TREATMENT AND CORROSION

CONTROL OF COOLING WATER

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Technical Note 5

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TREATMENT AND CORROSION CONTROL OF COOLING WATER

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SECTION 1

COOLING WATER TREATMENT

INTRODUCTION

This document is based on the practical experience of chemical engineers working in the field in the main industrial centres in the United Kingdom, from small factory units with cooling systems of a few cubic metres, to large industrial complexes circulating millions of cubic metres of water per day.

For those who want a more detailed account of cooling water treatment techniques a reading list is given in Appendix 11.

It is expected that public water supply demand will reach 45 million cubic metres per day in the year 2005 and industrial needs will approach 400 million cubic metres per day. Much of this is already being recovered in re-circulation cooling systems. Some examples of industrial water requirements are:-

Industry Water Requirement

Electric Power 0.06 cubic metre per MJ (0.2 cubic metre per kilowatt hour)
Steel 180 cubic metre per tonne
Oil 30 cubic metre per tonne

More and more industry will be forced to use re-circulation cooling for such purposes as:-

Refrigeration Plant
Compressor Cooling
Engine Cooling
Furnace Cooling
Moulding Machinery Cooling
Distillation Processes
Condenser Cooling
Air Conditioning Plant
Fume Washing and Cooling
Chemical Processes
Food Production

Cooling in an open re-circulating system is mainly effected by evaporation in the tower. For every 6ºC decrease in temperature across the tower, approximately 1% of the circulation water will be evaporated, thus increasing the dissolved solids content of water in the system.

Water is circulated round the cooling system, through the process heat exchangers. Water is lost from the system by evaporation, by windage or drift (which includes spray carried over from the cooling tower), by leaks in the system and by purge to control concentration. Leaks from the process into the cooling system can also occur upsetting the chemical balance. For example, there may be leaks of ammonia, caustic soda or acid into the cooling water, as well as contamination from the atmosphere. It is important to monitor the cooling water. Very often the only indication the Plant Manager has of a process leak is from the cooling water.

The problems met with in cooling water systems are dealt with fully in subsequent sections.

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SECTION 2

CONTROL OF CORROSION, AND CHEMICAL ATTACK

2.1 Introduction

Corrosion of various parts of a cooling system may result if treatment is absent or inadequate and may lead to expensive replacement. Product contamination may also occur due to leakage of cooling water into the process stream.

While corrosion may be found in one part of the system, scaling and timber attack may exist elsewhere using the same cooling water. Therefore any proposed water treatment must take into account all the chemical and physical processes occurring in the system, and may have to be a compromise, bearing mind the economic factors.

In neutral and alkaline waters corrosion can occur because there are breaks in the protective oxide film on the metal surface, which permits a difference in potential to arise between the bare metal and the film, resulting in electro-chemical dissolution of the metal. The presence of oxygen facilitates this process, and any corrosive effect is therefore intensified by the re-aeration of cooling water during circulation through the cooling towers and storage tanks open to the atmosphere.

The chief causes of corrosion of metals by water are dissolved oxygen and dissolved carbon dioxide. The latter lowers the pH, permitting general acid attack but even if the water is alkaline the metal of the system can be affected by oxygen corrosion. Corrosion may take several forms, e.g. general wastage or pitting. In evaporative cooling water systems the water continually passes over the cooling tower where it becomes saturated with oxygen. It is impracticable and uneconomical to remove the oxygen from the cooling system water by the use of an oxygen scavenger so other methods of corrosion control must be used.

Corrosion inhibitors may be used in cooling systems to modify the electro-chemical process and control the corrosion. Natural scale formation due to hardness salts may also affect the electro-chemical process and provide a degree of corrosion control (see Appendix 3). The function of the corrosion inhibitor may be to provide an obstructive film at either the anode (resisting the entry of metal ions into solution), or the cathode (hindering the removal of electrons by ions in solution). For a fuller description of the mechanism of corrosion and corrosion control see Appendix 3.

2.2 Chemical Factors

Corrosion occurs when the metal reacts with other materials with which it is in contact, with resultant damage to and loss of the metal. The metal may go into solution and may subsequently precipitate as a corrosion product.

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The main chemical factors which influence the tendency of cooling water to corrode are mineral salt content, pH value and dissolved gases, notably oxygen and carbon dioxide. Gases including sulphur dioxide and ammonia, chlorine etc., may contaminate the system being either airborne or from the process itself. For example, a cooling tower downwind of a boilerhouse using heavy fuel oil would certainly be subject to a varying and low pH due to sulphur dioxide in the flue gases; a leaking ammonia condenser would contaminate the water circulation in its condenser system.

Other conditions which may modify the local environment of the metal surface are deposits of corrosion products, scale, and biological slimes.

2.3. **Physical Factors**

The main physical factors contributing to corrosion are temperature, dissimilar metals and suspended solids.

Temperature plays an important role in corrosion in that the speed of most chemical reactions increase with increasing temperature; thus corrosion in a corrosive environment can be expected to be most severe where temperatures are highest, for example at the hot surfaces of a heat exchanger.

Corrosion may occur because of the proximity of dissimilar metals, either by direct galvanic action between these metals, or the dissolution of one metal and subsequent plating out in other parts of the system. Dissimilar metals are hard to avoid in a system of any size or complexity. The factors involved include electrical conductivity of the circulating water, relative areas and location of the metals, and their position in the galvanic series (see appendix).

Suspended solids can deposit in pipelines and heat exchange equipment and produce areas isolated from the general environment. This encourages corrosion by permitting differential aeration. Unfortunately, the water velocity, particularly in heat exchangers and similar equipment, is usually lower than is necessary to avoid settling. It may be necessary to clean a cooling system chemically to remove mill scale and debris.

Chemical cleaning does not itself confer protection, therefore where a corrosive environment is indicated, a protective program must be implemented immediately after the clean.

2.4 **Biological Factors**

Reference to sulphate reducing bacteria is made under "Control of Microbiological Fouling". These bacteria together with sulphates, are present in most waters and if oxygen is depleted locally, e.g. beneath corrosion deposits, are able to reduce sulphates to sulphides.

Corrosion from this source may be of the pitting type, the pits being filled with soft, foul-smelling sulphides. The microbiologist can identify the bacteria from samples of water and corrosion products.

In estuaries and harbours where water is polluted with organic matter, depletion of oxygen may also occur, allowing these bacteria to become active.

In closed cooling systems where oxygen is always likely to be depleted a small amount of bactericide will prevent corrosion from this source.

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2.5 **Methods of Prevention and Control**

Corrosion may be controlled in a cooling system by adopting one or more of the following techniques:-

Suitable materials of construction
Controlled scaling
Use of inhibitors
Cathodic protection
Biological control (see Section 4)

Controlled scaling can be effected using the Langelier Index or Ryznar Equation (see Appendix 7). In broad terms these formulæ define the conditions under which a protective calcium carbonate film may be maintained. Unfortunately they are only an indication and it must be realised that because of the many factors involved, corrosive conditions may occur in one part of the system and scale may deposit in another. Because of the many complications it is common to employ an inhibitor to supplement the corrosion protection conferred by controlled scaling. Allowances must be made for the fouling factor of the equipment (Appendix 4).

Inhibitors have the function of modifying reactions at the metal surfaces. Corrosion inhibitors can be justified only in terms of cost effectiveness, but toxicity and pollution aspects must be taken into account. There is a wide range of inhibitors available (see Appendix 5).

In the cathodic protection of immersed metals, the tendency of the metal to go into solution (corrode) at the anode is opposed by the application of a counter potential or opposite EMF. This can be derived either from an external source such as a battery or rectifier, or from the electrons liberated by a readily corrodable (sacrificial) metal such as zinc or magnesium. The degree of protection is proportional to the applied current density (amps per square centimetre) up to that required for complete protection.

Properly applied, cathodic protection has the effect of considerably upgrading the corrosion resistance of metals and alloys. Protection is positive but only where the current is applied.

Resistant metals such as stainless steel and cupro nickel are normally too expensive to incorporate into an entire water cooling system, but may be used for components including for example heat exchangers. Protective coatings are now available for mild steel and if properly applied can be very successful. Plastics too are now used extensively, particularly for tower packing. The use of plastic piping may also be considered.

2.6 **Control Testing**

Regular control testing is an essential part of any programme designed to prevent scale and corrosion, and the frequency and type of test must be established and reviewed periodically. Most control tests have been designed for field use but they require care on the part of the operator. Normally proprietary chemicals are used and the consultant firm advising will provide details of tests, methods and frequency.

2.7 **Maintenance**

Regular cleaning and maintenance will do much to keep corrosion in check. Draining a system at regular intervals serves to rid the system of accumulated debris and is essential, particularly for small systems. For large systems circulating thousands of cubic metres per hour this is not always practicable and side-stream filtration is an alternative.

SECTION 3

CONTROL OF MINERAL SALT DEPOSITION, PARTICULARLY HARDNESS

3.1 Salts Causing Deposition

A number of mineral salts may lead to deposition of insoluble products in cooling systems and associated equipment. The principal ions are:-

Anions	**Cations**
Bicarbonate	Calcium
Carbonate	Magnesium
Hydroxide	Aluminum
Phosphate	Iron
Sulphate	Zinc
Silicate	

Most of the above ions will be present in the water supply used as make-up, but iron and to a lesser extend, aluminum and zinc can be produced by corrosion of the materials of construction within the system. Phosphate and zinc, and occasionally silicate, may be introduced as corrosion inhibitors.

Calcium carbonate is the most common, constituent of deposits found in cooling systems in hard water areas. It is produced by the decomposition of calcium bicarbonate which is present to some extent in all natural water supplies. The occurrence of magnesium salts in deposits is less common, although silica levels approaching 200 ppm may lead to the formation of magnesium silicate scale.

Calcium sulphate may be a problem unless care is taken to limit its concentration below its solubility.

Phosphate can form insoluble salts with all the cations listed, and pH control may be needed to avoid deposition.

Metal hydroxide are not often encountered, but can be found in cooling systems which are allowed to operate at high pH values. Iron hydroxide is formed as a result of corrosion processes but it is converted into hydrated iron oxide or rust.

3.2 Factors Affecting Deposition

Many factors, both chemical and mechanical, affect the extent to which such deposits constitute an operating problem. These are listed below and will be dealt with separately:-

pH value
Ion concentration
Temperature (water and metal surface)
Heat transfer
Water composition
Chemical treatment
Plant design
System residence time

3.2.1 pH Value

The operating pH value affects the solubility of almost all the salts mentioned above. In particular the tendency of calcium to form deposits of carbonate is dependent upon pH value.

The Langelier Index (see Appendix 7) gives a method of determining the tendency of a water to deposit calcium carbonate or take it into solution.

However, in most industrial systems there are considerable temperature variations and it may be more convenient to control the pH value of the water (by acid addition), below that at which calcium carbonate will come out of solution, and to counter the aggressive action by the use of a corrosion inhibitor. Alternatively, control can be achieved by the use of chemical, such as inorganic polyphosphates, to retard scale formation at what would normally be scaling pH levels (see Section 3.3.2.)

When phosphate is present, similar considerations apply in respect of calcium ortho phosphate.

In general, the higher the pH of the cooling water, the greater will be the tendency to form mineral salt deposits. Many control systems are therefore operated at pH values slightly below the saturation scaling index and corrosion is prevented by the use of an inhibitor.

3.2.2. Ion Concentration

The governing requirement is that the main scale forming salts are not allowed to concentrate to the level at which they become insoluble. Alternatively, the tendency of the salt to form deposits may be suppressed by a chemical additive.

Another objective in this control is that of operating the system at the maximum possible concentration factor, thus limiting water losses and keeping treatment costs to a minimum.

3.2.3. Temperature

Many of the depositing salts, especially calcium carbonate, have solubilities which decrease with increasing temperature. Metal surface temperatures play a major part in determining the rates of deposition, because thermal decomposition of calcium bicarbonate may occur, and the solubility limit of calcium carbonate be reached more readily. High flow rates are helpful in keeping surfaces free from scale.

3.2.4. Heat Transfer

Rates of deposition and corrosion are affected where the metal is subject to heat transfer, the rates of both being increased. Where high process-side temperatures exist, e.g. in furnace cooling, more stringent measures are needed to ensure clean metal surfaces; low hardness waters, good pH control and deposit control chemicals may all be necessary.

3.2.5 Water Composition

The mineral content of the water is of fundamental importance in determining the type and rate of deposit formation. It is recommended that the calcium carbonate scaling potential or Langelier Index be calculated, bearing in mind the concentration effect of evaporation, and the maximum water temperature in the system. This will frequently indicate the most appropriate treatment procedure and the maximum number of concentrations allowable.

3.2.6. Chemical Treatment

This is dealt with more fully elsewhere (see 3.3.2.) but there are certain effects upon deposition which require care. Phosphate has been mentioned, and as phosphate is encountered in many corrosion inhibitors, it must be remembered that even if the phosphate is added in the form of a polyphosphate hydrolysis to the ortho phosphate will occur in an open evaporative cooling system. Calcium phosphate can form deposits unless the pH value and calcium concentrations are controlled.

The addition of sulphuric acid for scale control increases the sulphate level, and this must be taken into account when assessing concentration factors, with respect both to the precipitation of calcium sulphate, and attack on concrete.

Chromates present no problem, unless the system is subject to contamination by reducing agents such as sulphur dioxide, which will produce insoluble chromium salts. Inhibitors containing chromate should be avoided in such cases. Care should be taken to minimise product leaks from refinery and petrochemical plants when chromate is used, since some of the contaminants may cause chromate reduction.

Where organic slime control chemicals are used, it is desirable to establish that these do not form insoluble substances with any other treatment chemical in use.

3.2.7. Plant Design

The effect of plant design is of importance in dealing with problems of mineral salt deposition. The major aspects are (a) water velocity and (b) surface condition.

The greater the water velocity, the less is the tendency for deposits to accumulate. Velocities should not be less than 1 metre per second, and as high as possible, consistent with the materials of construction. The level of suspended solids will affect the choice of velocity and metal. (See Appendix 4). Areas of very low velocity and "dead-legs", will tend to allow any salts which are precipitated to settle out, and provision should be made for flushing these areas.

It is desirable to keep heat transfer surface temperatures as low as is consistent with the process requirements, tower design and pumping costs. This is obviously tied in very closely with water velocities. Mineral salt deposition on metal surfaces may have an adverse effect on corrosion and fouling. Prevention therefore is of great importance.

3.2.8 Residence Time

The length of time during which a given volume of water is held in the system, calculated by the expression:

$$\text{Residence time} = \frac{\text{Total System Volume}}{\text{Purge + Windage Losses}}$$

3.3. Methods of Prevention and Control

3.3.1 Pre-treatment of Water

The most obvious method of preventing scale is to remove the main scale forming constituents from the make-up water by some form of softening. This will usually involve removal of all or part of the calcium and magnesium salts.

Cold lime softening of the make-up water may be employed; this removes most or all of the bicarbonates of calcium and magnesium and reduces the scaling potential of the cooling water considerably. It has the advantage of low chemical cost, but may require a large reaction vessel, and may also produce a water of high pH value, aggressive to certain metals, and to cooling tower timber where chlorination is employed. Therefore, pH adjustment of the cooling water may be necessary. Cold lime softening has the added benefit of reducing the turbidity and suspended solids of the make-up water.

Base exchange softening will remove practically all hardness salts, and minimise scaling. It is most applicable when dealing with small cooling systems in hard water areas. Its main disadvantage is that the water produced in the cooling system may be corrosive, and should be inhibited (see Section 2.5). High alkalinities (over 1,000 ppm) may damage timber by delignification, where chlorine is used. As stated above, the base exchange softening process removes most of the hardness, whereas it is only necessary to remove the bicarbonate hardness. However, for small systems, base exchange softening may be the only practical process. (see Appendix 9).

For medium and large installations, where the make-up water contains a substantial proportion of dissolved solids in the form of calcium and magnesium bicarbonates, scale control can be more readily effected by the de-alkalisation ion exchange process. This process removes all the bicarbonates, forming carbonic acid which is removed by degassing either in the cooling tower itself or in a separate unit. Acid is used as regenerant, and the process may be considered as a means of acid dosing outside the tower, without increasing calcium sulphate in the cooling water. Because the dissolved solids are reduced by an amount equal to the alkalinity of make-up water, a higher concentration factor can be allowed in the cooling water, thus saving on make-up, chemical treatment and purge. A suitable corrosion inhibitor will be needed, bearing in mind that the pH value of the cooling water could be below 7.0 (see Appendix 5)

Evaporation or desalination may be suitable processes where good quality water is scarce and adequate supplies of brackish or sea water are available.

3.3.2 Conditioning Treatment

For many years now, a typical method of cooling system scale control has been by acid dosing, usually sulphuric. This reduces bicarbonate hardness by chemical reaction, forming calcium and magnesium sulphate in its place. These are appreciably more soluble than the carbonates, and can be controlled by blowdown. It is usual to control the system water at a total alkalinity of below 100 ppm in terms of CaCo$_3$, in the pH range 6.0 to 7.0 and to apply a suitable corrosion inhibitor.

In an acid treated system, the amount of concentration and hence the quantity of water purged is usually determined by the solubility limit of calcium sulphate or phosphate. This system of cooling water control is well tried, and effective at cost levels which are usually acceptable. It is desirable to incorporate pH control equipment, which regulates the supply of acid automatically. Equipment of varying degrees of sophistication for this purpose is available.

pH control by acid dosing is not usually suitable for small cooling systems, due mainly to handling problems, and the cost of control equipment. As has been previously stated, for the small tower user in hard water areas, it is often convenient to soften the make-up water by the base exchange process, and provided the amount of mild steel in the system is small, the use of a corrosion inhibitor may not be necessary.

Alternatively, a scale suppressant can be used without softening, provided care is taken to avoid undue concentration of hardness salts. The use of scale suppressants in cooling water treatment is well established. Polyphosphates with or without tannins or synthetic organic materials have been used for many years, and where temperatures are moderate, have given successful results. Scaling is not completely inhibited, and there is always a degree of reversion to ortho phosphate, which has no scale prevention properties, and can lead to the formation of calcium phosphate deposits.

Synthetic organic compounds, many containing phosphorus, have found widespread use in cooling water treatment. These materials may often be referred to as phosphonates or polyol esters. They function in the same way as inorganic polyphosphates, but have greater scale control capacity at low dosage levels, and more importantly do not hydrolyse. Again, care has to be taken to avoid high hardness levels and high pH values. The Langelier Index is useful in these situations, as it can be assumed that scale control with these materials is effective with a positive index. The compounds are especially suitable for situations where acid dosing or external treatment is not practicable.

As will be seen from Table 1, there is little water saving to be achieved by increasing the concentration factor above 5.0 or 6.0, although this is sometimes possible, given good treatment control. Many systems are unable to achieve even a concentration factor of 5.0 because of unavoidable process or other leaks. As water costs increase, it will become more and more necessary to achieve optimum concentration levels, and this is only possible using one of the water treatment procedures recommended above, to prevent scale formation.

3.4 Economic Considerations

The selection of a method of scale control in a cooling system may be dictated by considerations other than economic. Costs of treatment are, however, important and a few comments on comparative costs are given below.

In general, three methods are available:-

1. External Softening
2. Acid Dosing
3. Chemical Conditioning

In terms of running costs, acid dosing will usually be the cheapest (see example below). The capital cost of control equipment must be considered, and this is likely to be in the range of £600 to £2,000. Additional costs for civil works, bulk acid storage installation, may also be involved. Acid dosing has the advantage of allowing system operation at a relatively high concentration factor, with savings on purge and inhibitor. It must be remembered that corrosion control will almost always be required, and the cost of this must be allowed for.

The use of scale control chemicals, on the other hand, will normally be effective with pH values up to say a maximum of 8.5 and it may not be necessary to add corrosion inhibitors. The cost of treatment varies, as many products are commercially available. When compared with acid dosing, the extent to which concentration can be extended may be limited, and the loss of water by purge may accordingly be higher.

External softening by base exchange is very convenient for small systems in hard water areas, and again capital expenditure will be required. Running costs for treating water of similar quality by de-alkalisation will be lower, but capital expenditure some two or three times greater. However, de-alkalisation will allow operation at high concentration factors, and thereby reduce make-up water and inhibitor costs. Inhibitors will almost always be required, and the cost of these should be taken into consideration; base exchange softened make-up may produce a high pH value water which may or may not need inhibiting.

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3.4.1 Calculation of Treatment Costs

As an example of the method used to calculate the costs involved in the various methods of treatment discussed above, a typical system with the following characteristics can be considered.

Water Circulation Rate $500m^3$/hr
Return Water Temperature 25ºC
Flow Water Temperature 20ºC

Make-up Water Analysis

Total Alkalinity, in terms of $CaCO_3$ 250 p.p.m.
Total Hardness, in terms of $CaCO_3$ 350 p.p.m.
Calcium Hardness in terms of $CaCO_3$ 300 p.p.m.
Magnesium Hardness in terms of $CaCO_3$ 50 p.p.m
Alkaline Hardness, in terms of $CaCO_3$ 250 p.p.m.
Non-alkaline Hardness, in terms of $CaCO_3$ 100 p.p.m.
Chloride, in terms of C1   40 p.p.m.

Sulphate, in terms of SO_4 80 p.p.m.
Silica, in terms of SiO_2 15 p.p.m
Dissolved Solids, as such   500 p.p.m.
pH, as such   7.5

Cooling Tower Construction   Wood

Type   Mechanical Draught

(a) pH Control by Acid Dosing and Use of Inhibitor

Sulphuric acid will be used, to destroy most of the alkaline hardness to make the water non-scaling with respect to calcium carbonate. In this case, therefore, the maximum allowable concentration factor will be set by the calcium sulphate, since the sulphuric acid added will convert the alkaline hardness (calcium and magnesium bicarbonate) into calcium sulphate. There is already about 80 p.p.m. calcium sulphate in the make-up; destruction of alkaline hardness by sulphuric acid will add a further say 230 p.p.m. calcium sulphate, making a total of about 310 p.p.m. calcium sulphate in the make-up. An acceptable concentration factor, in this case, will thus be 4.0, giving 1,200 p.p.m. calcium sulphate in the circulating water.

The purge requirement will therefore be 1.7 m^3/hour, including drift or windage and the total make-up 6.7 m^3/hour.

The amount of sulphuric acid needed is based upon the volume of make-up water. A corrosion inhibitor, of the zinc/chromate or phosphate type would be added to maintain a level of 50 - 100 p.p.m. in the circulating water, based upon purge to replace inhibitor lost in this way.

Approximate requirements are, per hour:

Sulphuric acid	1.6 kg (cost about 6p)
Inhibitor	0.1 kg (cost about 12p)
Water	6.7 m^3 (cost about 105p)
Additional cost	pH control equipment

(b) Scale Suppressant

Although system characteristics, e.g. velocities, maximum water temperatures etc. limit the degree to which this type of treatment will allow hardness concentration without fear of deposition, a reasonable figure in this instance would be a concentration factor of three.

This increases the purge requirement to 2.5 m^3/hour and the total make-up to 7.5 m^3/hour. Normal dosage rates of proprietary chemicals would be in the range 30-80 p.p.m. in the cooling water.

Approximate requirements are, per hour:

Scale Suppressant	0.15 kg (cost about 15p)
Water	7.5 m^3 (cost about 120p)

(c) Base Exchange Softening

The limiting factor on concentration would probably be alkalinity, to minimise delignification effects on the tower wood. If an alkalinity of up to 1,000 p.p.m. $CaCO_3$ is used, the concentration factor allowed would be four and water usage as in (a).

The addition of a corrosion inhibitor would depend upon metals in the system.

Approximate requirements are, per hour:

Regenerant salt	3.5kg (cost about 9p)
Inhibitors (if used)	0.2 kg. (cost about 12p)
Water	6.7 m^3 (cost about 105p)
Additional cost	Softening Plant

(d) De-Alkalisation

With the alkaline hardness removed from the make-up, the extent to which concentration may be allowed is considerably increased. Theoretically, about twelve could be achieved, but in practice operating cooling systems seldom exceeds a concentration factor of eight; this will be used for this example

The purge requirement now becomes 0.7 m^3/hour, and the total make-up 5.7 m^3/hour.

A corrosion inhibitor of the type mentioned in (a), is almost always used because of the aggressive nature of de-alkalised water.

Approximate requirements are, per hour:

Regenerant Acid	1.6 kg	(cost about 6p)
Inhibitor	0.05 kg	(cost about 6p)
Water	5.7 m^3	(cost about 75p)

The above examples are quoted as a guide, and may not necessarily be applied to any definite cooling system. They illustrate the methods in general use, and the order of costs involved.

SECTION 4

CONTROL OF MICROBIOLOGICAL FOULING

4.1. Introduction

The conditions inside a re-circulating cooling system are very often conducive to build up of micro-organisms, which in turn can lead to problems of heat exchanger fouling and a deterioration in tower performance. It is advisable to take steps to control the level of micro-organisms in the system.

The organisms which can give rise to problems can either be introduced by raw water make up or, being airborne, can be washed out at the cooling tower. Process contamination, particularly hydrocarbons, can act as a nutrient and result in high levels of activity in the system.

Since the Cooling water is generally warm and well aerated, conditions are often ideal for a rapid build up of the level of micro-organisms. During the Summer months the higher ambient temperatures result in a higher degree of microbiological activity in the system.

4.2 The Types of Organisms Encountered in Cooling Systems

The three main groups of organisms which may prove troublesome in re-circulating cooling water systems are (1) algae (2) bacteria and (3) fungi.

The mere presence of these organisms does not indicate a troublesome condition. Trouble is usually caused only by that portion which tends to clump and form slimy deposits, which may also entrap other suspended solids.

The organisms can be subdivided into three main groups of organisms which are likely to contribute to problems.

Algae	Blue/Green, Green Diatoms
Bacteria	Corrosive (Sulphate reducing)
	Iron depositing
	Slime forming
	Non-troublesome

Fungi Moulds
Yeasts

4.2.1. Algae

Flourish only in portions of the system exposed to light and air. The blue/green and green algae are primarily troublesome in restricting the flow of water, and air in some cases, in the cooling tower. Diatoms are composed largely of silica and deposits of diatoms closely resemble silt on analysis. These organisms are found in natural water supplies, and may form deposits in piping, filters, or similar equipment.

4.2.2. Fungi

Are important in that the organisms are extremely large, compared to bacteria, and they are apt to entrap other organisms, resulting in a voluminous, microbiological deposit. Both mould and yeasts may result from airborne contamination of the cooling water. Fungal rot of cooling tower timber must be guarded against.

4.2.3. Bacteria

Slime growths in heat exchangers are generally the result of bacterial formations. Not all bacteria are slime forming. The relative numbers of each particular organism present give a rough guide as to the severity of the problem, but of more importance is the trend in activity.

The corrosive group includes the sulphate reducing bacteria. These organisms are important because they reduce sulphate in the water to corrosive sulphide ion.

Some bacteria will oxidize nitrite and nitrate. As nitrite is sometimes used as an inhibitor against corrosion in cooling systems and may be rapidly destroyed by these bacteria, it is important to prevent their formation in systems treated in this way.

The iron depositing group are responsible for the formation of hydrous iron oxide deposits in cooling system piping.

The non-troublesome group is important in that it indicates that conditions are good for bacterial growths.

For determination of organism types and numbers, laboratory microbiological analyses are required. These are frequently carried out on a regular routine basis in large cooling systems, particularly in the petrochemical industry.

However, micro-organisms have certain characteristics that will permit a tentative identification on site. For example:-

Algae will normally form a green or blue/green slimy or rubbery, stringy deposit in sunlit areas, e.g. at the tower.

Mould will usually show up a grey stringy, fluffy or matted deposit in sheltered water moist areas.

Yeast may form a leather skin type deposit in the same area.

Slime forming bacteria will form grey/black gelatinous slimy deposits on wood, concrete and on heat exchanger surfaces etc.

Corrosive bacteria will usually form a black mass beneath deposits, sometimes evil smelling.

Iron depositing bacteria are usually typified by a rust brown slimy or gelatinous deposit.

The best technique to use for identification is a differential microbiological analysis. It tells what type and how many organisms are present in the sample.

4.3 Selection of Biocide

There is a wide range of biocides available for microbiological control in cooling systems. For example, chlorine, sodium hypochlorite, chlorophenols, amines, organo sulphurs, organo tine etc., are widely used. There are also many other compounds available.

Chlorine - It is very widely used for microbial control purposes in cooling systems. It is cheap, can be applied easily either as gaseous chlorine itself or as sodium hypochlorite (containing up to 15% available chlorine), and in the <u>normal pH range of 6 to 8</u> it acts as both a chlorinating and an oxidizing agent. Sufficient has to be added to overcome the chemical demand and provide a <u>free chlorine residual of 0.5 to 1 ppm</u>. Impurities are destroyed by either the chlorinating or the oxidizing reactions. The timber of the cooling tower may also be attacked by excess chlorine.

Most large plants have chlorinators installed. However, <u>where the cooling water</u> is subject to <u>contamination</u> by materials having a high chlorine demand, such as ammonia, the chlorination programme is often supplemented by a non-oxidizing biocide. Bis-thiocyanates and chlorophenols are often used as supplementary treatments.

Sodium hypochlorite can be used in small systems as a general purpose biocide. The main draw-back to its use is the raising of the pH value of the water. In addition, the use of hypochlorite does not disperse or penetrate the microbiological masses. For these reasons proprietary formulations which incorporate a dispersant as well as the biocide, are used frequently.

Chlorophenates - Chlorophenate based biocides are widely used in cooling water treatment, being particularly effective against fungi, algae and nitrite oxidisers. Their use however can raise a serious effluent problem.

Amines - This class included both long-chain and quaternary amines. They are good general purpose biocides, being effective over the normal pH range. Their strong cationic charge makes them effective dispersants, although this property may lead to foaming problems. They do not normally present any effluent difficulties..

Organo Sulphurs - Mainly used to combat slimes and fungi.

Bis-thiocynates - Good general purpose biocides, with minimum effluent problems. They are used at low dosage rates, and are particularly effective against slimes and corrosive bacteria. Now in widespread use.

Acrolein - Like chlorine, is a gas at normal temperatures and pressures. Unlike chlorine it is a non-oxidising biocide and is easily destroyed in effluent streams. It is toxic and flammable, and needs special feeding equipment.

Organo Tins - Broad spectrum biocides effective against slimes and fungi. Raises effluent problems.

Copper Salts - Not encountered in cooling water treatment because of potential corrosion problems due to plating out of copper on steel. Primarily used at low dosages to kill algae in reservoirs, storage tanks etc.

Each of the general types have different degrees of activity against specific classes of micro-organisms. Thus to get the best cost/performance, it is essential to take the advice of the supplier of the product to be used concerning the dosage rates to be maintained for a specific period. Otherwise excessive amounts of treatment chemical may be required for less than complete results.

Most microbiological organisms can build up a resistance to one particular biocide in the course of time. It is therefore desirable to change the type of biocide periodically.

4.4. Application Techniques

The variations in physical characteristics of cooling water systems are vary large. While a single slug addition of biocide may be best for one system, continuous addition may be the right answer for another. For example, chlorine is normally fed for a total period of one hour in 24, i.e. a 20 minute application each eight hour shift.

Addition of a specific biocide at the tower sump may be recommended for one system, while addition of the biocide to certain sections of the plant (where the problem is severe) might be advisable in other cases.

Other important factors that must be considered are effluent requirements, toxicity, and the effect on the corrosion and scale inhibiting program.

Finally, the degree of system contamination, and the extent of existing deposits, may dictate a high level of treatment for clean-up, with the ultimate objective of lower levels providing continued control. Care is required when starting a biocide treatment on a badly fouled system that dislodged organic slimes and growths do not cause blockages in pumps and waterways etc.

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SECTION 5

CONTROL OF FOULING - MUD AND SILT

5.1 Introduction

Fouling can be broadly divided into two categories:-

Environmental and Mechanical

Environmental fouling involves materials that are present in the system as a result of factors external to the system. These can be varying make-up water composition and contamination, geographical location, airborne or process contaminants. Usually system operators have little control over the factors causing environmental fouling. Examples of environmental fouling materials are silt, clay, mud, natural organics, soluble iron, phosphates, sand and debris.

Mechanical fouling is caused more by the system characteristics and generally results from variations in operations. Samples of mechanical fouling are corrosion products, clarifier carryover, calcium, iron or aluminum compounds, microbiological growths, product contamination and chemical incompatibility.

It is unusual to find fouling in a system which consists of only one of the constituents mentioned in the above two groups. Generally a mixture of two or more of the constituents will be found, since the presence of one constituent can lead to the generation of one or more of the others. For example, the deposition of silt or mud on the heat exchange surfaces can lead to the formation of corrosion products which can deposit at the same location, or be carried elsewhere in the system.

Heat exchanger tubes, headers, circulating lines, cooling tower distribution systems, and tower sumps can all be subject to fouling by mud and silt. The build up of material can be gradual or sporadic, and may be uniform or localized. Each system is sufficiently different in design and operation to justify separate investigation to determine causes and treatment to alleviate fouling problems.

As far as system design goes heat exchangers with the water on the Shellside are extremely prone to fouling. The baffles in the path of the cooling water in these heat exchangers provide stagnant areas where there may be a depletion of inhibition. This gives rise to a greater risk of deposition and an area where bacterial contamination can grow, and cause further blockages and general falling off of efficiency. Linear flow rates of at least 1.5 metres per second are recommended.

It must always be remembered that cooling towers are excellent air washers (scrubbers).

With forced or induced draught it is inevitable that quantities of dust, dirt or air-borne pollution will be drawn in and washed out of the air stream into the cooling water as it cascades down through to the tower.

Thus it will be realised that regular preventative maintenance is essential to the good house-keeping of the cooling tower and system generally. This takes the form of regular wash-outs of the cooling tower basin to remove the air-borne deposits as well as the hardness salts released from the water due to evaporation and make-up.

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To assist with the regular maintenance wash-outs the introduction of a polymer based chemical will greatly improve the sludge removal from the system as well as the tower.

The volume of deposit from water can be roughly calculated from the water analysis and make up.

The volume of deposit from the atmosphere is quite a different problem. There are many factors involved, such as:

Position of tower in relation to dust extracts, vents, process fumes or boiler stacks, building site (demolition), etc.

Position and height of one building to another will cause air disturbance and partial robbing of air which may induce air re-cycling with subsequent loss of efficiency.

Position of tower in relation to traffic on roads or within factory confines. Dry weather with passing traffic will create considerable problems which are not nearly so troublesome in wet weather.

Towers set in or above wells in large office blocks, hotels, hospitals, etc. often become heavily fouled by insect life in addition to dust, etc. due to upward air currents carrying fumes, fats, grease, etc. from kitchens and garages, etc.

The volume of dust in air as an average over the country varies greatly, as indicated in the table below.

The above table has been extracted from the Department of Trade and Industries Warren Springs Laboratory Reports giving a sample of sites and the winter and yearly averages for amounts of undissolved matter deposited.

The sites are grades as follows:-

Code 1 Purely industrial
Code 4 Commercial centre of town with regard to a particular factor
Code 9 Commercial centre of town (general)
Code 8 Low density housing area
Code 13 Open country (general)

The quoted figures were mg/m^2/day which have been calculated as tons/square mile/month, or lbs/100 sq. yds./month.

Thus for sulphur dioxide at Nottingham during the winter period the mean daily SO_2 content was 241 ugms/m^3 with the highest days figure of 969 ugm/m^3. On 7 days during the 6 months the 500 ugms/m^3 was exceeded.

Converting the given figures from ugm/m^3 to lbs/50,000 cu.ft. (Factor 3.1×10^{-6}) gives a mean daily SO_2 content of 7.5×10^{-4} lbs/50,000 cu.ft.

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Figures quoted for flue gas composition give SO_2 content of 300 - 3000 p.p.m. v/v which is equivalent to 8.6 x 10^5 - 8.6 x 10 ugms/m^3 compared with the above 2.41 x 10^2. Thus in comparison between commercial town centre atmosphere and flue gas there is a factor of between 3.6 x 10^3 and 3.6 x 10^4.

Thus it would appear that the effect of polluted, but homogeneous, air is small compared with that of drawing in flue gas into cooling tower from nearby stacks, before dilution to normal atmospheric conditions.

Considering the mean daily SO_2 figure of 7.5 x 10^{-4}lbs/50,000 cu.ft. and absorption in a cooling system; if there were 50 x 10^6 cu.ft. of air passing through a tower with 100% absorption then the water would pick up 0.75 lb SO_2 . Thus if the system capacity was 1000 gallons the alkalinity either carbonate hardness or sodium bicarbonate would be reduced by 117 p.p.m. as $CaCO_3$.

For example, using the Birmingham Code 1 as an example the deposit factor would be approximately 1g/100m/^{2}/hr, which roughly equals 1oz./24hr. Not much to worry about it can be said, but position a vent or dust extract within a 100ft, or so, or a prevailing wind from an industrial area and the volume of deposit would increase dramatically.

The closeness of contamination whatever the source will increase deposits within the system many times. Localised traffic movement, demolition, or boiler stack emission can also considerably increase these figures.

Regular maintenance must be based on practical experience of each individual system and washouts on a monthly basis are recommended, experience will indicate a greater or lesser frequency.

Fouling from environmental deposits such as mud and silt is more usual in large systems which are drawing water from canals, river or sewage effluent, as make up. Any open recirculating system is also wide open to airborne contamination such as cement, brick dust, etc., in areas of demolition and reconstruction as well as of cement manufacture. Systems in the country are likely to be heavily contaminated in dry weather with the dust from the fields, while near the sea fine sand particles can be troublesome.

At a colliery coal dust is certain to cause troubles. At foundries and steel works, oxide sludge contamination is a certainty. Contamination of this type will be airborne over several miles.

The smaller systems with cooling towers on a roof may be contaminated by sulphur, acid gases, dust and fumes from nearby vents, thus adding to corrosion potential, mud and silt deposits. Circulation of water containing fouling deposits of this type will soon lead to heat exchange problems, unless control is exercised.

5.2 Control of Fouling

5.2.1 Pretreatment

If the make up water contains a high concentration of suspended matter, then pretreatment is essential, using conventional filtration methods, such as pressure type filters with sand or anthracite/sand filter media. Further removal of finely divided suspended matter can be achieved by flocculation or sedimentation techniques using inorganic flocculants, such as alum or ferric salts and organic flocculants such as polyamides or poly-acrylamides.

5.2.2. Side Stream Filtration

This method is employed in some medium and large recirculatory systems. Between 1 and 5% of total recirculation water is passed through the filter to control the fouling in the system to acceptable limits.

5.2.3 Internal Chemical Treatment

The continual addition of a chemical antifoulant will minimise deposition within cooling water systems, the type of antifoulant used depending on the cause of fouling. The use of high molecular weight organic polymers such as polyacrylamides, will flocculate the finely divided deposit to give a floc with a density close to that of water, so that changes in water velocity and temperature do not cause the floc to settle out. The deposit is therefore carried through the system and removed by the purge control.

The use of dispersant, such as lower molecular weight organic polymers, will prevent the agglomeration of deposit particles which again will be removed by purge.

5.2.4. Cleaning

For small systems of only a few cubic metres capacity, it is essential to wash out the cooling tower sump regularly.

On stream cleaning can be carried out using a variety of products and methods. Polyelectrolytes can be effective for cleaning once-through systems, recirculating cooling systems, tanks, stand pipes, ballast tanks, long runs of piping and in freeing side stream filters partially blocked with mud and silt. Each problem should be investigated carefully to determine the best method which might for example include pH adjustment and frequency of dosing to effect the removal of residual deposits.

Dispersants (low molecular weight polyelectrolytes) can also be used in a desludging programme, particularly in recirculating cooling water systems, with a decrease in the pH during the period of operation. Purge must be increased to lower the factor of concentration during this desludging programme.

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SECTION 6

FACTORS AFFECTING ENVIRONMENTAL POLLUTION

The authorities are striving to raise the standards of pollution control, and this, coupled with increasing awareness of the seriousness of industrial pollution, means that the effect of cooling towers on the environment cannot be ignored.

While at present these controls may not be stringently applied in all cases, there is no doubt that legislative restrictions will increasingly be applied.

The following list indicates those factors most likely to contribute to pollution.

(a) Drift (windage)
(b) Chemical treatment
(c) Purge, uncontrolled losses and draining

The various elements within the given divisions are listed together with their associated hazards, order of acceptability, and typical methods of control. However, it must be emphasised that each location must be considered on its own merits, and that it is not possible to lay down universal standards. (see Tables).

A. Drift and Windage from Cooling Tower

	Factors Affecting	**Hazard**	**Control**
Drift or windage	Season	Drizzle in vicinity of tower	Lower air velocity
	Weather	Corrosion of immediate surroundings	Reduced load
	Load Siting Design	Local complaints Fog, Ice	Mist eliminators
Spray at ground level	Wind	Local wetness/corrosion Water loss	Side shields

B. Chemical Treatment

Material	**Hazard**	**Limits**	**Control**
Chromate	Toxicity to plant fish and animal life	Limits subject to negotiations with appropriate authority	Dilution Reduction and precipitation Ion
Phosphate	Nutrient for algae slime, etc., in streams.		Precipitation
Zinc/Tin	Toxicity to fish		Dilution

Tannins	Increases B.O.D.	Precipitation Dilution Holding pond
Biocides	Toxicity in streams	Dilution
Algae	to fish and micro-organic life, and sewage works	Holding ponds Replace by degradable biocide, e.g. chlorine, acrolein
Dispersants	Foam	Defoamer
Chlorine	General toxicity	Sulphur Dioxide Aeration

C. Blowdown and Loss Disposal

Constituent	**Possible Hazards**	**Limits**	**Control**
Dissolved Solids	Interaction with stream solids Nutrient for plant life	As mentioned in Section B, the limits imposed by the relevant authorities are so variable that precise or even approximate limit figures could be misleading. The advice of the appropriate authority and of an expert in the subject must be sought.	Dilution with an acceptable source
Suspended Solids	Sludge Nutrients		Filtration settlement lagoons
Immiscible liquids (oil, solvents)	Oxygen Depletion Unsightliness Flammability		Interceptors Chemical treatment (e.g. flocculation) Filtration Eliminate process leaks
Ecological change	(effect on subsequent use)		
Heat	Effect on fish Mist formation Oxygen depletion Effect on subsequent use		Cooling towers. Load reduction by air cooling heat exchange
Process Contaminants	B.O.D. Toxicity		Dilution Aeration for BOD treatment.

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APPENDIX 1

GLOSSARY OF TERMS

Absorption Inhibitor (see Inhibitor)

Alkalinity Capacity for neutralising acid, usually expressed in water analysis in terms of mg/1 $CaCO_3$. Alkalinity in water is predominantly in the form of bicarbonate. Carbonates and/or hydroxides with much smaller quantities of other ions can also contribute to alkalinity.

Anodic Inhibitor (see Inhibitor)

Bicarbonate A compound containing the HCO_3 ion (see Alkalinity).

Biostat Reagent which renders micro-organisms inactive without destroying them. When treatment ceases, growth may restart.

Biocide A reagent which destroys micro-organisms. Also used: Bactericide, Fungicide, Algaecide.

Bleed Off (see Appendix 6).

Blowdown (see Appendix 6)

B.O.D (see Oxygen Demand).

Cathodic Inhibitor (see Inhibitor)

Clarification In cooling water practice, clarification usually refers to the settling process, in which chemicals may be used, for removing suspended matter from the make up water. The process if carried out in clarifiers, sedimentation tanks or settling tanks , Also see Filtration (Appendix 10)

Closed System A cooling system in which the water circuit is enclosed except usually the header tank which has an air space above the water. Such a system is subject to negligible evaporative loss and make up is normally required only to replace leakages.

C.O.D. (see Oxygen Demand)

Concentration (see Appendix 6)

Conductivity (see Electrical Conductivity)

Coupons (see Appendix 4)

De-alkalisation (see Ion Exchange, Appendix 9)

De-ionisation (see Ion Exchange, Appendix 9)

Delignification Destructive action on timber resulting from chemical action which removes such compounds as tanning and lignins, leaving behind a low-strength matrix consisting mainly of cellulosic material.

Demineralisation (see Ion Exchange, appendix 9)

Deposit The terms deposit, scale and sludge have numerous connotations but in cooling water technology usually refer to material deposited on the heat-transfer surface or other important parts of the system. The term scale should strictly speaking refer to crystalline deposit such as calcium carbonate or calcium sulphate but is often used to cover a rather wider range of deposits sometimes including corrosion products, which are hard and not easily removed. This should not be confused with mill scale. A sludge is a much softer material and can normally be removed by a good jet of water. There are, however, many intermediate deposits which are more difficult to characterise and for these the term "deposit" is often sufficient. (see also Fouling).

Dezincification A type of corrosion of brass in which the copper is left behind, usually in a spongy discontinuous form.

Dispersants (Dispersives) Reagents usually added with other treatment chemicals to prevent accumulation of sludges.

Drift (See Appendix 6)

Electrical Conductivity (or Conductance) The current-carrying capacity of water, measured in terms of the current which flows when a constant potential is applied. The level of electrical conductivity is largely determined by the dissolved solids concentration. As corrosion is an electro-chemical process, any increase in conductivity will, in general, increase corrosion activity.

Evaporation (see Appendix 6)

Filtration (see Appendix 10)

Fouling Organic growth or other deposits on heat-transfer surfaces causing loss in efficiency.

Foaming The formation of stable bubbles. Foaming may interfere with water circulation and/or heat transfer.

Galvanic An expression used to describe the action of a bi-metallic or other couple in corrosion processes. In such a couple the less electro-positive (less "noble") metal is corroded. A typical example is copper/zinc.

Graphitization A form of corrosion of cast iron in which a carbon (graphite) matrix is left as a porous mass.

Hardness Hardness of water relates to the quantity of soap required to produce a lather. It is caused by metallic salts, which precipitate insoluble soaps, those of calcium and magnesium being important. Hardness is often divided into alkaline (temporary) and non-alkaline (permanent).

Inhibitor (Corrosion) A corrosion inhibitor is a reagent which will reduce the rate of corrosion in a cooling water system. (see Appendix 5).

Ion-Exchange A method of water treatment involving the removal of hardness salts or other ions. In the standard process, water is passed through a bed of ion-exchange resin until it is exhausted. The bed is then regenerated. The most frequently used processes are:

` Sodium Ion Exchange (Base Exchange)
Softening Process
Regeneration
De-alkalization
Demineralization (de-ionization)

Many types of ion-exchange plant are available for special purposes. (see Appendix 9).

Langelier Index (see Appendix 7)

Leaching The extraction of a soluble fraction from an otherwise insoluble material, e.g. leaching of preservative from treated timber or sulphate from concrete.

Make Up (see Appendix 6)

Mill Scale A layer consisting mainly of iron oxides which forms on the surface of wrought steel products during hot processing.

Nutrient A constituent of water which will feed micro-organisms. Examples are various carbon, nitrogen and phosphorous compounds but elements required in trace quantities can also be described as nutrients.

Open Re-circulating System (Evaporative Cooling system) - A cooling system in which cooling depends on the effect of the temperature drop when water is evaporated in a cooling tower or similar device.

Organic Carbon See Oxygen Demand

Oxygen Demand Various tests have been devised in an attempt to measure the organic purity of water, particularly wastewater. The results of the various tests depend on the nature of the contaminants and interpretation requires care. The tests commonly used include BOD, PV and COD.

BOD (Biochemical Oxygen Demand) - Reduction in oxygen content after a period of five days incubation. This is intended to reproduce the effect of a discharge to a stream. Its disadvantage is the time required.

PV (Permanganate Value) A more rapid but less accurate method of determination for the measurement of the oxygen demand of the water. A sample is incubated with dilute permanganate then determined. This test is sometimes known as "oxygen absorbed from potassium permanganate" and the temperature and incubation period are then usually quoted.

COD (Chemical Oxygen Demand) - This is a measure of the maximum possible oxygen-absorbing capacity and is determined by boiling a sample with dichromate solution and estimating the residual dichromate. This test is sometimes known as "dichromate value".

Organic Carbon Another method for determination of the organic quality of water depending on the oxidation of organic matter to CO_2 The normal techniques are not very satisfactory for routine use.

Passivation The formation of a protective film (visible or invisible) which controls corrosion.

pH Value Reciprocal logarithm of hydrogen ion concentration. Used as an indication of acid or alkali strength. At neutrality, pH value is approximately 7.0 at ambient temperature. Higher figures represent alkaline conditions and lower figures acidity. As the scale is logarithmic, a difference in pH of 1.0 indicates a difference in hydroxyl or hydrion strength of 10

Process Leaks Leakages from process plant may cause problems in cooling systems; examples include acids, alkalies, metallic salts and many kinds of organic matter. Acidity or alkalinity complicate the control of chemical treatment. Other contaminants may serve as nutrients for organic growths, form objectionable deposits on heat transfer surfaces, promote foaming or otherwise affect the performance of chemical treatment.

Purge (see Appendix 6)
PV (see Oxygen Demand)

Residence Time The average period of water retention in a cooling system.

Ryznar Index (see Appendix 7)

Scale (see Deposits)

Sedimentation (see Clarification)

Sequestering Formation of a soluble complex Examples of sequestering agents are
(Chelating) polyphosphates, NTA, EDTA, and certain hydroxy-carboxylic acids.

Side-Stream Filtration of part of the circulating water in a cooling system thus controlling build-up
Filtration of suspended matter.

Sludge (see Deposits)

Softening (see Ion-Exchange and Appendix 9)

Stability Index (see Appendix 7)

Stress Corrosion Cracking caused by an applied or internal stress in a corrosive environment.
Cracking Such cracking may be intercrystalline (intergranular) or transcrystalline (transgranular) depending on whether it follows the grain boundaries or cuts across the grains.

Synergistic When the improvement obtained by using two inhibitors (or other treatment chemicals) is better than the sum of the improvements obtained with the two materials individually the effect is said to be synergistic. The method may permit the use of lower concentrations of inhibitor than would otherwise be used.

Windage (see Appendix 6)

Thermal Conductivity (see Heat Transfer)

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APPENDIX 2

UNITS OF MEASUREMENT

Both metric and imperial units are in common use, but it is recommended that where possible, the metric system known as S.I/ (Système International d'Unites) devised by the International Organisation for Standards (I.S.O.) should be used.

S.I. is described as a coherent system built up from no more than six basic units:

Length	Metre (m)
Mass	Kilogramme
Time	second (s)
Temperature	degree Kelvin (ºK)
Electric current	ampere (A)
Luminous intensity	candela (Cd)

Standard prefixes are used for multiples and submultiples. The following are the most important:

10^6	mega M
10^3	kilo k
10^2	hecto h
10^1	deca D
10^{-1}	deci d
10^{-2}	centi c
10^{-3}	milli m
10^{-6}	micro µ

It is recognized that for many applications, metric units other than S.I., mostly with traditional background, may be used. For example, the litre, although not an S.I. unit, it a convenient measure of volume for many purposes and is likely to be widely employed, as are minutes and hours.

NOTES

1. Water Analysis, etc.

The unit mg/l (=g/m^3) is recommended but is identical with ppm (weight/weight) for solutions with a specific gravity of 1.00. For most water analysis, except sea water, the two units can be regarded as interchangeable.

Specific gravity should be expressed as such (unit·less) rather than in "degrees".

Sludge and suspended solids concentrations are expressed as w/v - mg/l or g/l. Water hardness is normally expressed as mg/l (ppm) $\mathrm{cacO_3}$ but various "degrees" of hardness are used, as in the following table.

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HARDNESS

Size	Mild Steel	Admiralty	Aluminium
1 in x 4 in	0.36	0.33	1.08
3/8 in x 3"	1.11	1.03	3.32

In water analysis, results are usually expressed in the ionic form, i.e. mg/l Ca or mg/l CO_3. In deposits, however, the oxide form is normally used and results are expressed (except for very small quantities) as percentages, e.g. % CaCO or % CO_2

2. Chemical Dosages, etc.

These are normally expressed as mg/l or g/m^3. This is equivalent to ppm when the s.g. of the water being treated is 1.00 (1 ppm = 1 mg/l = 1 g/m^3 = 1 lb/1000,000 Imp gallons).

3. Pressure

The Newton is not yet well-known as the unit of force and it is likely that kgf/cm^2 will be used for some time.

1 kg/cm^2 is commonly known as the "technical atmosphere" (at) "metric atmosphere".

1 at = 101.325 kN/m^2
= 14.2233 lbf/in^2

1 standard atmosphere (atm = 760 mm Hg at 273 ºK
= 0.968 kgf/cm^2
= 14.696 lbf/in^2

Hydraulic head may be expressed in metres (m)
1 mm Hg = 133.322 N/m^2
1 mm H_2O = 9.80665 N/m^2

4. Temperature

The S.I. unit is the degree Kelvin (ºK) and refers to the absolute scale. The Celsius scale (ºC) has the same temperature intervals and is likely to be widely used in practice. The words Centigrade is not used because in France it has another meaning.

Note, the expression "deg K" ("deg C" or "deg") should preferably be used for a temperature difference or interval.

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TREATMENT AND CORROSION CONTROL OF COOLING WATER

APPENDIX 3

THEORY OF CORROSION

Metal corrosion may be defined as the destruction of the metal by chemical or electrochemical reaction with its environment. In aqueous systems the process of corrosion involves two electrochemical reactions, in which one section of the metal surface becomes anodic or corroding to protect another area which becomes cathodic. The three conditions required for the electrochemical corrosion process to proceed are:-

- a potential difference on the metal surface
- a continuous conductive path over which the potential difference is available .
- a mechanism for charge transfer between (metallic electronic) and (aqueous electrolytic) conductors.

When a metal is immersed in a conducting liquid or solution, the formation of anodes and cathodes on the metal surface can be initiated from several sources, including lack of homogeneity in the metal or by an uneven coverage of oxide scale, caused by scratches or cracks in the protective oxide film. Different concentrations of electrolyte or oxygen, particularly at turbulent or quiescent areas on a section of the plant, may also produce anodic and cathodic areas. The anodic areas are areas of low potential where the metal atoms split up to form a metal ion with the release of electrons, the metal ions passing into solution, for example:-

$FeFe^{++} + 2e$ (Fe^{++} is a ferrous ion)

The anodic reaction is shown here as the conversion of metal into its corresponding ion, in this case a ferrous ion. This is a process of dissolution or oxidation and it is at these anodic sites that the metal loss occurs. The reaction as written is known as the "anodic half cell reaction". For the dissolution of the metal to continue electrons left behind on the metal surface have to be removed; this is accomplished by the presence of oxygen in neutral water conditions or hydrogen ions in acid water conditions, and occurs at the cathodes.

The cathodic areas are areas of higher potential than the anodes, and the processes in these areas are reducing, no metal being lost from these areas. The cathode forms the other half of the corrosion cell. In neutral or alkaline water conditions, oxygen is reduced in the cathodic area by reacting with the electrons to form hydroxide ions as follows:-

$O_2 + 2H_2O + 4e \quad 4OH$ (OH is a hydroxide ion)

In acid solution, where the water contains considerable concentration of hydrogen ions, the electrons react with the hydrogen ions to produce hydrogen gas:-

$2H^{+} + 2e \quad H_2$

Thus in order to prevent these corrosion processes occurring it is necessary to eliminate the presence of dissolved oxygen or hydrogen ions. The latter may be reduces to negligible proportions by ensuring that the system water is neutral or slightly alkaline. In open evaporative cooling systems it is impracticable to remove the dissolved oxygen from the cooling water and other methods of metal protection must be used, see section of methods of corrosion prevention.

The two half cell reactions described above have thus produced two independently soluble ions (ferrous ions and hydroxide ions). When these come into close contact they react with each other and form ferrous hydroxide:-

$Fe^{++} + 2OH \quad Fe(OH)_2$

The ferrous ions are readily oxidised to ferric ions Fe^{+++}, which react with the hydroxide ions to finally produce the familiar brown rust, hydrated ferric oxide. Since the corrosion products are not formed at the metal surface where the corrosion processes are taking place, little protection is afforded to the metal by their presence and the corrosion processes can continue. The rate at which a corrosion process occurs is usually controlled by the rate at which dissolved oxygen or hydrogen ions become available at the cathodic areas.

Types of Corrosion Commonly Encountered

(a) General Corrosion

As the name implies, this is the usual removal of metal evenly from the metal surface. For this to happen the anodic and cathodic areas on the metal surface are constantly changing with respect to one another.

(b) Pitting Corrosion

In this case the active anodic regions remain and do not become cathodic to any surrounding anodes. It is most severe where there is a large cathode and a small anode; the corrosion rate is controlled by the anodic reaction, since any electrons released by the anodic process are readily removed by the large cathodic area, which is available for the reductive processes to take place.

MECHANISM OF CORROSION

Outer layer: red basic ferric hydroxide

Inner layer: black ferrous hydroxide

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APPENDIX 4

STANDARDS OF MEASUREMENT OF CORROSION AND FOULING RATES

A. Methods for Determining Corrosion Rates

Various methods are available for determining the apparent corrosion rate of a system, and these are listed below, together with brief details of factors that should particularly be noted if repetitive results are to be obtained.

I) test coupons
II) test heat exchangers
III) electrical resistance methods
IV) polarisation methods
V) process equipment
VI) measurement of corrosion products in the system

However, it must be realised that the test conditions are not necessarily related to the actual conditions encountered in all parts of a system, and so the results must be treated in a comparative and indicative manner only.

Also. it is <u>not practical</u> to <u>correlate</u> results obtained by <u>one method</u> with <u>those obtained</u> by a different method. <u>Nevertheless</u>, severe <u>scaling or corroding</u> conditions can <u>quickly be indicated</u>, and the <u>effect of a treatment</u> or change on a <u>system evaluated</u>.

In the following notes particular attention has been given to the use of test coupons, as this is the most likely method to be in general use as the requirements are simple. The other methods covered usually require specialised instruments and so are used by consultants who have the necessary equipment.

I) Test Coupons

These consist of metal strips made from material similar to that of interest in the system. They are cleaned, weighed before installation, left for a specified period, removed, cleaned and re-weighed. The cleaning removes any scale and corrosion products, which can be separately analysed. The loss of weight is calculated in terms of corrosion occurring during the exposure time. Corrosion coupons not only provide a means of measuring corrosion rates, but also permit visual inspection for determination of the type of corrosion.

Coupon corrosion rates can vary widely depending on how the coupons are prepared, installed and evaluated. It is important therefore to consider these factors carefully in interpreting results, and a standard procedure is essential for comparative measurements. Single measurements in particular can be very misleading.

Units of Measurement

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Corrosion rate is normally expressed as weight loss per unit area per unit time (weight loss/area/time) or as depth of penetration of the metal in unit time. The common units are:

weight loss : mdd - milligrams per square decimeter per day
penetration : ipy - inches per year
mpy - mils (1/1000 inch) per year
mpd - mils per day

Weight loss is the basic measurement. Corrosion, assumed to be uniform is then calculated from weight loss, using the metal density in the calculation. Using the following factors, mdd can be expressed in terms of ipy or mpy:-

$$\text{ipy} = \frac{\text{mdd} \times 0.001437}{d}$$

$$\text{mpy} = \frac{\text{mdd} \times 1.437}{d}$$

where d = metal density in g per cubic centimeter

For Mild steel d = 7.86
admiralty d = 8.54
aluminium d = 2.72

This relationship is only valid where the attack is generally uniform over the entire surface. In localised pitting there may be only slight weight loss but severe penetration. In these cases where pitting or highly localised attack occurs, the weight loss figures may be supplemented by actual measurement of the pit depth, which can be expressed directly in terms of mils per unit time.

Coupon Preparation

It is essential that a standard preparation technique is employed, as a variation in method can have a significant effect on corrosion rates.

After initial stamping with its identification number, and the removal of all sharp edges a coupon should be degreased in petroleum ether, dipped in inhibited Hydrochloric Acid, washed with distilled water, rubbed lightly with jewellers rouge, again water washed, then in alcohol, and dried. After weighing, mild steel coupons are inserted in a plastic envelope containing a vapour phase inhibitor to prevent corrosion prior to installation. Admiralty brass coupons for example can be inserted in plastic envelopes direct, as negligible atmospheric corrosion will occur with this material.

Details of coupon number and initial weight are then recorded.

Coupon Installation

To duplicate actual system conditions, careful judgement must be exercised in choosing the sites for installation of the coupons. They must be mounted with plastic or other suitable non-conducting holders to ensure insulation from stray currents and electrolytic effects.

The plane of the coupon should be parallel to the flow direction, but it should not touch the wall of the pipe. It should be totally immersed at a location in the system where the flow rate is not turbulent, and is typical of the greater part of the system. The least preferred site is the tower basin or other stagnant area.

It is also preferable to site the coupon in a 'hot' line, such as the outlet from a heat exchanger. In other cases it may be desirable to set up a test rig simulating certain flow and temperature conditions.

On large systems, several sites may be chosen, representing various conditions in the system from minimum to maximum temperature.

Coupons are generally about 1" x 3" in size, with a thickness of ^{1}/8", although actual dimensions are not too critical. However, they should be standardized for comparative results. All corners and edges (including those of the mounting hole) should be rounded, to minimize stresses that may lead to localized corrosion, and misleading results.

Exposure Duration

At least 30 days exposure is essential for a realistic evaluation of corrosion rates, as it is apparent that even on well protected systems a relatively high initial corrosion rate occurs during the first few days of immersion.

It is usually the practice to insert several coupons together on a rig, so as to allow the removal of coupons at different, exposure times such as 30, 60 and 90 days intervals. By installing further coupons as earlier ones are removed, a continuous record of corrosion rates can be built up over a period of time.

Determination of Weight Loss

After removal from the system, coupons should be air dried as quickly as possible to prevent further corrosion. In the laboratory the coupons are scraped with a plastic knife to remove scale, corrosion deposits etc., degreased with petroleum ether and dried. The coupons are then additionally cleaned by dipping into inhibited Hydrochloric Acid, immediately washed with water then alcohol and dried. They are then re-weighed.

The final weight is subtracted from the initial weight to give the total weight loss.

Interpretation of Results

The most frequently used units to express corrosion rate is mils per year (mpy). This is determined from the weight loss by the equation:-

$$\text{Corrosion rate mpy} = \frac{\text{Area factor x Weight loss in milligram}}{\text{Days exposed}}$$

The area factor is calculated from the measured exposed surface area of the material. Typical values for coupons are:-

For other sized coupons, the area factor can be calculated from the formula:-

$$\text{Area Factor} = \frac{22.3}{cA}$$

where c = density of material in g/cm^3
A = exposed area of coupon in in^2

II) Test Heat Exchanger

This consists of a tube of the material under consideration being immersed in a stream of the cooling water. The temperature of the tube can be altered by passing steam or circulating heated oil through the tube to simulate heat exchange conditions, and accelerate any corrosive tendency. The cooling water flow rate can also be controlled to reproduce required conditions.

After set exposure times, the tube can be removed and examined as described previously for test coupons.

This method allows a quick evaluation of specific conditions in a system, and also is capable of reproducible results and comparisons of different materials.

An alternative is to run a heat exchanger in parallel with and under similar conditions as the main operating units; this can give excellent results but is more time consuming than the accelerated method above.

III) Corrosion Measurement by the Resistance Method

This method of corrosion measurement makes use of the fact that the electrical resistance of a material changes as corrosion takes place. Results are sometimes irregular, but are generally similar in trend to those obtained by coupons, and quicker.

A wire element of the metal of interest is mounted on a probe and exposed to the corrosive environment. As corrosion takes place the cross sectional area of the measuring element is reduced and its electrical resistance is increased.

A bridge balance circuit allows the element's resistance to be measured by comparing it with that of an internal reference element of the same metal which is coated to protect it from the corrosive environment. Since both elements are of the same metal the resistance change with temperature will be the same. The reference element therefore serves as an automatic temperature compensator.

The reference element's protective coating damps its response to temperature change relative to that of the non-protected element. This may cause non-repeatable readings in systems where temperatures fluctuate rapidly.

The readings obtained are easily converted to metal loss and the average corrosion rate in mils per year occurring during the time the readings were made can equally easily be determined.

The principal advantages of this method of corrosion measurement are:-

1. Measurements are non-destructive
2. Measurements may be logged or recorded continuously.
3. Inaccuracies due to coupon cleaning and weighing are eliminated.
4. A wide variety of probe elements allows selection of the required sensitivity and life.
5. The instrument required is easily operated and portable
6. Measurements may be made in gases or liquids above or below ground by use of special probes.

IV) Measurement of Corrosion by the Polarisation Method

When a voltage is impressed across two metal electrodes immersed in a conductive liquid a current will flow from one electrode through the liquid to the other electrode.

Within certain limits and conditions which the associated equipment takes care of the magnitude of this current will be proportional to the corrosivity of the liquid. This method can, of course, only be used in electrically conducting liquids and not in oils or gases.

The most important feature of this method is that changes in conditions which affect the corrosion rate are immediately indicated in the results, although it may take 24 hours to stabilize when first inserted in a system.

This type of test is very useful if the relative effects of a change in water treating chemicals are immediately required.

In addition to measuring the instantaneous corrosion rate, this instrument can also provide a measure of a water's pitting tendency. This is a qualitative rather than a quantitative measurement, but it can generally be stated that for satisfactory protection to be obtained, the pitting index as calculated should be less than the corrosion rate.

V) Measurement of Process Equipment

A practical means of observing the results of corrosion and the effect of treatment is by the periodic inspection of a specific unit or exchanger. This will only give a qualitative comparison, and obviously is not suitable where quick results are required. Photographic records of such examinations are very desirable for true comparisons to be made.

This method is only of value if backed up by other quantitative measurements, and is best used as a long term check on the effectiveness of a treatment programme.

VI) Corrosion Products in Systems

Regular analyses of a cooling water can give an indication of the corrosion occurring in a system. The constituents measured are normally those associated with the materials of construction, usually Iron, Copper and Aluminum. Various amounts of these elements can be expected to occur naturally in the feed water and due to other sources of contamination, but a change in level of the materials can give an indication of change in corrosion. As for the previous method, those measurements should be used in conjunction with one or other of the earlier monitoring systems.

B <u>Standards of Corrosion Rates</u>

Based on exposure times of at least 30 days for coupons and resistance methods, and comparative times for the other methods, corrosion rates may generally be rated as below:-

Above 10mpy	Poor or no protection
5-10 mpy	Moderate or doubtful protection
2-5 mpy	Good protection
Under 2 mpy	Excellent protection

These classifications refer to general corrosion only. In addition, the general appearance of coupons should be noted, with especial reference to pitting attack. This can be categorised thus:-

General etch - uniform attack
Localised attack - large isolated areas of corrosion
Pitting - small isolated areas of corrosion

The type of attack is usually further described as slight, moderate or severe.

C. Inhibitor Protection Rating

The following rating is given only as an approximate guide, as a great many substances can be used to give satisfactory protection if economic factors are not considered. However, it is necessary to balance acceptable corrosion rates with reasonably low costs, and the table should be considered in this context.

Classification of Inhibitor	**Corrosion Rate mpy**
Zinc/Chromate/Poly-Phosphate	Less than 2 mpy
Zinc/Poly-Phosphate, Nitrite	1 to 5 mpy
Natural & Synthetic Organic Based Inhibitors	2 to 10 mpy
Silicates	Greater than 5 mpy

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D Fouling Factors

Suspended solids from the raw water supply, from the air, or deposition and corrosion products can settle from the flowing cooling water on heat transfer surfaces. These deposits will not only reduce heat transfer but may also start or accelerate corrosion due to differential oxygen cells established beneath the deposits.

A further source of fouling can be attributed to micro-organisms, which can thrive in the warm, nutritive environment of cooling water system (see Section 4).

Fouling is normally differentiated from scale by the physical characteristics of the deposit, the former normally being generally softer, more voluminous and more subject to physical factor such as velocity and flow patterns. Nevertheless both fouling and scale contribute to reduction of heat transfer, the factors affecting this being given in Table 1

Table 1

Solids in raw make-up water
Process contamination
Type of corrosion inhibitor
Air-borne solids
Retention time
Temperature
Velocity
pH
Concentration Factor

Control limits depend upon the conditions in the system, but various processed organic formulations are available, designed specifically to minimize the effect of the various factors. Using such a treatment higher levels of fouling constituents can usually be tolerated for a given degree of fouling, or alternatively a cleaner system can be maintained. Typical levels of suspended solids that can be accepted to cause a minimum of fouling with and without treatment are given in Table 2.

Table 2

Exchanger	Carbon Steel Tubulars		Admiralty Brass Tubulars	
Treatment	No dispersant or antifoulant	With antifoulant	No dispersant or antifoulant	With antifoulant
Suspended Solids ppm	20 - 25	40 - 50	30 - 35	60 - 70

The <u>lower limit</u> should be <u>chosen</u> when it is essential for equipment to be maintained at the <u>designed efficiency</u> for long <u>periods of time</u>.

Adequate water velocities are of prime importance in minimizing fouling, and a minimum value of 3 f.p.s. is generally recommended.

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Methods for Detection and Monitoring of Fouling

(i) Visual inspection of open flumes, tower slats etc.

(ii) by measuring the increase in temperature difference between process and water side of equipment.

(iii) by measurement of vacuum deterioration in condensers.

(iv) inspection at constant intervals of known troublesome equipment; this should preferable be backed up by photographic records of the deposits.

(v) installation of a test heat exchanger in a slip stream of the cooling water, followed by periodic inspection. Care should be taken to reproduce process conditions, - temperature, velocities, etc.

Methods for Cleaning Fouled Equipment

(i) Mechanical - at unit shutdowns.

(ii) Chemical - dispersants, inhibited acid.

(iii) Physical - on line - rubber balls (Taprogge system)
  - reversing brushes (Mannesman system)
  - air rousing or bumping.
(iv) Physical - off line - air rousing or bumping

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APPENDIX 5

CLASSIFICATION OF CORROSION INHIBITORS

Inhibitors may be broadly classified as anodic, cathodic, or mixed. Their action is to modify the surface condition of the metal and as a general rule mixed inhibitors are more efficient in that a smaller amount is required to prevent corrosion. Anodic inhibitors may be dangerous if close control is not exercised since severe localized corrosion can result if insufficient inhibitor is present.

The following classification table is merely an indication of the types of chemical inhibitors which are available for corrosion prevention. The specific selection of an inhibitor requires adequate knowledge of its action and of the corrosion processes in the system under consideration. These factors would include operation, materials of construction, quality of water, concentration factor, and biological and effluent considerations. Generally commercially available corrosion inhibitors are often mixtures of one or more types.

ANODIC	Usage Level	Limitations
Sodium Nitrite	400 ppm to 1000 ppm Na NO_2	Conc. required depends on chloride level. Maintain at least 2 : 1 nitrite/chloride, main, 400 ppm. pH 7 - 9. Bacteria nutrient.
Sodium Chromate	500 ppm to 5000 ppm CrO_4	Chloride dependent, Max. 500 ppm. Sodium Chloride, dangerous inhibitor at low conc.; toxic; effluent disposal problem; used only above pH7
Sodium Silicate	20/40 ppm	pH 6.5 to 7.5
Sodium Borate	200 ppm	pH is buffered to 8 - 9.5. Used with nitrite in small closed systems
CATHODIC		
Zinc Salts	500 ppm min.	pH 6.5 to 7; Effluent problem

Polyphosphates Tanning	10/25 ppm 100 ppm 300 ppm	pH 6.5 to 7.5 Sludge problems in hot water. Most effective when pH = 8
MIXED INHIBITORS		
Zinc Chromate	15-20 ppm as CrO_4	Toxic pH 6.0 - 7.5
Chromate/ phosphate	15-20 ppm as CrO_4	Toxic pH 6.0 - 7.5
$Cr/Zn/PO_4$	15-20 ppm as CrO_4	Toxic pH 6.0 - 7.5
Zinc/ Phosphonate	3 ppm as Zn	Toxic to fish. pH 7.0 - 8.5
Zinc Polyphosphate	-15 ppm PO_4	Nutrient to micro-organisms pH 6.0-7.0
Filming amines	up to 100 ppm	Absorption inhibitor - protects by film formation.

Choice of Inhibitor

The choice of an inhibitor very much depends on:
- The conditions under which it has to function, with respect to water contaminants such as chloride ions.
- the temperature of the system.
- whether the system is closed or open.
- whether the system is large or small.
- the nature of the effluent problem.

TREATMENT AND CORROSION CONTROL OF COOLING WATER

Even with this information, the choice of an inhibitor is complicated. For example, for a large cooling water system (50 - 50000 m^3) the use of an anodic corrosion inhibitor is generally uneconomical since too high a concentration is required, though there are exceptions, for instance if the cost of the treatment is less than the cost of a plant shutdown due to corrosion. It is usually necessary however, to use an inhibitor which functions at low concentrations. At the present time inhibitors based on synergised chromate formulations appear to be the best, but these have the disadvantage of being toxic and thus present more effluent problems.

If a zinc/chromate inhibitor is used in a restricted effluent area, the chromate must be removed by reduction and precipitation, or by ion exchange, Polyphosphates hydrolyze and excessive use of this inhibitor can cause blockage in certain types of cooling systems by precipitation of calcium phosphate   The problem of hydrolysis becomes more acute as a temperature of 80º is approached.

Where cooling towers are situated in or close to residential areas, limitations may be imposed on the use to toxic inhibitors because of the loss of water from the system as a result of windage.

Before adopting any inhibitor, the River or Local Authority should be consulted regarding any limitations on effluent discharges.

APPENDIX 6

CONCENTRATION AND CONCENTRATION FACTOR

The term concentration is used in cooling water technology in two ways:-

1. As in standard chemical parlance it is used to indicate the amount of substance present in solution or otherwise; for example, 20 mg/l sodium chloride as solution in water or 2 g/m^3 ammonia in air.

2. The term concentration is also sometimes used in the sense of concentrating effect to describe the accumulation of dissolved solids in a cooling system subject to evaporation.

If, for example, 1 litre of water containing 230 ppm dissolved solids is reduced by evaporation to 500 ml and no precipitation takes place, the solids content will increase to 460 ppm, i.e. it concentrates by a factor of 2.0. If the water were reduced in volume still further to 250 ml the solids content would increase to 920 ppm. i.e. it would concentrate by a factor of 4. The expression "it concentrates twice" is ambiguous and should be avoided and the term "concentration factor" should be used.

Concentration Factor

Evaporative cooling systems are subject to two kinds of loss (a) evaporative loss and (b) loss in liquid form collectively known as wastage. This wastage can include leakage, deliberate removal for other applications and losses in droplet form in the air stream (known as drift or windage). In some systems, extra water must be wasted to limit the concentration factor; this is known as purge or blowdown.

$$\text{Concentration factor } (n) = \frac{\text{Wastage + evaporative loss } (E)}{\text{Wastage}}$$

$$\text{Wastage} = \frac{E}{n - 1}$$

$$\text{Make up} = \text{wastage + evaporative loss} = E + \frac{E}{n - 1}$$

The maximum value of n which can be permitted in any particular cooling system depends on several factors including maximum water temperature, composition of water supply, temperature drop in tower nature of chemicals applied and residence time.

In systems where the evaporative loss is not known, an approximate value can be obtained from the temperature drip in the cooling tower. Irrespective of the temperature of operation the evaporative loss for each 10 deg. C temperature drop in the tower is 1.8% of the circulation rate.

Example

Required concentration factor 1.8
Circulation Rate 1000 m^3/hr
Temperature Drop 15 deg. C
Evaporation (calculated) 27 m^3/hr
Leakage and drift = 20 m^3/hr. (measured by determining make up rate without purge).

Wastage required $\frac{E}{n - 1} = \frac{27}{1.8 - 1} = \frac{27}{0.8} = 33.75$ m^3/hr.

Make up required $E + \frac{E}{n - 1} = 27 + 33.75 = 60.75$ m^3/hr.

Purge required = 33.75 - 20 = 13.75 m^3/hr.
Definition of the other terms used in considering concentration effects is as follows:-

Concentration ratio (or "Cycles of Concentration") - concentration factor.

Drift (Windage) Physical loss of water caused by fraught of air through the tower. The magnitude of drift is largely determined by tower design and is much less in units where baffles are fitted. Some towers are also appreciably affected by weather conditions, especially side winds.

Purge (Blowdown or bleed off) Water removed deliberately from the cooling system to control the concentration factor.

Wastage = the sum of losses other than evaporation, i.e. drift, leakage, withdrawal for other purposes and purge.

APPENDIX 7

LANGELIER INDEX

The solubility of calcium carbonate and calcium bicarbonate in water is of particular importance because calcium carbonate is the most significant scale-forming compound. The solubility of calcium carbonate is affected by temperature and by other salts present but the factor of greatest significance in evaporative cooling systems is the aeration which takes place in the cooling tower, thus removing carbon dioxide. The point at which scaling occurs if often determined by temperature, but it can also occur occasionally at or near the aeration zone.

Many standard text books deal with this in detail, but the following is a very simplified interpretation (see Appendix 11).

Calcium carbonate is held in solution in water (at pH 5.5.- 8.5 by carbon dioxide). Part of the CO_2 helps to form the bicarbonate ion but excess carbon dioxide over that needed to produce the bicarbonate ion is needed to keep it in solution. If insufficient carbon dioxide is present, the bicarbonate will be unstable and some of it will decompose to precipitate carbonate and release carbon dioxide until equilibrium is reached. If excess carbon dioxide is present, it will be available for dissolving more calcium carbonate.

$$Ca\,(HCO_3)_2 \quad CaCO_3 + CO_2 + H_2O$$

Professor Langelier introduced the concept of "saturation pH value" or "pH"s, at which a water of any given composition (alkalinity, calcium content, dissolved solids) is in equilibrium at any given temperature. pHs can be calculated from physico-chemical data or an approximate value can be obtained by measuring pH value after bringing the solution into contact with calcite ($CaCO_3$) crystals and allowing time for equilibrium to be established.

The difference between the actual pH value and saturation pH is known as the "Saturation Index" or "Langelier Index".

Langelier (Saturation) Index = pH - pHs

If the Index is positive, the water is supersaturated and will tend to precipitate calcium carbonate. If negative, the water is capable of dissolving more calcium carbonate. If zero, the water is just saturated.

The Index affects corrosion only in so far as it affects calcium carbonate. If positive, corrosion will often be controlled but only if the calcium carbonate is precipitated in certain forms. In practice, many waters with a positive index are not corrosive but they may throw down a significant quantity of scale. In a system with a range of temperature, scaling at one point may indirectly bring about corrosion at other parts. Under some conditions a non-protective scale - usually permeable to dissolved oxygen or other constituents causing or accelerating corrosion - is formed.

The magnitude of the Index is not directly related to the behaviour of the water, but consideration of equilibrium conditions if often useful, taken in connection with other data, in assessing the conditions in a system. The equation also enables calculations to be carried out to assess chemical additions required to meet prescribed conditions. Generally speaking, however, the equilibria can only be interpreted accurately after a good deal of experience and considerable care should be exercised by the novice.

Reference may also be made to other formulæ based on the Langelier idea, but attempting to improve the quantitative basis. The most important of these is Ryznar's stability index 2 pHs - pH. Waters with stability index less than 6 tend to be scaling. The same care in interpretation is required as for Langelier.

APPENDIX 8

SIGNIFICANCE AND INTERPRETATION OF MICROBIOLOGICAL ANALYSES

These are many different types of chemicals available for the control of microbiological growths in cooling systems. Each of the general types of compounds used have ranging degrees of activity towards micro-organisms. For optimum results and to achieve the best cost/performance, the performance of the biocide must be matched with the type and degree of microbiological activity in the system.

Thus for every system there should be an effective way to monitor the effectiveness of the biocide program. The monitoring of heat exchanger performance, and visual inspections around the system and at the tower is one way. However, this approach may lead to false conclusions, since the fall off in heat exchanger performance could well be due to factors other than microbiological fouling, and conditions at the cooling tower may be quite different from those in heat exchangers. It can also be uneconomic, since if microbiological fouling is occurring, massive doses of biocides may be required to restore optimum conditions.

A better technique is through the regular measurement of the micro-organism concentrations by means of plate counts. The organisms usually counted include slime forming bacteria, sulphate reducing bacteria, a total bacteria count, algae and fungi. For each class, an "acceptable" concentration can be established for each cooling system.

Performing regular microbiological analyses will indicate:-

(a) The concentration of organisms of different types in the system.

(b) The effect of the addition of biocides on the organisms

(c) If the frequency and rate of treatment has to be changed to maintain control.

(d) The influence of nutritive contamination in the system.

The "acceptable" level of organisms present in the system can vary from plant to plant, but the following table shows some typical values that provide a basis for control.

Slime forming bacteria - not more than 10,000 organisms/ml
Sulphate reducing bacteria - none
Total bacteria - not more than 500,000 organisms/ml
Fungi - none

It should be emphasised that while these limits may be acceptable in some plants, different limits (higher or lower values for slime forming and total bacteria count) may be needed on other plants). In all cases, however, there should be an absence of sulphate reducing bacteria.

A single microbiological analysis only represents conditions at the time of sampling. Of more importance is the trend in organism activity. Results should therefore be plotted graphically to determine the minimum effective dosage of the biocide in the particular system, and to establish the minimum frequency of addition needed to maintain control in the system.

APPENDIX 9

ION EXCHANGE

Ion exchange materials arc polymeric compounds in the form of granules or beads 0.3 to 1.5 mm in diameter. They possess the unique property of being able to exchange ions attached to the matrix for ions in the solution surrounding them. Originally naturally occurring substances, such as zeolites or greensands, were used. Over the years these have been gradually replaced with synthetic materials such as sulphonated coals and resin polymers. The vast majority of the modern ion exchange resins are either based on phenol formaldehyde copolymers or polystyrene, but there are a few such as weakly acidic cation exchange based on polymethyl methacrylate

There are four main groups of ion exchange resins, weak cation, strong cation, weak anion and strong anion. The main characteristic in each of these particular four groups is as follows:-

(a) Weak Cation Resins

These are generally used in the hydrogen form after regeneration with dilute sulphuric or hydrochloric acid in water treatment. Their main function is the exchange of cations in solution associated with a weakly ionised acidic group, i.e. the calcium and magnesium ions attached to the bicarbonate radical as per the following reaction.

$$\begin{matrix} RH \\ RH \end{matrix} + Ca(HCO_3)_2 = \begin{matrix} R \\ R \end{matrix} > Ca + 2H_2CO_3$$

.

In the aforementioned reaction, the letter R is used to indicate the resin matrix and it can be seen that the temporary hardness of the raw water (the calcium and magnesium bicarbonate) have been converted to carbonic acid, which on passage down a degassing tower counter to the flow of air breaks down into carbon dioxide which is taken up with the air. Thus, not only has the temporary hardness been removed from the water treated, the total solids have also been reduced by the same quantity.

$$\begin{matrix} RNa \\ RNa \end{matrix} + CaCl_2 = 2NaCl + \begin{matrix} R \\ R \end{matrix} > Ca$$

This stage following weak cation exchange and degassing forms the flow sheet of the most common type of pretreatment of water for cooling systems and low pressure boiler make up and is known as de-alkalization/degassing/base exchange.

Strong cation resins regenerated with hydrochloric or sulphuric acid are capable of exchanging all ions in the solution, calcium magnesium and sodium for hydrogen ions, thus converting all the salt in the solution to the respective acids of the anions such as hydrochloric and sulphuric. Carbonic acid so formed can be removed as in the case of weak cation exchangers by degassing tower or if only in a small quantity may be removed by a strong anion exchange which will be discussed later. Cation exchange resins used in this way from the first stage of the process known as de-ionization.

$$\begin{matrix}RH\\RH\end{matrix} + CaSO_4 = \begin{matrix}R\\R\end{matrix} > Ca + H_2SO_4$$

(c) Weak Anion Resins

These are generally regenerated with sodium carbonate, or caustic soda though ammonia and saturated lime have been used. They have the property of absorbing the strong acids in the solution such as hydrochloric, sulphuric, nitric, etc., but will not absorb carbonic acid and silicic acid. Thus if water produced by strong cation exchange in the hydrogen form as above passed immediately through a column of weak anion exchanges de-mineralized water will be obtained but this will not be free from carbon dioxide or silica.

$$RNH_2 + HC! = RNH_3C!$$

Quality obtained after this stage assuming London water is the raw water to start with would have a conductivity of 15-20 microsiemens per metre.

(d) Strong Anion Resins

These ion exchange resins are always regenerated with the strong bases of which the only common one is caustic soda. They have the property of absorbing all anions in the solutions, be they strong - such as chloride and sulphate - or weak, such as carbon dioxide and silica, and thus are capable of giving fully de-ionized water, In this particular group there are two subdivisions known as Type 1 and Type 2. Type 2 resins are slightly less basic than Type 1 and normally have a greater efficiency with respect to use of regenerant but do not produce quite so high quality of water.

$$ROH + HCI = RCI + H_2O$$

(c) Mixed Bed

The ultimate treatment to produce extremely high quality de-ionized water is the mixed bed unit in which after individual regeneration with acid and caustic soda respectively, strong cation resin and strong anion resin Type 1 are mixed together in a single unit. A water quality superior to that of distilled water can easily be achieved. i.e. conductivity less then 1 microsiemens per metre.

The foregoing is a brief outline of ion exchange resins but is by no means complete. The selection of an ion exchange for particular duty depends on many things and it is possible that with the same raw water and requiring the same quality treated water, several different routes are equally possible.

Individual viability is dependent on the capital costs and running costs ratio at an individual site based on the availability of potential regenerants already on site, amongst other factors. For instance in the United Kingdom, hydrochloric acid is generally not used in preference to sulphuric acid because of a greater storage problem and higher costs. However, if hydrochloric acid is already in use on a site and sulphuric acid is not, then the ion exchange process will designed around hydrochloric acid. As hydrochloric acid is better as a regenerant than an equivalent quantity of sulphuric acid, this factor will affect the amount of resin in the units. When a problem arises with regard to water quality where it is thought possible that ion exchange may supply an answer, then a reputable water treatment company or ion exchange resin manufacturer should be consulted.

ROSE CORROSION SERVICES LIMITED

TECHNICAL NOTE 5

TREATMENT AND CORROSION CONTROL OF COOLING WATER

APPENDIX 10

CLARIFICATION AND FILTRATION

CLARIFICATION

The term clarification embodies a number of treatment processes designed to remove suspended solids and colour from water. The processes described may be used separately or in combination one with another, depending upon the condition of the water and the degree of clarification required. The processes may be applied to the raw water or to part of the circulating cooling water, to maintain the level of suspended solids below a prescribed limit.

1. Sedimentation

Coarse suspended material may frequently be removed from the water by passing it through a settling tank of sufficient capacity and retention time to enable the particles to settle under the effect of gravity so that the settled solids or sludge can be discharged to waste from the bottom of the tank and the supernatant clarified water from the top of the tank. This simple form of clarification without the addition of conditioning chemicals does not remove the soluble colouring material, and frequently may not remove the smaller and lighter particles in suspension. However, the removal of these latter substances can frequently be enhanced by the incorporation of coagulation and flocculation treatments.

2. Coagulation and Flocculation

The particles of suspended matter normally present in natural water carry a negative electrical charge on their surface which tends to maintain the fine particles in a state of dispersion, due to mutual electrical repulsion.

In order to enable the particles to come together and flocculate it is necessary to neutralize the surface charge and this is achieved by the process of coagulation. The coagulants commonly used in water treatment are salts of aluminum and iron which have the power to reduce the surface charger and also react under suitable conditions with the natural alkalinity of the water to form colloidal hydrolysis products, capable of attracting, entraining, and absorbing the fine suspended solids and organic matter.

The coagulants most commonly employed in water treatment are aluminium sulphate, sodium aluminate, ferrous sulphate, chlorinated ferrous sulphate, ferric sulphate and ferric chloride. In addition there are a range of chemicals generally described as polyelectrolytes which may sometimes be used separately or in conjunction with one of the previously mentioned coagulants to improve coagulation and flocculation. These polyelectrolytes may be inorganic flocculants such as polymeric silica, natural organic materials such as sodium alginate, modified tannins and modified starches, or purely synthetic organic materials based on polyacrylate and polyamides. The synthetic organic materials can be made to perform as coagulants and flocculants (cationic polyelectrolytes) or merely as flocculants (anionic polyelectrolytes).

In order to ensure complete precipitation of the coagulant it is essential to adjust the alkalinity and pH value of the water being treated by the addition of acid or alkali. Failure to do this may result in incomplete utilisation of the coagulant, the formation of large by relatively light and fragile floc particles, and the presence of residual soluble coagulant salt in the clarifies water. The latter situation may result in precipitation of the coagulant after the water has left the clarification plant, and the formation of suspended solids in the cooling system.

Although the processes of coagulation and flocculation may be capable of converting the fine suspended solids into large floc particles, the settling rate of the particles may still not be suitable for the throughput of the treatment process if the specific gravity of the floc particles is still close to that of the suspended water.

In order to increase the density of the individual particles the treatment may be carried out in a sludge blanket sedimentation tank or one in which sludge from earlier treatment is re-circulated to form a nucleus onto which new precipitate forms.

The sludge blanket and sludge re-circulation processes are normally carried out in a tank in which the products of previous treatment are maintained in suspension as a blanket or sludge pool, by an upward flow of the water being treated.

The high concentration of sludge maintained in the lower part of the tank ensures intimate contact of the freshly formed colloidal coagulant particles with older material which has become heavy due to ageing.

In the treatment of waters where the level of suspended solids is fairly low or where there is a considerable amount of organic colour to be removed, the use of a sludge blanket or sludge recirculation process will frequently enable very much greater throughputs to be obtained for a given size of clarification plant.

3. Filtration

Some natural waters and even water decanted from sedimentation vessels after coagulation and flocculation frequently contain small amounts of suspended matter which must be removed by filtration. A filter usually consists of a bed of granular material such as sand or anthracite, through which water flows in a downward direction. The suspended matter in the water is trapped on the surface or in the voids of the filter bed. As the bed becomes loaded with suspended matter the pressure loss through the filter bed increases due to constriction of the voids and eventually the filter must be taken out of service for cleaning, either when the headloss has become unacceptable or when the quality of the filtrate is no longer acceptable.

The filter cleaning operation usually consists of an air scour to agitate the filter bed and loosen the entrapped dirt, combined or followed by a backwash with water to expand and partially fluidize the bed to enable the dirt to be washed out.

In some filters, the filter bed may consist of a layer of coarse anthracite superimposed on a layer of fine sand, to increase the degree of in depth filtration, and increase the total capacity of the filter for suspended solids. In other filters the same requirement is met by operating the filter in an upward flow condition so that the water passes first through coarse filter material and then through progressively finer material as the bulk of the suspended solids are removed.

APPENDIX 11

BIBLIOGRAPHY