chloramines. The residual effect appears to be limited to halogens, usually chlorine based compounds (White, 1999).

The processes of oxidation and disinfection in water treatment are often inter-connected since many of the chemicals are used for both processes. Furthermore, most disinfectants are also strong oxidants and the effect of the chemical depends on the stage in the process at which it is added. Although the two processes cannot be completely separated, oxidation processes tend to predominate if the chemical is added early in the process (e.g. before coagulation), while disinfection processes generally take place when the chemical is added after treatment is essentially complete (i.e. after filtration).

As a result of the fact that most disinfectants are also strong oxidising agents, if there is no pre-oxidation in the plant, oxidation of compounds which have persisted through the treatment process can occur at the disinfection stage. This can result in problems such as manganese

precipitation in the reticulation system or the generation of taste and odour compounds at the chlorine disinfection stage where there has been no pre-oxidation. For this reason care should be taken to ensure that the water is adequately pre-oxidised early on in the treatment train.

8.2 Chlorine

A wide range of commercially available disinfectants/oxidants is available and the reactions that give rise to disinfection and oxidation are very varied, but the most widely used of these is chlorine. Chlorine is a member of a group of chemical elements called halogens, which also includes bromine and iodine. Both bromine and iodine products are also widely used as disinfectants (iodine is also used as an antiseptic), although their use in water treatment is limited. Bromine compounds are used primarily in industrial water treatment and iodine almost not at all.

There are three primary sources of chlorine:

1. Gaseous or liquid chlorine.
2. Sodium hypochlorite.
3. Calcium hypochlorite.

Once dosed into the water, they all react in the same way. Therefore, although the different types of chlorine will be discussed individually, the use of chlorine in water and the reactions that occur will be discussed as a single topic.

8.2.1 Gaseous (Liquid) Chlorine

8.2.1.1 General Description

Gaseous chlorine, or chlorine gas, is also referred to as liquid chlorine because when it is sold as a compressed gas in the familiar yellow tanks or cylinders that are present at many plants, it is in fact in a liquid state and only as it leaves the cylinder and the pressure reduces, does it vaporise into a gas. Chlorine gas (see Table 17) is a greenish-yellow gas with a specific weight of about 2½ times that of air, an atomic weight of about 35, and a boiling point of about minus 34°C at atmospheric pressure. However, it is highly corrosive in the presence of even slight humidity and because of its high reactivity and oxidation potential the gas can produce explosive reactions with ammonia and hydrogen (White, 1999). Chlorine gas has a very distinctive odour and is highly dangerous if inhaled in any quantity. The gas exists as molecules of two chlorine atoms and therefore the chemical formula for chlorine is Cl₂ and the molecular weight is 70. Chlorine does not occur naturally as a gas, because it is so reactive that it will react with almost everything that it comes into contact with. It is of course very soluble in water, which is an important factor in its use as a water disinfectant.

TABLE 17: Typical Properties of Chlorine Gas

Appearance	Green-yellow gas
Atomic mass	35.453 g/mol
Specific Gravity (20°C)	$3.21 \times 10^{-3} \text{ g/cm}^3$
Melting point °C	-101
Boiling point °C	-34.6
Solubility in water	3.1 l/l at 10°C

8.2.1.2 Manufacture

Chlorine is manufactured by the electrolysis of sodium chloride (table salt). Although this is a very simple chemical process, the manufacturing facilities necessary to do this on a commercial scale are technically complex and very expensive.

The production reaction is, however, very simple as shown in Equation [16]:



Salt, of course, is a solid material so the reaction is carried out in a salt solution called brine and so the complete reaction is as shown in Equation [17]:



The reaction gives rise to two important by-products, namely sodium hydroxide (caustic soda) and hydrogen.

The electrolysis reaction takes place in electrolytic cells. Older technology used what were called mercury cells because each cell had a layer of mercury in the bottom that acted as one of the electrodes. This technology tended to leave traces of mercury in the final products, and so it has now been replaced with membrane technology. The membranes in the cells separate the chloride and sodium ions as the salt solution is electrolysed and this results in the production of pure products. The hydrogen comes off as a gas and is collected in its own specialised production process. A modern chlorine production facility will consist of banks of numerous membrane cells linked to each other and obviously the more cells present, the higher the production volume.

The process involves dissolution of the salt (sodium chloride) in water to form the brine solution. The brine is then extensively purified before being fed to the electrolysis cells, since any impurities in the brine can result in costly damage to the membranes.

As the chlorine gas is generated it is collected and dried, generally using sulphuric acid, and then compressed into a liquid and stored in specialised storage vessels. From here it may be used in subsequent manufacturing processes or packed into tanks or cylinders for sale as liquid chlorine.

The 'chlor-alkali' balance is an important concept in the overall understanding of the pricing, marketing and availability of chlorine. It can be seen from Equations [16] and [17], that similar amounts of caustic soda and chlorine are produced in the reaction. Taking into account the molecular weights of the compounds, it is found that for 71 kg of chlorine formed, 80 kg of sodium hydroxide is formed.

In South Africa there is a shortage of sodium hydroxide (caustic soda) and large quantities are imported, therefore most chlor-alkali producers strive to produce as much sodium hydroxide (caustic soda) as possible. However, as shown above, for every ton of sodium hydroxide produced, approximately 888 kg of chlorine is also produced. This chlorine cannot simply be vented to atmosphere, but due to the high demand for sodium hydroxide (caustic soda), the production of chlorine tends to exceed the demand for chlorine. It is for this reason that chlor-alkali manufacturers seek alternative uses for the chlorine gas which is produced as a by-product in the manufacture of sodium hydroxide. Many of the chemicals used in the water and wastewater treatment industry (such as polyaluminium chloride, ferric chloride and chlorine gas) help alleviate the situation as chlorine is used in the production of these chemicals. Such products are often called chlorine sinks, and this is a very important factor in the chlor-alkali business.

Only two ingredients are used in the production of chlorine, namely salt and electricity. The salt used is imported and the electricity consumption is high, and therefore the two factors that impact most strongly on the process of chlorine are the exchange rate and the cost of electricity. The maintenance costs incurred in running a chlorine plant are also very high, partly due to the fact that membranes require periodic replacement and are very expensive, and the fact that the chlorine production facility is highly specialised and sophisticated, and requires regular maintenance and safety inspections.

8.2.1.3 Transportation and Storage

Since chlorine is highly toxic and (unlike the other chemicals discussed so far) it is a gas, chlorine requires highly specialised conditions in order to be transported. Chlorine is packed into cylinders, usually of 70 kg net capacity, or into tanks of 925-990 kg net capacity. These containers are then transported to the point of use where they are coupled, through a measuring device called a chlorinator, to the water system.

Once empty, the cylinder or tank is returned to the production site for refilling, and because these vessels are pressure vessels they are subject to legislation regarding testing and quality control. Furthermore, because the product itself is so hazardous, the transportation is also highly regulated, requiring specially trained drivers, specially equipped vehicles and trained

personnel at fire stations on major routes. Operation of a chlorine-filling installation, such as the production plant, is highly specialised and sophisticated.

In addition to the containers described above, a small number of facilities are equipped to receive chlorine in bulk. Chlorine is transported to these sites in specially constructed ISO tanks which are then either left on-site or discharged into a similar tank on the customer's premises.

Storage facilities for chlorine cylinders and tanks have to be designed and maintained to specific detailed standards in order to ensure compliance with safety regulations. These regulations cover aspects such as alarm systems, scrubbing systems, door and window seals, the provision of windsocks, breathing sets and emergency evacuation plans. The above is a brief summary of the complex issues around chlorine transportation and distribution, but more detailed information can be obtained from the manufacturers and suppliers of chlorine.

8.2.2 Sodium Hypochlorite

8.2.2.1 General Description

Sodium hypochlorite is manufactured in a wide variety of concentrations and in some cases is diluted after manufacture. Common household bleach is in fact a weak solution of sodium hypochlorite.

When chlorine gas is dissolved in water, it hydrolyses to produce hypochlorous and hydrochloric acids and it therefore reduces the pH of the water to which it is added. Sodium hypochlorite, however, is very alkaline and so raises the pH of the water to which it is added.

8.2.2.2 Large Scale Industrial Production

As described above, the process of electrolysing salt produces sodium hydroxide (caustic soda) and chlorine which are separated by a membrane cell. If these two products are recombined, and alkaline solution of sodium hypochlorite is produced, generally containing around 12% m/m as Cl_2 . The reaction is shown in Equation [18]:



There have been many attempts to replicate this membrane process on a small scale for the on-site production of hypochlorite for use at small works. As mentioned previously, membrane based plants are expensive to operate and maintain and are highly sophisticated, so do not lend themselves to small scale operation.

8.2.2.3 On Site Hypochlorite Generators

There are a number of on-site hypochlorite generators on the market. These do not employ membrane cells but instead use packs of specially coated metal electrodes that electrolyse

brine to produce sodium hypochlorite *in situ*. These plants work in exactly the same way as the swimming pool chlorinators that are widely available.

A disadvantage of these units is that they can only produce a 0.8% chlorine solution (compared to the 12% that a membrane plant produces), so in order to achieve the large volumes of chlorine necessary to treat larger plants, a large number of units needs to be constructed in banks, together with large brine tanks and power packs. Another disadvantage is that in the process of producing the sodium hypochlorite they also produce a large amount of sodium chloride, which can significantly increase the conductivity of the water to which the hypochlorite is added.

The formation of sodium hypochlorite in an on-site generator involves the reactions shown in both Equation [17] and Equation [18]. However, in this case both reactions occur simultaneously as shown in Equation [19]:



As a result of the sodium chloride production in the reaction shown in Equation [19], these units cause a noticeable increase in the TDS and conductivity. However, there are circumstances in which these units can provide a feasible means of chlorination and a number of such installations can be found at smaller water and wastewater works.

8.2.2.4 Industrial Scale Dissolution

As described above, the production of sodium hypochlorite involves the dissolution of chlorine in sodium hydroxide, either as it is produced or at some time after production. The production method described here involves the dissolution of chlorine gas in sodium hydroxide (caustic soda) at some stage after production, which is obviously possible using sodium hydroxide (caustic soda) and chlorine produced from two different sources. For example, in some cases it is more economical to transport 100% chlorine in gaseous (liquid) form and 50% caustic lye to a location, than to transport 12% sodium hypochlorite solution. In such cases, a facility is required for the dissolution of chlorine into the caustic lye, but this requires a fairly simple plant compared to the much more complex plant required for the manufacture of chlorine gas.

A similar process is used when chlorine cylinders are returned to the filling station, where they have to be vented of any residual chlorine before they are deemed sufficiently safe for the

inspection to be carried out. This vented chlorine cannot be released to the atmosphere so it is passed through caustic soda to produce sodium hypochlorite.

Since electricity forms a significant part of the cost of producing sodium hypochlorite, it remains, either directly or indirectly, a major cost driver in industrial scale dissolution. As in the other processes described above, salt is another major cost that needs to be considered for this process. The cost is also affected by the market cost of sodium hydroxide (caustic soda).

8.2.2.5 Chemical and Physical Properties

Table 18 below refers to sodium hypochlorite produced industrially at a chlor-alkali facility. This is the most commonly used form of hypochlorite in water treatment.

TABLE 18: Typical properties of sodium hypochlorite solution

Appearance	Greenish-yellow clear liquid
Odour	Typical strong chlorine smell
Specific Gravity at 20°C	1.23 minimum
Available Cl ₂ when dispatched _{m/v}	15% minimum
Available Cl ₂ when dispatched _{m/m}	12.5% minimum
Sodium hydroxide as NaOH _{m/v}	1.5% minimum

As can be seen from the SG, a litre of this solution weighs 1.230 kg and therefore the chlorine activity when expressed as mass per volume (_{m/v}) is greater than that expressed as mass per mass (_{m/m}) or grams per kilogram (g/kg). It is important to take this into account when calculating dosage rates.

8.2.2.6 Transportation and Storage

Sodium hypochlorite is very corrosive to stainless steel and so should not be transported in stainless steel tankers. Plastic or rubber lined tanks are acceptable and for storage, plastic or fibreglass is recommended.

Sodium hypochlorite has limited stability in storage and the available chlorine content decreases on a slow but continuous basis. Ironically the stronger the product, the more rapidly it loses activity and therefore household bleach is a fairly stable product, while industrial 12.5% product is much less stable and ideally should not be stored for periods longer than two to four weeks. The actual rate of decay will depend on factors such as temperature, sunlight and the presence of any impurities like iron, which accelerates the rate of decay. It is therefore important that storage systems are sized correctly to ensure that the stock is turned over frequently.

8.2.3 Calcium Hypochlorite

The most well known form of calcium hypochlorite that is available locally is HTH but the chemical is produced by many manufacturers worldwide. The products produced vary in

chlorine content from around 65% to 70% and may be supplied as granules, tablets or flakes. Calcium hypochlorite is therefore a highly concentrated form of chlorine, but if stored correctly is fairly stable and it is much easier to handle than chlorine gas. However, it can be a source of violent and dangerous chemical reactions if it accidentally comes into contact with organic chemicals and therefore proper storage is essential.

8.2.3.1 Production

Calcium hypochlorite is produced from the reaction of chlorine gas and lime (calcium hydroxide) and this reaction is shown in Equation [20] (Austin, 1984).



The quality of the lime used in the process is of critical importance as any of the impurities commonly found in lime can lead to a poor quality, unstable product. All South African calcium hypochlorite production relies on imported high quality white lime, generally sourced in Europe.

The manufacturing process is a potentially dangerous one that, like chlorine, requires a sophisticated plant and qualified and experienced personnel.

Due to the fact that high quality, imported lime is used in the process, both the cost of the lime and the exchange rate influence the local price of calcium hypochlorite. In addition to this, the factors which influence the cost of chlorine, namely salt and electricity, also affect the cost of calcium hypochlorite.

8.2.3.2 Chemical and Physical Properties

As we have mentioned above, the product is commercially available as a granular material, as a flake or in tablet form. The physical form in which calcium hypochlorite is supplied has no effect on the chemical properties and the typical specifications shown in Table 19 are for a common 65% and a 70% product.

TABLE 19: Typical Properties of Calcium Hypochlorite

	Common (65%) product	70% product
Appearance	White powder or granule	White powder or granule
Chlorine content	65% m/m min	70% m/m min
Moisture	4% max	5-10%
Iron	Approx 0.02-0.04% max	Approx 0.02-0.04% max
Water insolubles	25% max	15% max

8.2.3.3 Transportation and Storage

Calcium hypochlorite is generally packed in lined steel or plastic drums. It is safe to transport in the manufacturer's packaging but there are certain restrictions in terms of other goods that may be transported in the same load. This applies in particular to shipping containers where the packing of calcium hypochlorite with certain other materials may not be permitted. It is very important that calcium hypochlorite is stored in its original container with the lid correctly replaced and in an area where it cannot come into contact, deliberately or accidentally, with any other substance or with moisture.

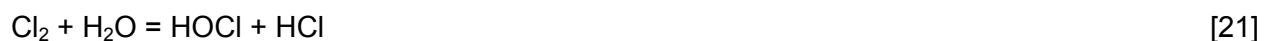
8.2.3.4 Application in Water Treatment

It is clear from the descriptions, especially of chlorine gas and calcium hypochlorite, that these are particularly dangerous chemicals and one may wonder why they are used at all in water treatment. It is in fact the very properties which make chlorine so hazardous that are also responsible for its effectiveness as a disinfectant.

Firstly, chlorine is a very broad spectrum microbicide, which means that it can kill a wide range of micro-organisms. Secondly and perhaps most importantly, chlorine provides a residual. This means that chlorine can be added to the water at the purification works and a measurable amount of chlorine will still be present in the water many kilometres from the plant. This is important in ensuring that no regrowth occurs in the reservoirs and distribution system and that there is still a small residual present when the water reaches the end user. The distribution system is protected by the residual effect of chlorine which persists through the reservoirs and pipe work for periods in excess of two days. This is generally long enough for most installations.

As mentioned previously chlorine is a highly reactive chemical and when added to water it hydrolyses to form hypochlorous acid and hydrochloric acid as shown in Equation [21]. Similarly the reactions of sodium hypochlorite and calcium hypochlorite are shown in Equations [22] and [23] respectively. The molecular masses are shown underneath the reactions, as these are required in calculations used to determine the relative costs of different sources of chlorine.

For chlorine gas



$$71 + 18 = 52.5 + 36.5$$

71 kg of chlorine gas will produce 52.5 kg of hypochlorous acid.

For sodium hypochlorite



$$74.5 + 18 = 52.5 + 40$$

74.5 kg of sodium hypochlorite will produce 52.5 kg of hypochlorous acid, but since sodium hypochlorite is purchased in solution form and not at 100% pure product, this needs to be accounted for. For example, a solution that is 12.5% as Cl_2 , contains 12.5 kg of chlorine per 100 kg of product. 12.5 kg Cl_2 corresponds to the following mass of NaOCl:

$$12.5 \div 35.5 \times 74.5 = 26.2$$

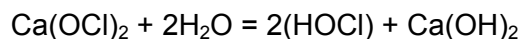
Therefore, if 74.5 kg NaOCl produces 52.5 kg hypochlorous acid, 26.2 kg of NaOCl will produce:

$$52.5 \div 74.5 \times 26.2 = 18.5 \text{ kg HOCl}$$

In other words, to produce 52.5 kg of HOCl using this solution,

$$52.5 \div 18.5 \times 74.5 = 211 \text{ kg solution would be needed.}$$

Calcium Hypochlorite



$$143 \quad + \quad 36 \quad = \quad 105 \quad + \quad 76$$

So 143 kg of calcium hypochlorite will produce 105 kg of hypochlorous acid.

Or 71.5 kg of calcium hypochlorite will produce 52.5 kg of hypochlorous acid.

For calcium hypochlorite containing 65% as Cl_2 , 100 kg material will contain 65 kg Cl_2 .

65 kg Cl_2 corresponds to the following mass of CaOCl:

$$65 \div 71 \times 143 = 130.9$$

Therefore, if 143 kg CaOCl produces 105 kg hypochlorous acid, 130.9 kg of NaOCl will produce:

$$105 \div 143 \times 130.9 = 96.1 \text{ kg HOCl}$$

In other words, to produce 52.5 kg of HOCl using this solution,

$$52.5 \div 96.1 \times 143 = 78.1 \text{ kg material would be needed.}$$

In summary therefore, to produce 52.5 g of hypochlorous acid we would need:

71 g of chlorine or

211 g of 12.5% commercial sodium hypochlorite or

78 g of 65% calcium hypochlorite.

The simplest way of determining the chlorine dose is to simply refer to the chlorine content and adjust accordingly for percentage Cl₂, since this is what determines how much product is required to achieve a particular chlorine dose.

Table 20 summarises some of the more important characteristics of chlorine gas, sodium hypochlorite and calcium hypochlorite.

TABLE 20: Comparison of chlorine gas, sodium hypochlorite and calcium hypochlorite

	Chlorine gas	Sodium hypochlorite	Calcium hypochlorite
Chemical formula	Cl ₂	NaOCl	Ca(OCl) ₂
Molecular mass	70	74	142
State	Gas	Aqueous solution	Solid
Chlorine content	100%	12.5% m/m	65-70% m/m
Shelf life	Years	Weeks	Months
Ease of use	Good with right equipment	Very easy	Must be dissolved first

Numerous studies can be found in the literature detailing the mechanism by which chlorine kills micro-organisms, but for the purposes of this guide, it is sufficient to know that chlorine oxidises or destroys micro-organisms essentially through oxidation of the cell membrane. This is however a simplistic explanation as there are many complex reactions that occur during chlorine disinfection.

When disinfecting with chlorine it is important to apply the correct dose, since under dosing may allow some pathogenic organisms to survive. Conversely over dosing can have adverse health implications and in the case of effluent discharges can affect the organisms present in the receiving waters and have an adverse impact on the environment. In fact the use of chlorine in wastewater effluent discharges is banned in some countries in order to prevent chlorine affecting the environment.

8.2.4 Effect of pH

The effect of pH on the reactions of chlorine and especially in terms of disinfection efficiency is very important and although the chemistry is complex, it is important to understand the basics. Figure 17 shows the relative proportions of HOCl and OCl⁻ in the pH range between 5 and 12 and shows that at pH values of between 6.5 and 8.5 both species are present. The proportions of the two species occur in about equal proportions at a pH of approximately 7.5. This is important in terms of disinfection efficacy, since HOCl is a far more effective disinfectant than OCl⁻ and so as the pH of the water increases, so chlorine becomes less effective as a disinfectant. This is important in ensuring both acceptable disinfection and cost effective utilisation of chlorine. Both HOCl and OCl⁻ are referred to as free chlorine.

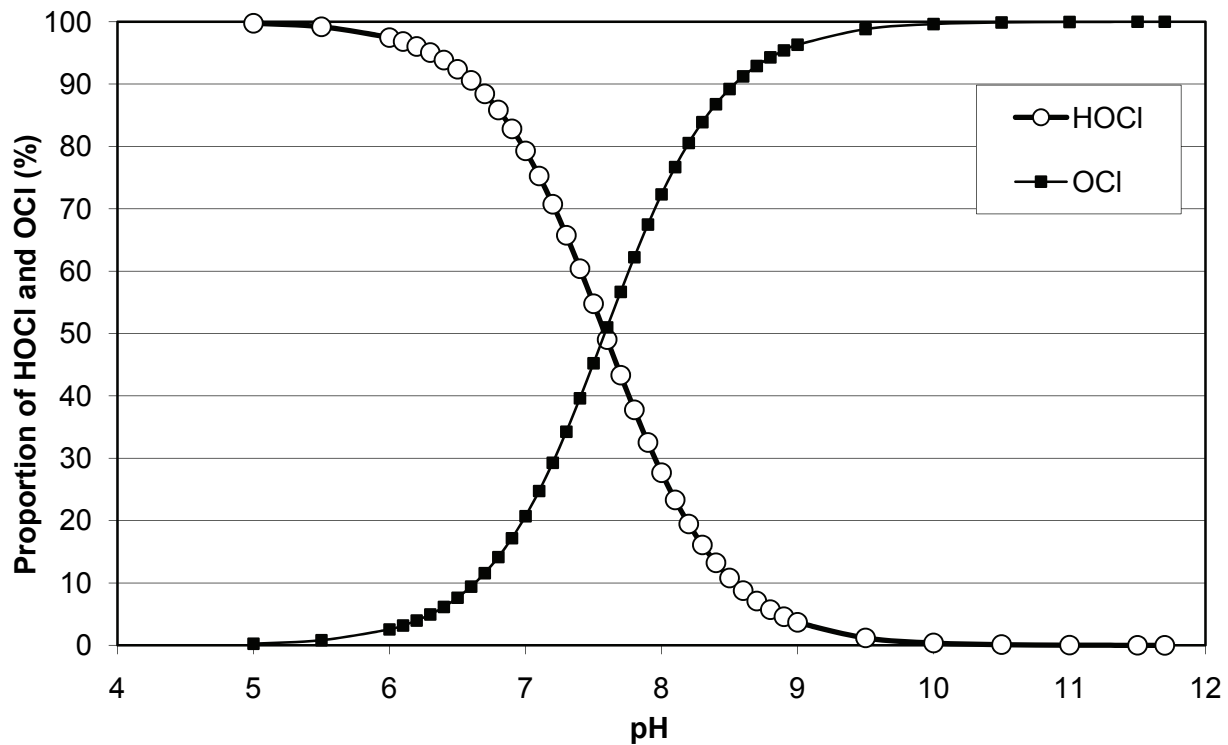
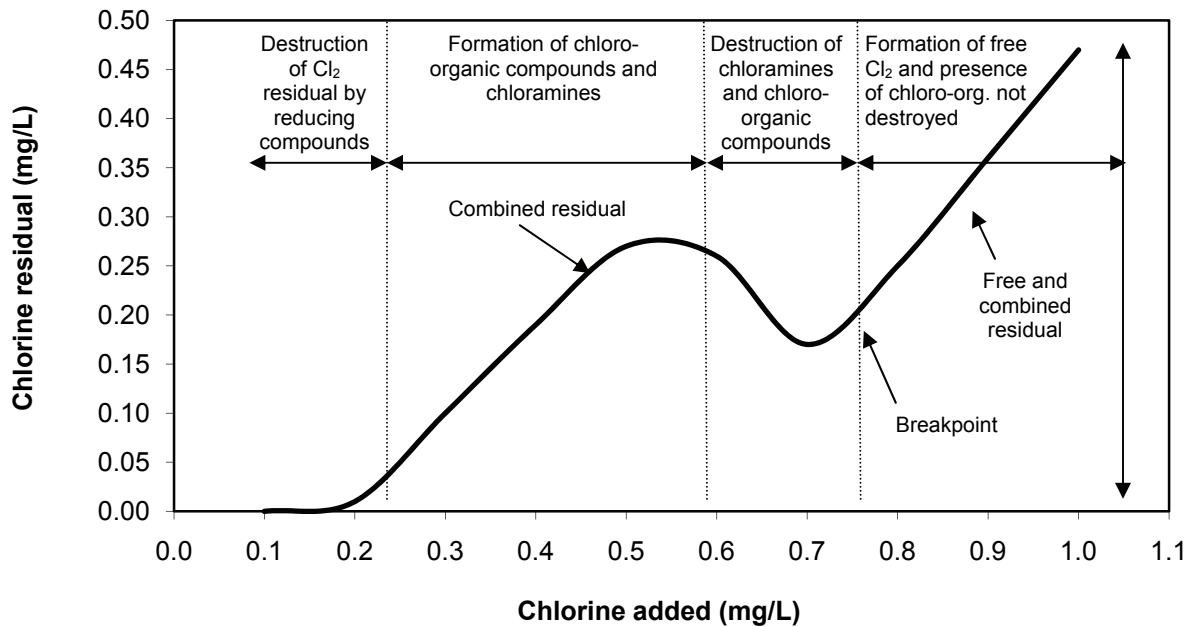


FIGURE 17: Relative proportions of HOCl and OCl⁻ in the pH range between 5 and 12 at 20°C (based on information from White, 1999)

8.2.5 Break-Point Chlorination and Chlorine Demand

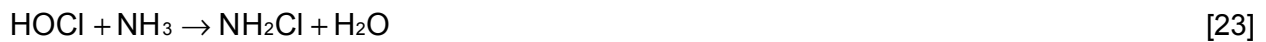
'Break-point chlorination' and 'chlorine demand' are two terms that are used widely in chlorine disinfection. Both involve complex reactions, but are concepts that are so critical to understanding chlorine disinfection that a description is needed before chlorine disinfection is discussed further.

The chlorine breakpoint is a very important aspect of chlorine chemistry and arises predominantly through the reaction of chlorine with ammonia nitrogen, but also with any other readily oxidisable compounds present in the water, such as Fe²⁺, Mn²⁺, H₂S and organic matter. A typical breakpoint curve is depicted in Figure 18.



**FIGURE 18: Typical chlorine breakpoint curve
(based on information from Metcalf and Eddy, 1999)**

The predominant reactions occurring here involve chlorine and ammonia nitrogen and result in the formation of three different types of chloramines by the following competing reactions:



Where:

NH_2Cl is monochloramine

NHCl_2 is dichloramine

NCl_3 is trichloramine

The reactions shown in Equations [23], [24] and [25] all involve the substitution of hydrogen atoms in the ammonia molecule with chlorine and all three reactions are highly dependent upon pH, temperature, contact time and chlorine to ammonia ratio (Morris, 1965).

Reaction [24], in which dichloramine is formed, is much slower than the formation of monochloramine (reaction [23]), but at pH values of between 7 and 8 which are typical of many surface waters, dichloramine will form if the chlorine to ammonia ratio is 10:1 by weight. Under these conditions, it can take up to an hour for 90% conversion to dichloramine to occur, but the reaction rate increases significantly if the pH is reduced. It is therefore possible to manipulate the reactions in order to produce the desired form of chloramines by controlling the chlorine to ammonia ratio and the pH of the water, a practice that is used when chloraminating water. Chloramination is discussed in more detail in Section 8.2.6 of this chapter. Chloramines, of which monochloramine and dichloramine are the predominant species, are referred to as combined chlorine.

As can be seen in the typical chlorine breakpoint curve depicted in Figure 18, as chlorine is added to water containing ammonia nitrogen and other readily oxidisable compounds, at pH and temperature conditions generally encountered in water and wastewater works, monochloramine starts to form. As the chlorine dose is increased and the chlorine to ammonia ratio increases, so dichloramine and even some trichloramine start to form. As the chlorine concentration is increased, so the ammonia nitrogen becomes more highly substituted by chlorine, until all the chloramines exist as trichloramine. All other oxidisable compounds present will also have been oxidised by chlorine at this point, resulting in complete reduction of all the chlorine present to chlorides. Trichloramine and chlorides have no oxidising capacity and hence provide no chlorine residual. This point is known as the breakpoint. At chlorine concentrations greater than the breakpoint, free residual chlorine occurs in the water and the most effective disinfection occurs. Chloramines also have disinfection potential, but are much less effective disinfectants than residual chlorine. The advantage of chloramines is that they have a much longer half-life than free residual chlorine, a property which is utilised in chloramination (White, 1999).

The breakpoint is important in chlorination of potable water, since optimal disinfection is only achieved at chlorine doses higher than the breakpoint.

8.2.6 The Use of Chlorine Disinfectants in Potable Water

Chlorine is most commonly added near the beginning of the water treatment process, primarily to act as an oxidant and to help control microbial growth through the plant, or it can be added near the end of the works for disinfection. It can also be dosed at a midway point in the plant and this is usually done in situations where there are elevated levels of organic contaminants.

8.2.6.1 Pre-chlorination

As its name suggests, pre-chlorination takes place near the beginning of the water treatment process, generally before the coagulant is added. The main objective of pre-chlorination is generally for oxidation and not disinfection. Another common example of pre-chlorination use is to destroy algae when high levels are present in the raw water. Live algal cells tend to be difficult to flocculate whereas dead algal cells are much more readily flocculated, and can therefore be more easily removed by settling or through flotation.

A disadvantage with pre-chlorination is that when the raw water contains raised levels of organic contaminants, such as the humic and fulvic acids that give rise to coloured water, chlorine will react with these compounds to form trihalomethanes (THMs), compounds which are suspected carcinogens (USPHS Report, 1970). This created a lot of negative publicity around water chlorination and resulted in a growing interest in alternative disinfectants. However, the real risks associated with THMs in water have so far been found to be low and a risk assessment conducted for the South African situation (Freese and Genthe, 2006) found that risks posed by THMs in drinking water at the concentrations that are commonly found in South Africa are well below the US-EPA acceptable risk level of 1×10^{-5} . In contrast, the risks incurred by not disinfecting a water supply are considerably higher and occur over a far shorter exposure period (days to weeks).

Pre-chlorination is also often used in the removal of iron and manganese in raw water sources. Soluble forms of iron and manganese are sometimes found in raw water sources, particularly when the dissolved oxygen concentrations in the water are low. When these soluble forms of iron and manganese enter the treatment plant they can, under certain conditions, pass right through the plant if not oxidised early in the process. If the iron and manganese are still in soluble form once the water has passed through the filters, then they can precipitate out of solution in the reservoirs or distribution system, resulting in staining of laundry, bathroom and swimming pool surfaces. A common way of dealing with this problem is to pre-chlorinate to enable sufficient time for the iron and manganese to undergo oxidation before the water passes through the filters. Manganese is oxidised at a much slower rate than iron, so even pre-chlorination is not always adequate for manganese oxidation. In such cases, it is necessary to use a stronger oxidant, such as chlorine dioxide or ozone. Potassium permanganate can also be used. For more information on the removal of iron and manganese see Chapter 3, Section 3.1.1.

8.2.6.2 Intermediate Chlorination

Intermediate chlorination takes place around the midway point in the treatment process, usually after sedimentation but before filtration. This is most often used when there are high levels of organic contaminants present as well as elevated concentrations of iron and/or manganese. If pre-chlorination is used in such situations, it can result in the formation of unacceptably high levels of THMs. One method of dealing with this is to remove pre-chlorination, coagulate and flocculate the water to remove as much of the organic contaminants and algae, etc. as possible and then chlorinate only after removal of this matter by settlement or flotation, but prior to the filtration. Provided there is sufficient contact time, the iron and manganese will be oxidised by chlorine to the insoluble forms, which can then be removed on the filters.

8.2.6.3 Post or Final Chlorination.

Post chlorination, as the name implies, is used at the end of the treatment process and is almost always for the purposes of disinfection. If the treatment process is performing optimally, the concentration of organic contaminants, particulate matter and soluble forms of iron and manganese should have been significantly reduced by this stage of the treatment process. This

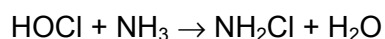
means that the potential for chlorine to react with compounds other than the micro-organisms is reduced and so disinfection will be more effective. It is important at this stage that sufficient chlorine is added to maintain a residual either until the end-user point of the distribution system or until the next point of chlorine addition in the distribution system. Large distribution systems are often designed with chlorine booster stations along the pipelines to ensure that a chlorine residual is maintained until the end-user point. However the system is designed, it is important that careful dose control is practiced to ensure that the chlorine concentration is adequate to ensure good disinfection and allow for an adequate chlorine residual, while at the same time not so high that the end user is subjected to chlorinous tastes and odours.

The chlorine dose required is obviously dependent on the quality of the water and especially the chlorine demand of the water. The chlorine demand is basically the amount of chlorine that needs to be added to a particular water in order to ensure that a free chlorine residual exists. The chlorine demand is affected by a number of factors, including the concentration of organic matter and other contaminants, pH, temperature and in the case of wastewater effluents, the concentration of ammonia and other contaminants. The term 'break-point chlorination' is often used in chlorine disinfection and essentially the 'chlorine demand' is the amount of chlorine required to reach the 'break-point'. Some of the concepts surrounding the chlorine demand and the chlorine break-point will be discussed in more detail in the subsequent section in which chloramination is described.

Most of the surface waters treated in this country have chlorine demand values of between 2 and 5 mg/l Cl₂, and since pre-chlorination is practiced at many plants the total chlorine demand is met through both pre-chlorination and post-chlorination. Typical pre-chlorine doses of between 1 and 2 mg/l Cl₂ are used together with post-chlorine doses of between 2 and 3 mg/l Cl₂. However, the only reliable means of determining the correct chlorine dose required is by either conducting chlorine demand tests on the water in a laboratory, or through trial and error on the plant adding chlorine until a free chlorine residual of the desired concentration has been achieved. Generally a chlorine residual of between 0.1 and 0.5 mg/l Cl₂ at the end-user point is desirable.

8.2.6.4 Chloramination

Chloramination is a disinfection procedure in which chlorine is used in conjunction with ammonia gas, and much of what is described here is similar to that described in Section 8.2.4 of this chapter, in which the terms 'break-point' and 'chlorine demand' were described. Chloramination is fairly widely used in the USA (Van der Kooij *et al.*, 1999) and it also finds application in South Africa, especially in situations where the reticulation system is extensive and retention times are long. The reason for this is that chloramines provide much longer lasting residuals than are possible with chlorine. Chloramination is based on the reaction of chlorine with ammonia which is described in Equation [26].



[26]

In practice chlorine and ammonia are added separately to the water, usually as chlorine gas and ammonia gas, ammonia solution or anhydrous ammonia. In some processes the ammonia is added first to prevent the formation of chlorinous taste and odour compounds and THMs. However, chloramines are far less effective disinfectants than chlorine, so some water treatment authorities prefer to add chlorine first, using a concentration that will allow the formation of a free chlorine residual, thus achieving breakpoint chlorination and effective disinfection. Ammonia is then added a short time later, generally at a chlorine to ammonia (m/m) ratio of between 3:1 and 6:1. This results in the formation of monochloramine. Higher ratios lead to the formation of dichloramine which imparts unpleasant tastes to the water and so are to be avoided. The advantages of chloramination are:

- Chloramine provides a long lasting residual, which is ideal for extensive reticulation systems.
- It can reduce formation of THMs and certain chlorinous taste and odour compounds.

However, monochloramine is a less effective disinfectant than free chlorine and if the process is not carefully controlled, inadequate disinfection can occur.

8.2.7 The Use of Chlorine in Wastewater Disinfection

Disinfection of wastewater is not an internationally accepted practice although disinfection of wastewater is often used in South Africa, since a requirement of the General Authorisation issued by the Department of Water Affairs and Forestry is that wastewater effluent discharges contain 0 faecal coliforms per 100 ml (DWAF), which is generally only achievable if the effluent is disinfected. To complicate matters, the DWAF General Authorisation for wastewater effluent discharges also imposes a limit on the chlorine residual present in an effluent of 0.25 mg/l Cl₂ and the DWAF Special Limits value for chlorine is 0 mg/l. The intention of these limits is to provide a balance between safe water in terms of human health and water that won't impact negatively on the environment.

Wastewater effluents generally contain ammonia and other oxidisable compounds in concentrations which are too high to allow for the breakpoint to be reached. In general, achieving a free chlorine residual in a wastewater effluent would require impractically and prohibitively high doses of chlorine, which would also result in a total chlorine (combined and free residual chlorine) concentration in excess of the General Authorisation. A total chlorine residual can be made up of free chlorine and combined chlorine, but for wastewater effluents is nearly always made up almost entirely of combined chlorine.

8.3 Bromine Compounds

Bromine is a member of the halogen group of chemicals along with chlorine and iodine and it is therefore not surprising that it can act as an oxidant and disinfectant. Bromine as an element is a reddish-brown liquid that is dangerous to handle.

Bromine can also be used in pure form, as it exists as a liquid at room temperature, but is a very dangerous and hazardous chemical to handle. It is more commonly produced from the oxidation

of ammonium bromide or sodium bromide to hypobromous acid using chlorine as the oxidant. However, whether used as liquid bromine or as produced by the reaction of chlorine and ammonium bromide, bromine has never been used to any extent in potable water disinfection, since it imparts a strong medicinal taste to the water (White, 1999). There have been reports of some large utilities, such as mines, in the USA using bromine for disinfection (Brits *et al.*, 1994), but this is still rare.

The two salts of bromine, namely ammonium bromide and sodium bromide do find application in the disinfection of wastewater and in disinfecting cooling tower waters. These salts are used in conjunction with a source of chlorine, commonly chlorine gas or sodium hypochlorite, and the chlorine then oxidises the bromide to hypobromous acid by the reaction shown in Equation [27] for the oxidation of ammonium bromide using chlorine gas:



The ratio of chlorine to ammonium bromide solution in practice has been found to be around 1.25 (i.e. molecular weight of Cl_2 is 71 and that of $2 \times \text{NH}_3\text{Br}$ is 194 and $194/71 = 2.7$). It is possible by optimising the reaction conditions to reduce the chlorine dose to about 25% of its normal dose.

Bromine species are better oxidising agents than the equivalent chlorine species (White, 1999), but the fact that bromine results in much lower residuals than equivalent doses of chlorine is a positive factor in terms of disinfection of wastewater effluents, where the emphasis is on trying to keep the chlorine residual within the General Authorisation limit.

However, a disadvantage of using bromine is that it has been found to form THMs more readily than chlorine, resulting in a shift from chloroform to bromoform (Lange and Kwaczynski, 1978). Bromine also becomes a more effective disinfectant as pH rises whereas the efficacy of chlorine decreases as the pH exceeds 7.6. For this reason the bromine/chlorine regime is worth considering, especially where the waste water pH is greater than 7.6.

8.4 CHLORINE DIOXIDE

8.4.1 General Description

Chlorine dioxide is a very powerful oxidising agent and therefore a very powerful disinfectant, although it is more widely used as a bleach in the paper making process than it is as a disinfectant in water treatment. Its use in water treatment is largely limited by its cost but it does have some unique properties that make it the product of choice in certain circumstances.

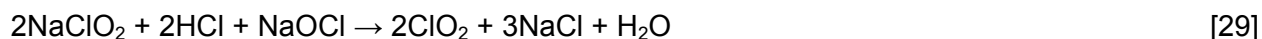
8.4.2 Manufacture

Generally for water treatment applications the chlorine dioxide is produced at the point of use by one of the following three methods shown in Equations [28], [29] and [30]:

The reaction of sodium chlorite with chlorine:



The reaction of sodium hypochlorite and sodium chlorite with hydrochloric acid:



The reaction of sodium chlorite with hydrochloric acid:



These reactions are often compared in terms of the efficiency of conversion in that there should be no chlorine produced and no unwanted by-products; based on this the reaction shown in Equation [29] is the most efficient, since its by-products are innocuous (sodium chloride and water). However, as can be seen, it requires 25% more sodium chlorite than the other two reactions in order to produce the same amount of chlorine dioxide. For the sake of completion it should be mentioned that large scale paper bleaching applications usually use different production reactions and tend to use processes in which the first step involves sodium chlorate as opposed to the chlorite.

The advantages of using chlorine dioxide as opposed to chlorine for disinfection are that it:

- Does not result in the formation of THMs (Lykins and Griese, 1986; Rav-Acha, 1984).
- Is excellent for the control of phenolic taste and odour problems (White, 1999).
- Is effective in the oxidation of manganese and iron (Aieta and Berg, 1986).
- Is a more effective viricide than chlorine (Tiff, 1977).
- Does not react with ammonia nitrogen (White, 1999).

Unfortunately there are also several disadvantages to using chlorine dioxide for disinfection. Chlorine dioxide:

- Is a relatively costly disinfectant.
- Is highly explosive and therefore cannot be transported and has to be generated on-site (Aieta and Berg, 1986).
- Can form by-products that pose a health threat, namely chlorite and chlorate (Condie, 1986; Griese *et al.*, 1991; Gordon *et al.*, 1990; Hautman and Bolyard, 1992).

The industrial process most commonly used for the generation of chlorine dioxide, as described above, involves the reaction of chlorine gas with sodium chlorite solution, and the reaction requires a small excess of chlorine (about 5%). If this is not carefully controlled, it can result in an excess of chlorine and so diminish any advantage in terms of limiting THM formation.

Sodium chlorite is not produced in South Africa and because of the potential explosion hazards associated with the powder material, it is commonly imported as a 25% solution. All the other components required are locally produced and are generally products of the chlor-alkali industry. Here too, electricity is a major cost factor in the industry.

8.4.3 Typical Properties

At concentrations of more than 15% in air, chlorine dioxide decomposes explosively into chlorine and oxygen and it is for this reason that it is always produced *in situ* and simultaneously dissolved in water. The typical properties of chlorine dioxide gas are listed in Table 21.

TABLE 21: Typical Properties of Chlorine Dioxide

Physical nature	Gas
Appearance	Orange-yellow
Molecular mass	67

8.4.4 Storage and Transportation

This is not really relevant to chlorine dioxide as it is not stored or transported. It is however appropriate to mention here that a 'stabilised' form of chlorine dioxide is sometimes marketed. This is in fact a dilute solution of sodium chlorite and it is 'activated' by the addition of dilute acid. This is not suitable for large scale application and does not occur in the water treatment industry.

8.4.5 Application in Water Treatment

Chlorine dioxide is an extremely powerful oxidising agent and as such it is an excellent disinfectant for water. It is particularly effective against *Giardia* spp. and *Cryptosporidium* spp., parasitic organisms which are of growing concern in potable water. The chlorine dioxide dosages required to effectively inactivate these organisms are lower than the chlorine dosages required. In fact the chlorine dosages required to inactivate *Giardia* spp. and *Cryptosporidium* spp. are too high to be practical in water treatment applications.

Because chlorine dioxide does not form THMs, it can be used for disinfection in situations where good oxidation is required, e.g. to oxidise iron and manganese, or remove taste and odours, but where the organic contaminants in the water would give rise to unacceptable THM formation were chlorine to be used. However, a chlorine dioxide residual of 0.4 to 0.5 mg/l has been found to cause taste and odour compounds (Water Quality and Treatment, 1990) and therefore using chlorine dioxide to provide a disinfectant residual in waters with moderate to high total organic carbon (TOC) concentrations can be problematic. However, in waters with a low oxidant demand, the chlorine dioxide residuals may persist for several days.

Typical dosages when chlorine dioxide is used as a disinfectant for water treatment applications range between 0.07 and 2.0 mg/l, and an Environmental Protection Agency (EPA) Report

(USEPA, 1998) found that the average chlorite and chlorate concentrations at plants using chlorine dioxide were 0.24 and 0.20 mg/l respectively. The USEPA recommends that the total chlorine dioxide, chlorite and chlorate concentration be less than 1.0 mg/l (USEPA, 1983).

It is obvious that chlorine dioxide can offer a number of advantages over chlorine in terms of both oxidation and disinfection. However it is not nearly as cost effective as chlorine, and in spite of the fact that the dosages of chlorine dioxide required for a particular application are lower than those of chlorine, it is still more expensive than chlorine. Added to this is the fact that chlorine dioxide needs to be generated on-site and the process involved requires trained staff, careful management and regular maintenance. For this reason the use of chlorine dioxide in large scale drinking water applications remains a niche market. Typically it will be used where there are high levels of algae or other organic pollutants that give rise to unacceptable THM concentrations when using chlorine, or in situations where there are high levels of soluble iron and/or manganese which cannot be adequately oxidised prior to filtration when using chlorine. Chlorine dioxide has found greater use in smaller applications such as food and drink factories where disinfection is very important but is not a major contributor to costs.

As mentioned above, chlorites and chlorates can be formed as by-products of disinfection with chlorine dioxide. Chlorites are also produced from the disinfection reactions that occur when using chlorine dioxide. The amount of chlorites permissible in water is limited to 1 mg/l so this also has to be taken into consideration when using chlorine dioxide.

8.5 OZONE

8.5.1 General Description

Ozone has the chemical formula O_3 . It is an unstable gas at ambient temperatures that immediately reverts to oxygen and for this reason has to be produced on-site and used immediately. Ozone has a typical smell that can be detected by humans at concentrations of as low as 0.01 mg/l and it is a severe irritant at concentrations exceeding about 1 mg/l. It is formed as a result of high voltage electrical discharge and can sometimes be detected at the time of lightning storms or close to other powerful electrical arcs.

It has been well documented in recent years that there is a layer of ozone in the upper atmosphere that acts as a filter for some of the sun's ultraviolet radiation, and as a result reduces temperatures at ground level.

8.5.2 Production

Ozone for water treatment is produced 'on-site' in an ozone generator by electric discharge at relatively high frequencies in dry air or dry oxygen. Efficient generators can produce up to 14% ozone in an oxygen stream. Generation from air requires very careful air filtration and drying of the air as a dew point of $-60^{\circ}C$ to $-70^{\circ}C$ is required if arcing of electrodes in the ozone generator is to be avoided.

Ozone generators are typically classified by:

- The control mechanism (either a voltage or frequency control).
- The cooling mechanism (either water, air, or water and oil).
- The physical arrangement of the dielectrics (vertical or horizontal).

Generators using pure oxygen are capable of producing ozone concentrations about four times higher than those using air but of course the additional costs of the oxygen have to be taken into consideration. The typical properties of ozone are listed in Table 22.

TABLE 22: Typical Properties of Ozone

Physical nature	Gas
Appearance	Colourless
Molecular mass	48

If oxygen is used to produce ozone, then the cost of this will be a significant cost factor in the price. However, as mentioned above, ozone generators can be designed to run on air, in which case no raw chemicals are required, but this definitely does not mean that there is no cost attached to using air as the raw chemical as the process required to dry the air to the required level requires expensive capital outlay, highly skilled staff and regular maintenance and refurbishment, and can in fact be more costly than using purified oxygen. The other cost drivers in using ozone are the cost of electricity and the depreciation costs of the generator itself.

An efficient commercial scale ozone generator is a highly sophisticated and expensive unit and the high capital cost is one of the factors that works against ozone becoming a widespread treatment option. The operation of the generator requires skilled staff and regular maintenance and refurbishment, which further escalates the cost of ozone.

8.5.3 Storage and Transportation

This is not applicable to ozone as it is always produced on-site. Transport of oxygen must be carried out according to the safety requirements of transporting pressurised, flammable gases.

8.5.4 Use of Ozone in Water Treatment

Ozone is used to oxidise various compounds such as iron manganese, as well as to disinfect water. It also results in a marked improvement in the taste and appearance of the treated water. For pre-oxidation purposes ozone dosages of around 1,5 to 3 mg/l are generally applied. For disinfection, a residual concentration of approximately 0.4 mg/l needs to be maintained for four minutes (ct of 1.6, where ct is the product of the ozone concentration and the time) to remove pathogenic bacteria and viruses. As mentioned above, ozone is also effective against *Giardia* cysts and *Cryptosporidium* oocysts, as it inactivates the cysts and oocysts, which are resistant to attacks by chlorine. Since ozone is one of the strongest oxidising agents and disinfectants known, it is a very effective disinfectant and destroys bacteria and viruses more effectively than

chlorine. However, its side effects and reaction products have not been researched as thoroughly as those of chlorine and the effects of its by-products are not as well known. It is known however that ozone does generate certain aldehydes and ketones in the oxidation process, some of which can be harmful.

Ozone is sparingly soluble in water relative to chlorine and its addition to the treatment stream is therefore more difficult than that of chlorine. Addition to the water is usually through diffusers or at the throat of a venturi on a recycle side stream. Efficient contacting with the water is essential if the production of large quantities of waste ozone requiring destruction is to be avoided. Unreacted ozone represents wastage of generation capacity and an additional cost to the treatment process.

In the early years of its use in water treatment, ozone was generally only added at the disinfection stage as a final disinfectant, sometimes supplemented with chlorine addition in order to provide a chlorine residual to protect the reticulation system. Over the years it has been discovered that the addition of ozone at such a late stage in the treatment process results in a breakdown of organic compounds, rendering these compounds more biodegradable and therefore allowing further biological action in the reticulation system. The general practice today is to add ozone at a pre-oxidation stage to oxidise most of the organic compounds so that they break down through the water treatment process and do not cause complications in the distribution system. Ozone can therefore be added as a pre-oxidant, intermediate oxidant or post disinfectant.

As previously stated, typical pre-ozonation dosages are between 1.5 and 3 mg/l and a residual dosage of 0.4 mg/l must be maintained for 4 minutes in order to achieve effective disinfection. This means that typical ozone dosage levels for water treatment disinfection are generally around 2 to 4 mg/l which is in the same range as those used for chlorine disinfection, but ozone is more expensive than chlorine and is usually only used when the need for a stronger oxidant or more efficient disinfectant outweighs the higher cost.

One of the main disadvantages in using ozone is that it has a very short-lived residual, and so needs to be used in conjunction with another disinfectant such as chlorine or chlorine dioxide to provide a longer lasting residual. For this reason the use of ozone as a disinfectant for potable water treatment is limited in South Africa, although there are niche applications where it provides a solution to a particular treatment problem. Ozone is, however, a popular disinfectant for potable water in Europe where it is commonly used in conjunction with granular carbon filters.

The lack of a long-lasting residual is only a disadvantage in drinking water treatment. In wastewater it is actually an advantage since as mentioned previously the presence of residual disinfectant in a wastewater effluent discharge can be harmful to the environment. This makes ozone an attractive option, from a technical point of view, for wastewater disinfection.

8.6 Summary of Disinfection

Disinfection is an important and complex topic in water treatment. As shown in this chapter all disinfectants have advantages and disadvantages, but the fact remains that more than 95% of treated potable water worldwide is still disinfected with chlorine and presently there are no other technologies available that can challenge chlorine in terms of cost effectiveness, disinfection efficiency and ease of use. Table 23 summarises the most important features of each of the disinfectants that were discussed in this chapter.

TABLE 23: Summary of Different Disinfectants

	Form	Use cost	Infrastruct ure cost	Residual effect	Shelf life
Chlorine	Gas	Low	Medium	Yes	Long
Sodium hypochlorite	Liquid	Medium	Low	Yes	Short
Calcium hypochlorite	Solid	Medium	Low	Yes	Long
Chlorine dioxide	Gas	High	High	No	None
Ammonium bromide	Solution	Medium	Low	Yes	Long
Ozone	Gas	Low	High	No	None

CHAPTER 9

ACTIVATED CARBON

9.1 General Description

Activated Carbon is used in water treatment either granular form, known as granular activated carbon (GAC), or in the form of a powder, referred to as powdered activated carbon (PAC). Do not confuse this with the abbreviation PAC when it is used for polyaluminium chloride.

Activated carbon is supplied in a range of different particle sizes and is also produced from a variety of raw material sources and to a wide range of specifications depending on the end use application. All activated carbons are 'sooty' black materials and are used in water treatment for the removal of unwanted organic contaminants. The most common application in South Africa is for the removal of taste and odour compounds, especially those produced by algal blooms that periodically occur in water impoundments during the hot, summer months. However, activated carbon will remove most organic pollutants, including pesticide residues and disinfection by-products such as THMs, activated carbon has wide application.

The organic contaminants are removed by adsorption on the carbon surface, a process in which dissolved organic compounds present in the water are chemically and physically bound to the activated carbon. This is an important point because the chemicals removed are therefore not suspended solids, which we would remove by coagulation and flocculation processes.

Activated carbon, particularly GAC, has many other industrial applications, the most prominent of which is probably in the recovery of gold in the mining industry, the demand for which far outstrips that of water treatment.

9.2 Manufacture

Several different raw materials are commonly used in the production of activated carbon; it can be produced from any carboniferous source but the most commonly used are wood, coal, shells such as coconut shells, and 'pips', e.g. peach pips. Each raw material imparts different properties to the carbon as will be discussed below.

Regardless of the starting raw material the production process for 'standard' water treatment activated carbons is similar and is represented in Figure 19.

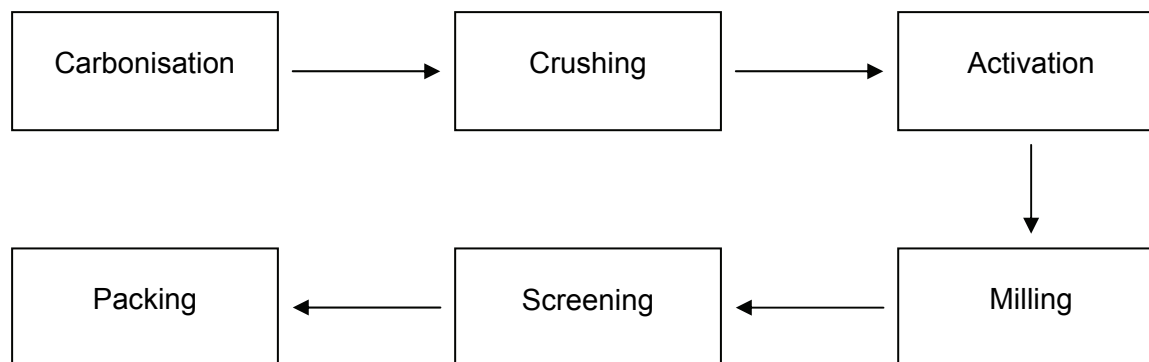


FIGURE 19: Schematic depicting the production process for 'standard' water treatment activated carbon

Carbonisation is the process of making charcoal in which the raw material is heated in an oxygen free atmosphere until it is all converted to carbon. The oxygen free atmosphere prevents ignition and simply reduces the raw material to what is commonly known as charcoal. Carbonisation or pyrolysis is generally carried out by heating the raw material to a temperature below 700°C in the absence of air to form a char. The material is then activated using oxidising gases such as steam, carbon dioxide, air and oxygen or using chemicals at temperatures of up to 1000°C (Sanks, 1978; Van Duuren, 1997). Activation can give rise to surface areas in excess of 2000 m²/g, although for potable water applications, activated carbon with a surface area in the region of 500 to 1500 m²/g is generally used. The physical properties of the carbon are dependent upon the raw material, as well as both the method and extent of activation used. In general, coconut tends to give rise to a dense structure containing only a few larger pores, while wood-based activated carbon has an open structure with many more, larger pores. The coal-based carbon usually has a structure somewhere between that of coconut and wood-based carbons (Greenbank, 1992). Experience has shown that coal-based and wood-based carbons are usually more effective for water treatment applications.

It is the high degree of porosity and the large surface area that accounts for the adsorptive properties of activated carbon and by changing the activating conditions, the size and number of pores can be controlled to produce a carbon suited to a particular application (Sanks, 1978). The pores in activated carbon are generally divided into two classes depending on size (Chemviron, 1974; Gregg and Sing, 1982; Sanks, 1978; Van Duuren, 1997).

- Micropores: <2 nm (i.e. <20 Å).
- Mesopores: between 2 and 50 nm (i.e. 20-500 Å).
- Macropores: >50 nm (i.e. >500 Å).

The micropores are responsible for most of the surface area providing activated carbon with its adsorptive properties, and in water grade carbons more than 70% of the available surface area is attributed to pores having a radius of less than 5 nm. Generally the external surface area of a typical water treatment PAC is insignificant compared to the surface area contained within the pores and therefore reducing the particle size, e.g. by grinding, will have a negligible effect on

the total surface area (Sanks, 1978). The same is true of GAC, and once ground the same tests used to assess PAC can be used to assess GAC as well.

As a general rule the smaller the pore, the more readily it will adsorb small molecules. Activated carbon made from coconut shells, for example, has a high percentage of micro pores and will therefore be efficient at removing small molecules like THM compounds. However, all activated carbons have a mixture of pore sizes and this mixture is called the pore size distribution.

9.3 Typical Properties

Before discussing the typical properties of activated carbons (described in Table 24 on page 96), some of the terms used to specify them need to be explained. Typically these terms are used to rate a carbon's ability to absorb molecules of different sizes and the most commonly quoted are described below.

9.3.1 Iodine Number

The iodine number gives an indication of the number of micro pores that a carbon possesses and is the most commonly quoted measure for water treatment applications. The iodine number is defined as the milligrams of iodine adsorbed by one gram of carbon when the iodine concentration is 0.02 N (American Society of Testing and Materials [ASTM] D4607). Although the iodine number is useful as a quality control parameter for comparing different production batches of activated carbon, its value is fairly limited in determining whether or not a PAC is suitable for a certain treatment objective. The problem with this test is that iodine is a small molecule that is well adsorbed and the test is conducted at high iodine concentrations, resulting in a loading that is much higher than that encountered in practice. For example, the iodine number specified for Chemviron Fitratorb 400 (a GAC) is 1050 mg/g which is equivalent to a weight loading of 105% w/w, while the typical loading achieved in most liquid phase applications is less than 20% w/w (Chemviron, 1998). Generally an iodine number of between 500 and 1000 would be expected for a water treatment carbon, with the most common range being around 600.

9.3.2 Methylene Blue Number

This test measures the capacity of an activated carbon to decolourise methylene blue and is also a measure of adsorption capacity. Two different types of methylene blue tests can be used, but whichever procedure is used the methylene blue number, like the iodine number, provides only an indication of the adsorption potential of the carbon and usually has only limited value in assessing the PAC in terms of operational performance.

9.3.3 Phenol Number

There are three different phenol number tests (for details see DIN 19603; ANSI-AWWA B600-96, 1996), but as with the iodine number and methylene blue number tests, it is difficult to translate the phenol number into plant performance. Not only is the loading of phenol during the

test much higher than for most contaminants that occur in water, but the phenol number value is also affected by pH.

9.3.4 Tannin Number

The tannin number test (AWWA B600-78, revised in ANSI/AWWA B600-90, 1991 and again in ANSI/AWWA B600-96, 1996) is defined as the concentration of activated carbon in milligrams per litre required to reduce the standard tannic acid concentration from 20 mg/l to 2 mg/l.

9.3.5 Molasses Number

As the name implies, this relates to a carbon's ability to adsorb molasses. Molasses is a large molecule representative of the colour molecules found in water, and a standardised test measures the reduction in colour of a standard molasses solution after contact with activated carbon. This is therefore a measure of the amount of large or macro pores in a carbon. The value is expressed as the 'molasses number' which is a factor of the percentage of colour removal. As with the other tests described above, it is not very effective in making accurate predictions regarding plant performance.

A major disadvantage with isotherm tests is that although they provide estimations and give an indication of whether a compound is adsorbable or not, they don't provide any design information, such as the required contact time. The isotherm tests described above are generally taken to equilibrium or are reacted for periods of time far greater than the contact time that the carbon has in typical water treatment and water reuse applications. This is one of the main reasons why these isotherm tests do not correlate well with full-scale operation. Most importantly, the total adsorbing capacity of a carbon gives no indication of the kinetics of the adsorption reaction, and since activated carbon generally has relatively short contact periods with the water (not more than 2 hours contact time when using PAC and perhaps only 10 to 20 minutes in the case of GAC), the rate of adsorption is critical. Generally the best way to evaluate a carbon is using laboratory simulation tests. For more information on these tests, refer Freese *et al.*, 2004 and to Linde *et al.*, 2003 regarding PAC evaluation.

9.3.6 Particle Size or Granulometry

There are specific guidelines defining PAC and GAC. Powdered activated carbon is defined by the ASTM as having a particle size of less than 0.177 mm which is equivalent to an 80 mesh sieve, while GAC are available in a variety of different particle sizes named, for example, 8 × 30 or 12 × 40. These numbers refer to sieve sizes, so that in the case of an 8 × 30 carbon, the particles will pass through a standard No. 8 mesh sieve but be retained on a 30 mesh sieve.

TABLE 24: Typical properties of activated carbons

	PAC	GAC
Raw Material	Wood or coal	Wood or coal
Appearance	Fine black powder	Black granule
Iodine Number	600-800	1000
Bulk Density	0.5	0.45
Moisture Content	5%	5%

9.3.7 Transportation and Storage

Activated carbon is generally packed in bags of 25 kg or 500 kg, but since it has a bulk density of around 0.5, a cubic metre of activated carbon weighs only 500 kg. There are no special hazards associated with its transport or storage, although PAC being a powder does pose a low explosion risk if the powdered carbon becomes airborne. All carbon dust is a respiratory irritant, so dust masks should be worn when handling activated carbon.

Activated carbon by nature adsorbs other chemicals and it is therefore important to store the product in unopened packaging in a dry environment. It is also important to avoid contact with other chemicals as this can also lead to fires. The stock and usage should be managed such that stock is turned over on a regular basis.

9.3.8. Use of Activated Carbon in Water Treatment

As mentioned earlier, activated carbon is used to remove organic contaminants from water, but it is also effective in the removal of chlorine from water and is used for this application by soft drink producers. In Southern Africa, PAC is used more often in water treatment applications than GAC, and it is used primarily for the removal of two taste and odour compounds, namely geosmin and 2-methylisoborneol (2-MIB). These compounds occur mainly due to the presence of two blue-green alga genera, *Microcystis* and *Anabaena*, that periodically proliferate during periods of hot weather in impoundments which have become enriched with nutrients (Wnorowski and Scott, 1992).

Both PAC and GAC can be used for the adsorption of contaminants present in water, but PAC is usually used for seasonal or sporadic incidents and GAC when activated carbon is required for extended periods of time.

Granular AC is generally more expensive than PAC treatment as construction of a GAC plant requires large capital outlay. However, GAC is more effective than PAC in removing organic compounds, partly because there is better contact between the water and GAC as the water is filtered through the GAC, and also because GAC is usually preceded by pre-treatment which reduces the load on the carbon. Despite this, PAC has a number of advantages over GAC, the main ones being the low capital cost of PAC and the ability to apply it only when it is needed (Najm *et al.*, 1990). This is particularly important in a country like South Africa where outbreaks of taste and odour compounds are usually seasonal and intermittent.

The advantage of GAC becomes evident when carbon addition is required over extended periods of time. PAC is not regenerated as a rule and therefore becomes very costly when used for long periods. It also provides a lower rate of organic removal than GAC, creates more sludge disposal problems and difficulties are often experienced in removing the PAC particles from the water (Sontheimer, 1976). Research conducted in this country has shown that if activated carbon is required for half the year or more, then GAC is more cost effective than PAC (Pryor and Freese, 2000).

Some of the advantages and disadvantages of the two product types are summarised in Table 25.

TABLE 25: Advantages and disadvantages of PAC and GAC

	Powder	Granular
Capital cost	Low	High
Product cost /kg	Relatively low	Relatively high
Product cost in use	Relatively high	Relatively low
Ability to 'stop-start'	Easy	Difficult
Efficiency	Good	Excellent
Need to regenerate	No	Yes

9.3.9 Using Powdered Carbon

From the discussions above, it is obvious that PAC is ideal for periodic or seasonal problems. Powdered activated carbon is prepared as a suspension in water and dosed using a conventional dosing pump. The strength of the suspension is not critical, but usually the suspension is around 10% m/v . The preparation seems fairly straightforward, but is, in practice, a little more complicated. Powdered activated carbon contains significant amounts of carbon dust and therefore the packaging needs to be opened under controlled conditions to avoid the dust from becoming airborne. Not only will the airborne dust pose a health hazard, but as mentioned previously there is a potential risk of a dust explosion if the critical concentration in air is reached and there is a source of ignition. As a result, although PAC is better suited to temporary or *ad hoc* usage, it is advisable to invest in an automatic or semi automatic make-up system. Such systems allow for the bag to be opened inside a closed cabinet containing a dust extraction system, and for the carbon to be added directly to the water whilst still in a dust controlled environment.

The decision regarding the point and rate of addition of PAC is based on a number of factors. The PAC needs to be added before the final flocculation stage since flocculation and sedimentation are needed to remove the carbon once it has done its work. On the other hand, it is wasteful to dose PAC at a point where it will adsorb compounds that would otherwise have been removed in the treatment process without the addition of PAC. Some plants have a primary and secondary flocculation and settling/flotation processes, e.g. a dissolved air flotation unit followed by a sedimentation unit. Under these circumstances the ideal point of addition is between the two stages. However, PAC can be added to the water at a number of sites,

although it is usually added at the influent or the rapid mix section. Powdered activated carbon can also be added to the flocculation basin influent or at the filter influent (Water Quality and Treatment, 1990). Plants using PAC doses of up to 50 mg/l can be found in the literature (Water Quality and Treatment, 1990), but not all plants can tolerate such high doses. Depending on the treatment train, coagulant dose and other factors, the amount of PAC which can be dosed on a plant may be less than half this before carryover from the clarifiers occurs.

The rate of adsorption of organics by carbon is relatively fast and therefore long contact times are not usually required. However, it should be established that the adsorption rate of the PAC being used is sufficiently rapid for the retention times experienced on the plant, otherwise the PAC will be ineffectively utilised.

Selection of the PAC dose rate is also very important, but accurate measurement of the concentration of taste and odour compounds, or whatever organic contaminants are being removed, requires highly specialised techniques, expensive equipment and skilled analytical staff, and these are often not available to the plant operating staff. For this reason, the PAC dose is generally set empirically, based on the minimum PAC dose at which the problem is resolved. For example, in the case of taste and odour problems the PAC dose is adjusted until there is no longer a detectable taste or odour to the water. Many plants will start at a predetermined dose, e.g. 20 mg/l, and then reduce this to a point where the PAC dose is at the lowest concentration that still removes all detectable taste and odour from the water.

9.3.10 Using Granular Carbon

Although PAC and GAC are used for the same reason, namely the removal of organic contaminants, the way in which they are applied is completely different. Granular activated carbon is always used in some sort of fixed filter bed. This may be a specially designed activated carbon filter or it may be an additional layer of carbon applied on top of a sand filter. The latter concept provides a relatively easy way to introduce carbon to a plant that was not originally designed for its use. It is important, though, that careful consideration is given to the dimensions and backwashing conditions, because since carbon is a lighter material than sand it can easily overflow out of a filter that does not have sufficient head space to retain it.

The design and sizing of a granular carbon filter involves both scientific and engineering expertise and in order to understand the concepts, the way in which carbon works needs to be considered. When the water first comes into contact with the carbon, adsorption of the organic compounds present in the water starts to occur. The percentage of the total organics removed at the first contact will depend on factors such as

- The granulometry (and hence surface area) of the carbon.
- The total amount of organics present.
- The pore size distribution of the carbon relative to the target molecules.
- The flow rate of the water.

The organics not removed at the first interface will carry on through the carbon bed and be continuously removed on a percentage reduction basis. If the filter is correctly sized, the organic contaminant concentration of the final water will be at an acceptable concentration. Eventually the carbon at the start of the filter will become fully loaded and water passing through it will not show any reduction. This interface of fully used carbon will pass through the filter bed until eventually the last carbon to come into contact with the water is also fully exhausted and the water passes through the carbon with no change in its organic content. This point is called the breakthrough point, and it occurs when the carbon's capacity to adsorb the target compounds is completely exhausted. This point is important in determining the size and flow rate characteristics of a carbon filter. Traditionally these characteristics are measured using isotherms (the Freundlich isotherm is the most common) and the information obtained from these is used to calculate the design criteria of a filter.

Once all the carbon has been exhausted it has to be removed from the filter and taken to a specialist facility for regeneration (the regeneration process is only applicable to GAC and not PAC, which is removed from the plant as part of the sludge on a continuous basis). The regeneration process involves filling a kiln with the carbon and heating it to temperatures around 600-800°C. There are a number of different designs for kilns, but the purpose of them all is to vaporise the pollutants that have been adsorbed onto the carbon, while at the same time limiting the amount of mechanical damage to the carbon.

Carbon can be regenerated several times in this way before it has to be discarded, and each time it is regenerated some of the carbon is lost and needs to be replaced with fresh carbon. Therefore there is always a percentage of new carbon in the bulk of the regenerated material.

Regeneration is an expensive procedure, especially if the regeneration facility is remote from the point of use. As a result the cost of regeneration must always be taken into consideration when comparing the use of powder and granular carbons.

9.3.11 Biological Activated Carbon

Before leaving the topic of carbon, mention should be made of Biological Activated Carbon (BAC). Whereas PAC and GAC refer specifically to the physical form of the carbon, BAC refers more to a particular process and actually involves the use of GAC.

Because carbon is so porous, it can easily act as a substrate on which bacteria and other micro-organisms can grow, and carbons used for BAC are granular carbons developed specifically to encourage this biological growth. They are used like conventional GAC in a fixed filter but the structure and pore size distribution is tailored specifically to a size and surface structure that will provide an ideal substrate for biological growth. This is especially important during backwashing, since the carbon needs to provide a suitable substrate for micro-organism attachment in order to minimise the loss of microbial organisms during the backwashing process.

Biological activated carbon systems are always designed as part of a process of which the first stage is ozonation. This process has been used primarily in Europe where organics contamination of surface waters with chemicals such as pesticides and phenols is more predominant. A problem which is often experienced when using GAC filtration is that pre-loading of background organic matter affects adsorption of the target organic contaminants. Background organic matter refers to all the organic matter present in the water other than the target organic pollutants. This background organic matter is usually present in much higher concentrations than the target pollutants and tends to adsorb onto the GAC before the target compounds such as pesticides, phenols or taste and odour compounds (Orlandini *et al.*, 1997). This results in more frequent regeneration of the GAC, which is both costly and time consuming (Hubele, 1986). Intermediate ozonation prior to GAC filters can be expected to lower background organic matter pre-loading on GAC by increasing the concentration of biodegradable organics, thereby allowing a larger proportion of the organics to be removed by biodegradation. As mentioned in Chapter 8, Section 8.5.4, ozonation of organic compounds breaks them down into smaller, more readily biodegradable compounds.

Whilst some carbons are actively developed with characteristics that favour microbiological growth there have also been examples of conventional granular carbon filters that have not been regularly maintained and regenerated, effectively developing into BAC filter beds.

The advantage of the BAC filter is that the carbon does not need to be regenerated as frequently, or possibly not at all, and this can be a significant cost saving. The filter does require regular backwashing, however, to prevent it from becoming clogged, but apart from this, can provide an attractive alternative to conventional GAC filtration.

CHAPTER 10

MISCELLANEOUS CHEMICALS FOR WATER AND WASTEWATER TREATMENT

In this chapter some of the chemicals that are used on a limited scale in water and wastewater treatment are discussed. Generally these chemicals are not used as widely as those discussed in the previous chapters of the guide, but are used for niche applications. Some basic information is provided here.

10.1 Copper Sulphate

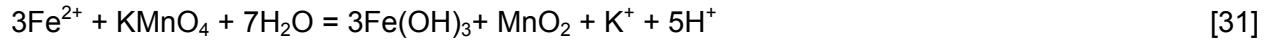
Copper sulphate is available as a blue material of a glassy, crystalline appearance. It has the chemical formula CuSO_4 and the molecular weight is 159.5 (i.e. $63.5 + 32 + (4 \times 16) = 159.5$). Copper is a microbicide and so is sometimes added to water to prevent the growth of algae. However, the use of copper sulphate must be carefully controlled as overdosing can cause poisoning of fish and other aquatic creatures. Normally dosages of 0.06 mg/l to 0.25 mg/l are sufficient for preventing the growth of algae. The toxicity of copper to fish is dependent on the total alkalinity of the water; the lower the alkalinity, the greater the toxic effect, so it is important that this be taken into consideration when using copper sulphate. It is not advisable to use copper sulphate in waters of very low total alkalinity, and in all cases its use should be supervised and recommended by qualified personnel. However, copper sulphate is an extremely fast acting and effective means of controlling algae in ponds and reservoirs.

When applying copper sulphate the objective is to treat the surface water, and this is best done by making a solution of about 5% and then applying by spraying either from a boat or a shore based system depending on the size of the impoundment or reservoir.

10.2 Potassium Permanganate

Potassium permanganate is supplied as a dark purple, glassy crystal having the formula KMnO_4 . The molecular weight is 158 (i.e. $39 + 55 + (4 \times 16) = 158$) and it is not very soluble in water (5-30 g/l at 20°C with contact times of 15 to 60 minutes), producing a dark pink solution when dissolved. It attacks ferrous metals and is generally used with protected steels and plastics and must be handled with care (wear goggles and gloves).

Potassium permanganate is sold in small quantities as an antiseptic under the name Gentian Violet and it is a strong oxidising agent. Its most common use in water treatment, perhaps paradoxically, is to remove manganese and iron (see also Chapter 3, Section 3.1.1). Permanganate will oxidise iron and manganese to convert soluble ferrous (2+) iron into the insoluble ferric (3+) state and soluble Mn^{2+} to the insoluble Mn^{4+} state. The oxidised forms will precipitate as ferric hydroxide and manganese hydroxide according to the reactions shown in Equations [31] and [32] (Degremont, 1991).



The theoretical potassium permanganate dose required for iron removal is 0.94 mg/mg of iron and 1.92 mg/mg of manganese although in practice it has been found that the required dose is generally below the theoretical. It is important to use the correct dose, since overdosing with permanganate will cause a pink colour in the final water. The reaction varies with the pH. Generally a pH of between 7.2 and 7.3 with a contact time of less than five minutes is ideal, but if the concentration of organic contaminants in the water is high and the permanganate becomes combined with organic matter, the reaction time will become much longer and then it may be necessary to increase the pH to above 8.5 to accelerate the reaction (Degremont, 1991).

Potassium permanganate is also used to remove taste and odour causing compounds. The required dose is anywhere between 0.25 and 20 mg/l , and whereas with iron and manganese removal the required dose can be calculated fairly accurately, this is not the case when using permanganate for taste and odour removal so extra care has to be taken to ensure that overdosing, and the resulting pink water does not occur.

For water treatment applications, the permanganate crystals are usually dissolved in water to produce a solution of about 3-5% strength which can then be dosed using a conventional dosing pump. Like ferric salts, potassium permanganate will stain everything with which it comes into contact and this fact should be considered when designing dosing installations.

Potassium permanganate is an expensive material and is not manufactured in South Africa. Furthermore it is known to be used in the production of certain banned substances so special import permits are required. These factors combine to make permanganate an expensive option for manganese removal.

10.3 Bentonite

Bentonite and kaolin are naturally occurring clays, which are added to water when the turbidity of the raw water is so low that adequately weighted flocs cannot be produced. Bentonite is the more frequently used, although the effects of both are similar. Bentonite used in water treatment is generally 'activated bentonite', which is bentonite clay that has been treated with a strong acid. The acid leaches out iron and aluminium from the bentonite structure leaving a porous particle structure not unlike a poor grade of activated carbon. Both sodium and calcium activated bentonites have use in industry, but the sodium bentonite has greater swelling properties in water and is therefore favoured for water treatment.

Generally, bentonite is added to the raw water prior to the addition of the coagulant so that it adds weight to the resulting floc and also acts as a seed for floc formation. Dosages of bentonite are often quite low being of the order of 1 to 5 mg/l. Bentonite can be added using dry screw feeders, but because of the time delay that occurs in adequately hydrating the bentonite, it is more usual to prepare an approximately 5% suspension (50 g/L) and to add this by means of positive displacement dosage pumps. Bentonite does not modify the pH or the chemical characteristics of the water apart from providing additional weight to the floc which is formed.

10.3.1 Sodium Fluoride

Sodium fluoride has the chemical formula NaF and the molecular weight is 42 (i.e. $23 + 19 = 42$) and as can be easily calculated, the percentage fluoride in sodium fluoride is $19/42$ or 45.2%. The solubility of sodium fluoride in water is 4%.

Sodium fluoride is widely used as a fluoridation additive in small drinking water plants but the handling and mechanical requirements of accurately preparing the solution make it less suitable for large scale operations.

10.3.2 Sodium Fluorosilicate

Sodium fluorosilicate is a solid material having the formula Na_2SiF_6 and the molecular weight of 188 ($(2 \times 23) + 28 + (6 \times 19) = 188$) and therefore the percentage fluoride contained in this chemical is 60.6%, so greater than that of sodium fluoride.

The advantage of sodium fluorosilicate is that it is generally a cheaper source of fluoride than sodium fluoride; but it is considerably less soluble, having a solubility in water of only 0.76%.

10.3.3 Fluorosilicic Acid

Fluorosilicic acid is the only chemical used for fluoridation that is supplied in liquid form. It has the formula H_2SiF_6 giving it a molecular weight of 144 ($(1 \times 2) + 28 + (19 \times 6) = 144$) and the percentage fluoride in this compound is therefore 79%. It is a very corrosive material and requires strictly controlled handling and dosing facilities, but if properly managed it provides an easy way to dose and control fluoride levels. Fluorosilicic acid has a very low pH and can negatively affect the pH of very soft waters. In such circumstances, the effect it will have on the pH of the water needs to be assessed to determine whether it will be a suitable chemical for use in fluoridation.

10.4 Sodium Aluminate

Sodium aluminate has the formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and is an alkaline form of soluble aluminium. Sodium aluminate is a coagulant in its own right and on certain types of water produces good results when used as a coagulant, rather than as a coagulant aid. The sodium aluminate reacts with the bicarbonate or carbon dioxide in the water to give an aluminium

hydroxide floc which coagulates in the normal way. Its use is preferred in waters that coagulate better at relatively high pH values although this is not always the case.

Sodium aluminate is also used as a floc aid, under certain circumstances the addition of sodium aluminate together with aluminium sulphate produces large flocs that coagulate and settle well. Sodium aluminate is available as a commercial reagent containing approximately 50% Al_2O_3 and is dosed at concentrations ranging from approximately 5 to 50 mg/l depending on the application. The higher dosages are generally employed when it is used on its own and lower dosages when used in combination with aluminium sulphate. Unlike nearly all other coagulants, sodium aluminate increases the pH of the water as it contains free alkalinity. The use of aluminium sulphate and sodium aluminate in combination can therefore be used where the pH of the water needs to be held reasonably constant.

10.5 Activated Silica

Activated Silica is a floc aid that increases the weight and size of flocs formed after the addition of the coagulant. It is prepared by acidification of sodium silicate which has the formula $\text{SiO}_2 \cdot \text{Na}_2\text{O}$. Sodium silicate is supplied as a viscous solution with a specific gravity of between 1.35 and 1.4 at a concentration of 24 to 28%. Preparation of activated silica involves several stages, these being acidification of the concentrated sodium silicate solution, ageing for a definite time and dilution of the resulting solution. Suitable acids for acidification and neutralization of part of the alkalinity are sulphuric acid, hydrochloric acid, aluminium sulphate, sodium bicarbonate and hypochlorous acid (aqueous chlorine). The supplier of the sodium silicate solution, frequently states the conditions for acidification, ageing and dilution. For laboratory purposes, approximately 31 ml of 29% sodium silicate solution can be diluted to 1 l to yield a 1.25% SiO_2 solution. Eighty millilitres of this solution, when added to a 100 ml volumetric flask, acidified with HCl to lower the pH to 5 and diluted to 100 ml gives a 1.0% SiO_2 solution which should be aged or activated for 30 minutes before being used directly as a coagulant aid. The dosage of activated silica when used under normal practice as a coagulant aid on a plant is usually within the range of 0.5 to 4.0 mg/l as SiO_2 .

10.6 Fluoridation Chemicals

The debate around fluoridation of water supplies to improve dental health has continued in South Africa for many years, but in spite of a rigorous campaign by its supporters it has not yet become mandatory. It is generally considered that a small quantity of fluorine or fluoride in drinking water (0.4 to 0.8 mg/l) promotes the formation of dental enamel and protects teeth against decay (caries). However, too much fluoride leads to the destruction of the enamel and results in fluorosis, a condition characterised by dental malformation, stained tooth enamel, decalcification of bone structure, mineralisation of tendons, digestive and nervous disorders, etc. These conditions occur in different people at very different levels of fluoride content. In general however, water containing more than 1.5 mg/l of fluoride should be rejected or treated.

Fluoridation of a water supply comprises the addition of fluoride to water and has the approval of the WHO and is practiced mainly in the USA, although cases are also quoted in Europe, Australia and South America. The process is not yet generally applied because it is not seen as being free from risk and has aroused much opposition in certain quarters.

Chemicals suitable for fluoridation are not readily available in South Africa, so these would have to be imported, although locally manufactured material may become available if there was sufficient demand.

Fluoride is introduced into the water by the dosing of a fluoride salt at a rate that gives a total fluoride concentration of 0.4 to 0.7 mg/l. Care needs to be taken to prevent overdosing, since as indicated above, the effects of overdosing have serious health implications. The equipment used should be failsafe and should involve the use of day tanks where limited quantities of the fluoride material are transferred from the main storage tanks per day. This limits the amount of fluoride that can be added to the water in a particular period of time and is an aid to preventing over dosage. The dosage pumps should also be sized so that they normally run at close to capacity thus eliminating the possibility of setting them too high and severely overdosing the water. Fluoride chemicals are highly toxic and care is required in its handling and dosage.

The point of addition of the fluoride is not critical as it will be in solution and is not susceptible to removal in the coagulation and flocculation processes at the concentrations of chemicals normally used. It would be preferable to add it at a point where it mixes in well and any pH effects can be corrected.

The most widely used chemicals for fluoridation are:

- Sodium hexafluorosilicate (Na_2SiF_6) is the most common.
- Hexafluorosilicic acid (H_2SiF_6) or one of its salts (e.g. sodium fluorosilicate).
- Sodium fluoride (NaF).

Fluoride chemicals are intrinsically very dangerous chemicals and the acid hydrofluoric acid is one of the most corrosive and dangerous chemicals in use. Application of hydrofluoric acid is theoretically possible, but its extreme corrosivity renders it almost impossible to handle safely. The choice of fluoride chemical should account for factors such as the quantity that needs to be distributed and what is economically available in the particular market. The use of the salts minimises this danger but careful control of the conditions under which these chemicals are used is extremely important.

APPENDIX

USEFUL CALCULATIONS AND EXPLANATIONS

11.1 Specific Gravity, Bulk Density, Density, Concentration and Tank Capacities

The terms SG, bulk density and density are used to describe 'density' in different materials:

- Specific Gravity is used for liquids (the SG is also known as the Relative Density).
- Bulk density is used for solid materials that are in a powdered, granular or some sort of particulate form.
- Density is used for solid materials like wood, metal, etc.

The SG of a liquid is the weight in grams of one millilitre (mℓ) of a liquid (this is of course the same as the weight in kilograms of one litre of the liquid). The SG of water is 1g/mℓ at 25°C and the importance of this will become apparent as we discuss concentrations below. For the sake of comparison, the SG of a solution of ferric chloride solution containing around 43% FeCl₃ is about 1.45 and the SG of an aluminium sulphate solution containing around 48% Al₂(SO₄)₃·18H₂O is about 1.33. The SG of polyelectrolytes like polyamine and polyDADMAC are around 1.15.

The bulk density of a material, e.g. polyacrylamide or activated carbon, is the weight of a specified volume of the material. This is usually expressed in terms of kilograms per cubic metre. Thus a cubic meter of polyacrylamide powder weighs about 700 kilograms and a cubic metre of powder carbon about 500 kilograms.

Knowledge of the SG or bulk density of a material is important for a number of reasons. Dosing pumps, for example, dose volumes not weights and their output is expressed in millilitres or litres per minute, so when measuring the output of a pump using a calibration tube, it is the volume output which is being determined. However, when discussing chemical dosages, the dose is expressed as mg/ℓ (also referred to as parts per million, or ppm) or kg/Mℓ. As mentioned above, the SG of water is one (at 25°C, although it is accurate enough to use an SG of one for the range of temperatures usually encountered in water and wastewater treatment), so 1 mℓ water weighs 1 g. Therefore if 1 mℓ water is added to 1 ℓ (1 ℓ contains one thousand milliliters), the result is 1 g/ℓ or 1000 mg/ℓ (i.e. one thousand parts per million regardless of whether weight or volume is used).

However, if 1 mℓ ferric chloride solution (SG 1.45) is added to a litre of water, 1.45 g of solution have been added to the water (i.e. 1 450 mg/ℓ or 1 450 ppm), although in terms of volume, the addition was 1 mℓ/ℓ. It is for this reason that the term mg/ℓ is more commonly used as it avoids any confusion.

In considering the output of a pump, having measured this in volume, it must then be converted back to mass. This is done by multiplying the volume by the relevant SG, since:

Mass = Density × Volume

Of course in the case of products where the SG is close to 1 the difference is going to be small, but in the case of heavier materials like iron salts and sodium hypochlorite, the difference can be significant.

A pump that is delivering 100 ml/min of ferric chloride (43% as FeCl₃) is delivering 145 g solution per minute. Therefore if, for example, a dose of 15 mg/l ferric chloride solution was required, for a plant with a raw water inflow of 6 Ml/d, the ferric chloride solution required would be:

$$15 \times 6 = 90 \text{ kg/d}$$

The SG of the solution is 1.45, and therefore $90 \text{ kg} \equiv 90 \div 1.45 = 62.1 \text{ l/d}$

$$62.1 \text{ l/d} = 62.1 \div 24 \text{ l/h} = 2.59 \text{ l/h} = 2.59 \div 60 \text{ l/min} = 0.043 \text{ l/min} = 43.1 \text{ ml/min.}$$

The pump output would need to be $(100 \div 145) \times 15 = 10.34 \text{ ml/min}$ ($10.34 \text{ l} \times 15 \text{ l}$). (The pump would be set at 43.1% to provide the correct volume of ferric chloride solution for a dose of 15 mg/l for a flow rate of 6 Ml/d.)

However, if the dose required is for example 15 mg/l ferric chloride and not 15 mg/l ferric chloride solution, the percentage ferric chloride contained in the solution would need to be taken into account. For a 43% ferric chloride solution, as ferric chloride dose of 15 mg/l is equivalent to $15 \div 0.43 = 34.9 \text{ mg/l}$ solution. Therefore for a plant with a raw water inflow of 6 Ml/d, the dose required would be:

$$34.9 \times 6 = 209.3 \text{ kg/d}$$

The SG of the solution is 1.45, and therefore $209.3 \text{ kg} \equiv 209.3 \div 1.45 = 144.3 \text{ l/d}$

$$144.3 \text{ l/d} = 144.3 \div 24 \text{ l/h} = 6.0 \text{ l/h} = 6.0 \div 60 \text{ l/min} = 0.100 \div 145 \times 15 = 10.34 \text{ ml/min}$$

($10.34 \text{ ml} \times 15 \text{ ml}$).

Therefore, the pump would need to be set at 100% to provide the correct volume of 43% ferric chloride solution for a dose of 15 mg/l as ferric chloride for a flow rate of 6 Ml/d.

Apart from dosing considerations SG is also important when considering delivery and storage tank capacities. Tank sizes are normally quoted in cubic meters, which in terms of water capacity is the same as mass, i.e. a 10 000 litre tank will also hold 10 000 kg of water. However, if the tank is to be used for products with a high SG, such as caustic soda, which has a SG of 1.5, then when the tank is full of caustic soda, the weight contained in the tank will actually be $1.5 \times 10\,000 \text{ kg}$ which is 15 000 kg – a full 5 000 kg or five tons more. It is therefore important that the tank is specified to hold 15 000 kg and not 10 000 l. In addition a normal 20 ton tank of

this solution will actually carry a load of 20 000 litres but needs to be able to support 22 250 kg, so the nominally 20 m³ tanker that is used to deliver the product will actually be carrying 30 tons of product if fully loaded, in which case it may be in contravention of road legislation.

Finally on this topic, it is important to understand the difference in the concentrations of products when they are quoted as containing a certain percentage active ingredient. For example the concentration of sodium hypochlorite is generally quoted in terms of percentage available chlorine. In the case of a solution with a SG of around 1, it is irrelevant whether the percentage is measured in terms of mass per volume or mass per mass. However, with a solution such as sodium hypochlorite, which typically has a SG of around 1.2, it is important that it is specified whether the percentage available chlorine is m/v or m/m.

For example, if a hypochlorite solution is specified as being 15% m/v, it means that the solution contains 150 g/l chlorine. However, the SG of this solution is 1.2, so 1 l actually weighs 1 200 g. This means that if we express the 150g/l chlorine as a percentage of the mass, we get:

$$(150 \div 1\,200 \times 100)\% = 12.5\% \text{ m/m}$$

The use of m/v or m/m is common with sodium hypochlorite, sodium hydroxide, ferric chloride and ferric sulphate and although both terms are acceptable, it is important to understand the difference in the terminology if the correct dose and pump delivery rate are to be calculated.

11.1.1 From Milligrams to Megalitres

When discussing dose rates and plant flow rates there are a number of ways in which they can be expressed. Plant flow rates are often quoted in litres per second, litres per minute, cubic metres per hour and megalitres per day. Fortunately the metric system makes conversion from one to the other very simple.

$$1\,000 \text{ ml} = 1 \text{ l}$$

$$1\,000 \text{ l} = 1 \text{ m}^3$$

$$1\,000 \text{ m}^3 = 1\,000\,000 \text{ litres} = 1 \text{ Ml}$$

$$1\,000 \text{ kg water} = 1\,000 \text{ l water} = 1 \text{ m}^3 \text{ water}$$

Some examples:

1. From cubic metres per hour to megalitres per day

$$45 \text{ m}^3/\text{h} \equiv 45 \times 24 = 1\,080 \text{ m}^3/\text{d}$$

$$1\,080 \text{ m}^3/\text{d} \equiv 1\,080\,000 \text{ l}/\text{d} \equiv 1.08 \text{ Ml}/\text{d}$$

2. From litres per minute to cubic meters per day to megalitres per day

$$2\,500 \text{ l}/\text{min} \equiv 2\,500 \times 60 = 150\,000 \text{ l}/\text{h}$$

$$150\,000 \text{ l}/\text{h} \equiv 150\,000 \times 24 = 3\,600\,000 \text{ l}/\text{d}$$

$$3\,600\,000 \text{ l/d} \equiv 3\,600 \text{ m}^3/\text{d} \equiv 3.6 \text{ Ml/d}$$

It is also useful to note the connection between mg/l and kg/Ml because laboratory tests used to determine dosage rates are usually carried out using units of mg/l, while the amount of product that will be used on the plant is normally expressed in terms of kg/Ml. Since a milligram is one millionth of a kilogram and a litre is a millionth of a megalitre, mg/l \equiv kg/Ml.

Therefore, a 20 Ml/d plant that requires a dose of 7 mg/l will consume 140 kg (i.e. 7 \times 20 kg) of chemical per day.

11.1.2 Calculating tank capacities

11.1.2.1 Cylindrical Tank

The formula for calculating the capacity of a cylindrical tank is:

$$\pi r^2 h$$

Where:

$$\pi = 3.143$$

r = the radius of the tank

h = the height of the tank

The radius is half the diameter and for practical purposes it may be easier to estimate the diameter. Therefore, a cylindrical tank with a diameter of 2.5 m and a height of 4 m will have a capacity of:

$$3.143 \times 1.25 \times 1.25 \times 4 \text{ m} = 19.644 \text{ m}^3 \text{ or } 19.644 \text{ l.}$$

If this tank is filled with water, it will hold 19 644 kg, but if it is filled with a polymer which has a SG of 1.15, the tank will need to hold a weight of 22 590 kg (19 644 \times 1.15).

11.1.2.1 Rectangular Tank

The formula for calculating the capacity of a rectangular tank is:

$$l \times b \times h$$

Where:

l = length

b = breadth

h = height

A tank with a length of 2 m, breadth of 2 m and height of 1.5 m will have a capacity of:

$$2 \times 2 \times 1.5 = 6 \text{ m}^3 \text{ or } 6\,000 \text{ l}$$

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