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**OECD SERIES ON EMISSION SCENARIO DOCUMENTS
Number 4**

EMISSION SCENARIO DOCUMENT ON WATER TREATMENT CHEMICALS

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OECD Environmental Health and Safety Publications

Series on Emission Scenario Documents No. 4

**EMISSION SCENARIO DOCUMENT ON
WATER TREATMENT CHEMICALS**

Environment Directorate

Organisation for Economic Co-operation and Development

June 2004

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The Environmental Health and Safety Programme co-operates closely with other international organisations. This document was produced within the framework of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC).

The Inter-Organization Programme for the Sound Management of Chemicals (IOMC) was established in 1995 by UNEP, ILO, FAO, WHO, UNIDO and the OECD (the Participating Organizations), following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. UNITAR joined the IOMC in 1997 to become the seventh Participating Organization. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organizations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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or contact:

**OECD Environment Directorate,
Environmental Health and Safety Division**

**2 rue André-Pascal
75775 Paris Cedex 16
France**

Fax: (33-1) 45 24 16 75

E-mail: ehscont@oecd.org

Explanatory notes

Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns and release pathways of chemicals used in the treatment of water in a number of areas to assist in the estimation of releases of chemicals to the environment.

This ESD should be seen as a 'living' document, which provides the most updated information available. As such, an ESD can be updated to take account of changes and new information, and extended to cover the industry area in countries other than the lead (the United Kingdom). Users of the document are encouraged to submit comments, corrections, updates and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org). The comments received will be forwarded to the OECD Task Force on Environmental Exposure Assessment, which will review the comments every two years so that the lead country can update the document. The submitted information will also be made available to users within the OECD web-site (www.oecd.org/env/riskassessment).

How to use this document

The user of this ESD needs to consider how the information contained in the document covers the situation for which they wish to estimate releases of chemicals. The document could be used as a framework to identify the information needed, or the approaches in the document could be used together with the suggested default values to provide estimates. Where specific information is available it should be used in preference to the defaults. At all times, the values inputted and the results should be critically reviewed to assure their validity and appropriateness.

Coverage

This ESD covers the use of chemicals to treat water in closed heating and cooling systems, open cooling systems, paper production and swimming pools. It deals with releases on initial treatment and through the life of equipment where appropriate. The methods included estimate releases to water only, and do not cover the releases from container residue.

The industry categories, use categories and biocidal product types relevant to this document are as follows.

Industry category	Use Category	Biocidal product type
6 – Public domain	14 – anti-scaling, deposition, corrosion inhibitor 39 – biocides, non-agricultural	2 – private area and public health area disinfectants and other biocidal products (swimming pools, air-conditioning) 11 – preservatives for liquid cooling and processing systems
12 – pulp, paper and board industry	14 – anti-scaling 39 – biocides, non-agricultural 43 – process regulators (coagulants, retention aids, defoamers) 0 – drainage aids	11 – preservatives for liquid cooling and processing systems

How this document was developed

The document is based on a report produced by the Building Research Establishment for the UK Environment Agency entitled 'Use Category Document - Water Treatment Chemicals'. The original purpose of the document was to provide information to be used in risk assessments for new and existing substances in the EU. Information for the original report was largely provided by practitioners in the industry with a wide breadth of knowledge and experience. Published sources are cited where appropriate, but most of the information did not come from such sources and was based on this knowledge and experience. Unless a specific source is cited for a piece of information, it should be assumed to be derived from the experience of the original authors. The information was collected for the original report over the period 1994-1997.

The OECD Task Force on Environmental Exposure Assessment selected this original document as suitable for development as an OECD-wide emission scenario document by revising it with additional information including where possible information from countries outside the EU. The formal consultation took place over the period of February to May 2002.

Comments on the document were received from Canada, Finland, Japan, the UK and United States. Finland and Japan provided information on the papermaking industry in their countries, and this has been added to the information already included. Information from a United States generic scenario for cooling tower system has been incorporated into the document. Some countries use different chemicals to those indicated in the original report. This is partly due to different practices, but also to the fact that use of chemicals changes as new products are developed, or existing products are found to present a higher risk to the environment. Where certain chemicals are used or not used has been indicated in the document.

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1. INTRODUCTION

1.1 Overview and purpose of document

1. This document is intended to provide information to be used for risk assessment of new and existing substances.

2. This document provides information on water treatment chemicals used in recirculating systems, their use and release. Four main use areas are considered.

- Closed cooling and heating systems (Section B)
- Open cooling systems (Section C)
- Systems within the papermaking industry (Section D)
- Swimming pools (Section E)

3. The amount of information available varies for each use category. Where possible a published source for information has been cited. However much of the information included comes from the experience of the authors (Iddon and Fielden) and from others consulted during the production of the report. Hence much of the information in this report appears without a specific reference.

1.1.1 *Cooling and heating systems*

4. Appliances and processes requiring cooling vary extensively from machinery compressors to air conditioning systems. The general principle of cooling circuits is that cold water enters the system and is heated by contact with hot surfaces within a heat exchanger.

5. Cooling water systems may be either 'once-through', in which the water is discharged to drains or rivers after heat exchange, or 'recirculating', in which the water is cooled by contact with a secondary fluid (air or water) before being recirculated to the system.

6. In a 'closed' recirculating system, the water is cooled in a second heat exchanger without coming into contact with the atmosphere. In an 'open' recirculating system, the hot water is cooled by partial evaporation in a cooling tower and then returned to the appliance.

7. Closed recirculating systems, i.e. without evaporation, require very little make-up water to maintain flows. However, open systems which do need make-up water and which tend to require more water treatment are more common.

8. Most cooling systems can be categorised using the above terms, with differences in the size of the system and the volume of water flow necessary for the system to be cooled efficiently. The size of the system, as well as the type of system, will govern the types and amounts of water treatment chemicals needed.

9. The highly visible, hyperbolic natural draught cooling towers associated with inland power stations are excluded from this report, since although they use very large volumes of water, these are not chemically treated.

1.1.2 Systems within the papermaking industry

10. Many paper mills are attempting to recirculate wastewater from the papermaking process. The water is used to homogenise the pulp for conversion to paper via the papermaking machine. The wire and press section expel a good proportion of the water, which can be collected and recirculated. These stages are called the 'wet end'.

11. The section of this report on papermaking is primarily concerned with water recirculating around the papermaking machine from the wet end, the problems associated with the water, the treatment chemicals added to the water to rectify those problems and the water discharged.

1.1.3 Swimming pools

12. In order to maintain recirculated swimming pool water in a condition which is safe and appealing for bathers it needs to be treated in a variety of ways to meet the desired chemical and bacteriological quality.

1.2 Problems associated with recirculating water systems

13. Generally, the potential problem areas for which chemical treatment of water is required in a recirculating system are scaling and general fouling, corrosion, and the growth of micro-organisms (which leads to fouling). There are also problems specific to particular systems which will be discussed in the relevant sections.

14. The methods of treatment used to overcome these problems generally fall into three groups: pre-treatment; chemical treatment; and physical treatment.

1.2.1 Corrosion

1.2.1.1 Characteristics

15. Corrosion in cooling water systems is an electrochemical process, which is the normal form of corrosion at or around a neutral pH (cooling water pH varies between 6.0 and 9.0, 8.3 in open systems). Acidic corrosion will only arise under exceptional circumstances, and galvanic corrosion can either be engineered out, or controlled by cathodic protection.

16. Corrosion removes some of the metal from a pipe or other surface exposed to a corroding medium. This process cannot be prevented entirely but loss of metal at a uniformly very slow rate over the whole surface area does not lead to problems. However, localised areas of corrosion can lead to rapid system failure even where the actual amount of metal lost is small.

17. 'Pitting' and 'tuberculation' (where a cap of corrosion products or microbiological matter forms over an area of pitting) are two of the most common forms of localised corrosion and are typical cooling water system problems. Crevice corrosion may also be seen in places where metals are connected with non-metallic materials.

18. All metals have a tendency to corrode. In cooling systems, the metals and alloys which are used are, in increasing order of corrosion resistance, carbon steel, galvanised steel, copper, admiralty brass, aluminium brass, cupro-nickel, stainless steel and titanium.

19. Corrosion cannot proceed unless both the anodic and cathodic reactions take place. The objective of corrosion control is to limit the extent of either or both of these reactions, so that metal loss is kept to an acceptable level.

20. In an open system there is a higher amount of dissolved oxygen getting into the system than closed systems. This enables the formation of more hydroxyl ions which combine with the metal ions to form corrosion products.

1.2.1.2 Causes

Corrosion is often associated with the following.

- Poor system design
- Ingress of air
- Debris/foreign matter remaining after poor pre-commission cleaning
- Acidity - presence of anaerobic bacteria
- Galvanic action - mixed metals of different electrochemical potential
- High chloride ion concentrations
- Grease and oil
- Unsuitable/inadequate water treatment

1.2.1.3 Effects

21. Corrosion causes practical problems such as reduction in heat transfer, reduced water flow, excessive wear on moving parts and, in extreme cases, plant failure due to leakage or structural damage. Pitting is particularly damaging as it can lead to rapid failure of equipment.

22. Corrosion by-products can lead to system fouling in low flow areas and form tubercles over corrosion sites, which promote pitting rather than uniform corrosion.

1.2.1.4 Control

23. The complete elimination of corrosion is an unattainable goal, but for practical purposes, wastage through corrosion must be kept at an acceptable level. Corrosion can be retarded by the addition of treatment chemicals or corrosion inhibitors which can act in one of the following general ways:

- Anodic inhibition: modification of naturally occurring metal oxide surface films to make them more protective.

- Cathodic inhibition: using the chemistry of corrosion cells to generate a protective film at the cathodic sites.
- Protective film-forming inhibition: the use of certain organic compounds which form a monomolecular layer over both anodic and cathodic areas and stifle or retard the corresponding corrosion reactions.

24. A formulated corrosion inhibitor will normally employ a combination of these inhibition processes, depending on the type of system and its operation.

Anodic

25. Chromate is the most efficient of the anodic inhibitors, especially when in combination with zinc ions. Ferrocyanide can be used to control pitting but the sludge generated may cause fouling. An additional problem arises if the water is chlorinated since ferrocyanide is converted to ferricyanide and corrosion is accelerated. Systems containing copper, steel and aluminium are not protected by chromate, so mixtures of sodium tetraborate and sodium nitrite are used. Nitrite is an anodic oxidising inhibitor. The orthophosphate ion can also behave as an anodic inhibitor by forming a film of iron phosphate on iron surfaces.

Cathodic

26. These include polyphosphates and zinc compounds including zinc polyphosphate and zinc aminomethylenephosphonate. Careful pH control is necessary when using these agents, since precipitation of zinc hydroxide and basic phosphates may lead to fouling.

Mixed anodic/cathodic

27. When corrosion anodes and cathodes are simultaneously inhibited, the ions in the formulations have a synergistic action. Product dosages can therefore be greatly reduced by the use of this synergistic effect. Examples include chromates, polyphosphates or phosphonates used in combination with the zinc ion.

Protective films

28. These are generally organic chemicals containing polar groups which are chemisorbed by metals, for example sodium 2-mercaptobenzothiazole in conjunction with polyacrylamides, and benzotriazole with polyamines, phosphoramides and phosphonium compounds. The concentration of chemical needed in the water is high, e.g. 50-150 mg/l.

1.2.2 Scale formation

1.2.2.1 Characteristics

29. Scaling is the crystalline growth of an adherent layer of insoluble salt or oxide on a surface where heat is exchanged. More often than not this is produced by the effect of increases in temperature on the solubility of salts in the water. Calcium carbonate is the most common constituent of deposits found in cooling systems in hard water areas. The occurrence of magnesium salts in deposits is less common; however, the presence of silica may lead to the formation of magnesium silicate scale. Other salts which may form in deposits in certain conditions include calcium sulphate, phosphates and metal hydroxides.

30. In open cooling systems, the concentration effect arising from evaporation can lead to the deposition (in the form of scale or amorphous deposits) of insoluble mineral salts of which calcium carbonate is most common.

1.2.2.2 Effects

31. The practical problems associated with scale formation are reduction in heat transfer resulting from the insulating nature of the scale deposits and reduced water flow resulting from blockages caused by scale build-up in the system.

1.2.2.3 Control

32. Pre-treatment methods used to control scale rely on the use of base exchange softening plants, i.e. ion exchange processes which exchange the calcium and magnesium ions in the intake water for sodium ions which form highly soluble compounds. Another method is to reduce the potential for calcium carbonate formation by converting part of the calcium bicarbonate in the make-up water to a more soluble salt by the addition of mineral acid, usually sulphuric. Such acid additions, which reduce the pH, may also be required to provide the correct environment for certain corrosion control chemicals.

33. The chemical control of scaling is achieved by the addition of active agents with either chemical or physical modes of action. The chemically active agents work in one of two ways, either by affecting the solubility of the scale or altering the growth mechanism of the crystals. In the first case, chelating or complexing agents may be used, for example oxydiacetates, iminodiacetates, oxydisuccinates, polyphosphates, phosphonates, phosphate esters, polyacrylates, NTA (nitrilotriacetic acid) and EDTA (ethylenediaminetetra-acetic acid). In the second case, sequestrants or anti-nucleating agents are used, which disturb the kinetics of natural crystal growth and prevent scaling. These agents include polyphosphates (also used for corrosion control), phosphate esters (good for calcium sulphate control but not as effective against calcium carbonate) and phosphonates.

1.2.3 General fouling

1.2.3.1 Characteristics

34. Fouling is a general term covering the loose, porous or gelatinous accumulation of particulate matter in the system. The particulate matter may consist of airborne dust and debris; mud, silt and clay; soldering flux, jointing compounds and grease; biological matter such as insects, pollen and plant material and microbiological slimes; insoluble corrosion products; reactions of water treatment chemicals with constituents of the water and with each other e.g. calcium phosphate, zinc phosphate; and process contaminants.

35. These may arise during the manufacture, storage and installation of components of the system, via the make-up water and via the cooling tower (which acts as an air-scrubber transferring particulate matter from the atmosphere to the recirculating water). Scale forming substances, as listed above, may also form at a location downstream from their initial production.

36. Deposits are produced by the laying down of insoluble matter in a location remote from that where it is formed and are frequently the result of changes in water velocities. For example, a sudden reduction in water flow rate can result in deposition of material which was previously held in suspension by the flowing water.

1.2.3.2 *Effects*

37. Scale and deposits can cause major operational problems in cooling systems. These include loss of efficiency, product loss or deterioration, and blockage of heat-exchangers and pipe work. They can be so severe as to cause tower collapse. In air-conditioning systems, the loss of efficiency can lead to inadequate temperature control within buildings and to plant trip-out. Fouling interferes with the flow of cooling water, reduces heat transfer, increases corrosion and leads to microbiological contamination. The particular problems of microbiological fouling are dealt with below.

38. At high flow rates, the tubes of the heat exchanger are likely to remain free of fouling, the material being swept away by the water flow. However, under low flow conditions, the insoluble material settles and accumulates and, when scaling is also heavy, both heat transfer and flow are severely curtailed.

1.2.3.3 *Control*

39. The chemical control of general fouling is achieved by the use of surface active agents to disperse insoluble substances and if possible bring them into colloidal solution. Synthetic dispersants include long-chain polymers with ionic groups, polyacrylates and polyacrylamides. Natural compounds such as lignosulphonates and other vegetable extracts (e.g. tannins) were widely used for this purpose but have now largely been replaced by synthetic dispersants.

40. Fouling may also be controlled by the physical method of filtration, and it is common practice to incorporate strainers or sidestream purification systems in cooling circuits to remove suspended particles. Further control of problems leading to deposition, e.g. corrosion and microbiological growths, can reduce fouling.

1.2.4 *Growth of micro-organisms, fungi and algae*

1.2.4.1 *Characteristics*

41. A major problem in open recirculating systems and, to a lesser extent, in once-through systems is the growth of micro-organisms as well as algae and fungi.

Fungi

42. They require air, water and carbohydrate for growth. In older wooden cooling tower systems, the carbohydrate was provided by the cooling tower structure itself, leading to decay of the wood.

Bacteria

43. These occur freely in the water circulating in cooling systems. Those causing major problems include slime-forming bacteria, sulphate-reducing bacteria, iron bacteria and pathogenic bacteria.

Algae

44. Algae can accumulate, particularly where they are exposed to sunlight. Large growths of algae can cause problems by blocking the air path in cooling towers, by blocking the water distribution nozzles on the cooling tower deck, by plugging piping and by accelerating corrosion and pitting.

45. Open systems receive bacteria from ambient air and make up water. The problems associated with microbiological activity are particularly relevant to open cooling systems, since it is these systems which can lead to outbreaks of Legionnaires' disease.

1.2.4.2 *Causes*

46. Micro-organisms, algae and fungi may arise in a cooling water system from a number of sources:

- May enter with the make up water or be carried with air
- May be present in original system components
- May be present with some forms of treatment
- May enter through open feed and expansion tanks

1.2.4.3 *Effects*

47. Problems arise when the micro-organisms are allowed to grow or flourish to excess leading to the formation of a biofilm on systems surfaces. This growth reduces heat transfer, induces highly localised microbial corrosion, reduces the effectiveness of corrosion inhibitors, leads to the fouling of the system, and harbours legionellae and provides an environment for its growth.

1.2.4.4 *Control*

48. In order to control microbiological growth in open cooling systems, a two fold control programme is necessary.

- Cleaning and disinfecting of the system twice a year.
- Dosing of system water with biocides to maintain protection.

49. Microbiological control chemicals fall into two categories, biocides, which kill the micro-organisms, and biodispersants, which enhance the performance of biocides through loosening microbial deposits which can then be killed or flushed away. The biodispersants also expose new layers of microbial slime or algae to the attack of biocides.

50. Biocides themselves fall into two groups: oxidising biocides, which can kill very quickly by oxidising cell materials; and non-oxidising biocides which need a longer contact time and act in different ways to kill organisms, e.g. by dissolving cell wall materials and interfering with cell metabolism.

Oxidising biocides

51. These include strong oxidising agents such as chlorine, bromine, chlorine dioxide and ozone. Chlorination is a well proven method of control which is used in conjunction with non-oxidising biocides and biodispersants. However, it loses effectiveness in alkaline waters and in the presence of contaminants such as ammonia, methanol and ethylene glycol. It is also corrosive towards common materials used in construction, e.g. stainless steel, and forms environmentally unacceptable degradation products. The use of bromine and chlorine dioxide overcomes many of these limitations. Ozone is not widely used in cooling water systems.

Non-oxidising biocides

52. These are more stable than the oxidising agents mentioned above and are active over a longer time period. Nevertheless, the concentration of these agents will also decrease with time as a result of water losses, the addition of make-up water and the removal of blow-down water, as well as through

degradation processes. Bacteria may build up a resistance towards biocides necessitating the use of more than one compound.

53. Oxidising biocides are widely used in condenser cooling systems and open evaporative cooling systems. Non-oxidising biocides are used in condenser water cooling systems employing evaporative cooling towers and also in closed recirculating systems. Biodispersants are used in all types of recirculating water system.

54. The risk of Legionnaire's disease from cooling systems means that the control of legionellae bacteria is a particularly important consideration. To control legionellae, the treatment regime should adequately control the amounts of scale and rust (which might protect bacteria in the system), sediments (which might prevent water treatment processes from working effectively) and bacteria and other organisms. This is usually achieved by the use of an appropriate overall treatment package including scale and corrosion inhibitors as well as the biocidal treatment itself.

1.3 Releases from the recirculating system

1.3.1 Formulation release

55. It is anticipated that the bulk of treatment formulations will be toll blended at sites away from the recirculating water site. However, there are some retention and drainage aids, biocides and inorganic acids supplied direct to the paper mill without going through a formulator.

56. It is estimated that during the formulating stage up to 2 % of the finished product will be lost. Losses derive from the blended product sticking to the blending equipment, washing out between batches and occasional spillages and leaks.

1.3.2 General release

57. Generally the potential release of treatment chemicals is system specific and depends on maintenance, monitoring and operating procedures on site.

58. The amounts of treatment chemicals present in wastewater depend on the concentrations and dosing levels for the treatment package as recommended by the chemical producer and the system installation company.

59. Varying degrees of wastewater treatment may or may not be provided on site or by a local sewage treatment works.

1.3.2.1 Once-through systems

60. These systems will not be considered in this document for two reasons. Firstly, they are not a recirculating water system. Secondly, due to the large volumes of water involved with once-through systems, typically no waste treatment other than settling is given to the discharged cooling water and no waste treatment chemicals are added. The most likely treatment chemical which may be added is to maintain a low chlorine residual.

1.3.2.2 Recirculating cooling systems

Open

61. For open recirculating systems, potential release to the environment will be via blow-down which may be discharged to estuarine waters, routed to an on-site treatment plant or to a local sewage treatment works. The preferred method of blow-down is a continuous low rate bleed using a flow control valve. The setting of the valve depends on the rate of concentration of dissolved solids in the cooling water and is set so that this concentration is below that at which scaling occurs. Blow-down is usually carried out after every 2-5 cycles of water through the tower.

62. It is not likely that blowdown will occur during or immediately after dosing of water treatment chemicals, as this will lead to the dilution of the biocide to below the optimum effective concentration. Excessive blow-down leads to the dilution of treatment chemicals and their waste in effluent streams, whereas insufficient blow-down will lead to over concentration of dissolved solids and result in scaling and often the precipitation of hardness salts on heat transfer surfaces.

63. Other potential releases of water treatment chemicals could arise from leakages in the system and a worst-case release scenario would involve complete system failure and the discharge of the water flow from the entire circuit. This may also occur at planned intervals as a result of shut-downs for system maintenance which necessitate the draining of the circuit.

Closed

64. In closed systems there should be little loss of water, thus requiring small amounts of make up water. A closed system, following routine monitoring and treatment programmes, is expected to lose approximately 1% of the system volume per month.

65. The larger volumes of losses occur at various stages of the systems life cycle such as commissioning of a new system, changes to an existing system and the uncontrolled losses that occur prior to bringing a system back on line.

66. Each of these stages may result in a total drain of the system volume along with the treatment chemicals. There may also be losses of cleaning agent and spillages of treatment chemicals.

1.3.2.3 Papermaking machine

67. The primary loss of water treatment chemicals will be from the 'wet end', discharged continuously whilst the machine is in operation. Although attempts are made to recirculate water from this stage, typically a good proportion is lost as wastewater. Volatile treatment chemicals may be lost through the paper drying process which follows the wet end.

68. Other losses from the papermaking machine include waste cleaning and biocidal compounds arising from the periodic 'boil out' of the papermaking machine.

1.3.2.4 Swimming pools

69. One of the essential aspects of pool management is to draw off a portion of the recirculating pool water and replace it with fresh water. Most swimming pools incorporate pressure sand filters which require backwashing as they become clogged up with filtrated solids. A portion of the recirculating water is used to backwash the system, which then needs replacing with fresh water. In the UK, recommended levels of water replacement are in the region of 10% of the pool volume per week (Aquabrome 1985, PWTAG 1990). In most cases this would be carried out by, or in conjunction with, backwashing the filter. Effluent arising from backwashing and diluting the system would typically be discharged to sewer.

2. CLOSED COOLING AND HEATING SYSTEMS

2.1 Description of closed systems

2.1.1 *General description*

70. A closed system recirculates water which is cooled or heated by chillers, boilers or other forms of heat exchanger. Water is supplied via header tanks or pressurisation units so the system water is not in contact with the atmosphere. As a result closed recirculating systems should have very low losses and require far less make up water than open systems.

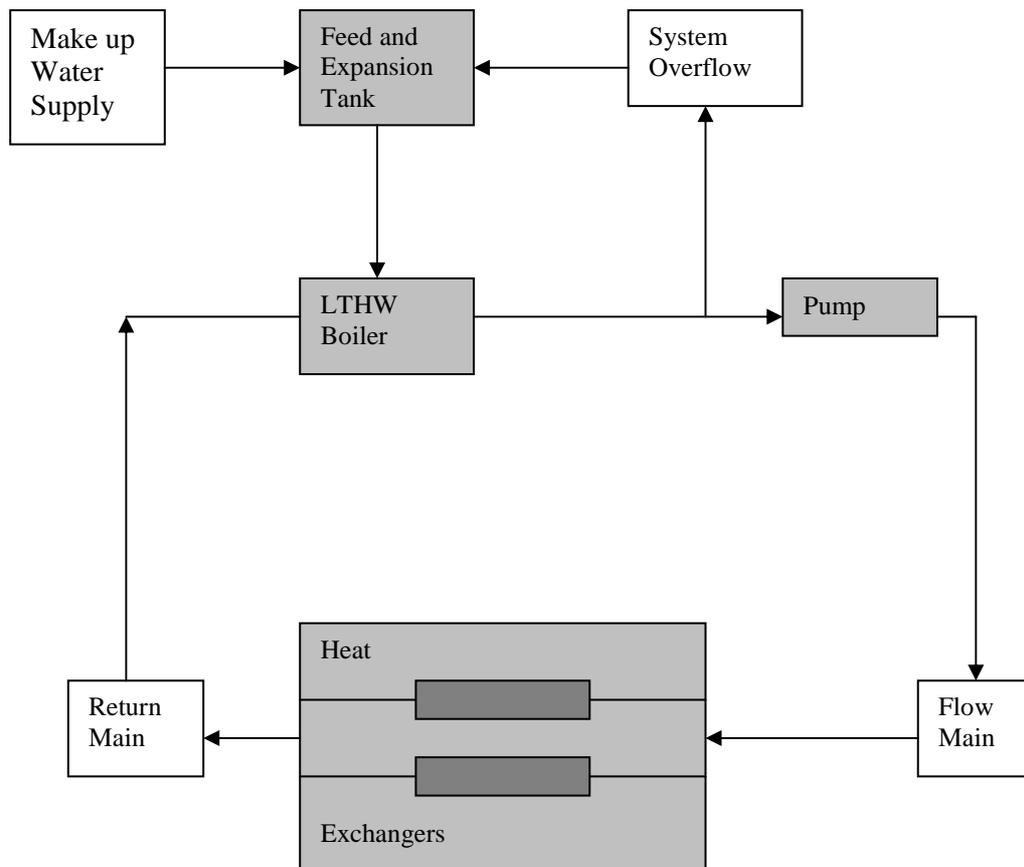
2.1.2 *Types of closed system*

71. Types of closed system are:

- 1) Chilled water and other cooling applications, usually operating around 5° C
- 2) Low and Medium Temperature Heating Water (LTHW/MTHW) Systems operating at temperatures between 80 and 120° C and pressurised by the head of water in the make up tank or a pressurisation unit.
- 3) High Temperature Hot Water systems where the temperature is above 120° C

72. Typical LTHW recirculating system may be pressurised by the head of water in the make up tank or by a pressurisation unit.

Figure 2.1 Typical Low Temperature Heating Water System



2.1.3 Losses

73. In theory, once a system has been carefully designed, installed, pre-commission cleaned and correctly treated with a suitable water treatment programme incorporating a compatible biocide, it should remain a sealed system requiring little or no make up water. Water losses from such a system should be minimal, typically around 1% of total system volume per month. This is assumed in the later calculations.

74. In practice, there may be other losses associated with the various stages in the system’s life cycle. This is especially true where a system is not routinely checked for problems or excess losses.

75. Four scenarios have been identified as potentially occurring during the life cycle of a closed system.

- New system pre-commission cleaning and filling with treatment chemicals.
- Changes or additions to new or existing systems.
- Design losses from correctly treated and monitored systems.
- Uncontrolled losses equal to or in excess of design loss due to irregular treatment or monitoring.

76. Generally releases from the system can be summarised under the following loss factors:

- L1 Release during the addition of the formulation to the system.
- L2 Design losses which are controlled as part of a routine programme.

- L3 Draining and uncontrolled losses resulting from lack of a routine programme.
- L4 Losses from the flushing process.
- L5 Losses from the chemical cleaning process.
- L6 Losses from the passivation process.
- L7 Losses arising from acid descale of the boiler.

The symbols L1 etc are used in the diagrams and text to identify the steps being considered.

77. Losses during formulation of the chemical treatment are estimated to be up to 2 % of the finished product. This would be released through the cleaning out of equipment at the formulator's site, not on the site where a closed system is installed.

2.2 The need for chemical inhibitor formulations

2.2.1 General comments

78. Recirculating closed chilled, cooling and heating systems are used in a wide variety of building applications. They provide warm and chilled air for air conditioning and serve radiators, 'Versatemp' units, fancoil units and finned perimeter heating circuits.

79. These systems are located in a variety of industrial, commercial and institutional sites. The problems associated with these systems lead to loss of chemicals and treated water irrespective of the location or size of the system. These problems have been discussed in general in the introduction, however there are aspects specific to these types of system.

2.2.2 Problems associated with heating systems

80. The main problems arising in heating systems are corrosion, scale deposition, microbiological fouling and sludges/suspended material.

2.2.3 Problems associated with Chilled and Cooling systems

81. Water induced problems in chilled and closed cooling systems differ slightly because of the lower temperatures. These lower temperatures tend to suppress microbiological activity. In addition, scaling requires higher system temperatures and heat transfer rates.

2.2.4 Effects of problems

82. Make up water to closed systems will be cold, aerated and may be hard water. Problems manifest themselves in a variety of different ways .

- Sludge, discoloration, suspended material in the system water when samples are drawn.
- Blocked sample or flushing points.
- Low water treatment chemical reserves found when routine sampling is carried out indicating loss of system water between water treatment service visits.
- High iron/copper levels in routine system waters drawn for analysis.
- Automatic control valves not responding.

- Fancoil/Versatemp units that fail to respond to control adjustments.
- Blocked strainers.
- Radiators that remain cold or are only partially hot.
- Blocked supply pipework from the make up tank or pressurisation unit.
- Failure of boilers or boiler sections.

83. The symptoms listed above may indicate increased system water losses, which may add to the loss of chemicals from the closed system.

2.3 Methods of dosing to closed systems

84. This section outlines the various methods of adding chemical formulations to closed systems. The dosing stage is an area of potential release of chemicals.

2.3.1 Manual dosing to a feed and expansion tank

85. A known amount of chemical is poured into the feed and expansion (F & E) tank by hand. The dose required is calculated from the estimated system volume and the dosing instructions issued by the chemical supply company, to obtain the required control reserves in the system water.

Advantages:

- Cheap and simple, no costs involved in the supply or installation of dosing equipment.

Disadvantages:

- Access to high level F & E tanks can be difficult, often reached via vertical ladders into roof spaces or high level plant rooms.
- Carrying 30 kg drums of chemical can be hazardous, may result in spilling chemical product or drum bursting if dropped.
- Spillages can occur when chemicals are transferred from drums to smaller containers (buckets).
- Further spillages are possible when open buckets are carried up ladders.
- F & E tanks may be high up in roof space with very little clearance between the top of the tank and ceiling, leading to spillages when inadequate clearance does not allow easy pouring.
- After adding chemical to F & E tank, system water must be partially drained off to draw the chemical from the F & E tank into the main recirculating system; also adequate time should be allowed for thorough mixing prior to retesting. This is time consuming and labour intensive.
- It is easy to overdose a system with manual feeding due to the probability of poor initial mixing (giving a low false reading) and reluctance of technicians to 'fine-tune' the dose volume.

2.3.2 *Manual dosing to pressurisation unit break tanks*

86. Partial draining of the system is required to reduce the pressure and trigger the pressurisation unit to cut in. The chemical is manually dosed into the unit break tank (usually located in a basement or top floor plant room) and is pumped into the system until the control set pressure is re-established.

Advantages:

- Easier handling of chemical, because break tanks for the smaller units are often at floor level.
- No requirement to decant chemical into smaller container, hence, less handling.
- With indicator coloured inhibitors it is easy to see when the chemical has been pumped out of the break tank.

Disadvantages:

- Pressurisation units are not designed to handle concentrated chemical solutions and may sustain damage, for example the diaphragm, pump impeller, non-return valve seating.
- Pressurisation unit pumps are not designed for continuous running or substantial system water loss make-up.
- The larger units may have break tanks that are boxed in and difficult to gain access to. This will require the transfer of chemical into smaller containers.
- Loss of chemical to drain with the requirement of partial system draining to activate the pump.
- The system must be allowed to recirculate and thoroughly mix before further tests are carried out to check on inhibitor reserves. Accurate dosing depends on correct sampling, testing and chemical volume calculations and measurements.

2.3.3 *Manual dosing using shot dose pots*

87. The dose pot is isolated from the recirculating system by a valve. Any contents are drained by opening the base drain valve and top vent. The drain is closed and the top fill valve is opened, allowing the pot to be filled through the tundish. When filling is complete, the top valve and vent are closed and the circuit valves are opened, allowing the differential pressure across the pot to draw the treatment chemical into the system.

Advantages:

- Simple and relatively inexpensive to install.
- Convenient locations can ensure ease of chemical handling.
- No change in system volume, hence pressure is constant.
- System water loss when dosing is confined to the volume of inhibitor concentrate added.
- Positive and rapid dosing of chemical to correct system conditions.

- Ideal for biocide dosing or additional alkali if pH levels too low.

Disadvantages:

- Chemical handling may be hazardous, may result in spillage.
- Dose pot must be completely filled to prevent air entering the system, leads to chemical waste if tundish overflows.
- Accurate dosing depends on site visits, representative sampling, testing and chemical volume calculations.
- System will be untreated between service visits.
- If only part dose pot chemical volume is required, problems with transfer of chemical and complete pot filling.

2.3.4 Manually initiated timer controlled dosing

88. A chemical dosing pump is linked to an electronic run timer to inject a specific volume of chemical into the system. The run timer is manually initiated as required, following the results of a system water analysis.

Advantages:

- Reduced chemical handling, therefore likelihood of spillage is reduced.
- Accurate dosing proportional to requirements should be possible.

Disadvantages:

- Dosing depends on:
 - i Frequency of site visits.
 - ii Representative sample being obtained.
 - iii Accuracy of test results.
 - iv Accuracy of pump setting.
 - v On / off switch control.
 - vi Calculation of measured quantity required.
 - vii Duration of chemical pumping.
- Additional dosing may overpressurise the system and cause automatic pressure release to drain, thus wasting treated water.
- With F & E tank, additional treated water may be forced back up into tank and eventually overflow to drain if not controlled.

2.3.5 *Automated dosing - conductivity control*

89. A conductivity sensor is installed in the recirculating system. The controller is adjusted to operate between control set points. Most chemical programmes contribute significantly to the conductivity and total dissolved solids of the system water and dosing pumps can be activated until the top limit is reached.

Advantages:

- Dosing is proportional to the system requirements.
- Chemical handling is minimal.

Disadvantages:

- Deposition on the conductivity sensor can 'blind' the electrodes and lead to dose malfunction.
- The wide temperature variations with closed systems running intermittently may lead to inaccuracies with the sensor and general sensor problems.
- Unexpected leaks from the system may prematurely drain the chemical reserve tank before a service visit is due.
- Control loops can be expensive.
- No provision for biocide dosing.
- The sensor must be located at the opposite end of the system to the injection point, or false or high readings may be obtained.
- If the sensor is located in a loop that is not always in use (AHU battery etc.) it may not record a representative system value and continue calling for additional dosing resulting in overpressurisation, waste of treated water etc.

2.3.6 *Proportional dosing*

90. A water meter in the make up line signals the dosing pump to run after a pre-set quantity of make-up water has entered the system.

Advantages:

- Allows excellent proportional control.
- Reduces chemical handling.
- Ensures chemical should be present if system suffers water losses.
- Can be used even if chemical inhibitor programme adds low or minimal additional conductivity to system water.

Disadvantages:

- Many water meters are not sensitive enough to respond to very low, but continuous make up demands.
- System may require a delayed action ball valve to eliminate errors due to low flow rates.
- If system leaks occur between service visits, chemical drums may become exhausted.
- More expensive and complicated to install than manual systems.
- No provision for automated biocide dosing.

2.3.7 Biocide dosing

91. Micro-organism activity within a closed system can reduce inhibitor levels and give rise to corrosion of system component metals.

92. An early warning indicator for some systems that micro-organism activity may be evident can take the form of loss of the bright pink phenolphthalein indicator colour (NB. not to be confused with low pH conditions). This should not be taken as positive proof, and routine bio-laboratory checks or the use of simple dip slides will more clearly indicate the need for a suitable biocide to be dosed.

93. Additions are usually single shot doses via an F & E tank, shot dose pot or the pressurisation unit.

2.3.8 Ethylene glycol dosing : chilled & closed condenser systems

94. Because of the volumes of ethylene glycol required to give antifreeze protection, between 25 to 33 % of system volume, it is essential that sufficient ethylene glycol is added after the pre-commission cleaning stage, and all system losses are made up with a suitable antifreeze/water mixture to maintain the degree of antifreeze protection. If glycol protected systems suffer losses, non treated make up water will continuously dilute the glycol ratio, necessitating a discharge of water/glycol mixture from the system to accommodate the neat glycol addition required to return the system to full strength. Additions will therefore be via specially designed glycol top up units, if installed; or by shot-dosing of neat glycol after sufficient has been drained off to allow full protection once refilled.

95. Ethylene glycol losses from closed systems are a real concern for the following reasons:

- The system protection is lost
- Glycol mixtures cannot be discharged to foul drains, they must be collected in drums and disposed of correctly.
- Disposal is labour intensive and costly.
- Glycols can act as nutrient for micro-organisms, so the system would need to be dosed with a suitable biocide.

2.4 Chemical treatments and formulations

96. This section discusses typical formulations and the individual chemicals which may be used.

2.4.1 *Make up water pre-treatment*

97. Systems should have been correctly pre-commission cleaned and flushed prior to final treatment dosing. Unless cost is no object, it would be wasteful to use softened, demineralised or reverse osmosis (R/O) treated water for such flushing operations.

98. In hard water areas, base exchange softening may be used for low pressure system make up water and deionised or reverse osmosis treated make up water may be used for high pressure systems.

99. Base exchange softening rejects dilute brine solution to drain during every regeneration, deionisation will produce neutralised effluent and R/O will concentrate entrained water parameters.

2.4.2 *Individual chemicals*

100. In order to establish the loss of individual chemicals from the system, the generally accepted use concentrations of currently used chemicals is given in Tables 2.1 and 2.2.

101. The listing for biocides and dispersants in Table 2.2 is not exhaustive but includes those in most common current use. The majority of the chemicals listed are used in hot water systems. Treatments for chilled water systems are normally blends of borate with nitrite or molybdate plus biocide.

2.4.3 *Formulations*

102. When marketed, the individual components are in a stable form, fully soluble in the aqueous phase and chosen because they form a compatible blend within the formulation.

103. Early attempts to create an all purpose chemical water treatment formulation were unsuccessful due to incompatibilities such as differing relative solubilities. These initial formulations never formed truly homogeneous liquid treatments.

Table 2.1: Corrosion inhibitors used in closed systems.

Chemical	Use concentration (mg/l)	Function/metal protected
Sodium nitrite	800 – 1200	
Sodium borate	50 – 500	and pH buffer
Sodium molybdate	100 – 500	
Sodium silicate	10 – 100	
Triethanolamine phosphate	100 – 500	Aluminium
Mercaptobenzthiozole	2 – 10	Copper
Tolyltriazole	2 – 10	Copper
Benzotriazole	2 – 10	Copper

Table 2.2: Chemicals used in closed systems.

Chemical	Use Concentration (mg/l)	Function
Sodium sulphite	50 – 100	Oxygen scavenger
Hydrazine	1 – 10	Oxygen scavenger
Diethylhydroxylamine	1 – 10	Oxygen scavenger
Methylethylketoxime	1 – 10	Oxygen scavenger

Tannins	50 – 150	Oxygen scavenger
Cyclohexylamine	5 – 20	pH control
Morpholine	5 – 20	pH control
Sodium hydroxide	300 – 500	pH control
Disodium phosphate	30 – 100	Scale control
Trisodium phosphate	30 – 100	Scale control
Sodium polyacrylate	50 – 150	Dispersant
Sodium polymethacrylate	50 – 150	Dispersant
Polymaleic acid	50 – 150	Dispersant
Polymaleic acid - sulphonated styrene copolymer	50 – 150	Dispersant
Quaternary ammonium compounds	10 – 100	Biocide
Glutaraldehyde	5 – 50	Biocide
Isothiazolones	5 – 50	Biocide
Ethylene glycol	25 to 33 %	Antifreeze

104. Early problems were experienced with phosphate sludges when the mixtures were used in hard water areas. Another oversight concerned micro-organism activity that utilised parts of the formulations as nutrients. This led to blockages when the filamentous material was pulled into the system distribution pipework.

105. Formulations have been evolved that are capable of working with the variety of different water qualities, providing excellent protection for mixed metal systems. For conventional closed systems, the different metals that may require protection include cast iron, mild steel, galvanised steel, copper, brass, bronze and aluminium (radiators and heat exchangers).

106. The following table (Table 2.3) gives the breakdown of a commercially available inhibitor mix for systems that do not contain aluminium. A 25 litre drum (approx. 30 kg) of this type of inhibitor formulation is recommended for treating just over 2,000 litres of closed system water.

Table 2.3: A commercially available formulation.

Component	Approximate %	Amount per 25 litre drum
Softened Water	70	21 kg
Phenolphthalein indicator	0.1	0.03 kg
Sodium hydroxide	5	1.5 kg
Sodium silicate	0.5	0.15 kg
Sodium nitrite	11	3.3 kg
Sodium tetraborate	3.5	1.05 kg
Sodium polyacrylate	0.3	0.09 kg
Mercaptobenzthiazole	0.1	0.03 kg
Sodium nitrate	8	2.4 kg

The overall value for active ingredients in this formulation is 4.3 kg/m³.

2.5 Losses from closed systems

2.5.1 *Listing of phases in the life cycle of closed systems*

107. This section sets out the worst case scenario for chemicals being released from closed recirculating systems. The steps in the life cycle are shown in Figure 2.1.

108. The following scenarios will be considered.

2.5.2 New systems.

2.5.3 Changes to systems.

2.5.4 Existing systems - controlled losses.

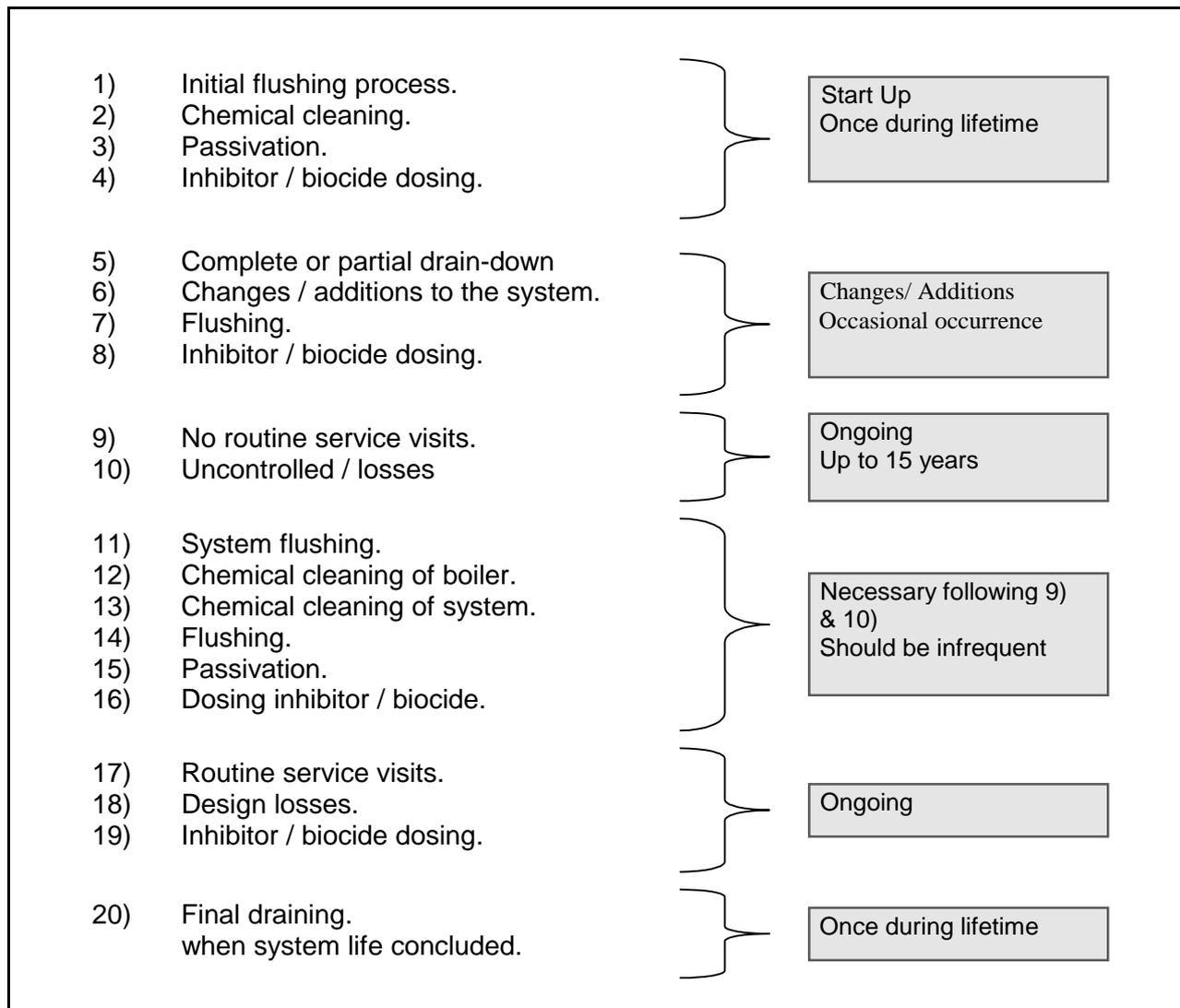
2.5.5 Existing systems - uncontrolled losses.

109. Within each of these scenarios there are subdivisions based on the loss factor for a given stage. For example the first scenario is titled "2.5.2 New Systems"; within this scenario the releases associated with the passivation process are under the title "2.5.2.3 passivation". Where this process is repeated in other scenarios, for example 2.5.5 existing system - uncontrolled losses, it will retain its original numerical heading i.e. 2.5.2.3 passivation.

110. Estimates of release quantities in these scenarios are based on the experience of workers in the industry.

111. Most of the steps described below are discrete events, occurring either once in the lifetime of a system or at infrequent intervals. These can be considered to be intermittent releases. Although the actual period of release for some may be relatively short, the mixing of the release in the drainage and sewer systems means that the emission can be considered to be more spread out in terms of the time over which it reaches the environment. A duration of one day is suggested for estimating emission rates for these steps.

Figure 2.1: Lifecycle of a typical closed system

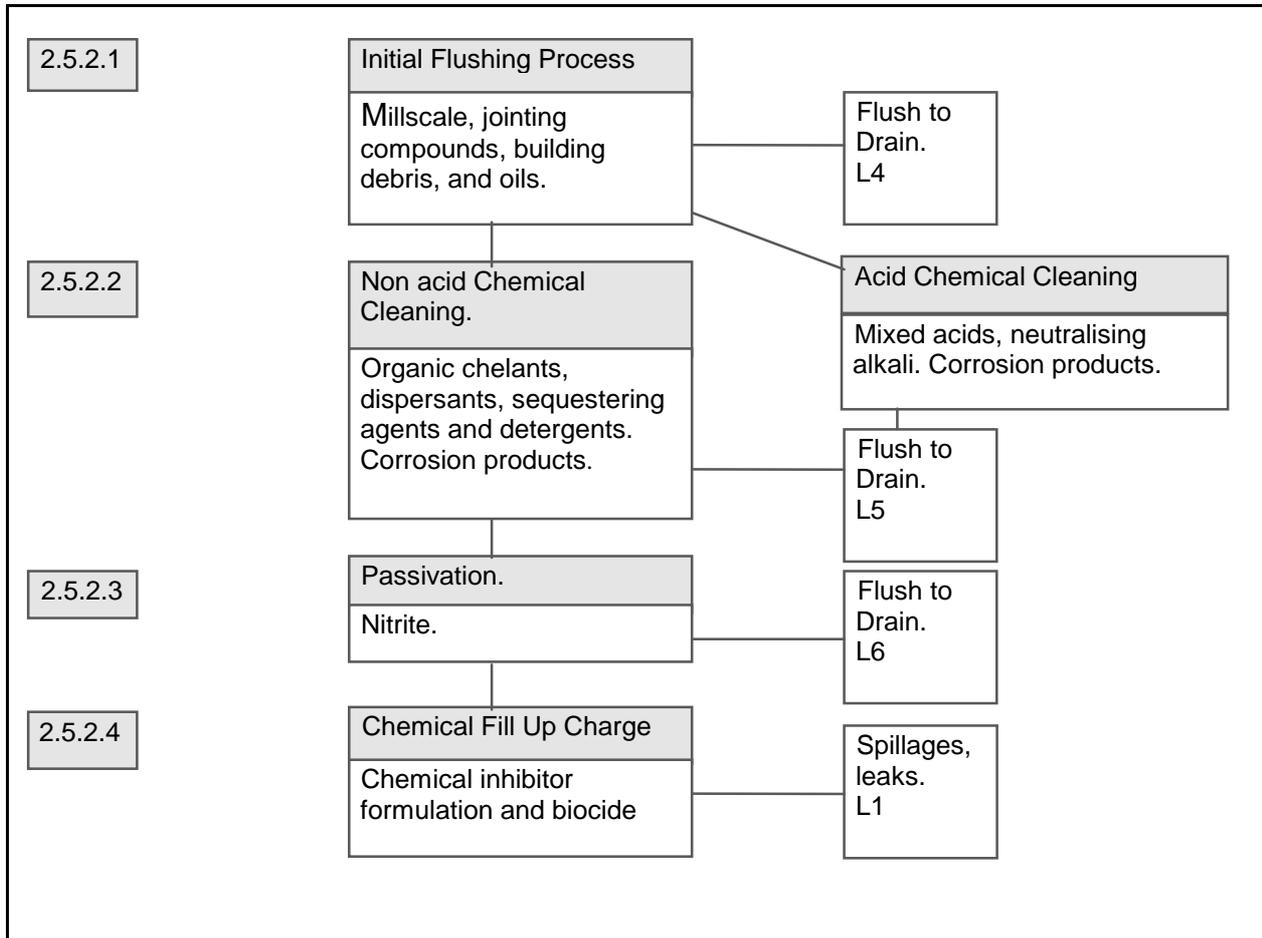


2.5.2 New systems : pre commission cleaning and chemical fill up charge

112. Figure 2.2 shows the basic theoretical method for preparing a system prior to client handover. Ideally this preparation stage would be followed by regular site visits to sample and test the system water, making additions of treatment chemicals and biocide if control levels are not being maintained. Such a routine will quickly highlight problems within the system such as corrosion or scaling or bio-fouling that may be due to system water losses. This would be carried out on a regular basis, generally every 3, 4, 6 or 12 months of system life.

113. In Figure 2.2 the unshaded boxes indicate the nature of releases from the particular stage, these will now be described in greater detail.

Figure 2.2: New systems



2.5.2.1 Process: Initial flushing (L4)

114. Water is used to flush the new system of material which may have been deposited during construction (care is taken to avoid deposits if possible) such as swarf, metal filings, jointing compounds, PTFE tape, solders, fluxes in components and millscale, oils and greases inside pipework.

115. A rough indication of the level of contamination is 500 - 1000 mg/l (0.5 - 1 kg/m³). Although this is expressed as a concentration, much of the material removed in this step is likely to be in solid form. These releases are not related to the use of water treatment chemicals, and are not considered further in this document.

2.5.2.2 Process: chemical cleaning (L5)

Non-acid cleaning

116. Formulated products containing organic chelants, dispersant and surface active agents are dosed at 3 to 5 % vol/vol and allowed to recirculate for a number of days. During this chemical cleaning period, samples are regularly taken to check system conditions. Tests carried out include conductivity, total

dissolved solids, pH, iron (soluble and total) and copper levels. When values are observed to plateau out, the system is again flushed to drain.

117. Losses at this stage would include the organic cleaning agent and entrained corrosion products.

118. The amount of substance flushed to drain in step L5a can be estimated as follows.

$$Q_{subst, clean} = V_{system} \cdot F_{clean, water} \cdot C_{clean}$$

Explanation of symbols:

$Q_{subst, clean}$	= amount of substance flushed to drain after cleaning	[kg]	
V_{system}	= volume of system	[m ³]	See Section 2.6
$F_{clean, water}$	= fraction of system volume flushed to drain	[-]	Assume 1
C_{clean}	= concentration of cleaning substance	[kg/m ³]	

119. For the concentration C_{clean} information on the specific substance should be used where possible. The figure of 3 - 5% (30 - 50 kg/m³) given above applies to the complete formulation, but could be used as a maximum value for an initial calculation if on other information is available.

120. This release is a one-off release at this stage of the preparation of the system. Although the cleaning solutions may remain in the system for a number of days, the actual discharge will take place over a shorter period, which can be assumed to be one day for the purpose of calculating an emission rate. Hence:

$$T_{clean} = \text{time for cleaning emission} = 1 \text{ day as default}$$

and

$$E_{clean, water} = Q_{subst, clean} / T_{clean}$$

121. In addition to the release of chemical, there will also be corrosion products removed from the system included in the discharge (loss step L5b). An indicative concentration for these products is 500 - 2,000 mg/l (0.5 - 2 kg/m³). These are not directly related to the chemicals used in water treatment, but an emission rate for them could be estimated in the same way as above.

Second process (alternative): acid cleaning

One of these acids would be used (v/v):

Hydrochloric Acid	Dosed at	10 - 20 %
Phosphoric acid	Dosed at	10 - 20 %
Sulphamic Acid	Dosed at	5 - 20 %
Ammoniated Citric	Dosed at	10 - 20 %
Acetic Acid	Dosed at	5 - 20 %
Formic Acid	Dosed at	5 - 20 %

122. Upon completion of the acid clean, the acid will be neutralised to pH 7 to 8.5 with sodium hydroxide whilst being flushed to drain. The main products discharged would be the sodium salts of the acids used (losses L5c), together with soluble iron and copper salts (losses L5d). Indicative concentrations

for these are 100 - 200 kg/m³ for the neutralised acid slats, and 0.5 - 2 kg/m³ for the soluble iron and copper salts. If required, emission estimates for these using the formula for non-acid cleaning releases, substituting the relevant salt concentration for the cleaning agent concentration. The same assumptions about the fraction of the system volume discharged and the time period for emissions could be made.

2.5.2.3 Process: passivation (L6)

123. The clean metal surfaces are at their most potentially active with regard to vulnerability to oxidation/corrosion initiation. Hence, passivation with a high nitrite level is carried out to form a stable film on the metal surface. The amount of substance flushed to drain in step L6 can be estimated as follows.

$$Q_{subst, passiv} = V_{system} \cdot F_{passiv, water} \cdot C_{passiv}$$

Explanation of symbols:

$Q_{subst, passiv}$	= amount of substance flushed to drain after passivation	[kg]	
V_{system}	= volume of system	[m ³]	See Section 2.6
$F_{passiv, water}$	= fraction of system volume flushed to drain	[-]	Assume 1
C_{passiv}	= concentration of cleaning substance	[kg/m ³]	Default 1-2

124. This is also a discrete event. The emission rate can be estimated from $Q_{subst, passiv}$ by assuming that emissions take place over one day (as in Section 2.5.2.2).

2.5.2.4 Process: first chemical inhibitor system fill up charge (L1)

125. The formulation of the fill up charge will be similar to the typical mix described in Section 2.4. There will be changes where individual water treatment companies substitute alternative chemicals to perform the same generic function. Corrosion inhibitors tend to be considered to be the most necessary ingredient. The amount of substance flushed to drain in step L1 can be estimated as follows.

$$Q_{subst, fill} = V_{system} \cdot F_{fill, water} \cdot C_{treat}$$

Explanation of symbols:

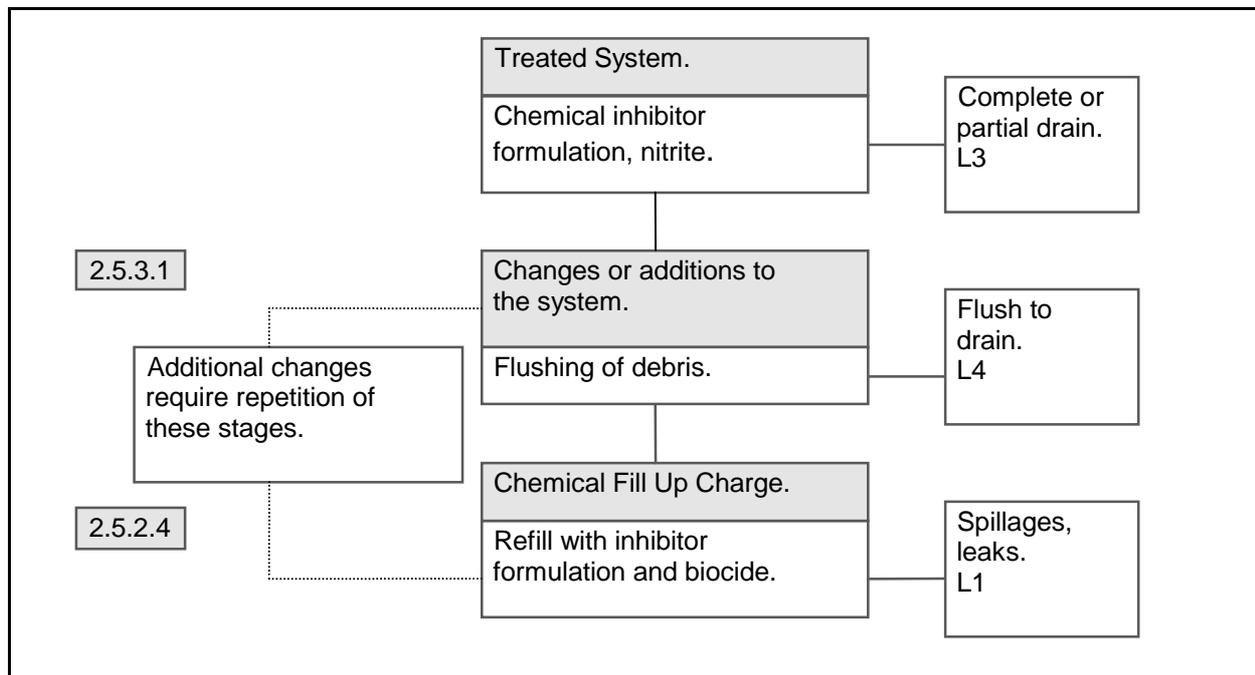
$Q_{subst, treat}$	= amount of substance flushed to drain on filling	[kg]	
V_{system}	= volume of system	[m ³]	See Section 2.6
$F_{fill, water}$	= fraction of fill up charge lost to drain	[-]	Default 0.005
C_{treat}	= working concentration of substance in treated system	[kg/m ³]	See Tables 2.1 & 2.2

126. Note that the concentration of substance is that in the water in the system at the working concentration, and not that in the formulation used. Again this is a discrete event, and emission rates can be estimated from $Q_{subst, treat}$ as in Section 2.5.2.2.

2.5.3 Changes or additions

127. If a system needs to be added to or altered, which is frequently the case in a recently installed system, it will need to be partially or completely drained (Figure 2.3).

Figure 2.3: Changes or additions to a system



128. If a system needs modification after having been pre-commissioned cleaned and having received initial system chemical dosing, problems can arise if the contractor or client refuse to fund further cleaning or treatment costs, relying on simple flushing and refilling prior to handover.

129. This may result in the system being left without any chemical treatment present or with no programme of regular water treatment system checks, leading to potentially uncontrolled water losses from the system over a long period of time. This could also cause the boiler plant or another part of the system to fail resulting in another round of chemical cleaning and inhibitor/biocide dosing.

2.5.3.1 Process: drain down of chemically treated system (L3)

130. This step is necessary before cutting in additional valves, making further additions, adding drainage or flushing points etc. It should be assumed that the treatment chemicals are present at their working concentration when the system is drained. As a worst case it should be assumed that the whole of the system is drained, but estimates for partial draining can also be made.

131. The amount of substance flushed to drain in step L3 can be estimated as follows.

$$Q_{subst, drain} = V_{system} \cdot F_{drain, water} \cdot C_{treat}$$

Explanation of symbols:

$Q_{subst, drain}$	= amount of substance released to drain	[kg]	
V_{system}	= volume of system	[m ³]	See Section 2.6
$F_{drain, water}$	= fraction of system volume drained	[-]	Assume 1
C_{treat}	= working concentration of substance in treated system	[kg/m ³]	See Tables 2.1 & 2.2

132. The draining of a system is likely to be an intermittent event, and lead to a discrete release. As above (Section 2.5.2.2), the duration of the release can be assumed to be one day for calculation purposes.

133. After draining down the necessary additions or changes will be made. The system will then be in a similar state to the new system, and will be flushed out as in Section 2.5.2.1, with releases of material as discussed in that section (losses L4). The system will then be refilled, with the possible losses from the first charge of treatment chemicals as described in Section 2.5.2.4 (losses L1).

2.5.4 Existing systems

134. The following scenarios in Figure 2.4 assume that the system has been correctly pre-commission cleaned and chemically dosed as shown in Figure 2.2.

2.5.4.1 System with regular site checks

Continuous losses (L2)

135. Around 1 % loss per month is anticipated from an existing system being routinely checked and treated. The loss of water is made up with water from the feed and expansion tank. Emissions are estimated as follows (losses L2).

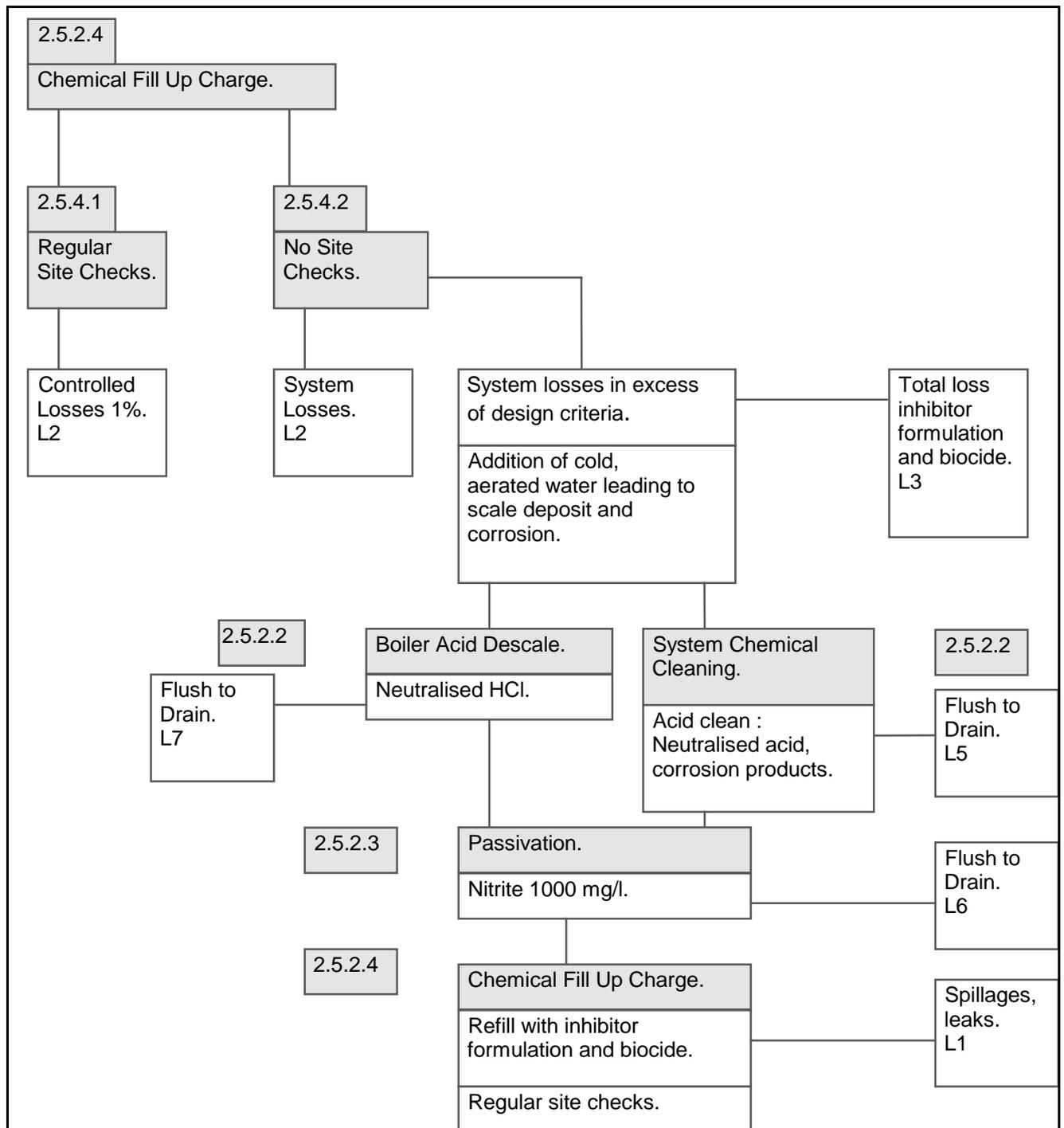
$$E_{subst,routine} = V_{system} \bullet F_{routine,water} \bullet C_{treat}$$

Explanation of symbols:

$E_{subst,routine}$	= emission of substance to drain	[kg/day]
V_{system}	= volume of system	[m ³] See Section 2.6
$F_{routine,water}$	= fraction of system volume lost in routine operation	[d ⁻¹] Default 0.0003 d ⁻¹
C_{treat}	= working concentration of substance in treated system	[kg/m ³] See Tables 2.1 & 2.2

Note: daily release fraction corresponds to 1% per month.

Figure 2.4: Existing systems



Dosing (L1)

136. There may be spillages or leaks when adding the formulation by whichever dosing method is employed. The method used will to some extent determine the frequency with which such additions need to be made, and also the volume of formulation which is added. In general, the less frequent the additions

the larger the volume needed. As a worst case, it can be assumed that the addition is the same as required for a first fill. The losses can then be estimated in the same way as in Section 2.5.2.4 for first fill. In a well-maintained system such additions will only be required at significant intervals, and so releases from such dosing should be considered as discrete releases. A duration of one day can be assumed for calculating emission rates.

2.5.4.2 *System with uncontrolled losses*

No site checks

137. The treated water will be lost at 1% per month or greater (through corrosion, leaks etc.) and might not be treated subsequently. Losses are the same as for a system with regular checks, but the reduction in protection will eventually lead to problems in the system. It is then more likely that the system will need to be emptied and brought back on line as described below. The continuous losses can be estimated as in Section 5.4.1 (losses L2) above.

Bring the system back on line

138. In order to bring the system back on line and then to follow a routine checking and dosing programme the system needs cleaning, passivating and refilling with formulation. Inhibited HCl is used to clean the boiler in these circumstances, this is followed by neutralisation with sodium hydroxide. Realistically a 30 kg mixture would be used every five years for a boiler serving a 5,000 litre capacity system. Quantities for other systems would be in proportion to their capacity (larger systems tend to be served by a number of boilers of this size). The discharge would probably contain neutralisation products and corrosion products, as described in Section 2.5.2.2 under acid cleaning (losses L5c and L5d).

139. Cleaning is followed by passivation (Section 2.5.2.3, losses L6) and refilling with treatment chemicals (as first fill, Section 2.5.2.4, losses L1). These steps, including cleaning, can be considered as discrete steps.

140. Once the system is operating with controlled losses the releases will match those of 2.5.4.

2.6 Market size in UK and Europe

2.6.1 UK systems

141. The total number of closed systems in the UK is estimated to be 100,000, of which :

- Chilled/ cooling 25,000
- LTHW/MTHW 60,000
- HTHW 15,000

142. The distribution of the sizes of these systems is shown in Table 2.4.

Table 2.4: Estimates of numbers within each capacity range (UK).

System	Capacity										Total
	0 to 2,000 litres		2,001 to 4,500 litres		4,501 to 9,000 litres		9,001 to 20,000 litres		20,001 to 45,000 litres		
	%	No.	%	No.	%	No.	%	No.	%	No.	
Chilled	40	10	40	10	15	3.75	3	0.75	2	0.5	100%
LTHW/M	50	30	30	18	10	6	8	4.8	2	1.2	100%
HTHW	5	0.75	25	3.75	35	5.25	30	4.5	5	0.75	100%

Note: No. = number of systems. expressed in 000's

143. Not all closed systems receive treatment chemicals; those that do not are irrelevant in terms of system losses. Table 2.5 indicates the percentage of each type of system in the UK which is treated, broken down into size classes.

Table 2.5: Percentage of systems that are treated (UK).

System	Capacity				
	0 to 2,000 litres	2,001 to 4,500 litres	4,501 to 9,000 litres	9,001 to 20,000 litres	20,001 to 45,000 litres
Chilled	20	35	65	80	95
LTHW/M	25	30	55	85	95
HTHW	65	55	75	95	95

144. Those systems that are treated can be sub divided into those with regular checks (leading to controlled losses) and those without. Table 2.6 gives the percentage of treated systems without regular checks, by type and size.

Table 2.6: Percentage of systems with uncontrolled losses (UK).

System	Capacity				
	0 to 2,000 litres	2,001 to 4,500 litres	4,501 to 9,000 litres	9,001 to 20,000 litres	20,001 to 45,000 litres
Chilled	60	50	50	30	20
LTHW/M	80	75	70	60	50
HTHW	25	20	15	10	5

2.6.2 Systems in France & Italy

145. Treatment technology for hot water boilers and chilled water systems is similar to that in the UK

2.6.3 Systems in Germany

146. Demineralised water is frequently used in closed systems to reduce the need for chemical treatment. In some instances there has still been evidence of corrosion resulting in the need to have some chemicals supplied. These are currently restricted to blends of phosphate and sulphite, phosphates, and silicate and tannins. Molybdate inhibitors were introduced but have now fallen out of use.

2.6.4 *Systems in Austria*

147. This country traditionally uses sacrificial anodes (magnesium or zinc) to control corrosion.

2.6.5 *Systems in Scandinavia*

148. Scandinavian buildings tend to be heavily insulated and utilise energy conserving technology, therefore hot water boilers tend to be smaller than for the UK. Also, much of the heating is supplied by combined heat and power schemes, which are not considered in this report. Conventional hot water boilers and chilled water systems use nitrite based inhibitors or blends of silicate and phosphate.

2.6.6 *Systems in Southern Europe*

149. The use of air conditioning units tends to be fairly recent. Where treatment chemicals are used they tend to be silicate/phosphate, sulphite or tannin.

2.7 Individual chemical release scenario examples

150. Using the capacity sizes for closed systems along with information pertaining to chemical use concentrations and stages of release, it is possible to estimate the typical loss of an individual chemical from a closed system. Throughout the EU, discharge is typically to the sewerage system. There may be some discharge to coastal waters in Southern Europe.

151. In order to cover a spectrum of release possibilities the following chemicals will be used:

- Sodium nitrite - as corrosion inhibitor* and as passivation chemical.
- Sodium polyacrylate - as dispersant*
- Organic cleaning agent - as used in new system preparation.

* Constituent of treatment formulation

152. Releases will be characterised as discrete (lost over short period of time) or continuous (constant amount lost continuously).

2.7.1 *Sodium Nitrite*

153. Assume a 30,000 l (30 m³) capacity system.

New system

$$\text{Passivation (L6)} \quad Q_{\text{subst, passiv}} = V_{\text{system}} \bullet F_{\text{passiv, water}} \bullet C_{\text{passiv}}$$

$$V_{\text{system}} = 30 \text{ m}^3$$

$$F_{\text{passiv, water}} = 1 \text{ (default)}$$

$$C_{\text{passiv}} = 1000 - 2000 \text{ mg/l (1 - 2 kg/m}^3\text{), Section 2.5.2.3}$$

$$Q_{\text{subst, passiv}} = 30 - 60 \text{ kg (discrete loss).}$$

Loss would be over a short period, assumed to be one day for calculation purposes, so the emission rate is 30 - 60 kg/day.

$$\text{Fill-up (L1)} \quad Q_{\text{subst, fill}} = V_{\text{system}} \bullet F_{\text{fill, water}} \bullet C_{\text{treat}}$$

$$V_{\text{system}} = 30 \text{ m}^3$$

$$F_{\text{fill, water}} = 0.005 \text{ (Section 2.5.2.4)}$$

$$C_{\text{treat}} = 800 - 1200 \text{ mg/l (0.8 - 1.2 kg/m}^3\text{), Table 2.1}$$

$$Q_{\text{subst, fill}} = 0.12 - 0.18 \text{ kg (discrete loss)}$$

Loss would be over a short period, assumed to be one day for calculation purposes, so the emission rate is 0.12 - 0.18 kg/day.

Changes or additions

$$\text{Drain (L3)} \quad Q_{\text{subst, drain}} = V_{\text{system}} \bullet F_{\text{drain, water}} \bullet C_{\text{treat}}$$

$$V_{\text{system}} = 30 \text{ m}^3$$

$$F_{\text{drain, water}} = 1 \text{ (assumed)}$$

$$C_{\text{treat}} = 800 - 1200 \text{ mg/l (0.8 - 1.2 kg/m}^3\text{), Table 2.1}$$

$$Q_{\text{subst, drain}} = 24 \text{ to } 36 \text{ kg (discrete loss)}$$

Emission rate would be 24-36 kg/day assuming release over one day.

Fill-up (L1) - as above for new systems

Existing - controlled

$$\text{Design losses (L2)} \quad E_{\text{subst, routine}} = V_{\text{system}} \bullet F_{\text{routine, water}} \bullet C_{\text{treat}}$$

$$V_{\text{system}} = 30 \text{ m}^3$$

$$F_{\text{routine, water}} = 0.00033 \text{ d}^{-1} \text{ (Section 2.5.4.1)}$$

$$C_{\text{treat}} = 800 - 1200 \text{ mg/l (0.8 - 1.2 kg/m}^3\text{), Table 2.1}$$

$$E_{\text{subst, routine}} = 0.008 - 0.012 \text{ kg/day (continuous release)}$$

Fill-up (L1) - this is assumed to involve the same amount of formulation as at the initial fill-up, and so the emission are as above for L1, i.e. $Q_{\text{subst, fill}}$ is 0.12 - 0.18 kg (discrete loss).

Existing - uncontrolled

Losses during use will be the same as for controlled releases, as in L2 above.

Losses to drain will be the same as those for draining before changes to the system, as L3 above.

Passivation losses will be as for L6 above, and fill-up losses will be as L1 above for filling a new system.

2.7.2 Sodium polyacrylate

154. For this example assume system has capacity of 20,000 l.

New system

$$Fill\text{-}up\ (L1) \quad Q_{subst,fill} = V_{system} \bullet F_{fill,water} \bullet C_{treat}$$

$$V_{system} = 20\ m^3$$

$$F_{fill,water} = 0.005\ (Section\ 2.5.2.4)$$

$$C_{treat} = 50 - 150\ mg/l\ (0.05 - 0.15\ kg/m^3),\ Table\ 2.2$$

$$Q_{subst,fill} = 5 - 15\ g\ (0.005 - 0.015\ kg)\ (discrete\ loss)$$

Loss would be over a short period, assumed to be one day for calculation purposes, so the emission rate is 5 - 15 g/day.

Changes or additions

$$Drain\ (L3) \quad Q_{subst,drain} = V_{system} \bullet F_{drain,water} \bullet C_{treat}$$

$$V_{system} = 20\ m^3$$

$$F_{drain,water} = 1\ (assumed)$$

$$C_{treat} = 50 - 150\ mg/l\ (0.05 - 0.15\ kg/m^3),\ Table\ 2.2$$

$$Q_{subst,drain} = 1\ to\ 3\ kg\ (discrete\ loss)$$

Emission rate would be 1-3 kg/day assuming release over one day.

Fill-up (L1) - as above for new systems

Existing - controlled

$$Design\ losses\ (L2) \quad E_{subst,routine} = V_{system} \bullet F_{routine,water} \bullet C_{treat}$$

$$V_{system} = 20\ m^3$$

$$F_{routine,water} = 0.00033\ d^{-1}\ (Section\ 2.5.4.1)$$

$$C_{treat} = 50 - 150\ mg/l\ (0.05 - 0.15\ kg/m^3),\ Table\ 2.2$$

$$E_{subst,routine} = 10 - 30\ g/day\ (0.01 - 0.03\ kg/day)\ (continuous\ release)$$

Fill-up (L1) - this is assumed to involve the same amount of formulation as at the initial fill-up, and so the emission are as above for L1, i.e. $Q_{subst,fill}$ is 5 - 15 g (discrete loss).

Existing - uncontrolled

Losses during use will be the same as for controlled releases, as in L2 above.

Losses to drain will be the same as those for draining before changes to the system, as L3 above.

2.7.3 *Organic cleaning agent*

155. For this example assume 9000 l system capacity

New system

Non Acid Clean (L5a) $Q_{subst, clean} = V_{system} \cdot F_{clean, water} \cdot C_{clean}$

$$V_{system} = 9 \text{ m}^3$$

$$F_{clean, water} = 1$$

$$C_{clean} = 30 - 50 \text{ kg/m}^3$$

$$Q_{subst, clean} = 270 - 450 \text{ kg (discrete loss)}$$

This can be converted to an emission rate assuming that discharge takes place over one day, i.e. 270 - 450 kg/day.

Use of this cleaning agent is not anticipated in other areas.

3 OPEN COOLING SYSTEMS

3.1 Description of open systems

3.1.1 General description

156. The introduction of cooling towers into the UK began during the first quarter of this century, stimulated by the development of large power generating stations on inland waterways which needed extremely high volumes of water for turbine condenser cooling. Cooling tower use spread into the general heavy industry sector. From the beginning of the second half of the century, the use of cooling towers has accelerated because of the demands of the air conditioning industry. As compared with other methods of cooling, e.g. air cooling, wet cooling towers use less energy, are quieter and have a lower weight. In some cases, they can achieve lower temperatures.

157. The cooling effect of a cooling tower is produced predominantly by the evaporation of water. Warm water from the process is sprayed from the top of the tower through a pack, usually made of plastic, which permits the formation of small water droplets and thin films of water. The large surface area allows sufficient water/air contact for evaporation to take place, which cools the remaining water as it provides the energy needed for evaporation. Dissipation of this reject heat is provided by means of a fan. This fan may be located at the top of the tower (induced draught) or at the side (forced draught). The cooled water is collected in a tank at the base of the tower and is pumped back through the process. The water lost by evaporation amounts to approximately 1% of the flow rate for every 6° C temperature drop across the tower. This loss has to be replaced by fresh make-up water.

158. One function of a cooling tower is to conserve water. For example, a process which needs 1,000m³/hour of cooling water flow could use this volume on a once through basis. For the same flow rate, by recycling the water through a cooling tower, the water usage would be between 10-50 m³/hour.

3.1.2 Losses from the system

159. Treated cooling system water may be lost from the system in a number of ways:

- a) *Drift - the spray (plume) produced from the top of an evaporative cooling tower.*
- b) *Windage - Physical loss of water from a cooling tower caused by draught of air or wind.*
- c) *Bleed or purge - Water deliberately removed from a cooling system to control the concentration factor of dissolved solids.*

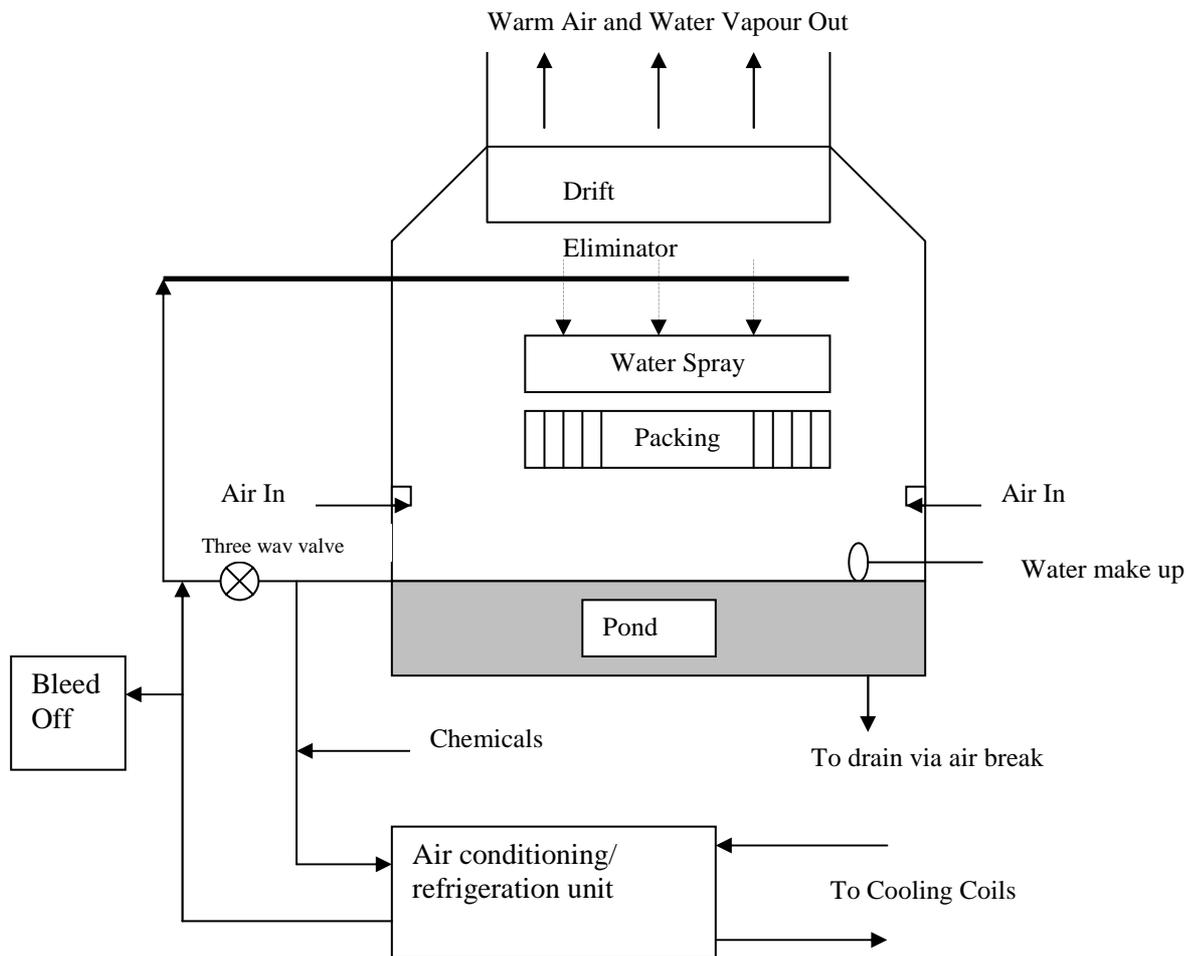


Figure 3.1 Cooling Tower Layout

160. Evaporation causes the soluble constituents of the water supply to concentrate. This must be controlled to prevent excessive deposition of mineral salts which become insoluble due to the joint effects of increased concentration and lower temperature. The maximum concentration allowable for any specific cooling tower system varies according to the quality of the water supply and the operating conditions. The ratio of the maximum concentration of dissolved solids in the recirculating water to the concentration in the make up water is called cycles of concentration. In order to keep the dissolved solids concentration below the maximum value a portion of the circulating water is discarded. This is known as blowdown. Blowdown losses are replaced by fresh make-up water and are calculated using the following equation:

$$\text{Blowdown} = \frac{\text{Evaporation}}{\text{Concentration Cycles} - 1}$$

$$\text{Total make-up} = \text{Evaporation} + \text{Blowdown}$$

161. In the nomenclature used for variables in this document, these terms are represented by:

Blowdown = $FLOW_{blowdown}$
 Evaporation = $FLOW_{evap}$
 Concentration cycles = N_{cycles}
 Total make-up = $FLOW_{total}$

162. There is an additional loss of water caused by drift and windage. This loss is estimated from the circulation rate by use of a factor.

$$FLOW_{windage} = FLOW_{circul} * F_{windage}$$

Explanation of symbols:

$FLOW_{windage}$	= loss of water in air	[m ³ /hour]	
$FLOW_{circul}$	= circulating flow rate in system	[m ³ /hour]	Assumed as 3.5x capacity
$F_{windage}$	= fraction lost to air	[-]	See below

163. Depending on the type of drift and mist elimination equipment fitted, these losses may be small. For the UK, a loss of 0.01% of the recirculation rate in the system is suggested (i.e. $F_{windage}$ is 0.01%). In the US, a loss rate of 0.1% is recommended where more specific information is not available. These releases can be considered to be to air. The drift loss has significance in potentially leading to the spread of infectious bacteria, such as *Legionella pneumophila*.

164. It is also possible that chemicals could be lost through volatilisation. Most of the chemicals used are expected to have low volatility. If volatilisation is considered to be possible, the Henry's law constant of the substance could be used to compare the volatility relative to that of water, and an estimate of the chemical loss rate made from the evaporation rate for water.

3.2 Treatment chemicals

3.2.1 The need for chemical treatment

165. The problems encountered in open cooling systems have been largely covered in the introduction. The main problems suffered by these systems include:

- Corrosion
- Scale deposition
- Microbiological fouling and associated health risks
- Sludge and suspended material

3.2.2 Chemical dosing

166. The actual dosing point in the system should ensure the rapid mixing of the chemicals with the bulk of the cooling water. Methods of dosing include:

- Manual, e.g. a once-daily shot. Chemicals are added to the system by hand. This can create large fluctuations in system concentration and may not be advisable.

- Continuous. In large capacity cooling systems where loads are steady and system conditions change very slowly, it may be acceptable to have continuously running dosing pumps. In this case, adjustments to the dosage rate are usually required infrequently and can be made by adjusting the pump stroke rate or by changing the strength of the treatment chemical. However, on smaller systems or in circuits where the cooling duty is large in relation to water content, conditions can change very rapidly and dosing must always be proportional to the system duty.
- Timer controller. Timers can be varied to run the dosing pump more or less frequently as required at times when system parameters are predicted to change.
- Proportional dosing. This is the best and most accurate method of dosing, since the changing operating parameters are reflected in the dosing rate and the correct amount of chemical is continually present in the system. This type of dosing is carried out by water meter control.
- Biocide dosing (independently from other chemicals). Either continuous or shot/ slug dose. Typically a system will be dosed at least weekly using two alternating biocides to protect against a wide spectrum of micro-organisms. Dosing will be more frequent if laboratory testing or dip slides indicate this is necessary. The biocide must be added at a point which ensures even distribution around the whole system, e.g. in the cooling tower pond or at the suction side of the recirculating pump.

167. The dosing methods adopted will attempt to maintain constant concentrations of scale control, fouling control and corrosion inhibiting chemicals throughout the whole cooling water circuit at all times. Thus, any release of water from the circuit, e.g. through leakage and blow-down, should always contain the concentration of treatment chemical as specified for the system by the treatment package. This will be the case unless a system malfunction means that mixing is not occurring properly and 'slugs' of treatment chemicals circulate through the cooling water circuit.

168. Biocide concentrations tend to fluctuate more widely between a maximum at the time of addition to a minimum just before addition of the next programmed dose. Thus, any release of water through leakage or blow-down will contain varying quantities of active ingredient depending on when the last dose was applied and on the rate of degradation/disappearance of the chemical from the system. For the purpose of estimating a release the maximum concentration should be assumed.

169. The dosing method adopted should be compatible with the whole treatment package specified for the system and should be able to cope with the addition of all treatment chemicals, i.e. continuous addition of one set of chemicals and occasional dosing with another.

3.2.3 Formulations

170. Until about 1950, cooling water treatment in the UK was practically unknown, with the exception of chlorination of industrial cooling systems for microbiological control. Small amounts of scale control additives, e.g. tannin and sodium polyphosphate were also used. As system design became much tighter and energy and water costs increased, the need for more effective water treatment was recognised. The market for treatment chemicals is highly competitive and there continue to be significant advances in the technology, many of which are driven by environmental concerns.

171. For smaller systems scale and deposit control chemicals will be supplied as a single package, formulated with corrosion inhibitors. For larger systems, greater flexibility is obtained by separating the dosage of corrosion control from scale and deposit control additives. Multi-functional formulations are

frequently used because scale and deposits are rarely of a single species. Biocides are always dosed separately. Therefore the treatment chemicals will be considered under the individual function groups:

- Corrosion control
- Scale and deposit control
- Microbiological control

3.2.4 Individual Chemicals

3.2.4.1 Corrosion control chemicals

172. In order to give a general indication as to the levels at which a new chemical may be dosed, Table 3.1 shows corrosion inhibitors in current use and their typical use concentrations.

173. A number of different phosphates are used in order to maintain the ortho and polyphosphate concentrations shown in Table 3.1. These phosphates include trisodium phosphate, disodium phosphate, trisodium polyphosphate and tetrasodium pyrophosphate.

Table 3.1: Corrosion inhibitors.

Chemical	Use Concentration (mg/l)
Sodium phosphate ^a	ortho and polyphosphate at 5-25
Zinc chloride or sulphate	Zinc at 2 - 10
Sodium molybdate	Molybdate at 2 - 15
Sodium nitrite	50 - 150
Sodium silicate	5 - 25
Phosphonobutane-1,2,4-tricarboxylic acid	5 - 20
Hydroxyethylidene diphosphonic acid	5 - 20
Hydroxyphosphonoacetic acid	5 - 20
Amino tri(methylene phosphonic acid)	5 - 20
Mercaptobenzthiazole, tolyltriazole, benztriazole	}Used interchangeably as }copper corrosion inhibitors 1 - 5

Note: a) A number of different phosphates are used in order to maintain the ortho and polyphosphate concentrations shown. These phosphates include trisodium phosphate, disodium phosphate, trisodium polyphosphate and tetrasodium pyrophosphate.

174. With the exception of phosphonobutane-1,2,4-tricarboxylic acid, hydroxyethylidene diphosphonic acid, hydroxyphosphonoacetic acid and methylene phosphonic acid, all these chemicals are stable under use conditions and will be discharged largely unchanged. The four phosphonates will undergo a degree of hydrolysis during use in the cooling system to form orthophosphate ions.

3.2.4.2 Scale and deposit control chemicals

175. Scale and deposit inhibitor chemicals are often dosed together. Table 3.2 gives typical use concentrations of chemicals which are currently used. Several of the inhibitors are multi-functional, in that they control scale and deposits e.g. phosphino polyacrylates.

Table 3.2: Scale and deposit inhibitors.

Chemical	Use concentration (mg/l)
Polyacrylic acid	5 - 20
Polymethacrylic acid	5 - 20
Polymaleic acid	5 - 20
Polyethylene glycol	5 - 20
Maleic acid - styrene copolymer	5 - 20
Maleic – methylvinylether	5 - 20
Maleic - ethylacetate – vinylacetate	5 - 20
Tannin	10 - 100
Phosphino polyacrylates	5 - 20
Phosphonobutane-1,2,4-tricarboxylic acid	2 - 10
Hydroxyethylidene diphosphonic acid	2 - 10
Phosphate esters	2 - 10
Amino tri(methylene phosphonic acid)	2 - 10
Diamine tetra(methylene phosphonic acid)	2 - 10
Diethylene triamine penta(methylene phosphonic acid)	2 - 10
Sulphonated polystyrene	5 - 20
Sulphonated styrene – acrylate copolymer	5 - 20
Sulphonated styrene – maleic copolymer	5 - 20
Allyl sulphonate – maleic copolymer	5 - 20
Lignosulphonates	10 - 100
Hydroxy phosphono acetic acid	2 - 10
Polyacrylamide	5 - 20
Partially hydrolysed polyacrylamide	5 - 20
Polyethylene imines	2 - 10
Poly isopropanyl phosphonic acid	2 - 10

176. All of the chemicals in this list are stable and remain chemically unchanged in cooling water systems, with the exception of those containing phosphorus, i.e.:

- Phosphino polyacrylates
- Phosphonobutane-1,2,4-tricarboxylic acid
- Hydroxyethylidene diphosphonic acid
- Phosphate esters
- Amino tri(methylene phosphonic acid)
- Diamine tetra(methylene phosphonic acid)
- Diethylene triamine penta(methylene phosphonic acid)
- Hydroxy phosphono acetic acid

- Poly-iso-propenyl phosphonic acid

177. These decompose to produce phosphate ion which may then react further with calcium to form insoluble calcium phosphate. The most unstable are the phosphate esters and amino tri (methylene phosphonic acid). Free halogen accelerates the decomposition of these phosphorous compounds.

3.2.4.3 Microbiological control chemicals

Cleaning and disinfecting

178. Due to a series of highly publicised outbreaks of Legionnaires' Disease and related diseases over the past 10-15 years, a number of guidelines on safe operation have been published by the UK Health & Safety Executive. The guidelines include recommendations for periodic cleaning and disinfection of cooling systems and cooling towers, and the following steps are advised:

- Chlorinate the system water to a level of at least 5 mg/l and allow to circulate for at least 5 hours. Drain system.
- Clean the system. This will involve physical and mechanical procedures but may also need chemicals, such as inorganic acids.
- Refill the system with fresh water and dose with chlorine to a level of 5-15 mg/l. Circulate for at least 5 hours.
- Drain the system. Refill and commence normal treatment.

179. Every 5 to 10 years, it may be necessary to acid clean the system. Typically 10% solutions of acids, such as hydrochloric, sulphamic and formic are circulated through the system. The discharge of these acid solutions will consist of any unreacted acid plus their calcium salts, dissolved iron oxide and any insoluble materials which may have been lodged in the deposit matrix. Such discharges will normally be to sewer.

Biocides

180. The term biocide embraces the more specific terms algicide, bactericide, fungicide, sporicide and virucide, (but not pesticides). Different biocides may require different contact times and concentrations to be effective, and may only work against certain selected organisms.

181. Water systems may have biofilms, biofilm fragments, scale and corrosion debris, pipework and deadlegs which may allow protection against biocide action. Free-living amoebae may act as reservoirs for *Legionella pneumophila*, affording protection against such disinfectants as chlorine and allowing apparent re-seeding of water systems with legionellae.

182. It is recognised that effective biocide dosing to ensure control of micro-organisms within cooling systems can only be achieved through well-managed water treatment regimes that encompass all aspects of system management. There are two separate classes of biocide, oxidising and non-oxidising.

Oxidising biocides

183. Wide spectrum, rapid kill capability by oxidation of cell materials

- Advantages: Quick kill at low cost
 Little or no foam
 Offers complete spectrum protection
 May have a lower potential for adverse environmental effects than some non-oxidising biocides.
- Disadvantages: pH problems with chlorine
 Biodispersant needed
 Tend to be corrosive.

184. Oxidising biocides are the most commonly used type of biocide, accounting for over 90% of those used. Within the oxidising range, the biocides in most use are based on chlorine or bromine, which liberate hypochlorous or hypobromous acids on hydrolysis in water. These acids are powerful biocides capable of oxidising organic matter e.g. enzymes or proteins, associated with microbiological populations, resulting in the death of the micro-organisms.

185. It is anticipated that an oxidising biocide will kill micro-organisms in a matter of minutes, followed by hydrolysis of any residues. It may be necessary to dose biodispersants alongside oxidising biocides to enable the product to penetrate slimes and biofilms via the surfactants' dispersing properties. Table 3.3 summarises the oxidising biocides in current use, their recommended use concentrations and an indication of quantities being consumed in the UK .

Table 3.3: Oxidising biocides.

Chemical	Use concentration (mg/l)	Use in UK (tonnes/year)
Sodium hypochlorite	1 - 5	6731
Calcium hypochlorite	1 - 5	
Sodium dichloro isocyanurate	1 - 5	19
Trichloro isocyanuric acid	1 - 5	23
Hypobromous acid/ hypobromite (made in situ)	1	5
Sodium bromide	1 - 5	356
1,3 dichloro 5,5 dimethyl - hydantoin	0.2 - 5	286
1- bromo 3-chloro 5,5-dimethyl - hydantoin	0.2 - 5	
Iodine/ hypoiodous acid	0.3 - 1.5	*
Iodophors	*	*
Chlorine dioxide	*	13
Peracetic acid	1 - 5	1
Hydrogen peroxide	1 - 5	1
Ozone	0.02 - 0.2	*

Note: * Value not known.

Non-oxidising biocides

186. These have a slower kill capability and require a longer contact time. They have different modes of action for example dissolving cell wall materials or interference with cell metabolism.

Advantages: Easy to apply
Act over wide pH range
Penetrating solution

Disadvantages: Expensive
Less environmentally acceptable
Foaming
Susceptible to degradation.

187. Non-oxidising biocides are normally more stable than oxidising biocide. The concentration of a non-oxidising biocide in a system may fall due to water loss and/or by degradation of the active substance.

188. Table 3.4 summarises non oxidising biocides in current use, their recommended use levels and approximate consumption in the UK.

Table 3.4: Non oxidising biocides.

Chemical	Use concentration (mg/l)	Use in UK (tonnes/year)
Chlorinated phenols	50	13
ortho- phenylphenol		
Sodium dimethyl dithiocarbamate	11 - 20	< 1
Disodium ethylene dithiocarbamate	11 - 20	< 1
bis-dimethylthiocarbomoyl disulphide		
Methylene thiocyanate	0.75 - 5	2
2,2-dibromo-3-nitropropionamide (DBNPA)	1 - 50	17
5-chloro 2-methyl-4-isothiazolin -3- one	1 - 30	13
2-methyl 4-isothiazolin 3-one	1 - 30	4
2-bromo 2-nitropropane 1,3-diol	200 - 1500	
2-thiocyanomethylthio- benzothiazole (TCMTB)		
Glutaraldehyde	1 - 50	56
Formaldehyde release agents		
Alkyl trimethyl ammonium chloride	6 - 10	
Dialkyl dimethyl ammonium chloride	6 - 10	4
Alkylbenzyl dimethyl ammonium chloride	6 - 10	21
Poly[oxyethylene (dimethyl imino)- ethylene (dimethyl imino)- ethylene dichloride]	3 - 50	2
Alkyl 1,3-propylene diamine salt		
Poly (hexamethylenebiguanide) hydrochloride	21 - 50	8
Tributyl tetradecylphosphonium chloride		10

Algae inhibitors

189. Triazines are typically used to specifically target algal growth, for example, 2-chloro-4-tributylamino-6-ethylamino 5-triazine.

3.3 Chemical release

190. With the exception of some oxidising biocides which have a degree of volatility, e.g. chlorine or ozone, cooling water treatment chemicals are discharged to the environment as blowdown or bleed-off. In the UK approximately half of these discharges are to sewer and the remainder are to estuaries or to sea. Much of the cooling water blowdown discharged on the UK coasts or to estuaries is treated before discharge. Blowdown losses can be considered to be on a continuous basis although they may in fact take place over a short period every hour.

191. The discharges to estuary, and in a few cases to sea, are largely from the industrial complexes which have developed on the rivers Forth, Tyne, Tees, Humber, Thames, Severn, Mersey and Clyde. There is also a small number of discharges to inland waterways.

192. Throughout the rest of the EU there is little difference in the types of chemicals used. There are restrictions in Germany, Belgium and the Netherlands regarding allowable levels of organic halogen compounds and chemical oxygen demand of the discharges from a cooling water system. In addition Belgium may be introducing a tax on discharges of phosphorus, and Germany requires that the discharges from a cooling water system are tested for toxicity.

193. With the exception of the countries with little or no coastline, e.g. Germany and Austria, the pattern of blowdown discharge closely resembles that in the UK. There is a general split between discharges to estuarine and coastal waters and those to in-house and inland treatment plants. There is less treatment of cooling water discharged to coastal areas in Italy and Greece than in the UK. The amount of treatment is likely to increase as new regulations come into force regarding discharges to the Mediterranean and the North Sea.

3.3.1 Market size (UK)

194. There are an estimated 50,000 units of installed base and evaporative cooling towers at 25,000 sites (see Table 3.5), averaging two units per site. It is estimated that around 3000 new units will be installed each year, mostly in the small to medium range (4540 to 227000 litre capacity). Of the installed systems it is estimated that two thirds are on industrial sites and one third on commercial sites. The main end use sectors and applications are given below:

Manufacturing

Food and drink processing	Refrigeration, process cooling.
Rubber and plastics	Process cooling
Petrochemicals	Refrigeration, process cooling
Chemicals and paints	Cooling compressors
Metal manufacture & engineering	Process cooling

Commercial & institutional

Offices	Air conditioning, standby generator cooling
Grocery, supermarkets	Air conditioning, refrigeration.
Cold stores	Refrigeration.

Table 3.5: Capacity range of installed base cooling towers.

Capacity in litres	Installed number	Percentage
0 to 4,540	12,500	25
4,540 to 22,700	7,500	15
22,700 to 227,000	25,000	50
227,000 and over	5,000	10
Total	50,000	100

3.3.2 Individual chemical release examples

195. Typically the flow rate of a system will equal around 3.5 times the capacity every hour.

The following assumptions will be made relating to the system :

Parameter	Symbol	Value for example	Comment
System volume	V_{system}	100 m ³	Ranges in Table 3.5
Water circulation rate	$FLOW_{circul}$	350 m ³ /hour	3.5x system volume
cycles of concentration	N_{cycles}	3	Typical value
Evaporation loss	$FLOW_{evap}$	3.5 m ³ /hour	1% of circulation rate

Cleaning and disinfection

196. Before or during cleaning there will be a drain out of the system volume, accompanied by the treatment chemicals.

i. Drain out of system

Assume:

- System is dosed with corrosion inhibitor, scale and deposit inhibitor and non-oxidising biocide.

Loss to drain can be estimated by the following formula.

$$Q_{subst, drain} = V_{system} \cdot F_{drain, water} \cdot C_{treat}$$

Explanation of symbols:

$Q_{subst, drain}$	= amount of substance released to drain	[kg]	
V_{system}	= volume of system	[m ³]	See Table 3.5
$F_{drain, water}$	= fraction of system volume drained	[-]	1 for complete draining
C_{treat}	= working concentration of substance in treated system	[kg/m ³]	See Tables 3.1 to 3.4

197. For the corrosion inhibitor, sodium silicate, C_{treat} is 5 - 20 mg/l (0.005 - 0.02 kg/m³) from Table 3.1. The amount released, $Q_{subst, drain}$, is therefore 0.5 - 2.5 kg. Similarly, releases of polyacrylic acid, a scale and deposit inhibitor, are also 0.5 - 2.5 kg (same use rate, from Table 3.2), and for the non-oxidising biocide alkylbenzyltrimethyl ammonium chloride, releases are 0.6 - 1.0 kg (use rate in Table 3.4).

ii. Cleaning and disinfecting

198. Here the main chemical to be lost is chlorine, assume:

- Average level of free chlorine 10 mg/l (0.01 kg/m³) (= C_{clean})
- System filled and drained twice, potentially within 24 hours.

199. The losses can be estimated with the same equation as above, but with C_{clean} in place of C_{treat} . Also the discharge of water is two volumes of the system. This gives a release of 2 kg chlorine per clean and disinfection.

200. Releases from these steps will occur over a limited period of time. To convert the quantities released to emission rates, a time period of one day is suggested. These releases will also only occur infrequently.

Normal operation

201. In normal operation, losses to water are related to the blowdown rate, and losses to air are related to the drift/windage rate.

For blowdown
$$FLOW_{blowdown} = \frac{FLOW_{evap}}{N_{cycles} - 1}$$

For this example, $FLOW_{blowdown} = 1.75 \text{ m}^3/\text{hour}$.

Emissions to water are given by the following equation.

E_{water}	$= FLOW_{blowdown} \cdot C_{treat} \cdot 24$	$\frac{FLOW_{evap}}{N_{cycles} - 1}$	Explanation of symbols:		
[kg/day]		E_{water}	=	emission	rate
				in	water
$FLOW_{blowdown}$	= blowdown rate			[m ³ /hour]	See above
C_{treat}	= working concentration of substance			[kg/m ³]	See Tables 3.1 to 3.4
24	= constant to convert from hours to days			[hour/day]	

202. As an example, the corrosion inhibitor sodium silicate is dosed at 5 to 25 mg/l (0.005 - 0.025 kg/m³). Losses of this substance are estimated as 0.21 - 1.05kg/day.

For windage and drift losses

$$FLOW_{windage} = FLOW_{circul} * F_{windage}$$

and

$$E_{air} = FLOW_{windage} \cdot C_{treat} \cdot 24$$

Explanation of symbols:

E_{air}	= emission rate to air	[kg/day]	
$FLOW_{windage}$	= windage rate	[m ³ /hour]	See above
C_{treat}	= working concentration of substance	[kg/m ³]	See Tables 3.1 to 3.4
24	= constant to convert from hours to days	[hour/day]	

203. As an example, the scale and deposit inhibitor polyacrylic acid is dosed at a concentration of 5 - 20 mg/l (0.005 - 0.02 kg/m³). Assuming a fraction of loss in windage and drift of 0.1%, the emission rate is 0.042 - 0.17 kg/day.

3.4 Recycling

204. There is currently no recycling of cooling water chemical treatment from the cooling tower discharge (blow-down or bleed-off). However, a brief review of this subject will help to put it into perspective.

205. The only attempt to recycle chemical treatment was in the period when corrosion inhibitors based on zinc chromate were used. In the UK these inhibitors predominated between 1960 and 1980 and the attempts at recycling and recovery were made because the alternatives to zinc chromate were less effective and often more costly.

206. The only practicable process, which recovered only the chromate, used ion exchange. Cooling tower blow-down was passed through an anion exchange resin, which was regenerated with caustic soda. The sodium chromate in the regenerant was returned to the cooling tower.

207. Another process developed in the metal plating industry was used to remove chromate and sometimes zinc to avoid the undesirable environmental impact of discharge. The cooling tower discharge was acidified and treated with a reducing chemical such as sulphur dioxide, sodium bisulphite or ferrous sulphate. In this way, the chromate ions were converted into trivalent chromium ions. The water was then made alkaline by addition of lime or caustic soda to a pH value of 8.5-9.5. Chromium hydroxide and zinc hydroxide were both precipitated and removed by sedimentation and filtration. The treated water was then suitable for discharge.

208. Another technology relevant to this topic was developed particularly in the USA to recycle blow-down water and provide so-called "zero-discharge" cooling systems. This process involved treating the blow-down with lime or with lime and sodium carbonate to reduce hardness and alkalinity. Although ions such as chlorite, sulphate and silica were unchanged, the process allowed the cooling system to operate at much higher cycles of concentration.

209. At the present time, the use of membrane technology is being studied, in particular the use of reverse osmosis membranes. If cooling water blow-down is treated in a reverse osmosis plant, the resultant treated water, with about 90% of its soluble salts removed, can be recycled. Such a procedure will almost always require a filtration step ahead of the reverse osmosis membrane and will be restricted to medium and large units where specific conditions make it financially desirable given the capital cost. The treatment chemicals listed in this report will also be removed to the same extent as all the other soluble material and so no chemical recycling takes place.

4 PAPERMAKING SYSTEMS

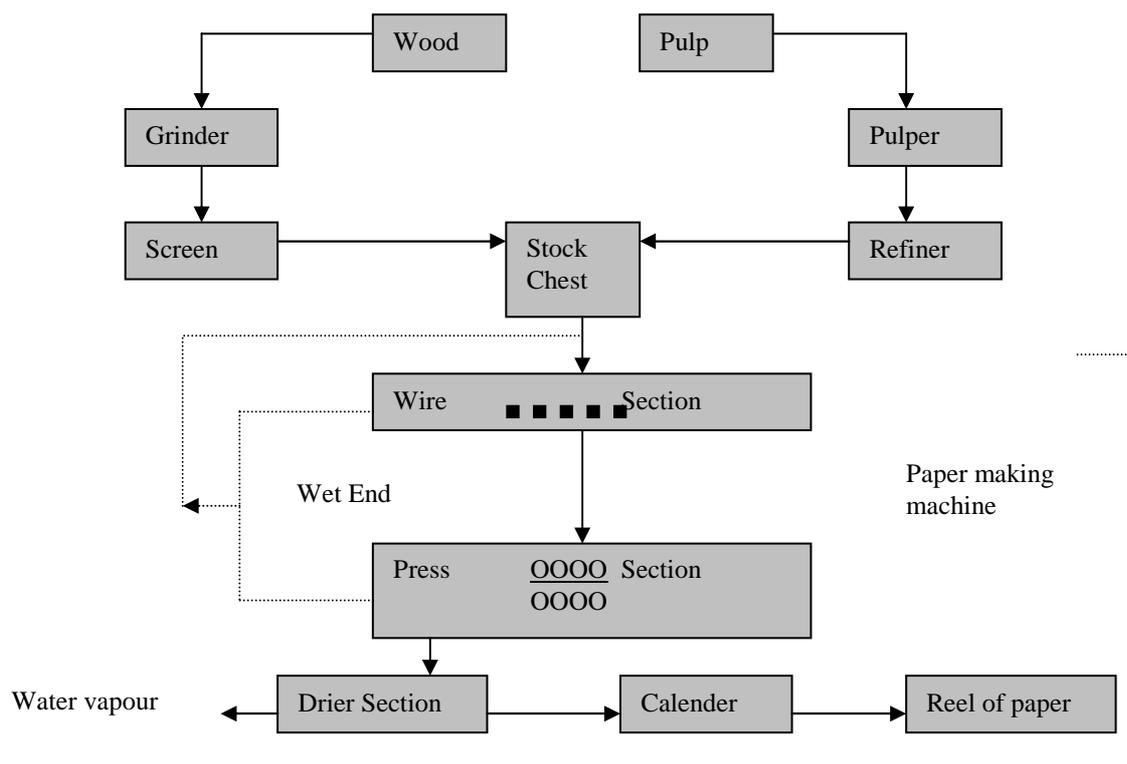
4.1 Description of papermaking systems

4.1.1 General description

210. The paper making process is shown in Figure 4.1. This report is only concerned with the area where water recirculation occurs, resulting in water treatment.

211. As Figure 4.1 shows, the area of water recirculation is encompassed by the term ‘the wet end’ and does not include the initial pulping processes. It should therefore be assumed that discussions regarding chemical use and wastewater relate to the paper making machine, unless otherwise specified. This section is relevant to sites which take in pulp from other sources to produce paper, board etc. It can also be used for the paper-making section of integrated plants, where pulp is produced on the same site, but does not cover this pulp production step.

Figure 4.1 Paper making process



212. Raw material in the form of wood pulp or waste paper (from external sources or the mill itself) is homogenised at a level of about 1 to 3 % in water. This liquid is first of all distributed on to a continuously moving wire mesh. This allows the fibres to begin the formation of a paper sheet and much of the water to drain through the mesh.

213. The next process is for this incipient sheet to pass over a felt where it is rolled to express more water. These two processes are known as the ‘wet end’. The sheet, which now contains 50 to 60 % water

by weight, then proceeds over a series of steam heated rotating cylinders, where most of this remaining water evaporates.

214. During this process, chemicals are added to fulfil a variety of functions, and the number of such chemicals exceeds 1,000 in the UK paper industry. Some of these chemicals are used to give specific properties to the finished product, e.g. starch, size, fillers, pigments, wet and dry strength additives. These substances are dealt with in an emission scenario document included in the EU Technical Guidance Document (EU 1996).

215. This report therefore discusses that group of chemicals which is used to control water related problems. The different functions will be described in individual sections.

216. It should be noted, however, that the chemicals used to give specific properties to the paper can contribute considerably to effluent contamination by BOD, COD and suspended solids.

4.1.2 Losses from the system

217. From UK experience, in the past water was used on a once through basis at the rate of about 50 m³ per tonne of product. In recent years the industry has invested considerably in procedures to recycle water by 'closing up' the whole of the mill water system. This has been done largely by the introduction of devices known as save-alls, which are essentially tanks placed beneath the wire and felt press sections so that water from these two sections is collected and recycled. While it is obviously more difficult to collect the water removed in the heated section by evaporation, some mills are attempting to do this.

218. Water which is recirculated from the wet end may be treated in an attempt to overcome the problems highlighted in the following section. It is anticipated that large amounts of water will be lost from the papermaking machine despite efforts to recirculate it. This will be lost from the system throughout the stages of paper manufacture, currently estimated to be around 30 to 35 m³ wastewater per tonne of product. Losses can vary within and between countries, see Section 4.4.1.

219. Loss of water through evaporation will be of little consequence for chemical release, except where volatile treatment chemicals are concerned.

4.2 The need for chemical treatment

4.2.1 Overview

220. The problems associated with the water at paper mills differ somewhat from the previous sections. The areas which will be detailed in terms of treatment chemicals are as follows:

- Influent and effluent water treatment.
- Drainage and retention aids.
- Defoamers
- Deposit control
- Biocides

4.2.2 Influent and effluent water treatment

221. Many paper mills abstract water from their own supply, such as a nearby watercourse. Since this water may contain unacceptable levels of solids and bacteria, it may be necessary to treat the water prior to

use in the paper making machine. Any contaminants may adversely affect the quality of the paper product and encourage micro-organism growth.

222. Paper mills which utilise their own private water supply may need to treat with coagulating, sedimentation, filtration, and disinfecting chemicals. Chemical flocculants and coagulants are also used where the effluent is treated on site, assisting in sedimentation, dewatering of sludges produced in sedimentation and sludge digestion processes.

4.2.3 *Drainage and retention aids*

223. When the dilute pulp suspension enters the wire section, the bulk of the water is drained away. The more effectively this is done, the less energy will be needed in later stages to remove the remaining water through presses and evaporation. Drainage can be improved by treating the water with the appropriate chemicals.

224. The draining process carries with it some fibre and other valuable constituents. It is important that as much as possible of these are retained on the wire to enable them to be incorporated into the finished product. Retention can be enhanced by the use of certain chemicals.

4.2.4 *Defoamers*

225. Surface active materials present in the paper making process can reduce surface tension to a level at which foam build-up occurs on the machine. This can affect product quality, disrupt production and, in severe cases, cause machine shut down. The foam can also occur in the effluent treatment plant and reduce its effectiveness. Therefore chemicals are added to the water to inhibit foam production.

4.2.5 *Deposit control agents*

226. The conditions under which a paper machine operates can be complex, with wide variations in temperature, the use of many different substances, and the possibility of interaction between these and impurities in the pulp or recycled waste. As with the other recirculating water systems, there can be a problem of scale deposition in hard water areas.

227. Deposits can occur at any location, are frequently mixtures of two or more species, and can adversely affect the quality of the paper product and cause operational problems. Due to the complex nature of the system, a wide variety of chemical additives is employed to reduce deposition to acceptable levels. These chemicals include surfactants, dispersants, solvents and chelating agents.

228. Felt conditioners comprise a similar group of compounds, which are used to maintain the condition of the felt of the presses. Without these conditioners the felt can become block like and less effective at removing water.

229. Periodically it may be necessary to clean the paper making machines using high concentrations of deposit control and felt conditioning agents. This is called 'clean out' or 'boil out' and requires the paper mill to be shut down, typically between changes of paper grade production.

4.2.6 *Biocides*

230. A paper machine provides a congenial environment for many microbiological species to develop, because it is wet, warm and contains a multitude of nutrients. These species can build up into very large gelatinous masses, which adversely affect paper quality and eventually lead to breaks. Where deposits exist, anaerobic conditions can develop beneath them. Corrosive bacteria may then proliferate and can

cause severe corrosive attack on materials of construction. Biocides are used to reduce the number of bacteria entering the paper making machine and maintain low levels in the recirculating water.

4.3 Chemical dosing

4.3.1 Dosing methods and storage

231. **Manual dosing** of chemicals, by hand, in batches is only used in a small number of paper mills. Spillage can occur during the transfer from drums to the container used for measuring and pouring.

232. **Pumped dosing** is the method most commonly used. Biocides are dosed intermittently, whereas other chemicals tend to be dosed continuously. Pumps may be reciprocating, diaphragm, peristaltic or worm gear. Leaks can occur as a result of faulty valves and O- rings, and damaged pipework.

233. **Chemical storage** - Chemicals are supplied in a wide range of containers from 25 litre pails to 100 litre drums to 1 tonne tanks. Pumping may be direct from container or via a storage tank. Spillages can occur during transfer and there is usually a residue of around 1 to 2 % left in containers . Typically 100 litre - 1 tonne containers are returned to the supplier.

234. Recent developments have seen the introduction of five tonne bunded storage vessels filled by road tanker. The bund should contain any spillages, especially where pumps and control equipment are integrated into the storage area. Spillages should be kept to a minimum by avoiding drum handling and chemical transfer on site.

4.3.2 Chemical treatments

235. Examples of chemicals used in particular stages of the process and for different purposes are included in this section. It should be noted that these are based on practice in the UK at the time the original document was produced, and may or may not be relevant for other countries or for current practice. Where information has been provided on chemicals used or not used in other countries this has been included in the document, but all chemicals mentioned should be treated as examples.

4.3.2.1 Influent and effluent treatment

236. Table 4.1 gives the chemicals typically used to provide treatment of incoming water and effluent.

237. The dosage rates given in the table for this group of chemicals are expressed in mg/l. In the other sections, dosage rates will be expressed in the conventional industry nomenclature of kg per tonne of product.

Table 4.1: Chemicals used for influent and effluent treatment.

Chemical	Function	Use Concentration (mg/l)
Sodium hypochlorite	Biocide	0.5 - 5 free chlorine
Sodium bromide*	Biocide	0.2 - 2 free bromine
Bromochlorodimethyl hydantoin (BCDMH)	Biocide	0.2 - 5 free halogen
Chlorine dioxide*	Biocide	0.2 - 2
Ozone*	Biocide	0.2 - 2
Aluminium sulphate	Coagulant & flocculent	5 -100
Ferrous/ferric sulphate	Coagulant & flocculent	5-100
Polyaluminium chloride	Coagulant & flocculent	5-50
Polyaluminium silicate sulphate	Coagulant & flocculent	5-50
Poly-dimethyldiallylammonium chloride (Poly-DMDAAC)	Coagulant & flocculent	1-50
Polyacrylamide (PMA)	Coagulant & flocculent	0.2-10

* - these are little used in Japan

4.3.2.2 Drainage and retention aids

238. A number of chemicals are added which have the effect of modifying the disposition of fibre so that more of it stays on the wire and drainage of water is enhanced. These chemicals are known as drainage and retention aids and are used in almost all mills. Table 4.2 indicates the ones currently in use.

Table 4.2: Drainage and retention aids.

Chemical	Usage (kg/tonne paper)
Poly-dimethyldiallylammonium chloride (Poly-DMDAAC)	0.1-2
Polyacrylamide (PMA)	0.1-2
Cationic starch	0.1-2
Polyethyleneimine	0.1-2
Bentonite clay	0.1-2
Sodium silicate	0.1-2

239. All the chemicals in Table 4.2 have similar functions, except bentonite clay which assists in sedimentation rather than initiates it. Sodium silicate is used in conjunction with one of the polymers, poly-DMDAAC, PMA, cationic starch or polyethyleneimine. These chemicals are not very interchangeable, with one usually being more suitable than others, based on the conditions at the mill.

4.3.2.3 Defoamers

240. There is considerable commercial sensitivity in this area and the list in Table 4.3 may not be complete. Usually only one of these chemicals is used. It is likely that new compounds would be used in this function.

Table 4.3: Defoamers.

Chemical	Usage (kg/tonne paper)
Mineral oil*	0.1-1.0
Siloxanes	0.01-0.2
Fatty acids, aliphatic alcohols and their polyethers	0.01-1.0
Fatty acid amides	0.1-1.0

* - not used in Japan

4.3.2.4 Deposit control

241. The compounds in Table 4.4 are frequently supplied as blended products. Many chemical suppliers make a point of custom blending deposit control agents for specific mills or even specific machines.

Table 4.4: Deposit control/cleaning agents.

Chemical	Function	Usage (kg/tonne)
Phosphoric acid Hydrochloric acid Potassium hydroxide	pH control	*
Ethylene oxide/ propylene oxide block polymers	Surfactant = dispersing agent	0.1-2.0
Nonylphenol ethoxylates ^a	Dispersing agent	0.1-2.0
Propylene glycol	Solvent	0.1-2.0
Ethylene glycol	Solvent	0.1-2.0
Dimethyl formamide ^b	Solvent	0.1-2.0
Alkyl aryl polyether	Dispersing agent	0.1-2.0
Alkyl polyglycol ethers	Dispersing agent	0.1-2.0
Phosphonates and phosphate esters	Calcium scale control agent	0.1-2.0
Sodium lignosulphonate ^b	Pitch and resin dispersal	0.1-2.0
Alkyl phenol ether sulphate	Dispersing agent	0.1-2.0
Heavy aromatic naphtha	Solvent	0.1-2.0
Alkyl and aryl sulphosuccinates	Dispersing agent	0.1-2.0
Ethylenediaminetetraacetic acid	Calcium scale control agent	0.1-2.0

Note: * The quantity required will depend on the natural pH of the system and the pH needed for operation, in particular the sizing process.

^a use declining in some areas

^b little used in Japan

242. Alternative substances used in Japan include malic acid, citric acid (pH control and scale control agent), poly2-hydroxy propyl N, N dimethylammonium-chloride (pitch control agent), polyacrylic acid (pitch and scale control agent), polyethylene glycol alkylether (pitch control agent), poly diaryl dimethyl ammonium chloride (pitch control agent).

243. All of these compounds are used intermittently at higher levels, typically 10 times higher than those given in Table 4.4, for machine and felt cleaning i.e. clean out or boil out. The frequency of these operations varies considerably from mill to mill.

244. A typical formulation used for the cleaning out of a paper machine is given below :

Propylene glycol	10%
Ethylene oxide/PO block polymers	5%
Aryl sulphosuccinates	5%
Phosphoric acid	5%
Remainder is water	

245. Many mills use proprietary compounds which are typically 2 to 10 % sodium hydroxide and 1 to 5 % non-foaming surfactant. Where a mill is located in a hard water area an acid clean, using a formulation similar to that tabulated above, would be used. In paper and pulp mills, where there may be a pitch problem, sodium lignosulphonates could be incorporated in the cleaning formulation at 10 to 20 %.

246. A typical dosing rate for cleaning formulations is 5 to 10 kg formulation per tonne of paper produced. The spent cleaning solutions are disposed of to sewer or to the mill effluent treatment plant.

4.3.2.5 Biocides

247. A wide variety of chemicals are used to control micro-organisms. They are used singly or in blends, and dosed intermittently, normally for a few hours each day. It is usual that alternate doses will contain different biocides. As new biocides are developed they tend to be more effective and/or less of a concern for the environment, and so replace the older ones. Table 4.5 has examples of biocides used in the UK compiled in 1995. Table 4.6 has a more recent list of biocides used in Japan.

248. The same chemicals are also used for microbiological control in some of the materials added to a paper machine, particularly starch solutions, where growth can be particularly rapid and lead to degradation of the starch.

249. Table 4.1 indicated the biocides which are used for disinfection of the mill supply water. However effectively this disinfection is carried out, bacteria will still enter the machine system from the atmosphere and from raw materials, especially pulp.

250. Biocides covered in this section differ in their function and are known as machine biocides. They have a short retention time in the paper making machine and hence are unlikely to degrade significantly in use.

Table 4.5: Machine biocides in UK 1995.

Chemical	Usage (kg/tonne)
Sodium bromide	0.05-0.15
Bromochlorodimethylhydantoin (BCDMH)	0.01-0.05
2-Bromo-2-nitropropane-1,3-diol (BNPD)	0.1-0.5
5,5-Dichloro-2,2-dihydroxydiphenylmethane	0.2-1
Methylene bis thiocyanate	0.01-0.05
Quaternary ammonium compounds and polyquaternary ammonium compounds	0.2-1

Bromonitrostyrene	0.2-1
Glutaraldehyde	0.1-0.5
5-Chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one	0.05-0.2
Sodium dimethyldithiocarbamate, disodium ethylene bis dithiocarbamate	0.1-0.5
Dodecylguanadine hydrochloride	0.1-0.5
Dibromonitrilopropionamide	0.1-0.5
Bis (trichloromethyl) sulphone	0.03-0.25
2-(Thiocyanomethylthio) benzothiazole	0.1-0.5
3,5 Dimethyl-tetrahydro-1,3,5-2H-thiadiazine-2-thione	0.1-0.5

Table 4.6: Machine biocides in Japan, 2001

Chemical	Usage (kg/tonne)
4,5-Dichloro-1,2-dithiol-3-one	0.1-0.5
2,2 Dibromo-2 nitro-ethanol	0.1-0.5
Bis bromoacetoxy-2 butene	0.1-0.5
1,2 Benzoisothiazoline-3-one	0.1-0.5
Bis-bromoacetoxyethane	0.1-0.5
2 Benzoimidazole carbamamic methylester	0.1-0.5

4.4 Market size and wastewater production

4.4.1 Overview

251. In the UK the paper industry produces about 5,000,000 tonnes of paper and board per annum, from about 100 mills. A breakdown of the production rates is given in Table 4.7.

252. Allowing for evaporation loss and for water used in steam generation, it is generally considered that the minimum water consumption is around 5 m³ per tonne of product. The average UK usage is between 30 to 35 m³ per tonne of product. The amount of wastewater related to production is given in Table 4.6.

253. Although the bulk of wastewater is from the paper machine, there may be other wastestreams to consider:

- Coated paper/board production produces a coating wastewater which can be discharged with the papermaking wastewater.
- On site pulping discharge is typically handled separately from the papermaking wastewater.
- Deinking liquor is always discharged along with paper machine wastewater.
- Uncontaminated cooling water is discharged separately or used as process supply water.

254. Water costs to the industry vary, with effluent charges running at somewhat higher levels. At the middle and higher costs, there are obvious incentives to close-up (collect and recycle water) for economic reasons. UK paper mills have had to demonstrate that water is being used and discharged to the best practicable environmental standards from 1996.

Table 4.7: UK paper production and wastewater flow.

Annual production (tonnes / year)	Daily production (tonnes per day)*	Number of mills	Total wastewater flow (m ³ /day)	Average w.water per mill (m ³ /day)
up to 5,000	up to 16.67	12	2,230	186
5,000 to 10,000	16.67 to 33.33	11	43,350	3941
10,000 to 25,000	33.33 to 83.33	25	66,800	2672
25,000 to 50,000	83.33 to 166.67	21	58,600	2790
50,000 to 100,000	166.67 to 333.33	15	125,020	8335
100,000 and over	333.33 and over	16	150,500	9375
Total		100	446,500	

Note: * Assumes 300 days operation per year

255. Table 4.8 gives an indication of the paper production industry throughout the EU in 1994.

Table 4.8: Paper production in EU countries 1994.

Country	Paper production (ktonnes/y)	Number of paper mills	Average mill production (ktonne/y per mill)
Austria	3,603	28	129
Belgium	1,202	15	80
Denmark	311	4	78
Finland	10,880	45	242
France	8,672	150	58
Germany	14,429	190	76
Greece	300	25	12
Ireland	36	1	36
Italy	6,699	300	22
Luxembourg	0	0	0
Netherlands	3,011	32	94
Portugal	949	75	13
Spain	3,504	140	25
Sweden	9,286	50	186
UK	5,817	100	58
EU	68,699	1155	59

256. More detailed and recent information is available from a survey of Finnish paper mills conducted in May 2001 (Sirkka, 2001). The 37 mills which are members of the Finnish Forest Industries Federation were sent a questionnaire and twenty four responded. The average production among these was 1,144 tonnes per day, with a range of 55 - 3,300 tonnes per day. Hence sites in Finland are generally larger than those in the UK. The average water use rate was 16 m³/tonne of paper. Mills typically operate for 346 days per year.

257. In Japan, the average water use is larger, at 100 m³/tonnes of paper, though this depends on the grade and on the pulp used. In more modern and efficient integrated mills this is reduced to around 50 m³/tonne of paper. The average production tonnage is 200 tonnes/day.

4.4.2 Wastewater treatment

258. Many paper mills have some form of effluent treatment, which may or may not affect the quantity and nature of water treatment chemicals leaving the site. In the UK approximately one third of paper mills, mainly at the larger end of the scale, treat their effluent prior to discharge. Some paper mills discharge directly to an estuary, or to sea, these tend to be larger paper producers.

259. Effluent treatment is either primary, or primary and secondary. Primary treatment involves sedimentation and secondary treatment, in the UK, involves the activated sludge process. This form of treatment is entirely aerobic. Further closing-up of the water cycle would permit anaerobic sludge digestion, which has the benefit of producing methane for use as a fuel.

260. Within the EU standards may be set at a national level or on a local basis. In most EU countries, some form of wastewater treatment is typically employed, either on-site or at a sewage treatment works. However, in some countries with extensive coastline (e.g. Greece, Spain), there are considered to be significant amounts of untreated paper mill effluent discharged to the coastal waters.

261. In the event of a new chemical being affected by effluent treatment, Table 4.9 gives a breakdown of paper mill wastewater treatment in the UK.

Table 4.8: Summary of wastewater treatment at paper mills in the UK

Level of treatment	Sewer	Freshwater	Estuary/sea	Total number of mills
No effluent treatment	13	0	2	15
Primary effluent treatment	23	11	8	42
Primary and secondary effluent treatment	2	21	14	37
Total number of mills	38	32	24	94

262. In Finland, 68% of the mills responding to the survey (see Section 4.4.1 above) have activated sludge treatment. Others had chemical or mechanical treatment, or a combination of both. Integrated mills (which include pulping) need active sludge treatment, while mechanical and/or chemical treatment is sufficient when only paper or board is produced.

263. In Japan, most mills discharge water to river or to sea after treatment according to local or national regulations. Most integrated mills use activated sludge treatment and flocculation/coagulation. A few mills have only primary treatment.

4.5 Chemical release scenario examples

264. Using the information in Tables 4.1 to 4.8, it is possible to produce examples of water treatment chemical release at a paper mill. The capacities in these examples are based on the UK values above.

4.5.1 Influent and effluent treatment chemicals

265. Table 4.1 contains information on the concentrations at which chemicals are used. In order to estimate releases, the volumes of water treated are needed. For effluent treatment, information on effluent flows for different sizes of paper mill is included in Tables 4.7 and 4.8. As noted in Section 4.4.1, some water is lost in the mill through evaporation, and so the inflow volume of water is greater than the waste water flow. Section 4.4.1 suggests a value of 5 m³ water lost per tonne of paper produced.

266. The equations for calculating releases from these stages of water treatment are as follows.

For effluent:

$$E_{waste_water} = FLOW_{waste_water} \cdot C_{treat}$$

Explanation of

symbols:

E_{waste_water}	= emission rate to waste water	[kg/day]	
$FLOW_{waste_water}$	= flow rate for waste water	[m ³ /day]	See Table 4.7
C_{treat}	= working concentration of substance	[kg/m ³]	See Table 4.1

Note: concentrations in Table 4.1 are in mg/l, so a factor of 10⁻³ required to convert to kg/m³.

267. This calculation assumes that there is no removal of the substance as part of the on-site treatment.

For influent:

$$E_{waste_water} = FLOW_{water_in} \cdot C_{treat}$$

$$FLOW_{water_in} = FLOW_{waste_water} + Q_{paper} \cdot VOL_{evap}$$

Explanation of symbols:

E_{waste_water}	= emission rate to waste water	[kg/day]	
$FLOW_{waste_water}$	= flow rate for waste water	[m ³ /day]	See Table 4.7
C_{treat}	= working concentration of substance	[kg/m ³]	See Table 4.1
$FLOW_{water_in}$	= flow of water used in paper mill	[m ³ /day]	
Q_{paper}	= quantity of paper produced each day	[tonnes/day]	See Tables 4.7 and 4.8
VOL_{evap}	= volume of water lost by evaporation	[m ³ /tonne]	5m ³ /tonne as default

268. This calculation assumes that there is no loss of the substance from water during the paper mill production process. Note that although the calculation involves the quantity of water lost to the air through evaporation the estimated release of chemical is to water.

Examples:

269. For these examples the following values are assumed or calculated.

Q_{paper}	16.67 tonnes/day (small mill from Table 4.7)
$FLOW_{waste_water}$	186 m ³ /day - corresponding water release from Table 4.7
VOL_{evap}	5 m ³ /tonne as default
$FLOW_{water_in}$	186 + (5*16.67) = 269 m ³ /day

270. For the treatment of influent water, use of sodium hypochlorite gives a concentration of free chlorine of 0.5 - 5 mg/l (C_{treat} , from Table 4.1). Hence release from the treatment of water is:

$$E_{waste_water} = 269 * (0.5 - 5) * 10^{-3} = 0.135 - 1.35 \text{ kg/day}$$

271. For the treatment of effluent, aluminium sulphate is used as a flocculant at a concentration of 5 - 100 mg/l (C_{treat} , from Table 4.1). Hence the release to waste water is:

$$E_{\text{waste_water}} = 186 * (5 - 100) * 10^{-3} = 0.93 - 18.6 \text{ kg/day.}$$

272. As this treatment process produces a precipitate, it may be more realistic to consider this as a release to solid waste rather than to water.

4.5.2 Drainage and retention aid

273. For chemicals which are used in the actual production of paper or other products, the use rates are expressed in terms of the amount of the product made. As a result the calculation approach is a little different to that above.

$$E_{\text{waste_water}} = Q_{\text{paper}} \bullet Q_{\text{treat}} \bullet (1 - F_{\text{ret}})$$

Explanation of symbols:

$E_{\text{waste_water}}$	= emission rate to waste water	[kg/day]	
Q_{paper}	= quantity of paper produced each day	[tonnes/day]	See Tables 4.7 and 4.8
Q_{treat}	= quantity of treatment substance used per tonne of paper produced	[kg/tonne]	See Table 4.2
F_{ret}	= fraction of treatment substance retained on paper	[-]	Default assume 0

274. Note that some chemicals used in this area may be at least partly retained in the paper. For these a fixation rate to the paper should be incorporated to reduce the amount of substance calculated to be released - this is included above as F_{ret} .

275. For this example the following values are assumed:

Q_{paper}	83.33 tonnes/day (medium sized mill from Table 4.7)
Q_{treat}	0.1 - 2.0 kg/tonne for sodium silicate
F_{ret}	0 (assumed)

276. The emission rate of the substance is $83.33 * (0.1 - 2.0) * 1 = 8.3 - 167 \text{ kg/day}$

4.5.3 Further examples

277. Emissions from other uses of chemicals in the paper mill can be estimated in the same way as in Section 5.2. The examples below all assume the same size of paper mill as above, i.e. producing 83.33 tonnes/day.

Scale control agent:

Ethylenediamine tetraacetic acid: from Table 4.4, the use rate (Q_{treat}) is 0.1 - 2.0 kg/tonne.

Estimated releases are $83.33 * (0.1 - 2.0) * 1 = 8.3 - 167 \text{ kg/day}$.

278. When used in machine cleaning, the level of use of the substance could be up to 10x higher than in the example. This would be an infrequent process, and the releases from it should be considered as intermittent.

Use of a formulation in paper machine operation:

279. Section 4.3.2.4 includes a formulation for a blended product used in paper machine operation. This is used at 5 - 10 kg/tonne paper, which can be used as Q_{treat} . Emissions of the formulation are therefore $83.33 * (5 - 10) * 1 = 417 - 833$ kg/day. Emissions for individual components of the formulation will be in proportion to their content in the formulation. So propylene glycol is present at 10%, hence emissions are 42 - 83 kg/day. The other active components are present at 5%, so the emissions for each are 21 - 42 kg/day.

4.6 Recycling

280. Efforts are now being directed to develop so called "zero discharge" paper mills, which have no aqueous effluent. So far none exists in the UK, because problems associated with complete closing up require very considerable investment and technology.

281. It is typical for water to be recycled after primary treatment, in fact primary sedimentation equipment can be used as save-alls. Generally water from secondary treatment is not recycled.

282. The main purposes of this recycling are water conservation, and reduction of effluent. There is an additional benefit to be gained by recycling of fibre fillers etc. which finish up in the product and have a commercial value. As noted these types of chemical are not considered here; emission scenarios for these are to be found in the EU Technical Guidance (EU 1996). The average water use figures have already taken some account of water recycling and this will affect releases calculated on the basis of concentrations. However it should be assumed for emission calculations that there is no significant recycling of water treatment chemicals and hence no resulting lower dosing of those chemicals.

5 SWIMMING POOLS

5.1 Description of the system

283. Swimming pools can be divided into many categories: public (indoor, outdoor or combined), therapeutic baths, whirlpools, private and public pools. In addition, the replacement of swimming pool water can occur through three processes: fill and draw, flow-through and re-circulation. Where swimming pool water is recirculated and constantly reused, this water is contaminated by bathers, with the additional possibility of airborne contamination. The combination of warm water temperatures and the presence of organic matter result in ideal conditions for micro-organism growth and transfer between bathers. Pool maintenance and water treatment must be scrupulous to prevent infections of the eye, skin and urinary tract.

284. To maintain a pool in a fit state of use, the water must be continuously filtered, disinfected and replaced. Filtration and disinfection are interrelated; the less efficient the filtration the greater the disinfectant usage required.

5.2 Filtration

5.2.1 *Description*

285. Filtration is required to reduce the turbidity of the water. It also has a secondary function of reducing the amount of disinfectant needed and making disinfection more effective. In heavily used pools filtration and disinfection need to run continuously.

286. Continuous circulation of the pool water by pumping through a filter removes suspended soil. For heavily used pools the filtration needs to be at a reasonably slow rate to ensure effective soil removal. A recommended maximum of 24.5m³ water/m² filter surface area/hour is given (DOE 1987).

287. Periodically the collected particles must be removed by backwashing the filtration plant. This is considered the ideal time to remove 10% of the recirculating water volume for the backwash and to draw in fresh water. It is recommended that this is carried out weekly (Aquabrome 1985). Effluent resulting from these activities will normally be discharged to sewer.

5.2.2 *Filtration plant*

5.2.2.1 *Pressure sand filters*

288. A typical slow rate pressure sand filter has about 0.6 m of sand on a gravel bed containing a perforated collecting pipe system. A high rate filter has around 0.3 to 1.5 m of sand bed and requires less space than a slow rate filter. These systems are suitable for all types of pool and the use of more than one filter unit allows the pool to be in use during a backwash. The collected solids will be discharged as effluent during the backwash.

289. It is estimated that in the UK pressure sand filters are used by 94% of swimming pools. (PWTAG 1990).

5.2.2.2 *Pre-coat filters*

290. In pre-coat filters, the filter material is a thin layer of diatomaceous earth or perlite particles on a rigid, porous surface. When the pre-coat is blocked with dirt it is thrown away as solid waste and replaced with a new pre-coat filter. This system has advantages of space-saving and convenience but is quite costly to maintain.

5.2.2.3 *Pad filters*

291. Filter pads are discarded as solid waste when dirty. The lack of backwashing and subsequent pool water dilution makes pad filters only suitable for lightly loaded pools.

5.3 Disinfection

5.3.1 *Description*

292. The aims of disinfection in a swimming pool are to keep micro-organisms to a minimum and to ensure that any pathogenic or harmful micro-organisms are rapidly destroyed to prevent transfer to bathers. Many disinfectants are also capable of oxidising organic matter.

5.3.2 *Disinfectant types*

293. Traditionally chlorination is used for the disinfection of swimming pools. Agents used include chlorine gas, sodium hypochlorite, calcium hypochlorite, chlorine dioxide and chlorinated isocyanurates. Other disinfectants include liquid bromine, bromochlorodimethylhydantoin, ozone and residual chlorine, polymeric biguanides and UV irradiation.

294. Table 5.1 gives an indication of the current use of disinfectants by swimming pools in the UK based on a survey of 1500 swimming pools (PWTAG 1990).

295. Generally sodium hypochlorite and calcium hypochlorite are used because satisfactory chlorine residuals, pH values and microbiological quality can be easily maintained using them. The water can be easily balanced (see Section 5.4.1) which reduces clarity and scaling problems brought on by calcium carbonate salts.

5.4 pH Adjustment and other chemical treatment

296. Table 5.2 shows the chemicals which are used in the treatment of pool waters and are considered unobjectionable on health grounds by the Committee on Chemicals and Materials (UK Drinking Water Inspectorate).

Table 5.1: Disinfectant use.

Disinfectant	Percentage of pools
Sodium hypochlorite	55.1%
Calcium hypochlorite	18.9%
Chlorinated isocyanurate	8.9%
Ozone + hypochlorite	6.2%
Chlorine gas	5.3%
electrically generated hypochlorite	2.0%
Bromine	1.4%
Polymeric biguanide	0.5%
Sodium hypochlorite + chlorinated isocyanurate	0.5%
Chlorine dioxide gas	0.5%
Bromochlorodimethylhydantoin	0.4%
Sodium hypochlorite + copper/silver ion	0.2%

Notes: Calcium hypochlorite rarely used outdoors
 33% of outdoor pools used chlorinated isocyanurate
 Use of Chlorine and chlorine dioxide gas not recommended by the UK Government.
 Polymeric biguanide is not suitable for heavily loaded pools.
 Sodium hypochlorite + copper/silver ion not considered suitable for heavily loaded pools.

Table 5.2: Chemicals used in swimming pools.

Function	Chemical
pH adjustment	Calcium carbonate, calcium hydroxide, calcium oxide, calcium dioxide, hydrochloric acid, magnesium carbonate, magnesium hydroxide, magnesium oxide, phosphoric acid, potassium carbonate, potassium hydroxide, sodium bicarbonate, sodium bisulphate, sodium carbonate, sodium hydroxide.
Flocculant/ coagulant	Aluminium, aluminium sulphate, bentonite, ferric chloride, ferric sulphate, sodium aluminate.
Raise calcium hardness	Calcium chloride.
Algicide	Copper sulphate, quaternary ammonium compounds, polyoxyimino acid compounds.
Filtration	Diatomaceous earth.
Ion exchange/ water softener	Sodium chloride, sodium hexametaphosphate, sodium phosphate.
Corrosion inhibitor	Sodium silicate.
Chlorine neutraliser	Sodium thiosulphate.

5.4.1 Water balancing

297. Water balancing is necessary to achieve a set of conditions for the pool which will not cause scaling or corrosion. Water is balanced taking into account the relationship between temperature, bicarbonate alkalinity, calcium hardness and total dissolved solids in water with the ability to deposit scale.

298. A typical set of values to aim for is:

pH 7.4-7.5
Temperature 28 °C
Total alkalinity 100-120 ppm as CaCO₃
Calcium hardness 200-300 ppm as CaCO₃
Total dissolved solids less than 1000 ppm

299. The Langelier Balance was developed to indicate values allowing pH, temperature and total dissolved solids to be balanced against bicarbonate alkalinity and calcium hardness. A negative balance figure shows the water is corrosive and a positive figure shows the water is scale-forming. Pools typically aim for a low positive balance reading. (ISPE 1989)

5.4.1.1 Alkalinity

300. Total alkalinity is measured as the total amount of alkaline compounds (such as carbonates, bicarbonates and hydroxides) in pool water. Less than 80 ppm alkalinity can cause fluctuating pH, corrosion, eye irritation and green water. Greater than 160 ppm alkalinity can make pH adjustments difficult and cause cloudy water (Aquabrome 1985).

301. Total alkalinity can be raised by 10 ppm as CaCO₃ by the addition of 1.8 kg sodium bicarbonate per 100 m³ pool water. Total alkalinity can be lowered by 10 ppm as CaCO₃ by the addition of 1.8 kg sodium bisulphate per 100 m³ pool water (Aquabrome 1985).

5.4.1.2 Calcium hardness

302. Usually measured as calcium carbonate, low levels of calcium hardness can cause etching of the plaster from the pool walls and increased corrosion. The ideal range is 200 to 300 ppm CaCO₃, higher levels resulting in scaling, cloudy water and eye irritation.

303. Calcium hardness can be raised by 10 ppm through the addition of 1.5 kg calcium chloride per 100 m³ pool water. Lowering calcium hardness can be achieved by adding fresh water with a lower calcium level (Aquabrome 1985).

5.4.1.3 pH adjustment

304. This may be necessary to balance the water or for the following reasons (DoE 1987):

- The bactericidal action of most disinfectants is at an optimum in a given pH range (for example chlorination is less effective at pH > 8).
- At pH levels below 7, the water becomes increasingly corrosive towards metal components. Low levels can cause eye and skin irritation.
- At pH levels above 8, increased precipitation of hardness salts occurs. High levels can cause eye and skin irritation.

305. The chemical used for pH adjustment will depend largely on the disinfectant in use. For acidic disinfectants, e.g. chlorinated isocyanurates, sodium carbonate may be added. For alkaline disinfectants, e.g. sodium hypochlorite, an acidic chemical such as hydrochloric acid may be added.

5.4.2 Coagulants/flocculants

306. Coagulants are used to improve the filtration of pool water. The formation of a coagulate from suspended and colloidal matter keeps turbidity to a minimum. Use of a coagulant will cause the filter media to clog up more quickly, therefore the system will require more frequent backwashing and hence more make-up water will be used.

307. The decision to use coagulant is largely dependent upon the bather load of the pool. For large or heavily loaded pools it is recommended that between 1.5 to 2.5 mg/l of a coagulant such as aluminium sulphate is added to the pool water on the inlet side of the filtration system. Coagulants tend to be acidic in nature and may increase the requirement for pH adjustment (DOE 1987).

308. In the UK it is estimated that 77% of swimming pools use a flocculent/coagulant, normally aluminium sulphate (PWTAG 1990).

5.4.3 Algicides

309. Algal growth can affect outdoor pools and indoor pools exposed to sunlight. Once formed algae can be difficult to remove. Therefore, it is often necessary to have a programme of dosing with an algicide.

310. In the UK, two types of algicide have been approved for use in swimming pools, based on quaternary ammonium and polyoxyimino compounds. Dosing levels should ensure that the amount of active chemical being discharged in the pool effluent does not exceed 0.05 mg/l in the water course at point of discharge (DOE 1987).

5.4.4 Evaporation reducers

311. There are products on the market which claim to reduce evaporation of water from swimming pools, thus saving heat and reducing condensation. These act by forming a thin film over the water surface (DOE 1987).

5.4.5 Make-up water/dilution

312. The backwashing of swimming pool filtration systems will require the addition of some make-up water, but it may be necessary to dilute pool water further. It is recommended that regular replacement of pool water with fresh make-up water is carried out at a rate of up to 30 litres per day per bather (DOE 1987). In France, Sweden and Austria there is a legal requirement for minimum water replacement of 30 litres per bather per day, in Belgium this figure is 20 l/bather/day.

313. In practice, in the UK, it is estimated that many swimming pools work to a water replacement figure of 10% pool volume per week. Around one third of pools backwash within three day intervals, around half backwash at intervals of between 4 and 7 days. (PWTAG 1995).

5.5 Chemical dosing

314. Over half of the UK's swimming pools are reported to use automatic dosing systems, these are switched off for backwashing and routine maintenance. Of the rest, 35 % use manually adjusted dosing pumps and 11 % are dosed by hand (PWTAG 1995).

315. Figure 5.1 indicates the point at which certain chemicals are added.

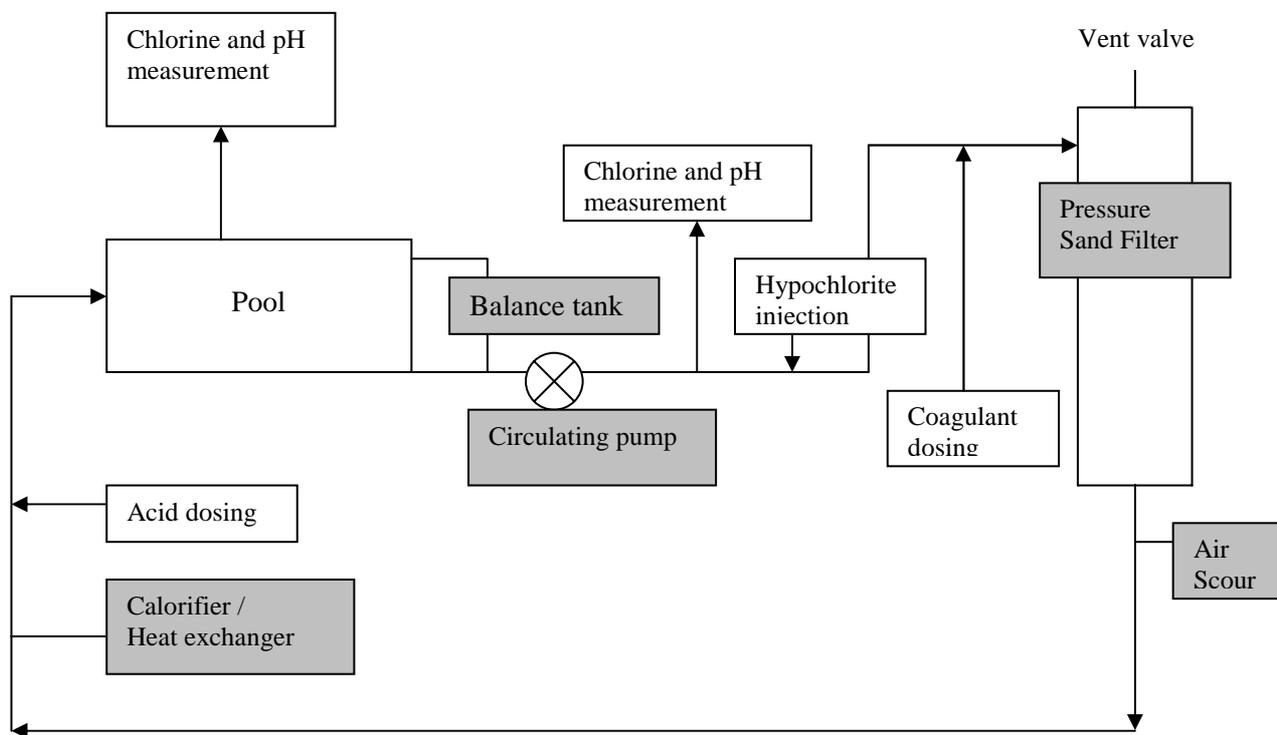


Figure 5.1 Swimming pool doped with sodium hypochlorite

5.5.1 Pool size and Distribution

316. Table 5.3 provides an estimate of the range and size of pools in the UK (information from ISRM 1995 and Piscean 1995).

Table 5.3: Pool size and Distribution.

Pool Type	Capacity (m ³)	Estimated number in the UK
Domestic	60 to 300	up to 50,000
School	450 to 700	up to 5000
Public	700 average	1,400
Olympic	up to 1,200	10

5.5.2 Release scenario examples

317. The absence of dosing rates for chemicals used in swimming pools makes it difficult to provide examples. When assessing a specific substance, information on the recommended dose level or working concentration to produce the required effect will be needed.

318. In the event of a new chemical for use in swimming pools being introduced it is recommended that the following figures could be used to provide an estimate of release:

Typical Release scenario:

$$E_{\text{water}} = \frac{C_{\text{treat}} \cdot V_{\text{pool}} \cdot F_{\text{replace}}}{7000}$$

Explanation of symbols:

E_{water}	= release rate to water per week	[kg/day]	
C_{treat}	= working concentration of substance	[mg/l]	
V_{pool}	= volume of pool	[l]	See Table 5.3
F_{replace}	= water replacement rate	[week ⁻¹]	0.1 typical for UK
7000	= conversion factor, week-day and mg-kg	[-]	

Estimates of pool volumes can be found in Table 5.3.

319. To estimate water replacement based on recommended levels for a given country the minimum water replacement (e.g. 30 litres per bather per day) needs to be related to the number of bathers in a given pool size (e.g. recommended maximum of 1 bather per day per 2 m³ (PWTAG 1990)). For the UK this equates to 10,500 litres recommended water replacement per day for a pool of 700 m³ capacity. Over seven days this equates to 73.5 m³, just over 10% of the pool volume.

320. It is expected that effluent discharged from swimming pools will normally go to public sewer.

321. Backwashing of the filters to clean them can also result in release of water containing chemicals. A volume of 10% of the pool volume is suggested This will be released over a shorter period of time, and one day is suggested.

322. A further scenario which can be considered in the discharge of the total volume of the pool, for example for major maintenance. Chemicals can be assumed to be present in the water at their usual working concentrations. Such a release should be treated as intermittent.

REFERENCES

Aquabrome 1985 Aquabrome handbook for UK pool managers.

Au C.O. 1995 Applications of wet end paper chemistry. Chapman and Hall.

BRE 1993 Preliminary Use Category Study on chemicals used in water cooling systems. Report for the DoE.

DOE 1987 The treatment and quality of swimming pool water. HMSO.

EU 1996 Technical Guidance Document in Support of Commission Directive 93/67/EEC on Risk Assessment for New Substances and Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances. Luxembourg: Office for Official Communications of the European Communities, 1996.

ISPE 1989 Design & planning of swimming pools, yearbook 1989. Institute of Swimming Pool Engineers.

IWS 1982 Code of practice for cooling water treatment The Industrial Water Society.

PWTAG 1990 Survey of swimming pool water management standards. Pool Water Treatment Advisory Group.

Experience of industry

Mike Iddon and Tom Fielden (the authors of the original report) have extensive knowledge, experience and contacts in the field of water treatment chemicals. This was utilised to formulate most of the information in this document. In addition the following organisations were consulted:

The Sports Council
Institute of Sport and Recreational Management
Institute of Swimming Pool Engineers
Swimming Pool and Allied Trades Association
Drinking Water Inspectorate
Pool Water Treatment Advisory Group
Local County Councils