



ELECTROFLOCCULATION OF RIVER WATER USING IRON AND ALUMINIUM ELECTRODES

AUBREY NARE MASHAMAITE

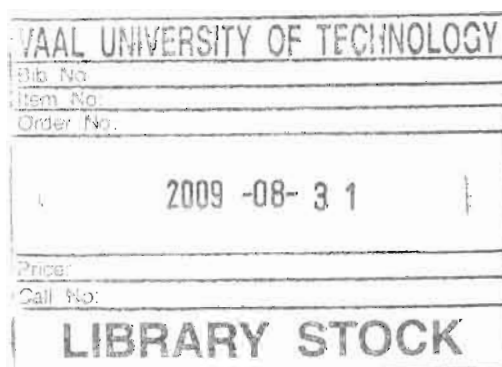
B. Tech (Chemical Engineering)

Dissertation submitted in fulfilment of the requirements for the Magister Technologiae
Degree in Chemical Engineering at the Vaal University of Technology

Supervisor: Dr. H.C. van der Merwe

September 2008

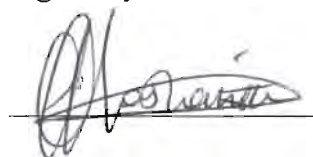
Vanderbijlpark



Declaration

This dissertation is my own, unaided work except where indicated to the contrary. It is being submitted for the M-Tech degree to the Department of Chemical Engineering at the Vaal University of Technology, Vanderbijlpark. It has not been submitted before for any subject, examination or qualification at any other educational institution.

Signed by student



Date

2008-09-24

Aubrey Nare Mashamaite

(YYYY-MM-DD)

9707409

Acknowledgements

It was a privilege to work with Dr. HC van der Merwe, and together with the co-operation I had from the Vaal University of Technology staff especially those in the Chemical Engineering, Chemistry and Research Departments. I would also like to express appreciation to the following individuals together with their departments and/or their companies: -

Mr James Parsons: Rand Water Technical Specialist – Research

Ms Olga Maleka: VUT B-Tech Student – Chemical Engineering

Ms Constance Tshisikawe: Sasol Infrachem Analyst – Process Laboratory

Mr Oswald Mahle: VUT Lecturer – Chemistry

Mr Josie Moabelo: Gold Fields Librarian – Library (Information)

Mr Reginald Fusane: VUT Research Technician – Chemical Engineering

I hope that some of their influence on my research is reflected in this dissertation. I wish to acknowledge the continued help and assistance of all the people around me (Family, Friends, Colleagues and my Mentor); they gave encouragement and their enthusiasm for my research was infectious, and I have retained interest which they generated over these many days.

Above all these people, I give gratitude to the Almighty God who gave me the serenity and courage to wake up each day and prove His power through this work.

Thanks

Abstract

A novel technology in the treatment of river water, which involves an electrochemical treatment technique to produce domestic or drinking water is being investigated using aluminium and iron electrodes in an electrochemical circuit. Coagulation and flocculation are traditional methods for the treatment of polluted water. Electrocoagulation presents a robust novel and innovative alternative in which a sacrificial metal anode treats water electrochemically. This has the major advantage of providing mainly active cations required for coagulation and flocculation, without increasing the salinity of the water. Electrocoagulation is a complex process with a multitude of mechanisms operating synergistically to remove pollutants from the water. A wide variety of opinions exist in the literature for key mechanisms. A lack of a systematic approach has resulted in a myriad of designs for electrocoagulation reactors without due consideration of the complexity of the system. A systematic, holistic approach is required to understand electrocoagulation and its controlling parameters.

An electrocoagulation-flotation process has been developed for water treatment. This involved an electrolytic reactor with aluminium and/or iron electrodes. The water to be treated (river water) was subjected to coagulation, by Al(III) and Fe(II) ions dissolved from the electrodes, resulting in flocs floating after being captured by hydrogen gas bubbles generated at the cathode surfaces. Apparent current efficiencies for Al and Fe dissolution as aqueous Al(III) and Fe(II) species at pH 6.5 and 7.8 were greater than unity. This was due to additional chemical reactions occurring parallel with electrochemical Al and Fe dissolution: oxygen reduction at anodes and cathodes, and hydrogen evolution at cathodes, resulting in net (i.e. oxidation plus reduction) currents at both anodes and cathodes.

Investigation results illustrate the feasibility of ferrous and aluminium ion electrochemical treatment as being a successful method of water treatment. Better results were achieved under conditions of relatively high raw water alkalinity, relatively low raw water turbidity, and when high mixing energy conditions were available.

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Chapter 1: Introduction and Problem Statement

1.1 Introduction

Increasing concern is being expressed about the quality of fresh ground and surface waters and oceanic waters in our environment. One of the priority uses is, of course, ingestion of water by humans. Consequently, it is demanded that potable water should have a quality to meet a rather rigid regimen of standards as set by the Department of Water and Forestry in conjunction with the Department of Health. On the other hand, it has been recognised that natural waters have uses other than for drinking by man. For example, water quality is extremely important to freshwater and marine aquatic life, for industrial and agricultural uses, and for recreation and aesthetic uses. These latter uses of water have moved the governmental and scientific communities to establish criteria for these various uses of natural waters (Faust, 1981).

National Drinking Water Regulations are legally enforceable standards that apply to public water systems to protect drinking water quality by limiting the levels of specific contaminants that can adversely effect human health and are known or anticipated to occur in public water systems (Bojic *et al.*, 2004).

Legislation and regulations of South Africa and abroad drive water management philosophies. South African fresh water aquifers are increasingly being challenged by industrially produced wastes that are routed to water sources such as rivers, dams, etc. To remove these pollutants from water sources requires special treatment before it is ready to be utilised for consumption.

There are many different water treatment methods (generally referred to as treatment processes) that can be used, each on its own, or in combination with others to treat water for domestic use. One method of treatment by which colloidal particles of water are destabilised (i.e. the nature of the colloidal particles is changed) so that they form flocs through the process of flocculation that can be readily separated from water is called coagulation.

Destabilisation is achieved through the addition of chemicals called coagulants to the water. Coagulants used in water treatment include aluminium sulphate, ferric chloride, lime, and polyelectrolytes (Bojic *et al.*, 2004)

The natural resources of South Africa are limited, therefore the use and reuse of water is becoming an increasing concern. Cost-effective methods are required to treat a wide range of pollutants in a diverse range of situations. Coagulation and flocculation are traditional methods for the treatment of polluted water. In these processes, coagulating agents (e.g. alum or ferric chloride) and other additives (e.g. polyelectrolytes) are dosed to produce larger aggregates, which can be separated physically. This is a multi-stage process that requires considerable land area and a continual supply of chemicals. A more cost-effective method to clean a wide range of polluted water, on-site, and with minimal additives, is required for sustainable water management (Bojic *et al.*, 2004).

Electrocoagulation treatment of water may fit this description. Electrocoagulation involves dissolution of metal from the anode with simultaneous formation of hydroxyl ions and hydrogen gas occurring at the cathode. Electrocoagulation has been proposed since before the turn of the century with Vik *et al.* (1984) describing a treatment plant in London built in 1889 (for the treatment of sewage by mixing with sea water before electrolysis). In 1909, in the United States, J.T. Harries (Vik *et al.*, 1984) received a patent for wastewater treatment by electrolysis with sacrificial aluminium and iron anodes. Matteson *et al.* (1995) describe a device of the 1940's, the 'Electronic Coagulator' which electrochemically dissolved aluminium (from the anode) into the solution, reacting this with the hydroxyl ion (from the cathode) to form aluminium hydroxide. The hydroxide flocculates and coagulates the suspended solids thereby purifying the water. A similar process was used in Britain in 1956 (Matteson *et al.*, 1995) in which iron electrodes were used to treat river water.

Presently electrocoagulation is marketed by a small number of companies around the world. A variety of designs have been employed with no dominant design. Often the electrocoagulation units are used simply as a replacement for chemical dosing systems and do not take advantage of the electrolytic gases produced in the electrocoagulation process. It is clear that electrocoagulation has the capability to remove a large range of pollutants under a variety of conditions ranging from suspended solids (Matteson *et al.*, 1995), heavy metals

(Osipenko and Pogorelyi, 1977), petroleum products (Amosov *et al.*, 1976), colour from dye-containing solution (Do and Chen, 1994), aquatic humus (Vik *et al.*, 1984), and de-fluoridation of water (Mameri *et al.*, 1998).

1.2 Problem Statement and Motivation

The treatment of water is an area which is, and was, extensively researched. Because of technological, developmental and economical impact there is a need for new efficient and cost-effective flocculation methods. As a result, the evaluation of electrochemical technique in river water treatment to remove suspended solids that meets the requirements of South African Legislation, had to be investigated.

The purpose of this study was to investigate the feasibility of electrochemical dissolution of iron and aluminium ions in river water to achieve electroflocculation and/or electrocoagulation. The investigation did not include the economic consideration relevant to the use of this electrochemical treatment technique.

The objectives of the project:

- Assess and demonstrates the ability of the electrochemical process as a process for the removal of phosphates, suspended solids and other pollutants from river water to produce drinking (domestic) water;
- Investigate and evaluate the electrochemical characteristics and mechanism of water treatment under regulated parameters with no chemical reagents used in the process.

The main aspects that must be taken into account when conducting the research are:

- The quality of water source (river water)
- The quality of the treated water to be produced (drinking water)
- Characterisation of electrochemistry (iron and aluminium electrodes)
- Current methods of flocculation (dosing of aluminium sulphate, ferric chloride, lime and polyelectrolytes)
- Operating factors (effect of pH, concentration, temperature and time studies)

Other factors (including change in parameters) arising from the experimental process will also be considered during the investigation.

Chapter 2: Literature Survey

2.1 Introduction

Due to rapid industrialisation, there has been an increase in the amount of effluent flowing into natural water bodies. Major contaminants found in water include biodegradable, volatile and recalcitrant organic compounds, toxic metals, suspended solids, plant nutrients (nitrogen and phosphorus), microbial pathogens and parasites (Bitton, 1994). Cooper (1993) also reported that runoff is regarded as an important route of entry of non-point pollutants in the surface water in agricultural areas. Runoff occurs during rainy seasons which last from April to December in the Western Cape. Runoff-related inputs usually lead to an increase of water levels, nutrients and total suspended solids (TSS). Pesticides may enter water-dissolved or particle-associated chemicals (Wauchope, 1978).

The discharge of nitrogen as nitrate and phosphorus as phosphate to inland rivers, lakes and dams causes massive growth of algae and plants due to the 'fertiliser type' effect of the phosphate and nitrate (Steyn *et al.*, 1975). This process is called eutrophication and disturbs the natural balance that exists in the water body. Phosphate is a more limiting factor than nitrate in eutrophication because some bacteria and algae are able to fix atmospheric nitrogen and convert it to the more oxidisable states of nitrates and nitrites for growth (Wentzel, 1990). Therefore, reducing phosphorus concentration to the lowest level is vital to the maintenance of unpolluted water supplies.

Many advanced treatments have been studied and electrochemical oxidation has been applied to many kinds of wastewater (Naumczyk *et al.*, 1996; Simmonson., 1997). This process is presented as an effective, selective, economical, and clean alternative for dealing with wastewaters bearing high loads of organic compounds, especially some bio-refractory organic pollutants. Such treatment produces total degradation of compounds to carbon dioxide and water or at least a considerable decrease in toxicity. A direct anodic process or an indirect anodic oxidation via the production of oxidants such as hydroxyl radicals, ozone, etc. usually destroys the organic and toxic pollutants present in wastewater (Simmonson, 1997).

This wastewater treatment technology, which involves an electrochemical technique to produce domestic or drinking water is to be employed in this investigation to treat river water using aluminium and iron electrodes in an electrochemical circuit.

2.2 Objectives of Water Treatment and Purification

Mankind has recognised the need to improve water quality as early as 2000 BC (American Society of Civil Engineers, 1990). The basic objectives of modern water treatment and purification plants would be to:

- produce water that is safe for human consumption,
- produce water that is appealing to the customer, and
- produce water at a reasonable cost.

The production of biologically and chemically safe water is the primary objective in the design of water treatment and purification plants and cannot be compromised. The principle contaminant in safe water is, in most of the cases, suspended solids. A strong correlation exists between the removal of suspended matter and micro-organisms. It is therefore not surprising that the main objective of surface treatment plants is the removal of suspended solids. Suspended solids consist mainly of clays, silts, bacteria, viruses, fulvic and humic acids, mineral and organic particulates. Their collective presence may be indicated by turbidity measurements (Pretorius *et al.*, 2001).

Appealing water is clear and colourless, pleasant to taste, odourless, and cool. The water should be non-staining, neither corrosive nor scale-forming and reasonably soft. Natural colour in water can normally be ascribed to the presence of humic and fulvic acids. They are strongly negatively charged hydrophilic colloids that will pass through conventional sand filters unless destabilised. Iron and manganese are inorganic species that may be of aesthetic concern (Pretorius *et al.*, 2001).

2.3 Laws and Regulations

The government of South Africa imposes strict regulations regarding the improvement of water supply, water resource management, and quality of water. Table 2.1 summarises the Acts governing the South African water legislation (DWAF, 1996).

Table 2.1: Summarized Acts governing the South African water legislation

Water Acts	Year
National Water Act [No. 36 of 1998] <ul style="list-style-type: none"> • <i>Fundamental Principles</i> <ul style="list-style-type: none"> - <i>Sustainability and equity guiding principles in protection, use, development, conservation, management and control of resources.</i> - <i>The need to share some water resources with other countries</i> - <i>The need to develop social and economic development through the use of water</i> - <i>The need to establish suitable institutions to achieve the purpose of the act</i> 	2000
Water Services Act [No. 108 of 1997] - 19 December <ul style="list-style-type: none"> • <i>Governs the supply of water</i> <ul style="list-style-type: none"> - <i>Water Services providers</i> - <i>Water services Authorities</i> • <i>Governs actions of Water Boards</i> • <i>Governs Water Quality</i> <ul style="list-style-type: none"> - <i>Water Services Act 1997 (Act No108 of 1997), Section 9(1) and 73 (1)(j)</i> - <i>Regulation relating to compulsory national standards (March 2001)</i> - <i>Use SANS 241 of 2005 or DWAF water quality guidelines</i> 	1999

2.4 Water Quality

‘Water quality’ is a term used to express the suitability of water to sustain various uses or processes. Any particular use will have certain requirements for the physical, chemical or biological characteristics of water; for example, limits on the concentrations of toxic substances for drinking water use, or restrictions on temperature and pH ranges for water supporting invertebrate communities. Consequently, water quality can be defined by a range of variables which limit water use. Although many uses have some common requirements for certain variables, each use will have its own demands and influences on water quality (Bartram and Ballance, 1996). According to DEAT (1999) there are three components that have been chosen as indicators of water quality for South African surface waters: phosphorus and nitrogen, which are good indicators of the level of domestic pollution in surface waters, and total dissolved solids TDS, which gives an indication of the salinisation or salt content of the water. Microbial contamination was also identified as a good indicator (DEAT, 1999).

“The composition of surface and underground waters is dependent on natural factors (geological, topographical, meteorological, hydrological and biological) in the drainage basin and varies with seasonal differences in runoff volumes, weather conditions and water levels. Large natural variations in water quality may, therefore, be observed even where only a single watercourse is involved. Human intervention also has significant effects on water quality. Some of these effects are the result of hydrological changes, such as the building of dams, draining of wetlands and diversion of flow. More obvious are the polluting activities, such as the discharge of domestic, industrial, urban and other wastewaters into the watercourse (whether intentional or accidental) and the spreading of chemicals on agricultural land in the drainage basin” (Bartram and Ballance, 1996).

A variety of human activities e.g. agricultural activities, urban and industrial development, mining and recreation, potentially significantly alter the quality of natural waters, and changes the water use potential. The effects of human activities on water quality are both widespread and varied in the degree to which they disrupt the ecosystem and/or restrict

water use. Deteriorating water quality leads to increased treatment costs of potable and industrial process water, and decreased agricultural yields due to increased salinity of irrigation water. Contamination of groundwater resources or of sediments deposited in riverbeds, impoundments and estuaries by toxic and persistent compounds can cause irreversible pollution, sometimes long after the original release to the environment has ceased (WQM, 1996).

According to WQM (1996), the persistent water quality problem is salination, which has two major causes, natural and anthropogenic. The origin of natural salination of river water is geological. A wide variety of man's activities are associated with increased releases of salts, some in the short and others in the long term. Immediate increases in salt concentrations result from point sources of pollution, such as the discharging of water containing waste by industries. Diffuse pollution, resulting inter alia from poorly managed urban settlements, waste disposal on land and mine residue deposits pose even a bigger problem, as it impacts over a larger area on the water resource. "The effect of diffuse pollution on groundwater is also often problematic in terms of remediation. Another major water quality problem is eutrophication which is the enrichment of water with the plant nutrients nitrate and phosphate. These encourage the growth of microscopic green plants termed algae. As nutrients are present in sewage effluent, the problem is accentuated wherever there is a concentration of humans or animals. The algae cause problems in water purification, e.g. undesirable tastes and odours, and the possible production of trihalomethanes or other potentially carcinogenic products in water that is treated with chlorine for potable purposes" (WQM, 1996).

A water quality issue which is receiving increasing attention among industrialised nations is pollution by metals and man-made organic compounds, such as pesticides and it is referred as micro-pollutants. WQM (1996) report that serious incidents of health impacts to man and animals have occurred at places throughout the world through uncontrolled exposure to these micro-pollutants. Pollution of this type tends to be highly localised and associated with specific industries or activities. Mining activities often expose pyrite containing rock formations to air and water to produce acid rock drainage. Due to the low pH of acid rock drainage heavy metals are mobilised. The Department of Water Affairs and Forestry has recently established a water pollution control works in the Brugspruit catchment, at huge

cost, to treat acid rock drainage emanating from abandoned coal mines. Another source of pollution is from Microbiological pollutants which is a water contamination by faecal matter and it is the medium for the spread of diseases such as dysentery, cholera and typhoid.

Erosion and sedimentation also have impact in quality of water, according to WQM (1996) an average sediment yields for South African catchments range from less than 10 to more than 1 000 tonnes/km²/annum. In some parts of the country erosion has increased by as much as tenfold as a result of human impacts. Apart from the loss of fertile agricultural soil, off-site damage like loss of valuable reservoir storage, sediment damage during floods and increased water treatment costs, have been largely ignored even though these are estimated to be in excess of R 100 million per year. Bartram and Balance (1996) describe the quality of water in terms of the concentration and state (dissolved or particulate) of some or all of the organic and inorganic material present in the water, together with certain physical characteristics of the water.

Contamination of the aquatic environment occurs when humans introduce, either by direct release to water or indirectly (for example through atmospheric pollution or water management practices), substances or energy that result in deleterious effects such as:

- hazards to human health,
- harm to living resources,
- hindrance to aquatic activities such as fishing, and
- impairment of water quality with respect to its use in agriculture, industry or other economic activities, or reduction of amenity value.

The importance attached to quality will depend on the actual and planned use or uses of the water (e.g. water that is to be used for drinking should not contain any chemicals or micro-organisms that could be hazardous to health).

2.5 River Water Quality

South Africa's hydrological regime is characterised by high variability, due to climatic conditions, and low water runoff, due to high absorption by soils (Walmsley 1991). An understanding of the discharge regime of a river is extremely important to the interpretation of water quality measurements, especially those including suspended sediment or intended to determine the flux of sediment or contaminants (Meybeck *et al.*, 1989). The discharge of a river is related to the nature of its catchments, particularly the geological, geographical, and climatological influences. Meybeck *et al.* (1989) add that the regime of a river is largely determined by the annual cycle of wet and dry seasons.

The great rivers of the tropics do not fall exclusively into any of these categories, because their drainage basins extend over many regions of differing climate and vegetation. According to Meybeck *et al.* (1989), erosion can be said to vary according to the following influences:

- amount and pattern of rainfall and resultant river regime,
- slope of the land,
- extent of destruction of vegetation,
- regeneration of vegetation, and
- soil type and resistance to the effects of temperature changes.

2.5.1 Vaal Dam water quality

Vaal Dam water quality data was retrieved and statistically analysed from Rand Water's database. The Engelbreghts weir water sample point was the only sample point available to characterise Vaal Dam water quality. A summary of water quality determinants exceeding the requirements (SABS 241: 2001) for class 0 and class 1 water is compiled in Table 2.2. The treatment objectives could therefore be defined through a comparison of water quality and drinking water requirements.

Table 2.2: Vaal Dam water quality determinants exceeding the potable water requirements as determined at the Engelbreghts weir. The SABS guidelines for Class 0 and Class 1 water are also included

Parameter	Unit	Vaal Dam water quality				Limits of SABS 241	
		Minimum	Maximum	Average	Median	Class 0	Class 1
DOC	mg/L as C	6.1	19.0	10.0	9.1	5	10
Turbidity	NTU	32	110	70	68	0.1	1.0
Al	mg/L as Al	<0.10	6.40	1.02	0.47	0.15	0.30
Fe	mg/L as Fe	<0.10	4.30	0.63	0.27	0.010	0.200
F ⁻	mg/L as F ⁻	0.15	2.90	0.23	0.18	0.7	1.0

The raw water turbidity is affected by seasonal changes as illustrated in Figure 2.1. A turbidity as high as 120 NTU can be experienced during rainfall seasons, while a turbidity as low as 30 NTU can be measured towards the end of the winter season. The variation in turbidity over an 18-month period is illustrated in Figure 2.1.

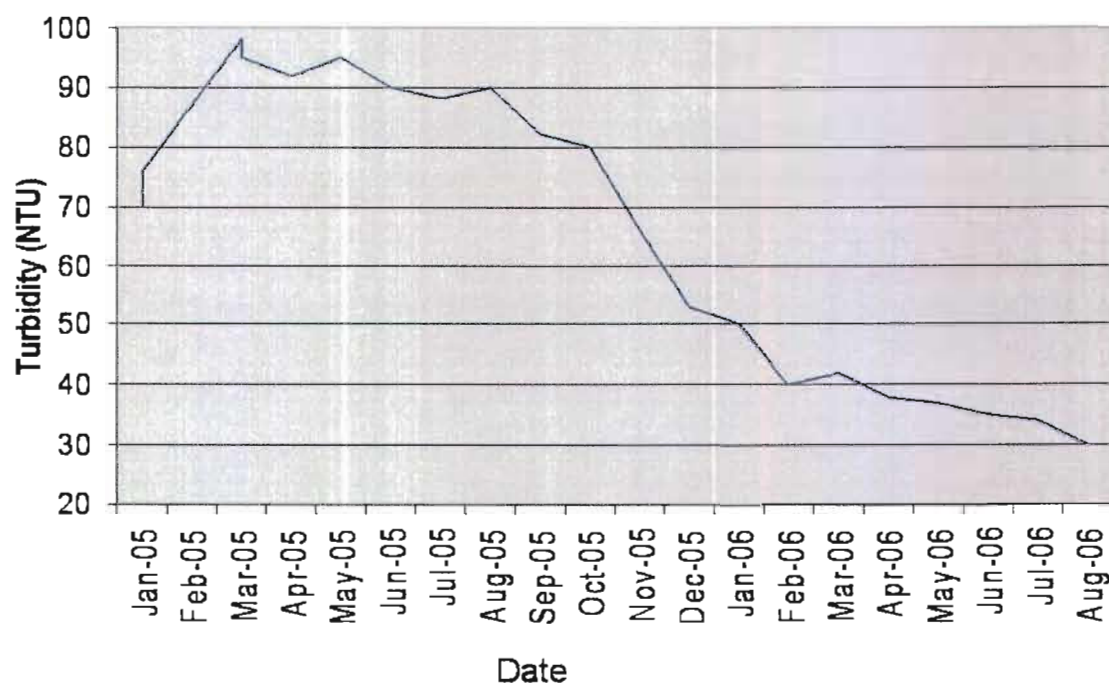


Figure 2.1: The variation in Vaal Dam turbidity as measured over an 18-month period

2.5.2 Natural processes affecting water quality

Although degradation of water quality is almost consistently the outcome of human conduct, certain natural phenomena can result in water quality. Natural events such as torrential rainfall and hurricanes lead to excessive erosion and landslides, which in turn increase the content of suspended material in affected rivers and lakes (Bartram and Ballance, 1996). Seasonal overturn of the water in some lakes can bring water with little or no dissolved oxygen to the surface. Such natural events may be frequent or occasional.

“Permanent natural conditions in some areas may make water unfit for drinking or for specific uses, such as irrigation. Common examples of this are the salinisation of surface waters through evaporation in arid and semi-arid regions and the high salt content of some groundwater under certain geological conditions. Groundwater is naturally high in carbonates (hardness), thus necessitating their treatment before use for certain industrial applications. Groundwater in some regions contains specific ions (such as fluoride) and toxic elements (such as arsenic and selenium) in quantities that are harmful to health, while others contain elements or compounds that cause other types of problems (such as the staining of sanitary fixtures by iron and manganese)”, Bartram and Balance (1996).

The nature and concentration of chemical elements and compounds in a freshwater system are subject to change by various types of natural processes, i.e. physical, chemical, hydrological and biological. The major environmental factors as stated by Bartram and Ballance (1996) are:

- distance from the ocean: extent of sea spray rich in Na, Cl, Mg, SO_4 and other ions,
- climate and vegetation: regulation of erosion and mineral weathering, concentration of dissolved material through evaporation and evapo-transpiration,
- rock composition (lithology): the susceptibility of rocks to weathering ranges from 1 for granite to 12 for limestone; it is much greater for more highly soluble rocks (for example, 80 for rock salt),

- terrestrial vegetation: the production of terrestrial plants and the way in which plant tissue is decomposed in soil affect the amount of organic carbon and nitrogenous compounds found in water, and
- aquatic vegetation: growth, death and decomposition of aquatic plants and algae will affect the concentration of nitrogenous and phosphorous nutrients, pH, carbonates, dissolved oxygen and other chemicals sensitive to oxidation/reduction conditions. Aquatic vegetation has a profound effect on the chemistry of lake water and a less pronounced, but possibly significant, effect on river water.

“Under the influence of these major environmental factors, the concentrations of many chemicals in river water are liable to change from season to season. In small watersheds the influence of a single factor can cause a variation of several orders of magnitude. These natural variations are reflected in the range of total dissolved solids in various water bodies. Total dissolved solids are the sum of the silica plus the major ions in the water. A close approximation of its value may be obtained by the measurement of electrical conductivity” (Bartram and Ballance, 1996).

2.5.3 Water use and water quality deterioration

Historically, the development of civilisations has led to a shift in the pattern of water use from rural/agricultural to urban/industrial, generally according to the following sequence: drinking and personal hygiene, fisheries, navigation and transport, livestock watering and agricultural irrigation, hydroelectric power, industrial production (e.g. pulp and paper, food processing), industrial cooling water (e.g. fossil fuel and nuclear power plants), recreational activities and wildlife conservation. According to Bartram and Ballance (1996) the water uses with the highest demands for quantity often have the lowest demands for quality i.e. drinking water, by contrast, requires the highest quality water but in relatively small quantities.

In order to counter the continuing deterioration of water quality and to meet the challenges of the future, the Department of Water Affairs and Forestry has adopted a receiving water quality objectives approach, consisting of a receiving water quality objectives approach for

non-hazardous substances and a pollution minimisation and prevention approach for hazardous substances. The receiving water quality objectives approach for non-hazardous substances accepts that the receiving water environment has a certain, usually quantifiable, capacity to assimilate waste without serious detriment to the quality requirements of its recognised users. However, if applied without the necessary precaution, the receiving water quality objectives approach for non-hazardous substances will inevitably lead to the deterioration of water resources to the point where they will be less fit for use by the recognised water user sectors. To counter the limitations of this approach, a precautionary approach was accepted to avert danger and minimise uncertainty and potential risk of undesirable impacts on the environment.

Human activities are the source of particulate, dissolved and volatile materials which may eventually reach water. Dissolved materials and many particulates are discharged directly to water bodies, while the particulate and volatile materials that pollute the atmosphere are picked up by rain and then deposited on land or in water.

2.5.4 Water and human health

Although water is an absolute necessity for life, it can be a carrier of many diseases. Paradoxically, the ready availability of water makes possible the personal hygiene measures that are essential to prevent the transmission of enteric diseases. Infectious water-related diseases can be categorised as waterborne, water-hygiene, water-contact and water-habitat vector diseases. Some water-related diseases, however, may fall into more than one category (Genthe, 2007).

Waterborne infectious diseases are those in which the pathogen, or causative organism, is present in water and ingested when the water is consumed. Most of the pathogens involved are derived from human faeces, and the diseases transmitted by consumption of faecally contaminated water are called “faecal-oral” diseases. All of the faecal-oral diseases can also be transmitted through media other than water, for example faecally contaminated food, fingers or utensils. The principal faecal-oral diseases are cholera, typhoid, shigellosis, amoebic dysentery, hepatitis A and various types of diarrhoea (Bartram and Ballance, 1996).

2.6 Drinking Water Quality

The provision of hygienic drinking water is one of the major contributions to the wellbeing of the human species. Many of the major human diseases can be attributed to waterborne micro-organisms, which, in the absence of adequate water treatment, are passed through a cycle of effluent discharge. The need for effective water treatment reflects the pressures of population growth and development of urban communities. Under conditions of low population density the surface and ground water remain relatively unpolluted and direct abstraction without treatment can be adequate, but large communities can easily pollute the natural fresh water resources and make treatment essential (Barnes and Wilson, 1983).

2.6.1 Water quality criteria

Municipal water will be used for several purposes - washing, drinking, waste disposal and as industrial water. The quality requirements will be set by the most critical of these uses, that is, human consumption (Barnes and Wilson, 1983). The criteria will reflect the need to produce water which is:

- hygienic with a minimum of pathogens and toxins,
- aesthetically acceptable and potable,
- non-corrosive to the distribution system, and
- which can be produced at the least cost.

To meet these requirements, several sets of standards have been proposed and are continually being revised. The specific concentrations as those which will not adversely affect water quality are suggested by Barnes and Wilson (1983).

2.6.2 Microbiological criteria for drinking water

Microbiological standards for drinking water are considered to be the most important and most widely quoted standards. Direct tests for pathogens are difficult because of the low number of pathogens present and the large number of different types of pathogens which can be present. A common standard is that the average number of coliforms is less than one per

100mL of sample with specification of statistical variation and sampling frequency (Barnes and Wilson, 1983).

2.6.3 Hardness criteria for drinking water

Water hardness is the state or quality of being hard caused by various dissolved salts of calcium, magnesium or iron. The range of water hardness varies from 0 mg/L of water to over 1712 mg/L. Water with 65 mg/L is considered very hard water. Much of the Ida area has water hardness ranging from 599 mg/L to 1455 mg/L. Most hardness test kits express test results as ppm of CaCO_3 . Currently there are no health standards for water hardness. Hard water precipitates carbonate mineral deposits, scale, and incrustations on pipes, hot water heaters, boilers and cooking utensils. Water hardness can cause other problems in the home such as increased soap consumption by preventing soap and detergents from lathering by giving rise to an insoluble curdy precipitation.

Water hardness can be lessened on a small scale by softening the water. This can be done with the addition of ammonia, borax, or tri-sodium phosphate mixed together with sodium carbonate. Hard water can be softened on a large scale by adding just enough lime to precipitate the calcium as carbonate to remove the calcium salts. Home water softeners commonly use natural or artificial zeolite minerals to soften the water. Zeolite minerals are hydrous aluminium silicates of sodium, calcium, potassium or barium naturally found in igneous rock (Barnes and Wilson, 1983).

2.6.4 Aesthetic criteria for drinking water

The production of drinking water which is aesthetically acceptable is generally regarded as necessary to assure users about the hygienic quality of the water. The physical tests for turbidity, colour, taste and odour are designed to ensure that the water will be potable and aesthetically pleasing. The general standards require the production of water which has properties within certain limits, for example less than 5 colour units and unobjectionable taste and odour. Specific chemicals are subject to additional restriction, for instance chlorine ions imparts a salty taste to water if present in concentrations greater than 200 mg/L while

phenolic compounds are restricted partly because of their tendency to form chlorophenols which are highly unpleasant odours (Barnes and Wilson, 1983).

- **Reactive Phosphorus**

Phosphorus is a non-metallic chemical element. Reactive phosphorus is the phosphorus that will react only with another substance. Phosphorus is found in many forms. In water, phosphorus is usually found as phosphates. Phosphates are formed when metallic atoms replace some or all of the hydrogen in phosphoric acid. The main sources of phosphates in groundwater and surface water include fertilizers, sewage, detergents and rainwater. The phosphates enter the water mostly as a result of surface runoff and bank erosion. The amount of phosphates that water can hold without becoming polluted varies. In a stream draining into a lake, the phosphates should not exceed 0.05 mg/L. In a lake the phosphates should not exceed 0.025 mg/L. A stream not flowing into a lake should also not exceed 0.025 mg/L. Phosphates exceeding these levels can be very harmful. If the phosphates exceed these levels algal growth can choke out other plants and completely take over the water. This is best avoided by using phosphate-free detergent to avoid fertilizer runoff and preventing stream bank erosion.

- **Total Phosphorus**

Phosphorus is usually present in river water as phosphates, and is in very small amounts unless there has been human-caused enrichment of the water. The natural scarcity of phosphorus can be explained by its attraction to organic matter in soil particles. Generally the lower the total phosphorus value in the water, the better. Total phosphorus includes organic and inorganic phosphate. Organic phosphate is a part of living plants and animals. Inorganic phosphates comprise the ions bonded to soil particles, and phosphates present in laundry detergents (polyphosphates). Phosphorus is considered to be a limiting factor in aquatic systems, meaning that it is not freely available for easy consumption by aquatic organisms. A river that is not flowing into a lake should not exceed 0.1 mg/L. Phosphorus is the major contributing factor in the process of eutrophication. Inputs of phosphorus come from erosion, fertilizers, detergents, and the draining of wetlands.

- **Suspended Solids**

Suspended solids are pieces of sand, silt and the fine organic matter of leaves, pieces of wood, etc. suspended in a stream or lake. The suspended solids in humid areas range from 0 ppm to 100 ppm. In arid areas the range can reach up to 100 000 ppm. Suspended solids can increase when stream flow increases. The faster-flowing water erodes the banks and because the stream is moving so fast, the suspended solids do not have a chance to settle to the bottom. Suspended solids are an important part of water quality. In excess they can smother the stream bottom life. When the water slows down, suspended solids settle out in stream pools and can fill lakes and reservoirs. High levels of suspended solids can make the water unusable in many ways. Pesticides and bacteria can attach to the suspended solids making them more readily transported. This can kill off the plants and animals downstream and make the water undrinkable to humans and wildlife alike.

- **Total Dissolved Solids (TDS)**

Rivers have solid particles called dissolved and suspended solids in them. The total dissolved solids (TDS) test measures the amount of particles that are dissolved in the river water. The USEPA standard is 500 mg/L or ppm. The TDS range from 20 to 2 000 mg/L in rivers and may be higher in groundwater. High levels in drinking water may cause objectionable tastes and have laxative effects. Water is tested for TDS because excessive amounts may be unsuitable for aquatic river life and poor for crop irrigation, in addition to being unsuited for drinking water. It may cause foaming or may corrode some metals. The quantity of TDS in a body of water depends on several factors, including the precipitation contributing to the body of water (Rainwater is almost pure with less than 10 ppm TDS.), the type of soil and rock the water passes over, and human activities. The major dissolved substances found in water that can cause the above problems are the positively charged ions of sodium, calcium, magnesium, potassium and iron and the negatively charged ions of chloride, bicarbonate, carbonate and sulphate.

- **Total Solids**

Total solids are the combined weight of both dissolved solids and suspended solids. The weighing can be performed on a Metler balance to ensure accuracy to a thousandth of a gram. All natural waters contain dissolved and suspended inorganic and organic substances.

The major dissolved solids are sodium, potassium, calcium, magnesium, chloride, sulphate, carbonate, bicarbonate and silica. The major suspended solids on the other hand include anything from silt and plankton to industrial wastes and sewage.

- **Turbidity**

Turbidity is the measurement of a lack of water clarity. Turbidity is the result of suspended solids in the water. A rough measure of turbidity can be made with a Secchi Disk, but more accurate measurements need to be taken with a turbidimeter. Turbidity is measured in NTUs, the abbreviation for nephelometric turbidity unit. A normal range for turbidity in river water has not been established. Turbidity in drinking water should be less than one NTU. The USEPA standard for drinking water is 0.5-1.0 NTU. Water treatment is required for drinking water when there is excessive turbidity. Water with high turbidity will appear to be murky or muddy. Turbidity in excess of five NTUs can be easily detected. Turbidity at that level may not affect your health, but water treatment may be desirable. Excessive turbidity may interfere with disinfection processes and is measured by municipalities to monitor the efficiency of public water supply filtration systems used to remove parasites and viruses in water.

2.6.5 Corrosiveness of drinking water

The major criterion used to control the corrosiveness of water is that of pH. In general, the water should be supplied slightly alkaline (pH 7 – 8.5) and with no free carbon dioxide (Barnes and Wilson, 1983).

- **Alkalinity**

Alkalinity is a measure of the quantity of compounds that shift the pH to the alkaline side of neutrality (above 7) or it is a measure of the capacity of water to neutralize acids. In the carbonate-bearing rock of Monroe County, most alkalinity is due to the presence of the bicarbonate ion which is derived from the dissolution of carbonates by carbonic acid. Minor contributors to alkalinity in the county include carbonate and hydroxide ions. Alkalinity is important because it buffers pH changes that occur naturally during photosynthetic cycles, water exchanges and the addition of acids to water. Raising the alkalinity almost always raises the pH. Alkalinity is measured in parts per million (ppm) or milligrams per litre

(mg/L). There are no standards established for surface or groundwater by the United States Environmental Protection Agency (USEPA). A range of 100 to 250 ppm for river water is considered normal. If the alkalinity of water is too high, the water can be cloudy, which inhibits the growth of underwater plants. Too high alkalinity raises the pH level, which in turn harms or kills fish and other river organisms.

- **pH**

pH is a general measure of the acidity or alkalinity of a water sample. The symbol pH stands for potential for hydrogen. The pH of water, on a scale of 0 to 14, is a measure of the hydrogen ion concentration. Water contains both H ions and OH ions. Pure distilled water contains an equal number of H and OH ions and is considered neutral (pH 7), neither basic nor acidic. If water contains more H than OH ions the water is considered acidic with a pH less than 7. If water contains more OH ions than H ions, the water is considered basic with a pH greater than 7. The USEPA standard range is 6.5 to 8.5. Stream water usually ranges from pH 6.5 to a pH of 8.5, an optimal range for most organisms. Rain-water by contrast is naturally acidic at about 5.6.

2.6.6 Water quality index

In 1970 the National Sanitation Foundation created a standard index to measure water quality. The Water Quality Index (WQI) can be used to measure water quality changes in a particular river segment over time, comparing water quality from different segments of the same river, and comparing water quality of different rivers. The results can determine if the river is healthy for particular uses. Certain tests, which are discussed here, must be performed, weighed, and added together to come up with the water quality value. The overall WQI values can be rated from the following Table 2.3:

Table 2.3: Water Quality Index rating

Percentage	Rating
100-90	Excellent
90-70	Good
70-50	Medium
50-25	Bad
25-0	Very Bad

A minimum of 50-58 would be required to meet most state water quality standards. A body of water can have high WQI, yet fail to meet state standards owing to a particular parameter. An example of this would be the high faecal counts in the River Raisin after storm events. An average WQI for the River Raisin in the Dundee and Ida area is >70, yet occasionally the faecal coliform counts are found in the thousands rendering the water quality below State standards for full body contact recreational use. The State and Federal standard for full body contact is 2 000 colonies or less per 100 mL of water.

2.7 Water Treatment by Hydrolysing Metal Salts

Aluminium and ferric salts are widely used as coagulants in water and wastewater treatment. They are effective in removing a broad range of impurities from water, including colloidal particles and dissolved organic substances. Their mode of action is broadly understood in terms of essentially two mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous precipitate of metal hydroxide. The relative importance of these two mechanisms depends on many factors, especially pH and coagulant dosage (Gregory and Duan, 2001).

Hydrolysing metal salts, based on aluminium or iron, are very widely used as coagulants in water treatment. These materials have been applied routinely since early in the 20th century and play a vital role in the removal of many impurities from polluted waters. These impurities include inorganic particles, such as clays, pathogenic microbes, and dissolved natural organic matter. As well as traditional additives such as aluminium sulphate ('alum')

and ferric chloride, other products containing pre-hydrolysed metal ions are now commonly used. These include a range of materials known as polyaluminium chlorides (Gregory and Duan, 2001).

Although the mode of action of metal coagulants is broadly understood, there are still some uncertainties, especially with regard to the nature of the active species, the role of dissolved salts in water, and the strength and break-up of aggregates formed. The mechanisms of action of pre-hydrolysed forms are also by no means fully understood (Gregory and Duan, 2001).

2.7.1 Colloid stability and instability

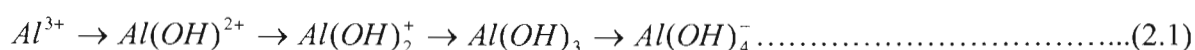
Particles in aqueous dispersions may interact in several ways, and their interactions determine whether the dispersion is stable or not. In this context, stability implies that the particles remain in a dispersed state for long periods, rather than forming aggregates (coagulation or flocculation). For long-term stability, some form of repulsion must operate between particles, otherwise, collisions of particles would result in attachment as result of the universal Van Der Waals forces of attraction. In water, particles are nearly always charged, and electrical repulsion between them may be responsible for their stability. A quantitative theory of colloid stability was developed by Deryagin and Landau (1941) and Verwey and Overbeek (1948) and now widely known as DLVO theory. There are other forms of interaction between particles, such as hydration and hydrophobic forces and effects associated with adsorbed polymers (Israelachvili., 1992), but these will not be considered here. DLVO theory treats colloid stability in terms of a balance between Van Der Waals attraction and electrical repulsion between particles. In practice, only the latter can be modified to a significant extent, and repulsion can be greatly affected by changing the ionic strength of the suspending medium or by modifying the surface charge of the particles. Increasing ionic strength effectively screens electrical repulsion and allows particles to approach each other more closely, so that Van Der Waals attraction may predominate. By adding salts that have specifically adsorbing counter ions (i.e., opposite in charge to the particles) the particle surface charge may be decreased or neutralized so that repulsion between particles is reduced or eliminated altogether. This can be an effective way of promoting coagulation and is often used in practice. In such cases, addition of excess

coagulant can cause charge reversal and restabilization of particles (Deryagin and Landau, 1941).

Another very important means of destabilizing particles is through the action of adsorbing polymers. Polymers of high molecular weight can adsorb simultaneously on two or more particles and bind them together by a process known as polymer bridging. The action of hydrolysing metal coagulants may be through charge neutralization effects or involve the binding of particles together by precipitated hydroxide (Deryagin and Landau, 1941).

2.7.2 The basic concept of hydrolysis of metal ions

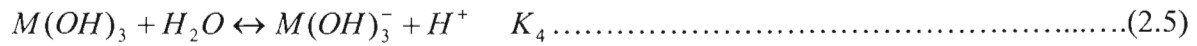
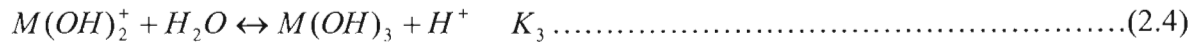
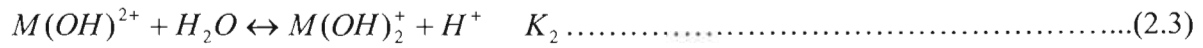
All ions in water are hydrated to some extent. In the case of Al^{3+} and Fe^{3+} , there is a primary hydration shell with six octahedrally coordinated water molecules, e.g., $Al(H_2O)_6^{3+}$. Hydrolysis of such ions is often represented as a sequential replacement of the water molecules by hydroxyl ions, and can also be thought of as a progressive deprotonation of water molecules in the primary hydration shell (Richens, 1997). The simplest representation, for Al^{3+} , omitting the hydration shell for convenience, is:



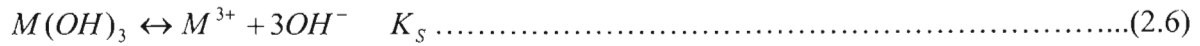
Since each step involves the loss of a proton, increasing pH causes the equilibria to be shifted to the right. Aluminium hydroxide has low solubility in water, and precipitation occurs at intermediate pH values. Further increase of pH causes the soluble aluminate ion to be formed. A similar sequence can be written in the case of Fe^{3+} . In this case, the hydroxide is much less soluble than aluminium hydroxide.

Because of the formation of insoluble hydroxides, the determination of hydrolysis constants is difficult, and there are significant discrepancies between published values (see e.g., Wesolowski and Palmer, 1994). Hydrolysis constants may be defined for the successive deprotonations in terms of the following equations:





It is also necessary to define the solubility constant for the solid hydroxide:



Although the most stable solid forms are gibbsite and goethite for aluminium and iron respectively, these reach equilibrium very slowly (up to several months or more). It is usual to take solubility constants for amorphous precipitates K_{sam} , since these form quite rapidly and are much more relevant in practical applications of coagulants. However, solubilities of amorphous hydroxides are not precisely known and only estimated values can be given. Table 2.4 gives values for hydrolysis and solubility constants (in pK form), taken from Wesoloski and Palmer (1994) for Al and from Flynn (1984) for Fe. The values are for conditions of zero ionic strength and 25 °C. Wesoloski and Palmer (1994) give extensive data for Al at other temperatures and ionic strengths.

Table 2.4: Hydrolysis and solubility constants for Al^{3+} and Fe^{3+} for zero ionic strength and 25°C. (Wesolowski and Palmer, 1994; Flynn, 1984)

	pK_1	pK_2	pK_3	pK_4	pK_{sam}
Al^{3+}	4.95	5.6	6.7	5.6	31.5
Fe^{3+}	2.2	3.5	6	10	38

As Martin (1991) pointed out, the hydrolysis constants for Al cover a much narrower range than those for Fe, which was ascribed to a decrease in coordination number for Al from 6 to 4, in passing from the hexahydrate to tetrahedral aluminate. For Fe, the coordination number remains 6 for all hydrolysed species. The effect on species distribution is quite marked, as shown in Figures 2.2.a and b, which show the proportion of Al and Fe species in soluble form, in equilibrium with the amorphous hydroxide. In the case of Al, the dominant species in solution changes from Al^{3+} to $Al(OH)_4^-$, over little more than 1 pH unit. In contrast, the corresponding change for Fe occurs over a range of more than 8 pH units and intermediate

species, such as Fe(OH)_2^+ and Fe(OH)_3 , can represent more than 90% of soluble forms at intermediate pH values.

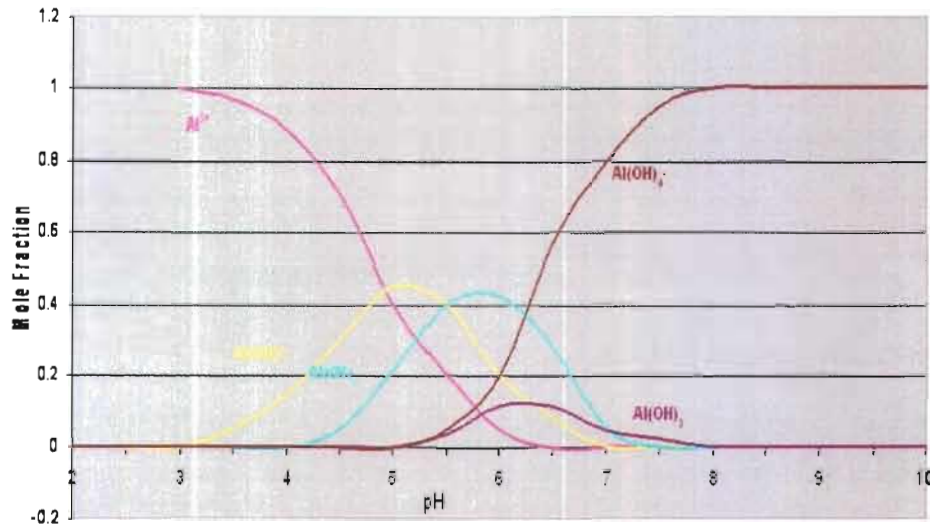


Figure. 2.2.a: Distribution of monomeric Al hydrolysis product as a function of pH (Courtesy of Martin, 1991)

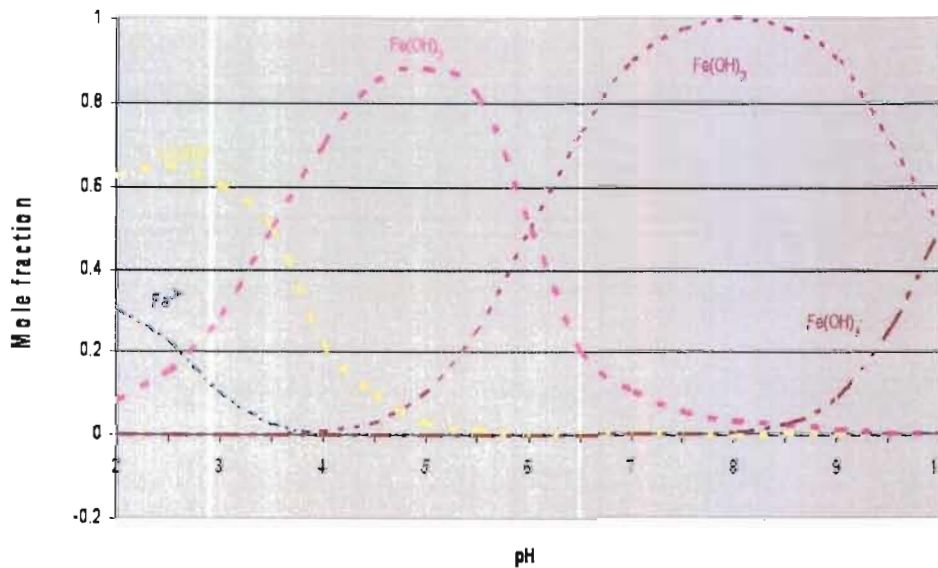


Figure 2.2.b: Distribution of monomeric Fe hydrolysis product as a function of pH (Courtesy of Martin, 1991)

From the standpoint of coagulation, the total amount of soluble metal species is important. For Al, there is a minimum solubility (about $2 \mu\text{M}$) in the region of pH 6. Ferric species show a much lower solubility (around 20 nM) over a rather broad pH range. These

calculations can be significantly affected by the presence of certain anions, which form complexes with Al and Fe. These include fluoride, phosphate, and sulphate, which can give increased solubility of the metals, especially at lower pH values (Reiber *et al.*, 1995).

As well as effects on equilibrium species distribution, some anions can modify the rate of hydroxide precipitation. An important example is sulphate, which can enhance precipitation of aluminium hydroxide (Hek *et al.*, 1978), essentially by association with highly charged polynuclear species, thereby reducing the free energy barrier to the formation of solid particles. This is essentially a catalytic effect, since basic sulphates were not detected in the precipitates. Hayden and Rubin (1974) found that the formation of settleable precipitates from aluminium sulphate solutions occurred over a much broader pH range than from solutions of aluminium nitrate. Another very important aspect is the complexation of metals with dissolved organic matter in natural waters.

2.7.3 Polynuclear species

As well as the simple monomeric hydrolysis products considered above, it is well known that highly charged metal ions can form a range of polynuclear species (Richens, 1997). For Al, these include $\text{Al}_2(\text{OH})_2^{4+}$ and $\text{Al}_3(\text{OH})_4^{5+}$, and there are equivalent species for Fe. Appropriate formation constants are known for the dimers and trimers, but at low total metal concentration they do not greatly affect solution compositions, such as those shown in Figures 2.2a and 2.2b. Various polymeric species, such as $\text{Al}_6(\text{OH})_{12}^{6+}$, have been proposed, but their existence has not been convincingly demonstrated. They might be regarded as intermediate forms in the conversion of soluble metal salts to solid precipitates. It is known that hydrolysis precipitation processes at ordinary temperatures are very slow and that true equilibrium can take months or years to achieve.

One polynuclear hydrolysis product of aluminium is now well established and of some practical importance. This is the so-called “ Al_{13} ” polymer, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, which can be formed by controlled neutralization of aluminium salt solutions. This has the Keggin structure, with one tetrahedral Al surrounded by 12 Al octahedra with shared edges. The

structure has been confirmed by ^{27}Al NMR studies (Akitt *et al.*, 1972), small angle X-ray methods (Bottero *et al.*, 1982), and potentiometric titration.

Another Al hydrolysis-polymerisation model involves the formation and condensation of hexameric rings, leading eventually to precipitation (Bertsch *et al.*, 1986), but this “core-link” model is now less popular, as a result of studies on the formation of the tridecamer species Al_{13} . However, the mechanism whereby Al_{13} is transformed into a precipitate is not fully understood (Bottero *et al.*, 1987).

The speciation of Al solutions can be conveniently studied by a timed colorimetric reaction with ferron reagent (8-hydroxy-7-iodo-5-quinoline sulfonic acid). This method was introduced by Smith (1971) and is based on the observation that different forms of Al react at varying rates with ferron. Mononuclear Al species (Al_a) react almost instantaneously and polynuclear species (Al_b) much more slowly. Colloidal or precipitated Al (Al_c) shows practically no reaction with ferron. The proportion of polynuclear species (Al_b) determined by the ferron technique corresponds quite well with results from membrane filtration tests (Gray *et al.*, 1995) and with the proportion of Al_{13} from NMR studies (Tang and Luan, 1996). Typically, the proportion of the various species is determined as a function of the degree of neutralization of the aluminium salt solution, B ($=\text{OH}/\text{Al}$). For 0.1 M AlCl_3 solution, titrated with 0.5 M NaOH, the proportion of Al_b increased from around 33 to 83% as B was raised from 1.0 to 2.5. For values of B above 2.5, the amount of precipitate (Al_c) increases significantly (Tang and Luan, 1996). In the same study, it was shown that the Al_b fraction was quite stable to dilution and to changes in pH, and only slowly converted to other forms.

2.7.4 Action of hydrolysing coagulants

2.7.4.1 Charge neutralization

A simple mechanism for destabilization of negatively charged particles is the specific adsorption of cationic species from solution. Since aluminium and iron salts give cationic hydrolysis products, charge neutralization is a possible reason for the action of these materials as coagulants. Adsorption of cations on negative surfaces may occur for simple

electrostatic reasons or by some form of surface complex formation. Since hydrolysing coagulants are effective for a wide range of particle types, including bacteria, clays, and many others, it is unlikely that a single adsorption interaction is responsible (Gregory and Duan, 2001).

It is commonly observed that particles can be destabilized by small amounts of hydrolysing coagulant and that optimum destabilization corresponds with the neutralization of particle charge (determined, for instance, by electrophoretic mobility). Larger amounts of coagulant cause charge reversal, so that the particles become positively charged and are thus *restabilised*. For relatively low particle concentrations, destabilization and restabilisation typically occur with just micro-molar concentrations of coagulant (Gregory and Duan, 2001).

If charge neutralization is the predominant destabilization mechanism, then there should be a stoichiometric relationship between the particle concentration and the optimum coagulant dosage (Stumm and O'Melia, 1968). At low particle concentrations, low coagulant dosages should be required. Under these conditions, coagulation rates can be very low, and it is found that higher coagulant dosages are much more effective. This is due to extensive hydroxide precipitation and a process known as sweep flocculation.

2.7.4.2 Sweep flocculation

Although particles may be effectively destabilized by charge neutralization, there are two disadvantages in water treatment:

- quite precise control of coagulant dosage is needed to give optimum destabilization;
- the particle collision rate and hence the coagulation rate depend on the square of the particle concentration and can be very low for dilute suspensions.

Both of these problems can be overcome if higher coagulant dosages are used, since considerable quantities of amorphous hydroxide precipitate are then formed. It has long been recognized (Packham, 1965) that, in many cases, optimal removal of particles from water is achieved under conditions of rapid hydroxide precipitation. In the case of aluminium coagulants, optimum pH conditions are close to the point of minimum solubility. Although

precise mechanisms are still not fully understood, it is clear that impurity particles are enmeshed in the growing precipitate and hence can be removed from water by sedimentation. This process has become known as sweep flocculation, since particles are “swept out” of water by an amorphous hydroxide precipitate (Gregory and Duan, 2001).

Sweep flocculation generally gives considerably improved particle removal than when particles are destabilized just by charge neutralization. At least part of the reason is the greatly improved rate of aggregation, owing to the increased solids concentration. Hydroxide precipitates tend to have a rather open structure, so that even a small mass can give a large effective volume concentration and hence a high probability of capturing other particles. It is also possible that binding of particles by precipitated hydroxide may give stronger aggregates (Gregory and Duan, 2001).

The different mechanisms outlined above (Gregory and Duan, 2001) have led to the definition of four zones of coagulant dosage, with the following consequences for negatively charged particles:

- Zone 1 - Very low coagulant dosage, particles still negative and hence stable
- Zone 2 - Dosage sufficient to give charge neutralization and hence coagulation
- Zone 3 - Higher dosage giving charge neutralization and restabilisation
- Zone 4 - Still higher dosage giving hydroxide precipitate and sweep flocculation

2.8 Ground Water and Redox Potential

Oxidation and reduction (Redox) reactions play an important role in the geochemical processes that occur in groundwater. Redox reactions are defined as reactions in which electrons are transferred. The species receiving electrons is reduced, whilst that species donating electrons is oxidized. Redox reactions determine the mobility of many inorganic compounds as well as biologically important materials such as nitrogen and sulphur. In addition, redox conditions govern the particulars for the biological degradation of complex hydrocarbon contaminants (Vance, 2002).

Redox potential is an intensity parameter of overall redox reaction potential in the system (similar in concept to pH), not the capacity of the system for specific oxidation or reduction

reactions. The redox value of standard half reactions (E°) and details of how to calculate redox capacity can be found in any elementary chemistry text (Vance, 2002).

Most work with redox reactions involves laboratory evaluation under static conditions; the focus is on solutions in closed systems that are in an equilibrium state. In groundwater with more than one redox couple the redox potential cannot be accurately measured unless the redox reactants are at thermodynamic equilibrium. However, environmental processes are typically in dis-equilibrium, caused by the following (Vance, 2002):

- flowing groundwater conditions,
- biological activity,
- redox reactions of light bioactive elements (C, H, O, and S) which most often involve the breaking of covalent bonds, a process that is normally slow, and
- electrochemical reactions of exposed active mineral surfaces.

Some redox reactions can take from 10 to 1000 years to reach equilibrium. Instead of measuring the redox potential from a field sample, the redox potential can be calculated using the relative concentrations and redox potential of major dissolved species. This is precisely the process used in fate and transport models utilized in support of risk assessments (Vance, 2002).

Groundwater typically contains both reduced and oxidized species, however what is termed the redox buffer capacity of an aquifer is normally dominated by the chemistry of the aquifer matrix:

- the oxidation capacity of the aquifer acts as a buffer to limit the transport of a plume in a reduced state that would be generated from hydrocarbon contamination or a landfill;
- the reduction capacity of an aquifer will buffer against attempts to increase the redox potential as part of the remediation program (such as air sparging or in-situ bioremediation) to address a contaminant plume;
- in most natural groundwater systems iron is the dominant (by 1 to 3 orders of magnitude) buffering species involved in redox reactions. In some organic rich aquifers TOC can equal ferrous iron as a reduction buffer.

The following inorganic oxidation reactions, described by Vance, (2002) will consume dissolved oxygen in groundwater:

- Sulphide Oxidation -



- Iron Oxidation -



- Nitrification -



- Manganese (II) Oxidation -



- Iron Sulphide Oxidation

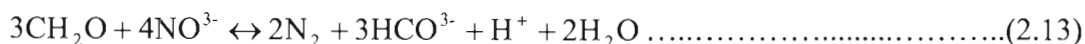


The following redox reactions will consume organic matter in groundwater:

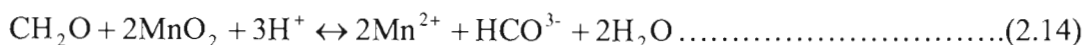
- Aerobic Degradation -



- Denitrification -



- Manganese (IV) Reduction -



- Ferric Iron Reduction -



- Sulphate Reduction -



- Methane Fermentation -



The above reactions are listed in order of decreasing Eh conditions as follows:

- Aerobic Degradation
+250mv and higher
- Oxygen - Nitrogen

-
- +250mv to 100mv
 - Iron - Mn (IV)
+100mv to 0mv
 - Sulphate
0mv to -200mv
 - Methane - Hydrogen
-200mv and lower

Water in contact with air will have an Eh in the range of 350mv to 500mv. Microbially mediated redox processes may decrease the redox potential to values as low as -300mv. A method of handling Eh data that has proven of particular value to the geochemist is the Eh-pH diagram, on which species oxidation state is plotted with variable Eh and pH conditions. The Eh-pH diagram works well in a qualitative fashion, but due to conditions previously discussed are usually unsuccessful when applied to quantitative applications. Vance (2002) illustrates the geologically important iron/water system. In addition to illustrating iron oxidation state, it shows how Eh in groundwater is governed at the upper range by the oxidation of water to O₂ and the lower range by the reduction of hydrogen ions to H₂.

2.9 Pourbaix Diagrams and Reactions in Aqueous Solution

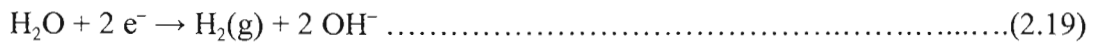
Water can act both as an oxidizing agent, in which case the water is reduced to H₂, and a reducing agent, with the attendant production of O₂. If a chemical species is to be stable in aqueous solution, it must not react with the water through a redox process. In other words, the oxidation and reduction potentials of the species must be such that it is thermodynamically unfavourable for the species to be either oxidized or reduced by the water (Coleman, 2003).

2.9.1 Stability of water

According to Coleman (2003) and Lower (2005), in an acid solution, the primary redox process occurs between H⁺ and metals producing metal ions and H₂. The potential for the reduction of H⁺ to H₂ is given by:



or, in neutral or alkaline solutions as



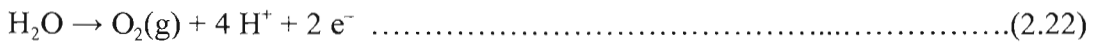
These two reactions are equivalent and follow the same Nernst equation

$$E_{\text{H}^+/\text{H}_2} = E_{\text{H}^+/\text{H}_2}^0 + \frac{RT}{nF} \ln \left(\frac{[\text{H}^+]^2}{P_{\text{H}_2}} \right) \dots\dots\dots(2.20)$$

which, at 25°C and unit H_2 partial pressure reduces to

$$E = E^0 - \frac{0.059}{2} \times 2 \text{pH} = 0.059 \text{pH} \dots\dots\dots(2.21)$$

Similarly, the oxidation of water



is governed by the Nernst equation

$$E_{\text{O}_2/\text{H}_2} = E_{\text{O}_2/\text{H}_2}^0 + \frac{RT}{nF} \ln(P_{\text{O}_2}[\text{H}^+]^4) \dots\dots\dots(2.23)$$

which similarly becomes $E = 1.23 - 0.059 \text{pH}$, so the E vs. pH plots for both processes have identical slopes and yield the stability diagram for water shown below in Figure 2.3.

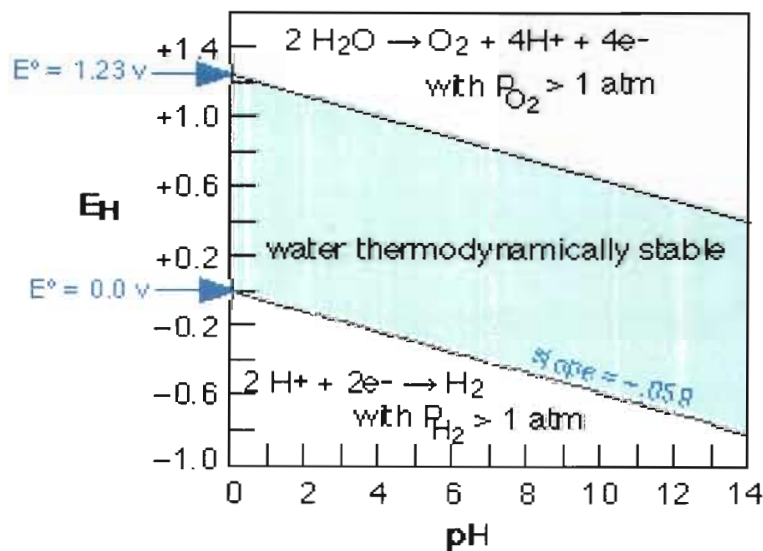


Figure 2.3: Stability (Pourbaix) diagram for water (Lower, 2005)

The two E^0 values shown at the left refer to "standard" conditions of unit H^+ activity ($\text{pH}=0$) and gas pressures of 1 atm. At combinations of pH and E that lie outside the shaded area, the

partial pressures of O_2 or H_2 exceed 1 atm, signifying the decomposition of water. The unity partial pressures are of course arbitrary criteria; in a system open to the atmosphere, water can decompose even at much lower H_2 partial pressures, and at oxygen pressures below 0.2 atm. Fortunately, these processes are in most cases quite slow (Lower, 2005).

Coleman (2003) adds that in practice it turns out that the reduction potential referred to above in Figure 2.3 needs to be at least 0.6V higher than predicted due to a kinetic phenomenon known as the overvoltage (or overpotential). This "extra energy demand" is always found when gases are involved in the redox processes, and is also associated with the complexities of transferring 4 electrons at once, as in the oxidation of water (Coleman, 2003).

The diagram in figure 2.4 below shows how the potentials for reduction and oxidation of water vary with pH. These are the inner two lines that slope downward from low pH to high pH. The pH scale only runs from 2-10. For both oxidation and reduction of water, an additional line is shown that lies 0.6V above (for oxidation of water) or below (for reduction) the theoretical E. This pair of lines represents the potentials including an approximation for the overvoltage. Lastly, there is a pair of vertical lines at pH = 4 and 9. These are reflective of the fact that most natural waters have a pH somewhere between these limits. The second plot emphasizes the region bounded by the upper and lower potential lines and pH 4 and 9. This region is frequently referred to as the stability field of natural waters (Coleman, 2003).

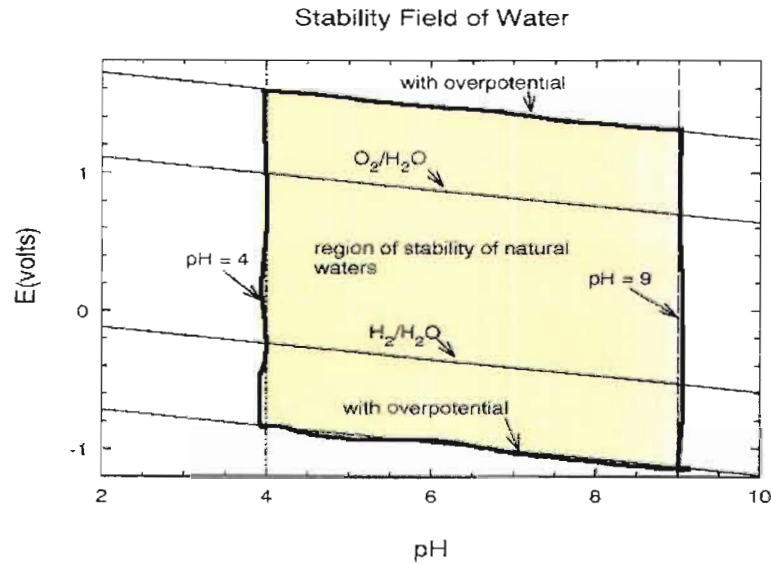


Figure 2.4: Reduction and oxidation potentials of water versus pH by Coleman (2003)

A Pourbaix diagram is an attempt to overlay the redox and acid-base chemistry of an element onto the water stability diagram. The data that are required are redox potentials and solubility products. The next diagram (Figure 2.5) shows approximate redox and acid-base behaviour for various types of natural waters. This diagram can be used in conjunction with the Pourbaix diagrams above to explain and predict a number of phenomena. For example, in Lake Waban and similar bodies of water, vertical mixing of material in the lake is greatly retarded by temperature gradients. At the surface, you would expect to find Fe present, mostly as $Fe_2O_3(s)$, but as the solid settled to the bottom, where there is far less oxygen, and probably organic matter from decay, it is likely that the iron will be reduced to Fe^{2+} . The ions migrate upwards and are deoxidised to $Fe_2O_3(s)$.

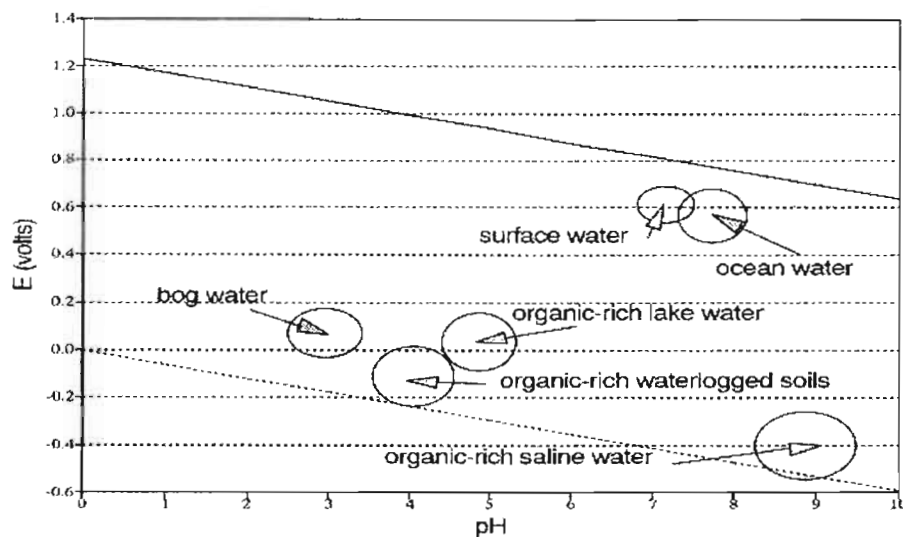


Figure 2.5: Approximate redox and acid-base behaviour for various types of natural waters (Coleman, 2003)

2.9.2 Pourbaix diagrams for iron

Not only is iron common, but it is also reactive and readily reflects changes in surrounding Eh/pH conditions. This is particularly true in soil and groundwater systems that have been environmentally impacted with hydrocarbons. In groundwater systems iron occurs in one of two oxidation states: reduced soluble divalent ferrous iron (Fe^{+2}) or oxidized insoluble trivalent ferric iron (Fe^{+3}). The modern atmosphere has 21% oxygen, causing most of the iron in shallow subsurface soils to be in the oxidized ferric state (Vance, 2002).

Ferric hydroxide ($\text{Fe}(\text{OH})_3$) is the direct result of ferrous iron oxidation and precipitation. With time, ferric hydroxide is mineralised. The principal forms of mineralised ferric iron found in soils are:

- amorphous hydrous ferric oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$),
- maghemite ($\gamma\text{-Fe}_2\text{O}_3$),
- lepidocrocite ($\gamma\text{-FeOOH}$),
- hematite ($\alpha\text{-Fe}_2\text{O}_3$), and
- goethite ($\alpha\text{-FeOOH}$).

The above iron oxides are listed in order of decreasing solubility, which also reflects increasing crystallinity. Amorphous hydrous ferric oxide at neutral pH and oxidizing Eh conditions has a solubility of 0.6 µg/L, which is three orders of magnitude greater than that of goethite. However, high concentrations of iron in groundwater are not rare; other processes are at work.

2.9.2.1 Iron Complexing

Ferrous iron is soluble as a cation, ferric iron is only slightly soluble. However, ferric iron can form soluble complexes with many inorganic and organic ligands, including compounds that are the byproducts of the biodegradation of aromatic petroleum hydrocarbons (catechols, which are organic acids resulting from aromatic ring cleavage). The yellow/orange colouration of groundwater at some sites contaminated with petroleum hydrocarbons is due to these ferric-catechol complexes.

It is important to remember that complexed ions typically react more slowly than uncomplexed ions. This impacts the behaviour of ferrous iron. Ferrous iron can normally be oxidized to ferric iron in minutes (see below for more details). Complexed ferrous iron may take months to complete the same reaction. This has profound implications for the fouling of groundwater injection systems. Humic acid, fulvic acid and tannic acid are examples on non-contaminant organic complexes. Phosphate also serves as a very effective complexing agent for iron.

2.9.2.2 Iron Oxidation

The time required for uncomplexed ferrous iron to undergo oxidation to the ferric state is dependent on many factors, the dominant being pH, temperature, dissolved oxygen level, and the presence of other soluble ions. The lower the pH and temperature the longer the time required for completion of the oxidation reaction. Increasing dissolved oxygen decreases the time required for oxidation. For example:

- At pH 7.0, 90% Fe^{+2} oxidation requires 1 hour at 21° C and 10 hours at 5° C,
- At pH 8.0, 90% Fe^{+2} oxidation occurs in 30 seconds At 21° C,
- At pH 6.0 it requires 100 hours, and

- The critical dissolved oxygen concentration is 2 mg/L. below that ferrous iron oxidation occurs slowly.

The above reactions are often responsible for the iron fouling of air strippers treating iron rich groundwater. These reactions can also foul screens in poorly designed recovery wells pumping that groundwater.

Knowledge of the pH condition of the environment is not sufficient for predicting the form in which an element will exist in natural waters. Consideration should be given as to whether the aqueous environment is well aerated (oxidizing) or polluted with organic wastes (reducing). In order to add this variable, we must expand the predominance diagram to include the reduction potential of the environment as well as the pH. This type of predominance diagram is known as a Pourbaix diagram, E° -pH diagram, or pE-pH diagram (Jones, 1996).

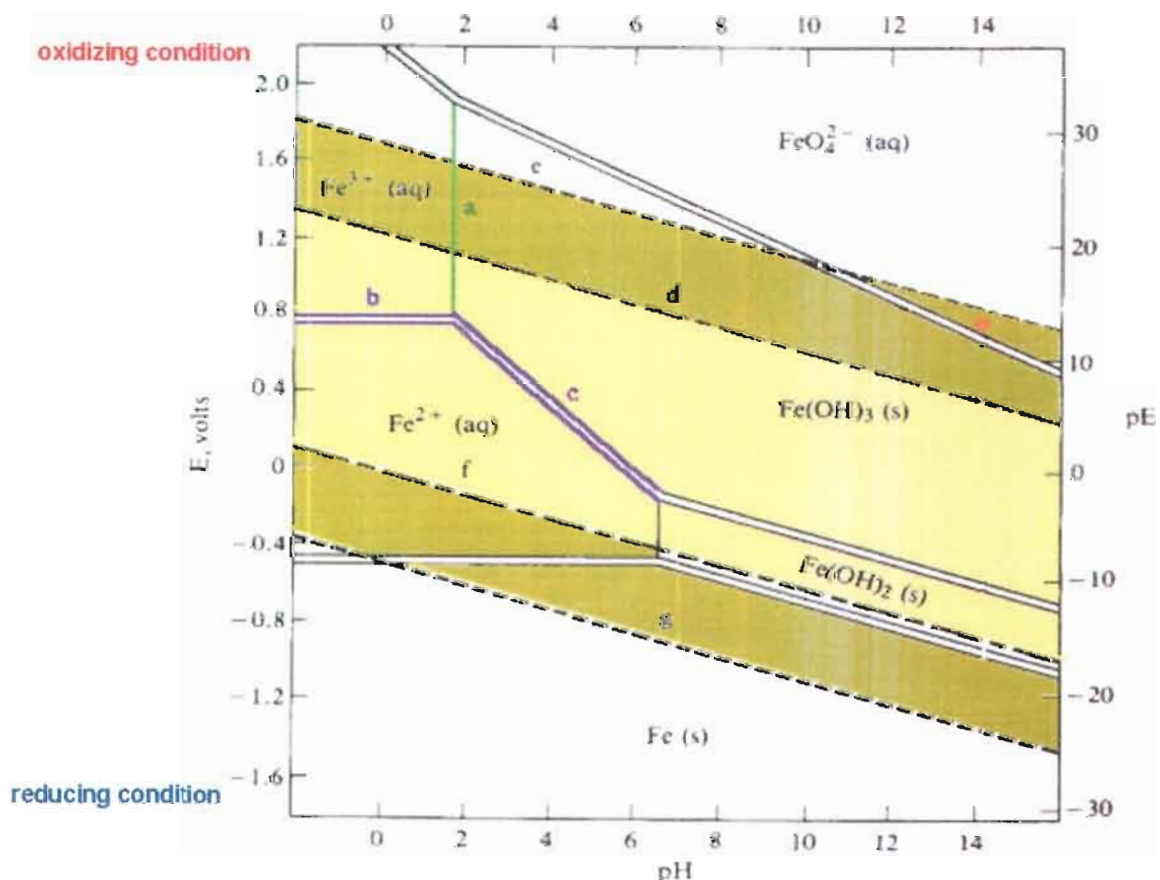


Figure 2.6: Simplified Pourbaix diagram for 1 M iron solutions

Low E or pE values represent a reducing environment. High E values represent an oxidizing environment. The pE scale is intended to represent the concentration of the standard reducing agent (the e^-) analogously to the pH scale representing the concentration of standard acid (H^+). PE values are obtained from reduction potentials by dividing E° by 0.059.

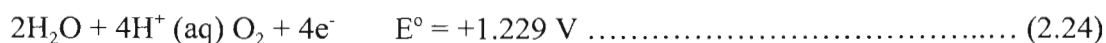
The key to features on the Pourbaix diagram on Figure 2.6 is as follows:

- Solid lines separate species related by acid-base equilibria (line a) -
 - line a shows the pH at which half of the 1 M iron is Fe^{3+} and half is precipitated as $Fe(OH)_2$.
 - Pourbaix diagrams incorporate Z^l/r calculations and acid-base equilibria.
 - the position of an acid-base equilibrium is dependent on the total concentration of iron.
 - reducing the total concentration of Fe^{3+} will reduce the driving force of the precipitation.
 - reducing the total iron concentration from 1 M to 10^{-6} M (more realistic concentrations for geochemists and corrosion engineers) shifts the boundary from pH 1.7 to pH 4.2.
 - In general, in more dilute solutions, the soluble species have larger areas of predominance.
- Solid double lines separate species related by redox equilibria (lines c & d) -
 - redox equilibria of species not involving hydrogen or hydroxide ions appear as horizontal boundaries (line b).
 - redox equilibria of species involving hydrogen or hydroxide appear as diagonal boundaries because they are in part acid-base equilibria (line c).
 - diagonal boundaries slope from upper left to lower right because basic solutions tend to favour the more oxidized species.

- Longer dashed lines enclose the theoretical region of stability of the water to oxidation or reduction (lines d & f) while shorter dashed lines enclose the practical region of stability of the water (lines e & g) -

- Dashed line d represents the potential of water saturated with dissolved O_2 at 1 atm (very well aerated water).

- above this potential water is oxidized to oxygen:



- theoretically water should be oxidized by any dissolved oxidizing agent $E^\circ > 1.229$.
- in practice, about 0.5 V of additional potential is required to overcome the overvoltage of oxygen formation (dashed line e).

- Dashed line f represents the potential of water saturated with dissolved H_2 at 1 atm pressure (high level or reducing agents in solution).

- Below this potential water is reduced to hydrogen:



- in practice, an overvoltage effect prevents significant release of hydrogen until the lower dashed line g is reached.

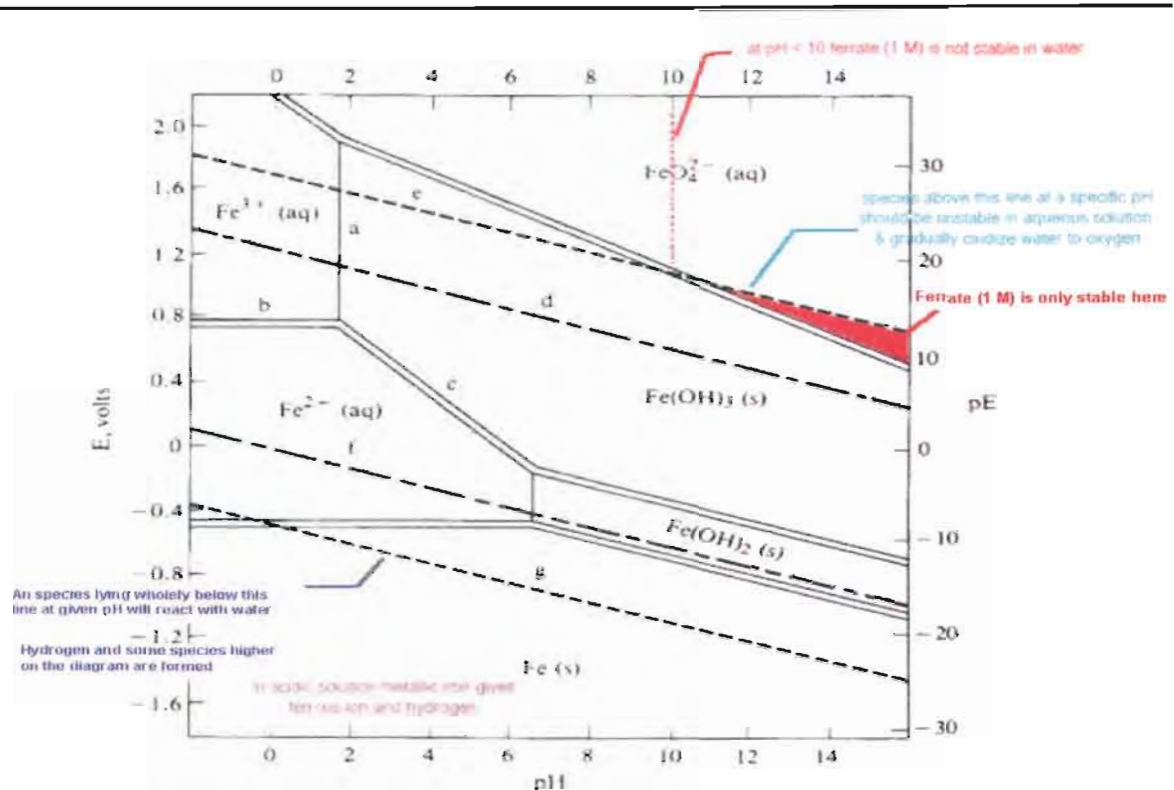


Figure 2.7: Pourbaix diagram indicating the stability and instability of ferrate

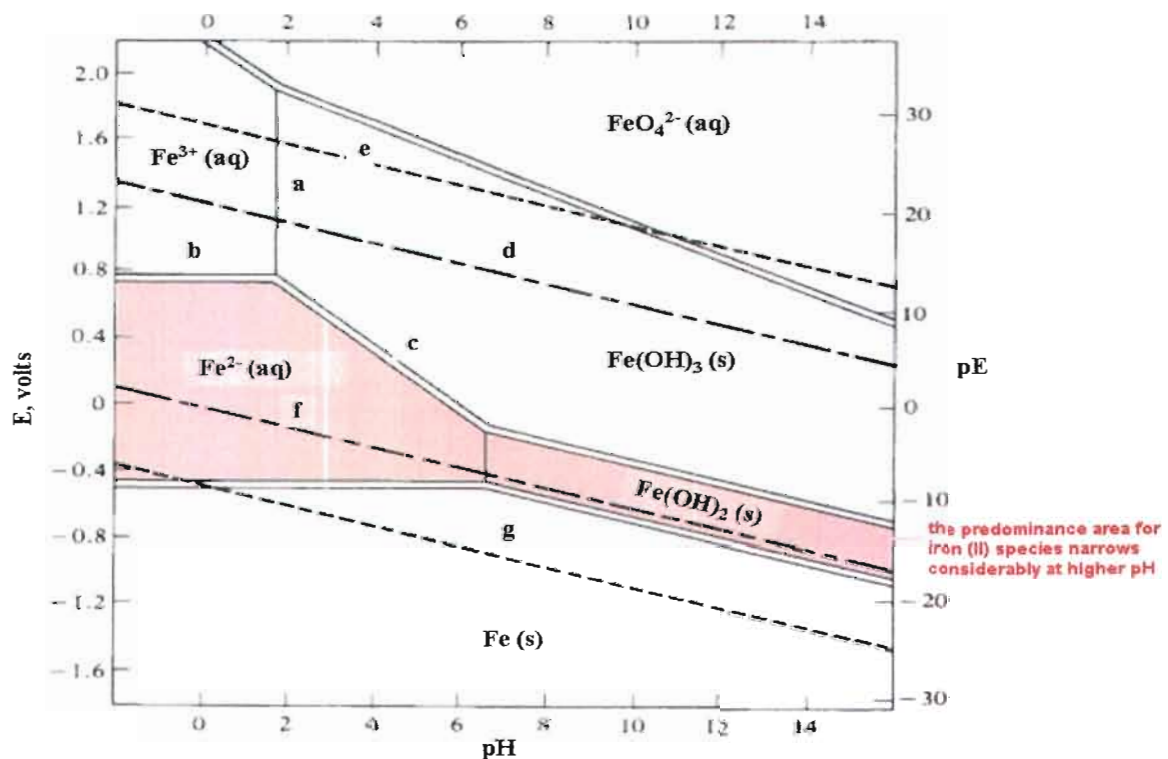


Figure 2.8: Pourbaix diagram indicating the predominant area for iron (II) species as it narrows with an increasing pH

2.9.3 Uses of Pourbaix diagrams

- Any point on the diagram will give the thermodynamically most stable (theoretically the most abundant) form of the element for that E and pH i.e. at $E = +0.8 \text{ V}$ and $\text{pH} = 14$ the predominant form is FeO_4^{2-} .
- The diagram gives a visual representation of the oxidizing and reducing abilities of the major stable compounds of an element:
 - Strong oxidizing agents and oxidizing conditions are found **ONLY** at the top of the diagram. The lower boundaries of strong oxidizing agents are high on the diagram.
 - Reducing agents and reducing conditions are found at the bottom of a diagram and nowhere else. Strong reducing agents have boundaries that are low on the diagram.
 - A species that prevails from top to bottom at the pH in question has no oxidizing or reducing properties at all within that range.

2.10 Electrochemistry (Background and Theory)

2.10.1 Introduction

Towards the end of the eighteenth century, Galvani and Volta discovered methods of producing electric current; the electrical energy was derived from chemically reactive systems, though the mechanism was not well understood. Volta's devices found uses in the reverse process of converting electrical energy into chemical energy (Davies, 1967). Water was decomposed into hydrogen and oxygen, and within few years, Davy had used the same process of electrolysis to isolate the alkali metals. Electrochemistry advanced rapidly from these beginnings, and its theoretical foundations took shape with the quantitative study of the electrolytic process by Michael Faraday in 1833.

Electrochemistry of solute systems deals with the exchange between an electrode and electron donors or acceptors present in the solvent and with ionic charge transfer through the solvent between two electrodes. A number of electrolytic reactions take place when there is an addition or subtraction of electrons from the solute. This is the reason why electrochemistry is used in the production of some organic and inorganic substances.

Two metallic conductors are immersed in an electrolyte solution. They are connected to a voltmeter and power-supplying source to make a complete circuit. Electric potential difference exists between the two electrodes and this leads the current to flow from the cathode through the external wires and the voltmeter entering the system again on the anode.

The potential difference between the two electrodes is directly proportional to the amount of ions dissolved in the solution when the electric current is flowing (Barrow, 1966). The chemical element that has a positive potential of reduction tends to be reduced, that is to acquire electrons, while the element that has a negative potential tends to be oxidized, that is to give up electrons.

2.10.2 Advantages and disadvantages of electrochemistry

Electrochemical techniques offer increasing degrees of accuracy and detection limits, often involving dramatically lower costs than other techniques. In addition, electrochemistry offers a series of advantages that in many cases can be used to make 'green' processes. Some include the minimization of waste emissions by improved process design involving the minimization of by-product formation, raw material usage, and energy consumption (Ibanez, 1994).

In this way, electrochemistry offers important degrees of:

- Environmental compatibility - Electrons are clean reagents per se and any chemical additive is not necessary,
- Energetic efficiency - Electrochemical processes are not subject to some limitations inherent in other processes,
- Cost - Among the reducing agents commonly employed, electrons have the lowest cost per unit of charge,
- Easy operational control and maintenance - In addition, electrochemical reactors normally do not require moving parts, and thus are mechanically simple and of relatively low maintenance,
- Versatility - The same electrochemical reactor can often be used for more than one purpose,
- Ease of automation - The main variables in electrochemical reactors are current and voltage that are ideally suited for process automation, optimisation, monitoring, and control,
- Friendly requirements - Contrary to other techniques or processes like incineration, supercritical oxidation, wet oxidation, etc., electrochemical techniques normally do not require high temperature or pressure, and
- Selectivity - An adequate combination of experimental conditions (electrolyte composition, temperature, degree of convection, applied potential, current) and reactor characteristics (shape, size, construction materials, electrode materials, membranes) can be judiciously selected so as to prevent or minimize energy waste and by-product

generation. Such by-products not only mean a waste of materials, but also introduce additional difficulties for their separation and/or disposal.

In spite of these advantages, there are also some challenges to be faced:

- Electrode materials may be prone to erosion, complexation, oxidation, wearing, or inactivation (the electrodes have to be substituted regularly due to the formation of a impermeable oxide, which reduces electro-flotation efficiency),
- Since most of the electrochemical processes are performed in aqueous solutions, solvent decomposition (that is, water oxidation/reduction) is often hard to avoid and thus there is a concomitant energy waste,
- The production of gases from the above decomposition (hydrogen and oxygen) may form explosive mixtures,
- The best electrode materials in terms of durability and inertness frequently involve precious metals, and this increases costs,
- Electricity dependency - the cost of electricity in many areas is prohibitive,
- Initial capital investment may be large, and
- The lack of knowledge or understanding of electrochemistry is perhaps the greatest hindrance for its utilization.

2.10.3 Electrolysis mechanism

Electrolysis involves passing an electric current through either a molten salt or an ionic solution. The ions are ‘forced’ to undergo either oxidation (at the anode) or reduction (at the cathode). Most electrolysis problems are really stoichiometry problems with the addition of an amount of electric current. The quantities of substances produced or consumed by the electrolysis process is dependent upon the following:

- electric current measured in amperes or amps,
- time measured in seconds, and
- the number of electrons required to produce or consume 1 mole of the substance.

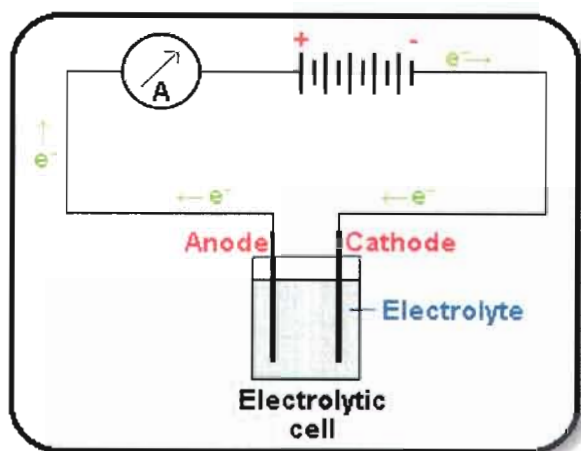


Figure 2.9: The electrochemical principle

2.10.4 Faraday's Law

In 1830, Michael Faraday published his experiment using the recently discovered voltaic column to decompose substances through the use of electric current. An electric current can pass through metals and many other substances without the substance itself appearing to suffer any material change; these are metallic conductors. When electricity passes through salt solutions or fused salts, on the other hand, the mechanism must be different, for where the current enters or leaves the liquid there is the evidence of chemical action having taken place; this is electrolytic conduction, and substances giving rise to such effects are termed electrolytes.

Electrolysis is an oxidation–reduction process involving a conversion of electrical energy into chemical energy. The electrolytic cell is a galvanic cell operation in reverse. The automobile battery is an example that acts as a collection of galvanic cells when delivering electric current, but acts as a collection of electrolytic cells when being recharged.

According to Delpierre and Sewell (2002) Faraday first described the qualitative relationship between the amount of electric charge (number of electrons) that has passed through an electrolytic cell and the amount of materials that has formed at the electrodes. Faraday's investigation of electrolytic conduction established the following two laws:

- In any electrolytic process the amount of chemical action is proportional to the quantity of the electricity passing the electrolytic conductor (The mass of substance reacting at an electrode is directly proportional to the total amount of electric charge that passed through the cell);
- The masses of different substances deposited or dissolved by the same quantity of electricity are in the proportions of their chemical equivalents (The masses of the substances reacting at the electrodes are in direct ratio to their equivalent masses).

The equivalent mass of a reacting substance is defined by Delpiere and Sewell (2002) as its mass that reacts with one mole of electrons in the oxidation-reduction process. The second law is a consequence of the stoichiometry of the balanced half reactions. Through exhaustive experimentation, the charge of a single electron has been determined to be 1.602×10^{-19} Coulombs (C). One mole of electrons has a total charge calculated to be 96 485C; this quality is defined as Faraday (F):

$$1F = 96\,485 \text{ C/mol } e^{-}$$

Faraday's Law predicts a linear relationship between electrochemical dissolution and/or deposition (plating) of metals. This is an exact science and concerns the variables of an electrical charge and mobile charged chemical ions. The relationship between electrical charge and mass is formulated as follows:

$$\frac{m}{M_w} = \frac{Q}{F} \dots\dots\dots(2.26)$$

- where m - mass of electrode dissolved (g)
 M_w - Molecular mass of metal electrode (g/mol)
 Q - Electrical charge (C)
 F - Faraday's constant (96 485 C/mol)

The constant F in the formula is the number of Coulombs (C) that will be required to deposit one gram of equivalent weight. Its evaluation from the above equation 2.26 requires a measurement of the weight of an element, of known atomic weight and valency, that is deposited by a known number of Coulombs, or, in practice, by a known current in amperes (A) flowing for a known number of seconds.

$$\text{Thus, } m = \frac{M_w \cdot I \cdot t}{z \cdot F} \dots\dots\dots(2.27)$$

- where m - mass of electrode dissolved (g)
- M_w - Molecular mass of metal electrode (g/mol)
- I - Electrical current through the circuit (A)
- T - Time (seconds)
- z - Valency of the element deposited
- F - Faraday's constant (96 485 C/mol)

Electrolysis can also be defined as the decomposition of water and other inorganic compounds in an aqueous solution by means of an electric current, the extent being proportional to the quantity of electricity passing through the solution. The positive and negative ions formed are carried by the current to the oppositely charged electrodes, where they are collected if wanted or released if unwanted. Metallic ions deposited on the electrode form a coating. A simple electrolysis is the separation of water into oxygen and hydrogen.

2.10.5 Electroflocculation

Electrocoagulation and electroflocculation are two techniques involving the electrolytic addition of coagulating metal ions directly from sacrificial electrodes. These ions coagulate with pollutants in the water, in a similar manner to the addition of coagulating chemicals such as alum and ferric chloride, and allow the easier removal of the pollutants. The electrolytic addition of these ions has a number of advantages over their addition chemically. There is no addition of anions meaning no increase in salinity of the treated water. The system produces half to one third of the sludge. Greater activity means fewer metal ions required and a wider range of pollutants can be removed. In electroflocculation, the pollutants are removed by the bubbles which are generated during the process, capturing the coagulated pollutants and floating to the surface. Appropriately constructed a single unit can be used to coagulate the pollutants and float them to the surface, from where they can be easily removed (Robinson, 1999).

Wastewater is the largest disposal problem associated with waste and by product production, being typically many tonnes of water per person per year in industrialised countries (Robinson, 1999). Yet the total amount of pollutant in the water is often much less than 0.1% (1 000 ppm). Great quantities of water are used to remove small amounts of pollutant. The magnitude of the waste problem could be considerably reduced if techniques which concentrated or removed the small amount of pollutant and left the majority of water in a condition suitable for reuse were used. Many different techniques are available, including a variety of filters, chemical dosing, reverse osmosis and similar. Many of these are either very pollutant specific or more expensive than dumping and using more water. These latter options are fast disappearing and new methods need to be sought. According to Robinson (1999), for a technique to be successful it needs to satisfy the following criteria:

- It must be cost-effective, producing results which are cheaper than dumping and purchasing more water. With water costs - for purchasing water and a similar price for disposing to sewer, both the capital and operating costs must be low and the results as good as tap water for the technique to be successful;
- It must remove the contaminants thereby producing water which can be reused in the same application, or as a replacement for water in another application;
- It must not in itself produce great amounts of waste;
- It must operate reliably and have low downtimes.

Electrolytically based processes appear to offer some of these advantages. These involve the passage of an electric current via sacrificial electrodes. Their operating costs are low because of the low cost of electricity and the element materials used. Many attempts have been made in the literature to take advantage of the potential associated with these capabilities, but with limited success. The process, usually known as Electrocoagulation (Stuart, 1946; Bonilla, 1947, Matteson *et al.*, 1995), involves the passage of an electric current, usually using aluminium electrodes. Aluminium goes into solution at the anode and hydrogen gas is released at the cathode. The aluminium coagulates with the pollutants which can then be removed, usually by either settling or filtration.

Some of the problems encountered with this technique have been associated with element lifetimes (Holt *et al.*, 1999). This has resulted in high operating costs and made the process

uneconomical and the potential benefits were lost. Recently these problems appear to have been overcome and at least one commercial electrocoagulation unit is available. A variation of the electrocoagulation process is one in which the gas generated by the process captures the coagulated pollutants and floats them to the surface. Known as electroflocculation, it offers the possibility of a one-step process, in which polluted water is pumped into a processing reactor, the pollutants are floated to the surface and the cleaned water is pumped out at the end of the process. Theoretically there are no chemicals to be added and no filters which need cleaning, enabling this process to have the potential to achieve the above goals.

Laboratory prototype reactors had been constructed in which preliminary work was undertaken to check the feasibility of the process and determine its viability to treat different types of wastewater. These results also enabled an understanding of the processes involved to be gained. Based upon the success of laboratory experiments, industrial scale units were field trialled in a number of different applications. Results by Bonilla (1947) indicated the ability to treat a variety of different types of water. Fats, oils and greases (FOGs) removal rates in excess of 99.95% have been achieved (Bonilla, 1947) and turbidity of rural clay water has been reduced to below 1 NTU, from values starting at greater than 500 NTUs (Packham, 1965). Bacteria removal rates in excess of 99% have been achieved from single stage reactors. The process appears to hold significant advantages for the treatment of wastewaters.

2.10.5.1 Theory of electroflocculation

Electroflocculation provides an alternative technique for the removal of pollutants from wastewater. The process involves the application of an electric current to sacrificial electrodes, usually aluminium, inside a processing tank. The reactions at the anode and cathode respectively are typically generating aluminium ions as a coagulating agent as well as gas bubbles. The well-known properties of the aluminium ions as a coagulating agent cause them to combine with the pollutants. The gas bubbles generated can capture the coagulated agglomerates, similar to the application in a dissolved air flotation (DAF) unit, resulting in most of the pollutant being floated to the surface. In theory, this electroflocculation process can be used as an alternative to DAF processing, with the added

advantage that there are no chemicals to be added. As is the case with DAF, there are no filters to be used for final pollutant removal.



In addition to the use of aluminium, other metals also have coagulating properties and can be used in place of aluminium. The use of these in conjunction with or independently of the use of aluminium, offers several potential advantages associated with the electroflocculation process. Not the least of these is that the aluminium/metal coagulating cation is added without the addition of an anion. This means that the whole process is carried out without any substantial effect upon the salinity of the water. Additionally, the sludge produced by Electrocoagulation is reduced by a factor of 2 or 3 over the use of chemical coagulants (Musquere *et al.*, 1983). Furthermore, experiments suggested that electrolytically added aluminium ions were much more active than chemically added aluminium ions (Donini *et al.*, 1994), meaning that less aluminium was required and that this process could be used to treat a number of different pollutants which could not be handled by chemical flocculants such as alum (aluminium sulphate).

Based upon these and other perceived advantages, considerable development work was undertaken with the objective of determining if the above-mentioned potential advantages could be converted into a practical system.

2.10.5.2 Electrode properties

2.10.5.2.1 Aluminium and its properties

Aluminium has the atomic number of 13 with atomic weight of 26.981; it has a melting point of 923.437 K, density of 2.7 grams per cubic meters and it appears as a solid metal at room temperature. Although aluminium is the most abundant metal in earth's crust it is never found free in nature. All of the earth's aluminium has combined with other elements to form compounds. Two of the most common compounds are alum, such as potassium aluminium sulphate ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), and aluminium oxide (Al_2O_3), about 8.2% of the earth's crust is composed of aluminium (Waterwell, 2005).

Aluminium and its alloys have a high affinity for oxygen. This means that clean, bare aluminium forms an oxide film in a minute when exposed to air. It is difficult to plate onto an oxide film with good adhesion. The normal natural oxide film formed on aluminium helps protect in normal outdoor environments. However, the oxide layer must be removed for good adhesion. This presents a problem when plating aluminium, as the oxide layer prevents the plate from sticking, but fortunately the oxide layer can be chemically removed. Aluminium is difficult to coat with most conventional electroplating and/or conversion coatings because it oxidises rapidly. Also, it acts as a cathode during the coating process, which leaves voids in the coating, causing corrosion. Another issue is that the thermal expansion of aluminium differs from most metal alloys used in plating. This factor causes most conventional plating products to peel, chip and flake (Waterwell, 2005).

The decoration and protection of aluminium and its alloys by the application of the electrodeposits or electroless deposits result in very attractive enhanced properties of the base metal with highly desirable surface attributes. Much effort has been put into the development of an efficient means of plating aluminium. The reasons for aluminium plating can be summarised as followed:

- Formation of an attractive finish,
- Increasing the corrosion resistance,
- Increasing wear resistance,
- Increasing of the surface hardness (electroless nickel), and
- Increasing of the solderability/ brazability.

The low specific gravity of aluminium, whereby approximately three times as many components may be produced from the same weight compared with ferrous or other common base metals, is an important economic factor which makes it well worth investigating the possibility of replacing heavier metal by the light alloys (Waterwell, 2005).

2.10.5.2.2 Iron and its properties

Iron is a chemical element and one of the most important metals in the world. The normal range for iron in freshwater is 0.1-0.5 ppm or mg/L. The accepted USEPA regulatory limit is 300 micrograms/L. If there is too much iron in the water, the water appears rusty. This water

has a metallic taste and it stains fixtures, utensils, and laundry. High concentrations of iron form reddish-brown ferric hydroxide sediments, coatings, and stains. Rust occurs when iron combines with the oxygen in water. A water softener in the home helps with this problem. Despite the problem of rusty drinking and wash water, iron is needed by our body. It helps carry oxygen throughout the body. Iron deficiency in the blood will cause body fatigue. Certain foods provide the human body with the iron that is required (Waterwell, 2005).

Iron is one of the most troublesome minerals encountered in domestic and commercial water supplies. The various forms of iron can leave stains and deposits that range in colour from yellow to brown, but commonly have a "rusty" colour. As organic residue, it may be grey to black, slimy to rock solid. Iron can also impart undesirable odours and tastes to water (Waterwell, 2005).

Iron occurs in many forms in natural water supplies. The most common forms are described as follows:

- **Dissolved Iron**

'Clear water' iron, is the most common form and the one that results in the most complaints by water users. This type of iron is identified after you have poured a glass of cold clear water. If allowed to stand for a few minutes, reddish brown particles will appear in the glass and eventually settle to the bottom (DNR, 2003). Ferrous bicarbonate $[Fe(HCO_3)_2]$ is found only in oxygen-free water. Dissolved iron is measured in parts per million (ppm). One ppm is equivalent to approximately 1/4 ounce of iron in 1 900 gallons of water. The recommended limit of iron in drinking water is 0.3 ppm and will begin staining at 0.5 ppm. Water containing iron can be clear and colourless when drawn. However, upon contact with the air, oxygen is absorbed and reacts with the dissolved iron to form insoluble ferric hydroxide (commonly known as rust). This clouds the water and colours it in shades of yellow to red-brown (Waterwell, 2005).

This reaction produces carbon dioxide as follows



The dissolution of the above carbon dioxide in water also forms carbonic acid. The presence of carbonic acid lowers the pH, and in low alkalinity water (2-3 gpg total solids) this can

cause some corrosion problems in the system. Filtration through a neutralization media is then required to remedy this. The neutralization medium commonly used is composed of calcium carbonate such as limestone or marble (Waterwell, 2005).

Small quantities (less than 0.5 ppm) of ferrous iron, in the absence of dissolved oxygen, may be removed by ion exchange water conditioning. If this method is used, a chemical resin cleaner is required to be added to the brine. This will help remove the exchanged iron and prevent any oxidized iron from fouling the resin bed. Ferrous iron, in higher concentrations, is most commonly removed by a two-step oxidation then filtration process. Chlorine, oxygen, and potassium permanganate are the most common oxidizers used. The filter media is most commonly manganese greensand (Waterwell, 2005).

- **Insoluble Iron**

When insoluble iron, or ‘red water’ iron is poured into a glass, it appears rusty or has a red or yellow colour. Insoluble iron can create serious taste and appearance problems for the water user. Because iron combines with different naturally occurring acids, it may also exist as an organic complex. A combination of acid and iron, or organic iron, can be found in shallow wells and surface water. Although this kind of iron can be colourless, it is usually yellow or brown. Insoluble ferric hydroxide in water produces a red water condition. It is found in some natural waters as a suspension of fine, denser-than-water particles. More often ferric hydroxide, in water, is formed when exposed to oxidizing conditions, like percolating from a spring, or being exposed to air at a water tap (DNR, 2003).

Another source of insoluble iron is from the action of bacteria. When iron exists along with certain kinds of bacteria, problems can become even worse. Iron bacteria consume iron to survive and leave a reddish brown or yellow slime that can clog plumbing and cause an offensive odour. You may notice this slime or sludge in your toilet cistern when you remove the lid. Bacteria can produce ferric hydroxide or iron carbonate as a waste product. Chlorine fed into the well or before the pressure tank will control this type of bacterial nuisance (DNR, 2003).

2.10.6 Possible electrochemical mechanisms

The pH, pollutant type and concentration, the bubble size and position, floc stability and agglomerate size all influence the operation of the electrocoagulation unit. The overall mechanism is a combination of mechanisms functioning synergistically. The dominant mechanism may vary throughout the dynamic process as the reaction progresses. The dominant mechanism will almost certainly shift with changes in operating parameters and pollutant types.

A current is passed through a metal electrode, oxidising the metal (M) to its cation (M^{n+}).



Simultaneously, water is reduced to hydrogen gas and the hydroxyl ion (OH^{-}).



Electrocoagulation thus introduces metal cations electrochemically, using sacrificial anodes (usually aluminium or iron). The cation hydrolyses in water forming a hydroxide with the dominant species determined by solution pH. Equations 2.33 – 2.36 illustrate this in the case of aluminium:



Highly charged cations destabilize any colloidal particles by the formation of polyvalent polyhydroxide complexes. These complexes have high adsorption properties, forming aggregates with pollutants.

Evolution of hydrogen gas aids in mixing and hence flocculation. Once the floc is generated, the electrolytic gas creates a flotation effect removing the pollutants to the floc - foam layer at the liquid surface.

According to Paunovic and Schlesinger (1998), the deposition reaction involves four types of issues. They are:

- Metal-solution interface as a locus of the deposition process,
- Kinetics and mechanism of the deposition process,
- Nucleation and growth process of metallic lattice (M lattice), and
- Structure and properties of the deposits.

The reduction of a metal, which occurs during the electrochemical deposition process, has been generalised as Equation 1 for a single metallic ion. Obviously, to reduce one mole of a given metal n moles of electrons are required. That is, the total cathodic charge used in the deposition Q (Coulomb) is the product of the number of gram moles of the metal deposited n , the number of electrons taking part in the reduction n_e , Advogadro's number N_a (the number of atoms in a mole), and electrical charge per electron Q_e (coulomb). Thus, the following equation gives the charge required to reduce m mole of metal:

$$Q = n \cdot n_e \cdot N_a \cdot Q_e \quad \dots\dots\dots(2.37)$$

Now, the product of the last two terms in this equation is the Faraday constant F . Therefore, the number of moles of metal reduced by charge Q can be obtained as:

$$n = \frac{Q}{n_e \cdot F} \quad \dots\dots\dots(2.38)$$

on the other hand, the total charge used in the deposition can be obtained as the product of the current I (Ampere) and the time of the deposition t (second) if the deposition current is held constant. Or, if the current varies during the deposition:

$$Q = \int I \cdot dt \quad \dots\dots\dots(2.39)$$

So, the number of moles deposited can be calculated as:

$$n = \frac{1}{n_e \cdot F} \int I \cdot dt \quad \dots\dots\dots(2.40)$$

There are a variety of ways in which species can interact in solution:

- Migration to an oppositely charged electrode (electrophoresis) and aggregation due to charge neutralisation,
- The cation or hydroxyl ion (OH^-) forms a precipitate with the pollutant,
- The metallic cation interacts with OH^- to form a hydroxide, which has high adsorption properties thus bonding to the pollutant (bridge coagulation),
- The hydroxides form larger lattice-like structures and sweep through the water (sweep coagulation),
- Oxidation of pollutants to less toxic species, and
- Removal by electro-flotation and adhesion to bubbles.

The inherent complexity of the process makes it difficult to model and control. Adequate scale-up parameters, a systematic approach to the optimisation and a priori prediction for the performance of the electrocoagulation reactor are yet to be established. The literature reveals that previously each new system has been considered on an individual basis. There has been little or no attempt to provide a holistic approach to electrocoagulation. In order to understand the mechanisms behind electrocoagulation, and thus control the system better, a holistic approach is required.

2.11 Chemical Issues

The control, operation, and chemical interactions of the system affect performance and reliability. Adding to complexity, the chemical interactions of the pollutants (type and concentration) with the electrode material, electrode passivation, and operational region should also be considered. This literature survey has not revealed a systematic approach to these issues.

2.11.1 Electrode material

The anode material determines the cation introduced into the solution. Several researchers have studied the choice of electrode material with a variety of theories as to the preference of a particular material. The most common electrodes were aluminium or iron plates as described by Holt *et al.* (1999).

Holt *et al.* (1999) compare the performance of iron and aluminium electrodes for removing colour from dye-containing solutions. Their conclusion was that the optimal electrocoagulation conditions varied with the choice of iron or aluminium electrodes, which in turn is determined by:

- Initial pollutant concentration,
- Pollutant type, and
- Stirring rate.

One group (Holt *et al.*, 1999) investigated the relationship between ‘size’ of the cation introduced and removal efficiency of organic waste. The size of the cation produced (10-30µm for Fe³⁺ compared to 0.05-1 µm for Al³⁺) was suggested to contribute to the higher efficiency of iron electrodes.

2.11.2 Electrode passivation

One of the greatest operational issues with electrocoagulation is electrode passivation. The passivation of electrodes is a concern for the longevity of the process. Passivation of aluminium electrodes has been widely observed in the literature (Holt *et al.*, 1999). The latter also observed that during electrocoagulation with iron electrodes, deposits of calcium carbonate and magnesium hydroxide were formed at the cathode and an oxide layer was formed at the anode. Holt *et al.* (1999) investigated various methods of preventing and/or controlling electrode passivation including:

- Changing polarity of the electrode,
- Hydro mechanical cleaning,
- Introducing inhibiting agents,
- Mechanical cleaning of the electrodes.

According to these researchers, the most efficient and reliable method of electrode maintenance was to periodically mechanically clean the electrodes which for large-scale, continuous processes is a non-trivial issue.

2.11.3 Solution pH

Solution pH determines the speciation of metal ions. The pH influences the state of other species in solution and the solubility of products formed. Thus, solution pH influences the overall efficiency and effectiveness of electrocoagulation. The pH of the solution can easily be altered. An optimal pH seems to exist for a given pollutant, with optimal pH values ranging from 6.5 to 7.5.

Chapter 3: Experimental Procedure

3.1 Introduction

All experiments were carried out at the Vaal University of Technology and where required, verifications were made. The experiments were performed on a bench scale. The investigation procedure involved a modification of glass beaker used as a reactor consisting of apparatus that included the electrode assembly and the auxiliary power supply.

The experimental procedure follows a simple electrolysis principle whereby electrodes are placed in river water. The electrodes are connected and supplied with power to complete an electrochemical cell. To determine the rate of dissolution of electrodes, during the course of the experiments the electrodes were weighed. The theoretical amount of metal dissolved (calculated using Faraday's equation for electrode dissolution) was compared with the weighed values of electrode dissolved. Aluminium and iron cations undergo hydration reactions in aqueous systems to an extent governed by the properties of the cation, the metal ion concentration and the $[H^+]$ concentrations. That is the "naked" metal ions do not exist in water, but occur as aqua complexes of varying degrees.

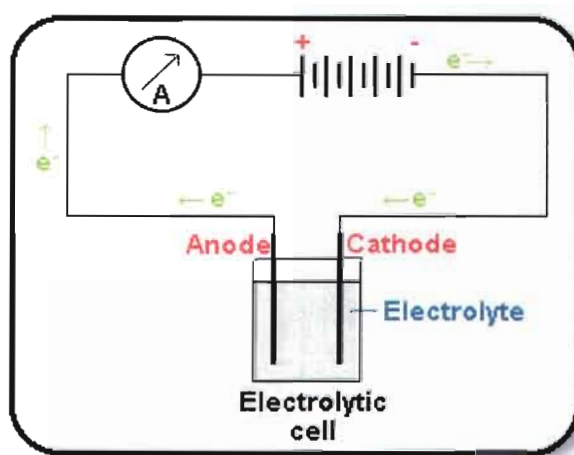


Figure 3.1: Electrolytic cell representing an experimental setup (Delpierre and Sewell, 2002)

The river water treated by the electroflocculation process during this project was purely natural and no simulation of river water specifications was made. Distilled water was only

used for cleaning of apparatus, for calibration and standardisation of analytical instruments. No chemicals were used for pH or any other operating parameter adjustment. All experiments were duplicated to validate the results. During the optimisation stage continuous agitation was used to investigate the effect.

Initially the parameters (iron, aluminium, pH, colour, conductivity, turbidity, solids (TDS and SS), as well as phosphates) were measured and compared against the guidelines as determined at the Engelbreghts weir reported in Chapter 2 on page 13, Figure 2.1. For electrolysis to exist, raw water (Vaal River water) was poured into a beaker; pre-weighed electrodes were immersed into the beaker (approximately 75% of the electrode depth was immersed). The equipment for variable measurement was immersed in the water in the reactor unless otherwise stated in which case representative samples were withdrawn from the mother solution for analysis at set time intervals. The inverter regulated the alternating current. Alternating current makes “self-cleansing” of the electrodes possible and provides favourable energy consumption during the electrolysis. The electrochemical reaction was allowed to proceed for a predetermined time. During the experiment iron, aluminium, pH, colour, conductivity, turbidity, solids (TDS and SS), and phosphates results were recorded against time. Changes observed are reported in the Chapter 4 and also in the Appendix A.

In order to alternate between the anode and cathode, a reverse-polarity switch was used. The switch reverses the direction of the current to alternate between the cathode and the anode as necessary. This was done every five minutes to allow the electrodes to corrode equally and to prevent the formation of a passive layer on the electrodes.

3.2 Operating Variables

Controlled variables include current passing through the circuit and the stirring rate (in some experiments agitation was not employed to test and check the influence). The DC power supply, model PS-305D was used to supply the direct current to the solution. The current was kept constant at a fixed value while the voltage was adjusted accordingly to keep the current at a given set value. The sample was stirred continuously using a magnetic stirrer in order to give an even distribution of ions in the solution for pH measurements. Where

agitation was employed the stirring rate was kept constant at 700 revolutions per minutes (the effect of variable agitation speed was not evaluated for this experimentation).

The measured variables in the treated water were iron, aluminium, pH, colour, conductivity, turbidity, solids (TDS), and phosphates. Procedures for analytical methods and operation of the analytical test instrument are summarised in Section 3.6.

3.3 Apparatus

Electrolysis involves passing an electric current through an ionic solution to ensure that ions are ‘forced’ to undergo either oxidation (at the anode) or reduction (at the cathode). For this electrochemical process, apparatus is needed to perform or fulfil this experiment. Figure 3.2 shows a photograph illustrating how the apparatus is setup for experimentation.

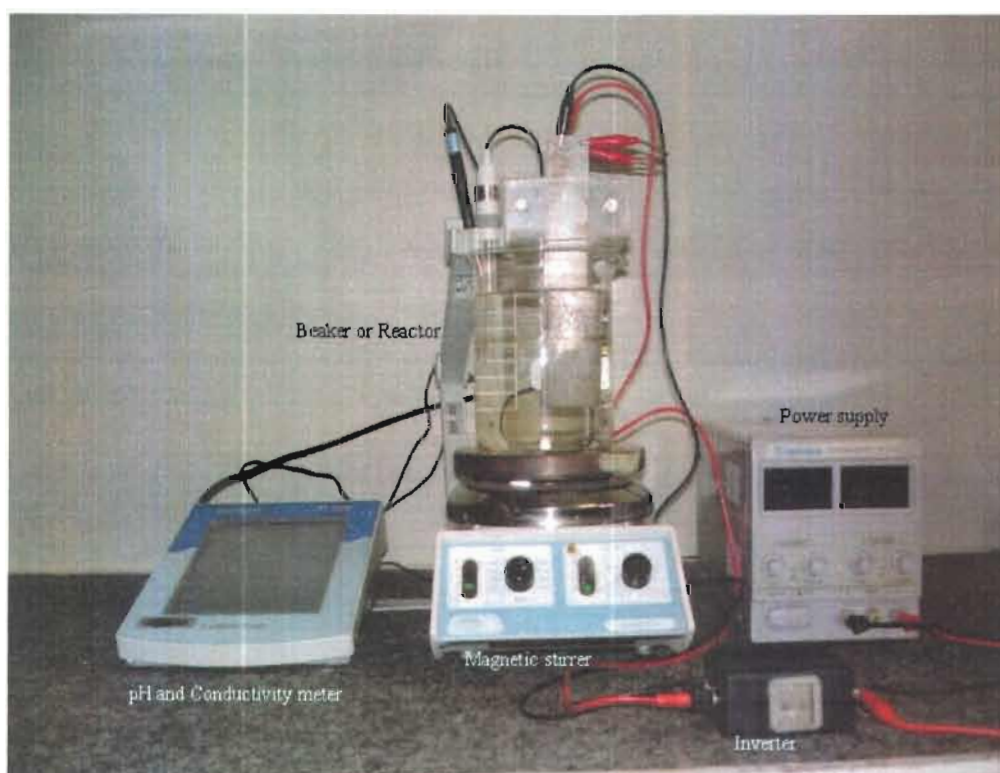


Figure 3.2: The experimental setup

List of apparatus, equipment, instruments and materials used for experiments

The apparatus as shown in Figure 3.2 includes the following:

- Aluminium electrodes
- Iron electrodes
- Electrodes holder
- Magnetic stirrer
- River water (as electrolyte)
- Glass beakers
- Volumetric cylinder
- Auxiliary Power supply with Ammeter, Voltmeter and power connecting cables – Model PS-305D
- Inverter - Reverse polarity switch
- Bench top weighing scale
- Conductivity meter
- pH meter - Cyberscan 5000
- DR 2000 spectrometer
- Varian Spectr AA-10 atomic absorption spectrometer

3.4 Cell Design

The cell design will affect all the figures of merit for an electrolytic process and as a result several factors had to be considered when designing the electrochemical cell. These considerations included simplicity (the cell design should meet the process requirement in the simplest way); in that way the following simple specifications were set to suit the design:

- Electrode materials: iron and aluminium
- Number of electrodes used per reaction cell = 2
- Distance between electrodes = 3 cm
- Electrode thickness = 1.5 mm
- Length of electrodes = 20 cm
- Breadth of electrode = 2.5 cm
- Length of electrode submerged = 15 cm

- Area submerged per electrode = 0.0077625 m^2 (77.625 cm^2)
- Reactor volume = 1000 mL (1 Litre)
- Stirring rate = 700 revolutions per minute (rpm)



Figure 3.3: The electrochemical cell

3.5 Experimental Procedure

The glassware was washed with ten percent hydrochloric acid and rinsed with distilled water before the experimentation commenced. For re-use of electrodes, used electrodes were first washed with ten percent hydrochloric acid, rinsed with distilled water and left to dry off. Then the following generic step-by-step procedure was followed for each test:

- Weigh electrodes before commencing with experiments
- Measure and analyse raw water before commencing with experiments (ensure instruments are working well and are calibrated)
- Pour a measured amount of raw water into the beaker
- Clamp the metal electrodes into the electrode holder – the configuration should be the same as indicated in Section 3.4 Cell Design
- Immerse the electrodes into the water in the beaker
- Connect the power cables from the power source to the electrodes

- Set the timer for alternating the current through the circuit
- Switch on the power supply and recorder
- Record initial current flow and voltage
- Measure pH, turbidity, conductivity, TDS, colour, metal (iron and/or aluminium) concentration, and phosphates at specified time intervals
- Take and filter samples to perform analytical tests
- Monitor the change and record observations

3.6 Analytical Procedures

3.6.1 Operation procedure for Atomic absorption spectrometer

This method describes the safety precautions, controls and operating instructions for the Atomic absorption spectrophotometer Spectr AA-10.

3.6.1.1 Safety practices

A - Exhaust system:

- Fumes (some exhaust gases are toxic) and heat produced by the flame must be extracted by means of an exhaust system.
- Equip the blower with a pilot light located near the instrument to indicate when the blower is on, or use some other device for this purpose

B - Cylinders:

- Compressed gases should be stored and handled strictly in accordance with relevant safety codes.
- Fasten all cylinders securely to an immovable structure or a permanent wall.
- Store, or move cylinders in a vertical position only.
- The area in which cylinders are stored must be adequately ventilated to prevent toxic or explosive accumulations.
- Always locate cylinders away from heat or ignition sources. Cylinders have pressure relief devices which will release the contents of the cylinder if the temperature exceeds 52 °C.
- Always ensure that you have the right cylinder before connecting the cylinder to the instrument.

- Use only approved regulators and hose connectors. Remember that left-hand thread fittings are used for fuel connections; right-hand fittings are used for support gas connections.

C - Precaution with acetylene:

- Since acetylene is a flammable gas proper precautions should be taken when using it.
- Never run acetylene at a pressure higher than 105 kPa. At pressures above this level acetylene can explode spontaneously. Include a flash arrestor in the line.
- Never pass acetylene through copper tubing or brass tubing containing more than 65% copper since this may provoke explosion. Do not use any tubing which reacts chemically with acetylene.
- Never bring acetylene into direct contact with silver, liquid mercury, or gaseous chlorine.

D - General precautions:

- Perform leak tests every month by applying a soap solution to all joints and seals.
- Arrange gas hoses so that they will not be damaged, stepped on, or have things dropped on them. Inspect all hoses regularly.
- A drainage tube must be connected to the drain outlet on the liquid trap and led to a suitable waste vessel.
- Never attempt to light a burner unless the liquid trap is full. The standard liquid trap supplied is for use with aqueous solutions. A vent tube must be connected to the vapour vent on the liquid trap and led to a location where vapours may be safely discharged when vapours are toxic.
- Never view the flame or hollow cathode lamp directly. Always use protective eyewear – preferably with side shields. (Hazardous ultra-violet radiation is emitted by flames and hollow cathode lamps).
- Do not leave a flame unattended.

E - Burners:

- Burners are clearly identified by the fuel / oxidant combination for which they are intended. Always fit the correct burner. Never attempt to use an air-acetylene burner for nitrous oxide-acetylene.

- Whenever you change burners remember that the burner you have just used may be very hot. Always use protective gloves unless you are absolutely sure that the burner is cool enough to handle safely without gloves.
- Always operate with the flame shield closed and the sample compartment front panel in place.

F - Lighting a flame:

- Follow instructions provided (section 3.6.1.6). Turn the gases on and off in the right order.
- At the end of the day close off the acetylene supply at the cylinder.

3.6.1.2 Apparatus and gases

- Cylinder of acetylene
- Cylinder of air or compressed air.
- Regulators for the gases.

3.6.1.3 Summary of practice

- In flame atomic absorption spectrophotometry, a standard or sample solution is aspirated as a fine mist into a flame where it is converted to an atomic vapour consisting of ground state atoms. The flame provides energy to the ground state atoms allowing them to absorb electromagnetic radiation from a series of very narrow sharply defined wavelengths. Light from a hollow cathode lamp or other source consisting of the characteristic monochromatic radiation generated by excitation of the element of interest is passed through the flame. Light from the source beam is isolated by the monochromator and measured by the photodetector. The amount of light absorbed by the analyte is quantified by comparing the light transmitted through the flame during nebulisation of a known concentration of the analyte to light transmitted during nebulisation of a solution that does not contain any measurable concentration of the analyte.
- An atomic absorption spectrophotometer may have single or double system. The spectr AA-10 has a single beam system. The amount of light absorbed in the flame is proportional to the concentration of the element in solution.

- Calibration - The atomic absorption spectrophotometer is calibrated with standard solutions containing a known concentration of the element of interest. A calibration curve is constructed for each analyte from which the concentration in the unknown sample is determined.

3.6.1.5 Flame type

- Air-acetylene

For most elements the flame should be oxidising (non-luminous with a hazy blue inner cone). For some metals, particularly chromium, molybdenum and tin, a reducing flame (white, luminous) is required. The best flame condition may be found for each element by adjusting the gas flows and burner position until maximum absorbance is obtained while aspirating a standard solution known to give about 0,4 absorbance.

- Nitrous oxide-acetylene

This flame allows the determination of many refractory elements which cannot be determined in the cooler air-acetylene flame. It also provides better sensitivity and greater freedom from interference than air-acetylene for a number of elements, notably barium, calcium, chromium, molybdenum, strontium and tin. Flame composition and burner position is more critical, and small departures from optimum may cause severe loss in sensitivity.

Generally, a slight fuel-rich flame is required with a red zone approximately 2 cm high. A number of metals are appreciably ionised in the nitrous oxide acetylene flame but this interference can be countered by adding excess of potassium or caesium to the analytical solution (1000 – 2000 μg K or Cs per ml).

3.6.1.6 Lighting instructions

- Gas supply pressure

Set gas supply regulators to the following pressures:

Table 3.1: AAS Gas supply pressure ranges

	Recommended	Permissible range
	kPa	kPa
Acetylene	63	49 – 105
Air	350	245 – 455
Nitrous oxide	350	245 – 455

Once the flame is on, the regulator setting should be checked and re-adjusted if necessary.

3.6.2 Operation procedure for DR 2000 spectrometer

3.6.2.1 Platinum-Cobalt standard Method 8025 – Colour detection

Colour may be expressed as “apparent” or “true” colour. The apparent colour includes that from dissolved materials plus that from suspended matter. By filtering or centrifuging out suspended materials, true colour can be determined. The procedure describes true colour analysis. If apparent colour is desired, it can be determined by measuring the unfiltered water sample. The stored program is used for both forms of colour. The stored program is calibrated in colour units based on the APHA – recommended standard of 1 colour unit being equal to 1 mg/L platinum as chloroplatinate ion.

Collect samples in clean plastic or glass bottles. Most reliable results are obtained when samples are analysed as soon as possible after collection. If prompt analysis is impossible, fill bottles completely and cap tightly. Avoid excessive agitation or prolonged contact with air. Samples can be stored for 24 hours by cooling to 4 °C. Warm to room temperature before running the test.

Step by step procedure

- Assemble the filtering apparatus (filter, filter holder, filter flask and aspirator)
- Rinse the filter with 50 mL of demineralised water and discard the rinse water
- Pour another 50 mL demineralised water through the filter
- Fill a sample cell (the blank) with 25 mL of filtered demineralised water and discard excess
- Enter the stored program number for true colour. Press: **120 READ/ENTER**. The display will show **DIAL nm TO 455**
- Rotate the wavelength dial until the small display shows **455 nm**
- Press: **READ/ENTER**. The display will show **UNIT PtCo COLOUR**
- Pour 50 mL of sample through the filter
- Fill a second sample cell (the prepared sample) with 25 mL of filtered sample
- Place the blank into the cell holder and close the light shield
- Press: **ZERO**. The display will show: **WAIT** then **0. UNIT PtCo COLOUR**
- Place the prepared sample into a cell holder. Close the light shield and press: **READ/ENTER**. The display will show **WAIT** and then the results in platinum cobalt units will be displayed

3.6.2.2 Acid Persulfate Digestion Method 8190 – Phosphate detection

Phosphates present in organic and condensed inorganic form (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analysis. Pre-treatment of samples with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates are converted to orthophosphate by heating with acid and persulphate. Organically bound phosphates are thus determined indirectly by subtracting the results of an acid hydrolysable phosphorus test from the total phosphorus results.

This procedure must be followed by one of the reactive phosphorus (orthophosphate) analyses for the determination of phosphorus content of the sample. If the ascorbic acid (PhosVer 3) method is used to measure the reactive phosphorus, this method is USEPA approved for NPDES reporting.

Most reliable results are obtained when samples are analysed immediately. If prompt analysis is not possible, samples may be preserved for up to 24 hours by cooling to 4 °C. Warm to room temperature before testing.

Step by step procedure

- Enter the stored program number for reactive phosphorus-vial. Press: **535 READ/ENTER** for mg/L PO_4^{3-} . The display will show **DIAL nm TO 890**
- Rotate the wavelength dial until the small display shows **890 nm**
- Press: **READ/ENTER**. The display will show **mg/L PO_4^{3-} - Vial**
- Fill a Test 'N Tube Cuvette Vial with 5 mL of sample (run a reagent blank for this test. Use demineralised water in place of the sample; subtract this result from all the test results run with this batch of PhosVer.)
- Add 2 mL of 1.00 N sulphuric acid to the sample vial
- Using a funnel, add the contents of one Potassium Persulfate powder pillow for phosphonate to the vial
- Cap tightly and shake to mix
- Heat the sample vials for 30 minutes

- Remove vials and place in test tube rack and allow to cool to room temperature
- Remove caps from vials
- Add 2 mL of 1.00 N sodium hydroxide to each of the vials and wipe off any sodium hydroxide on the cap or threads
- Cap tightly and shake to mix
- Place the COD vial adapter into the cell holder with the marker to the right
- Clean the outside of the vial with the towel. (Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.)
- Place a sample in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.
- Press: **ZERO**. The display will show **0.00 mg/L PO₄³⁻ - Vial** (for multiple samples, zero on the first sample and record the blank value. Subtract the blank value from each sample value.)
- Remove the cap and using a funnel add the contents of one PhosVer 3 Phosphate reagent powder pillow for 10 mL samples powder pillow to the vial
- Cap tightly and shake to mix
- Press: **SHIFT TIMER**. A 10 minutes waiting period will begin
- After the timer beeps, clean the outside of the sample vial with a towel
- Place the prepared sample vial into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter
- Press: **READ/ENTER**. The display will show **WAIT** and then the results in mg/L PO₄³⁻ will be displayed

Chapter 4: Results and Discussions

4.1 Introduction

The results for the investigation of electroflocculation of river water are presented in this chapter. Iron and aluminium electrodes were ionised and dissolved into Vaal River water in an electric circuit for this investigational work (see Chapter 3). A number of laboratory experiments were carried out to determine the effect of the different parameters on electrochemical mechanism and to test whether the research – electroflocculation of river water could be a competitive method for river water treatment. The following will be reported on: The effect of continuous agitation as well as the effect of energy charged on the parameters (iron, aluminium, pH, colour, conductivity, turbidity, solids, and phosphates) in the river water. The efficiency of the electroflocculation treatment could therefore be calculated by comparing the theoretical amount of metal dissolved in water with the actual amount or concentration in treated water.

4.2 Effect of Continuous Agitation on River Water Treatment

Mixing is an important operation in any water purification process. It facilitates dispersion and homogenisation of added reagents with water and contacts between the particles leading to their combining into readily separable flocs. The efficiency of the water purification process is, therefore, dependent on the mixing conditions under which the formation of flocculent suspension takes place. The reasons are that the importance of the mixing intensity, its duration and flow characteristics on the properties of formed flocs such as their shape, size and compactness (density), are not yet fully appreciated and/or understood in engineering practice (Polasek, 2007).

According to Polasek (2007), the term mixing is confusing because it is used to describe transport mechanisms for both flash mixing (reagent dispersion and homogenisation with water mixing) and agitation (flocculation mixing) because each of these mechanisms requires different flow characteristics in order to take place with maximum efficiency. Whereas flash mixing should take place under conditions of mixing on macro-scale with

macro-turbulent eddies being formed, agitation should take place under conditions of mixing under micro-scale with micro-turbulent eddies being formed, resulting partial volumes of water being transferred over short a distance. Agitation takes place under high- or low-intensity agitation. Only the conditions of agitation can be characterised by velocity gradient, and uniform distribution of a velocity field throughout the volume of agitated water is produced.

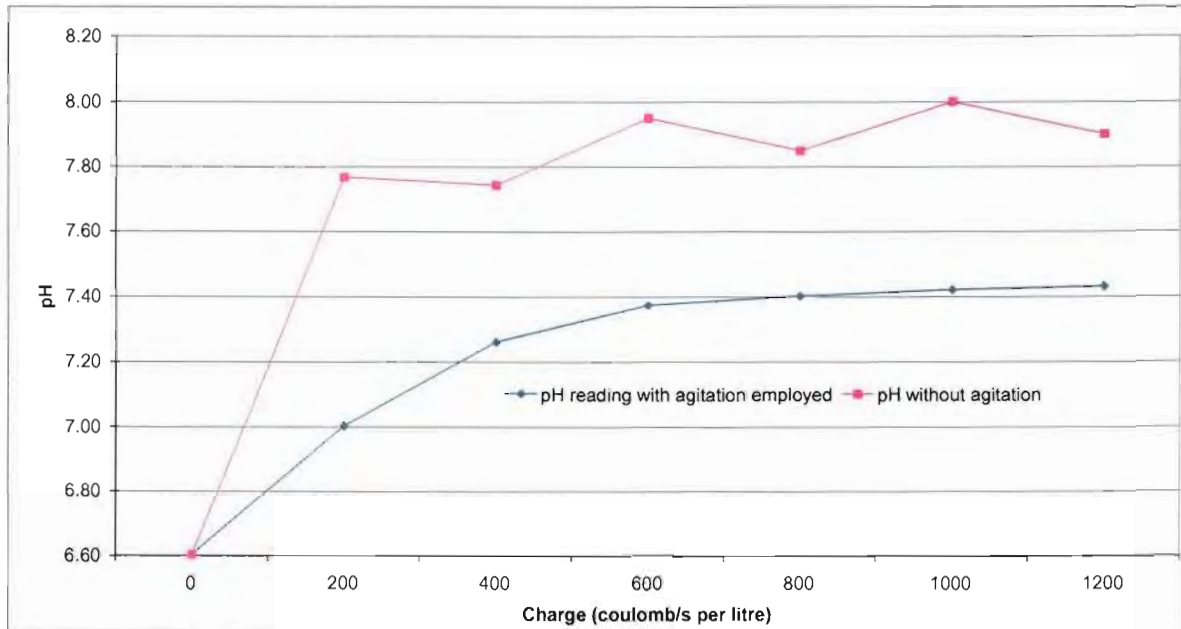


Figure 4.1: Effect of agitation on pH during electroflocculation of iron electrode

Results show a smooth exponential inclination of pH when agitation is employed during electroflocculation of river water whereas pH fluctuation was encountered when the water treatment is performed without agitation (Figure 4.1). Maximum removal of phosphate was also achieved when agitation is employed (Figure 4.2 overleaf). There were no significance changes or comparability in colour and turbidity results. Observations indicate that floc growth can be hastened by agitation.

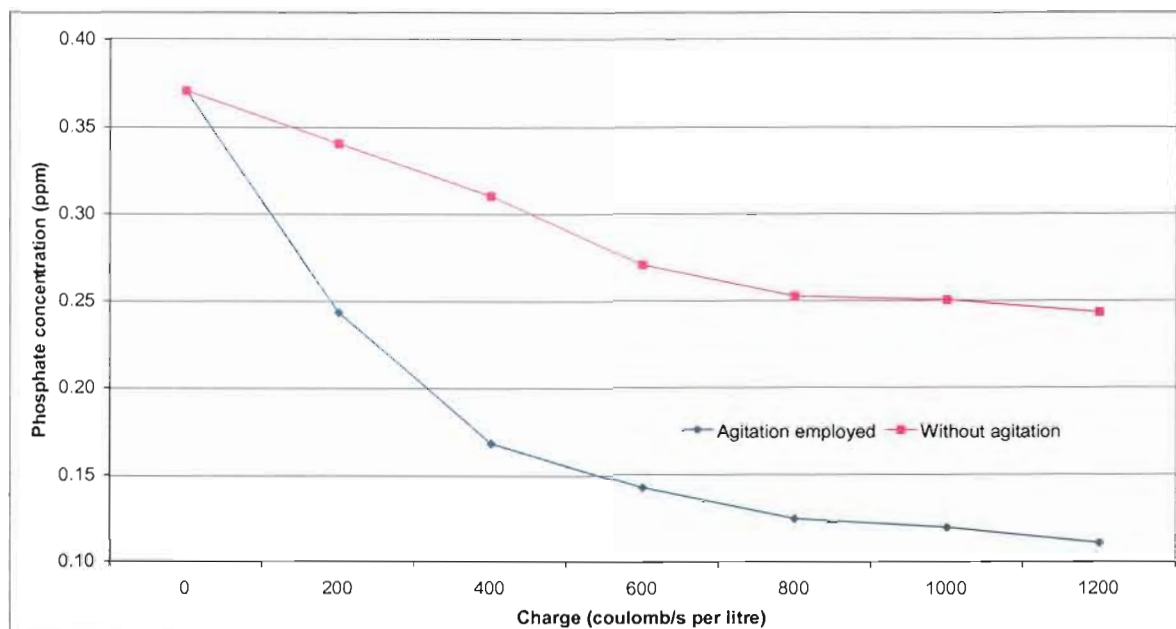


Figure 4.2: Effect of agitation on phosphate removal during electroflocculation of iron electrode

4.3 The Electrochemical Treatment of River Water using Iron Electrodes

During experimentation it was not clear as to which form iron will oxidised and hence after the data analysis it was indicated throughout the entire investigations that pH was always above pH6. Iron oxidation (see 2.9.2.2 Iron Oxidation on page 40 in Literature survey) explains the non-existence of iron (III) species formation under such conditions. It also indicates the predominant area for iron (II) species as it narrows with an increasing pH as illustrated in Figure 2.6 to Figure 2.8.

The river water treatment by electrochemistry is highly reliant on the pH of the solution which affects the surface charge of the electrodes, the degree of ionisation, current transfer and the speciation of the electrode species. The electrochemical behaviour of the iron ion was studied in aqueous solutions of different pH values using different dosing rates of ions and a fixed/constant amount of phosphate concentration in the solution. The results obtained are presented in Figures 4.3 to 4.9. It was observed that the maximum removal of phosphates was achieved at pH levels between 6.5 and 7.0, whilst less phosphate was removed with further increase in pH.

4.3.1 The effect of energy charged on iron dissolution

The theoretical amount of iron utilised is directly proportional to the amount of energy (expressed as charge). Trial experimentations have been conducted and charges exceeding 100 Coulombs per litre have been utilised. The initial optimisation was aimed to reduce power consumption to below 20 Coulombs charge per litre which was calculated theoretically (this is equivalent to 10 mg/L stoichiometric calculation of ferric chloride dosage in chemical treatment). In terms of mass representation the consumption of iron metal was projected theoretically to 3.443 mg per litre of water to be treated and 4.245 mg was achieved.

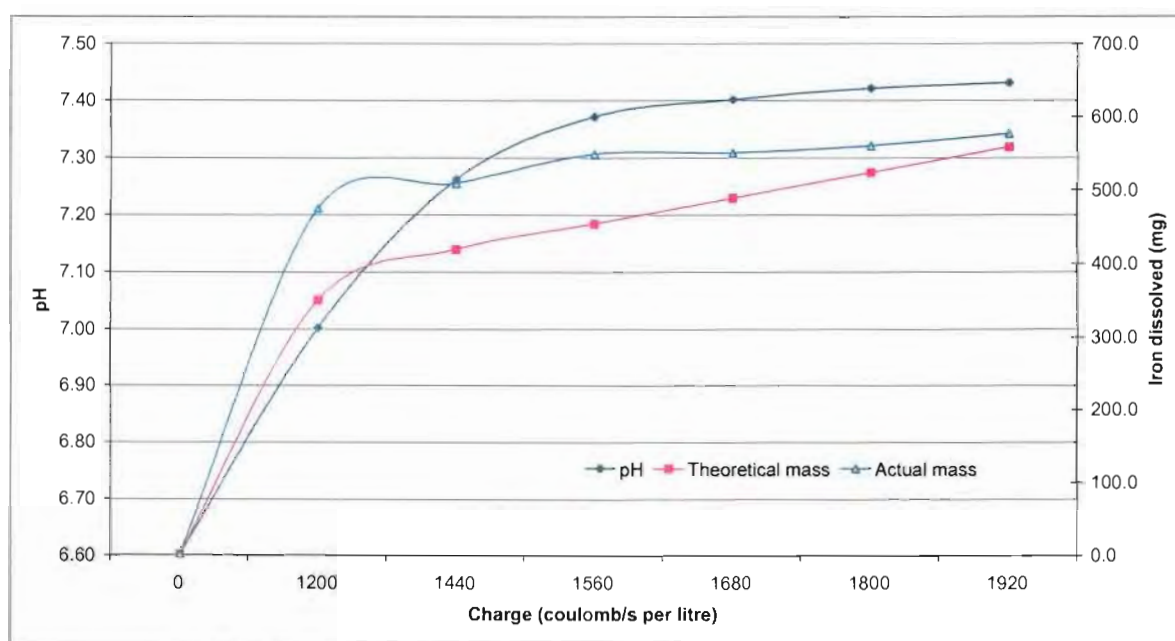


Figure 4.3: The effect of energy charged on the dissolution of iron (theoretical and practical) and the pH of the solution

The result above indicates near pH equilibrium at pH 7.4 where an energy consumption reached about 1680 Coulombs per litre. The comparison between the theoretical and measured iron dissolved shows huge distinction during the run but an overall error of about 3% was recorded at the end of the experimentation. The theoretical iron dissolution is represented by a linear expression (between 1200 to 1920 coulombs per litre) whereas the practical or actual measurement is not clearly defined.

4.3.2 The effect of energy charged on the water colour dissolution

Using an iron electrode as coagulant in water treatment resulted in a slight residual colour in treated river water, this was also observed in case of ferric chemical treatment (i.e. ferric chloride, ferric sulphate monohydrate). Figure 4.4 also indicates that as iron concentration in the water increased to an equivalent energy charge of 1440 Coulombs per litre, the colour improves and further increases in iron dosing then impact the colour negatively. This marginal change indicates the extent to which further experimentation for optimisation purposes could be employed.

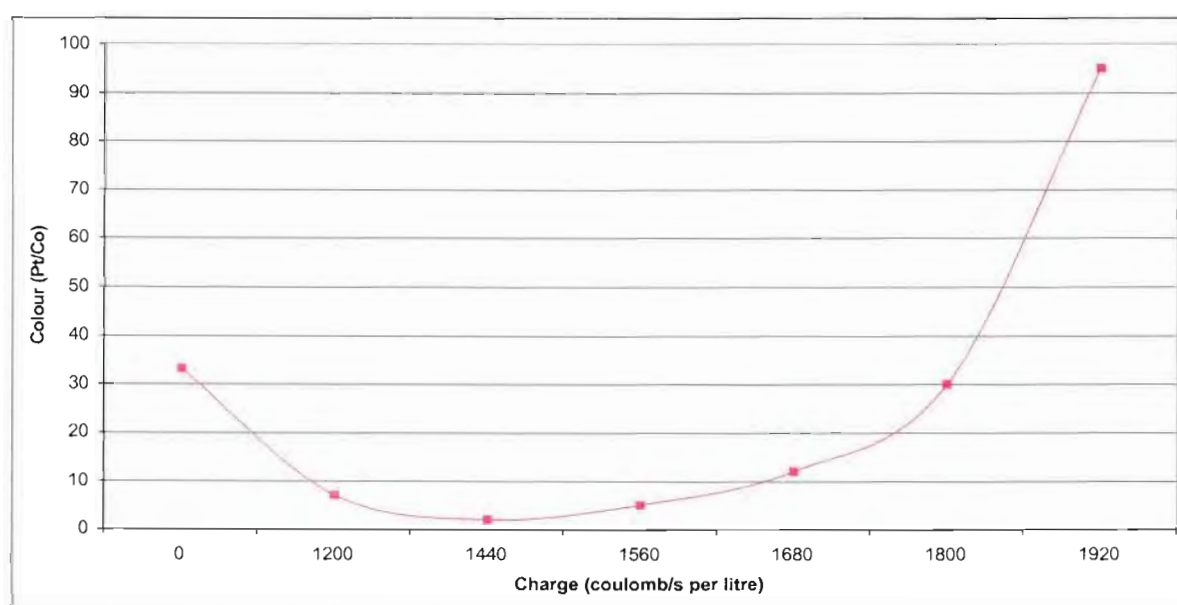


Figure 4.4: The effect of energy charged on the colour of the solution using iron electrodes

4.3.3 The effect of energy charged on conductivity

Electrical conductivity is measured in microSiemens/centimetre ($\mu\text{S}/\text{cm}$). A microSiemen is the same as a microhm. Conductivity of a water sample is a measure of its ability to carry an electric current. The more impurities (total dissolved solids) in water, particularly salts, the greater its electrical conductivity. By measuring the conductivity of a water sample, the amount of total dissolved solids in the sample can be determined. To convert the electrical conductivity ($\mu\text{S}/\text{cm}$) of a water sample to the concentration of total dissolved solids (ppm) in the sample, the conductivity must be multiplied by a factor of between 0.54 and 0.96 for

natural waters. The value of this factor depends upon the type of dissolved solids. A widely accepted value to use when determining this type of dissolved solids is 0.67.

$$\text{TDS (ppm)} = \text{Conductivity } (\mu\text{S/cm}) \times 0.67$$

An increased dosing of iron in river water seems to be constantly improving the electric conductance of water. Figure 4.5 illustrates the coordination of this effect, whereby six sets of the test were performed at different charging rates, as a result of which it has been observed that the higher the charge, the lower the conductance will be.

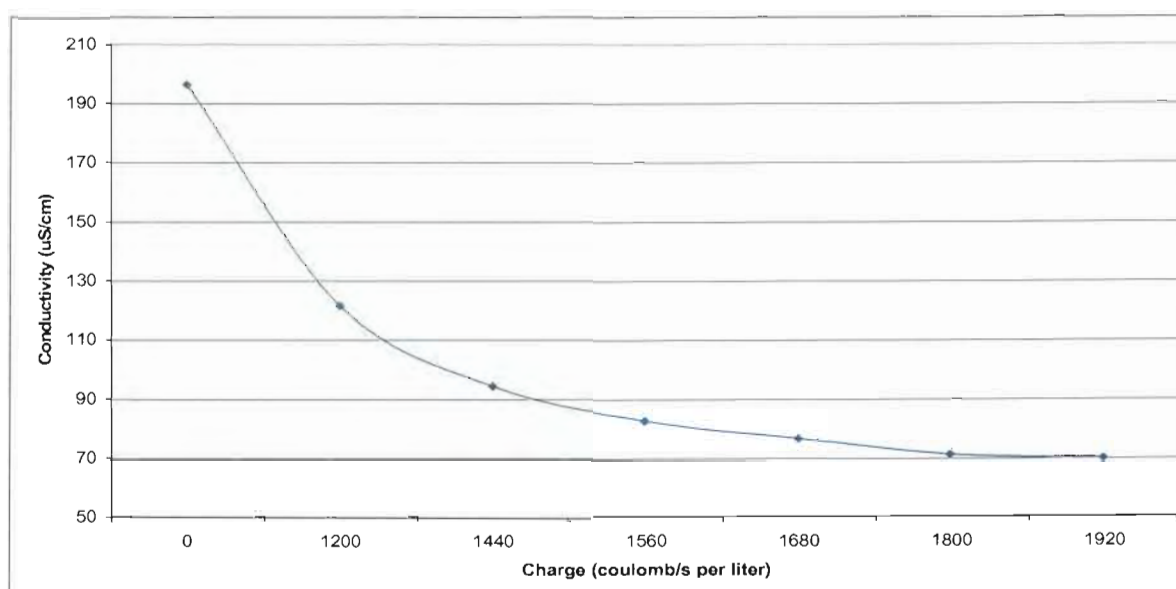


Figure 4.5: The effect of energy charged on the solution conductivity using iron electrodes

4.3.4 The effect of energy charged on turbidity

A successful application of iron (ferric ion) in water treatment was also indicated in Figure 4.6 by reducing the turbidity of river water to an average of 0.44 NTU. During this period in question the raw water turbidity varied from 60 to 40 NTU. This variation is indicated with different dosage rates of ferrous ion in river water. The results are presented in terms of dosage rate in milligram per litre and not as charge as in the previous result.

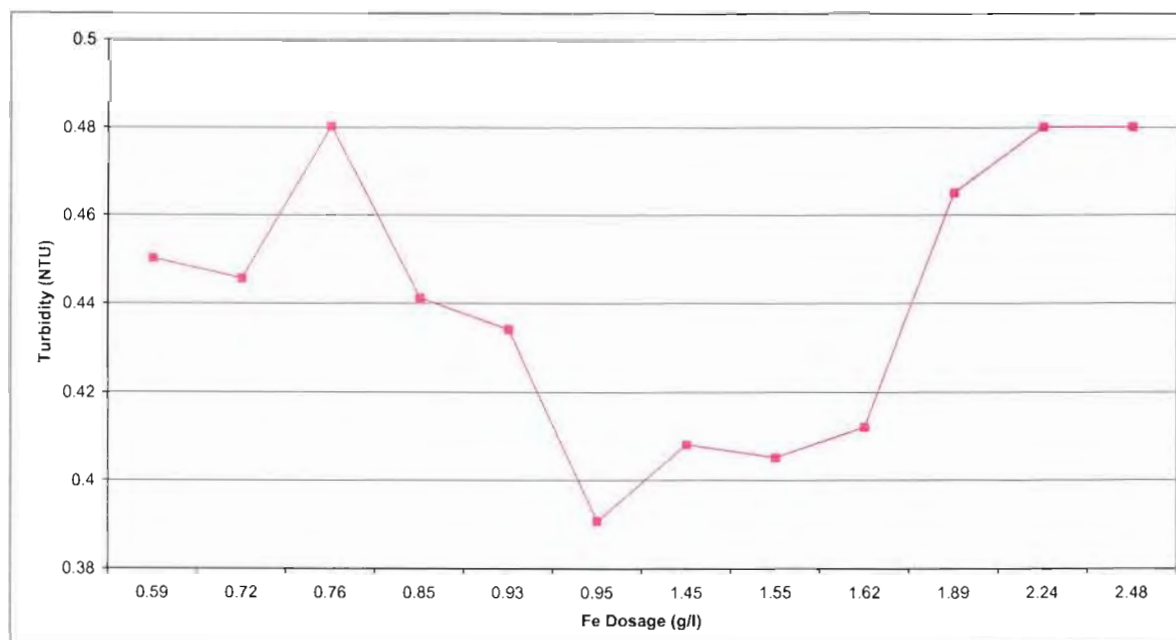


Figure 4.6: The effect of energy charged (represented by dosing rate) on the solution turbidity using iron electrodes

4.3.5 The effect of energy charged on total dissolved solids

Similarly to the conductivity as indicated in sub section 4.3.3, an increased dosing of iron in river water seems to be constantly decreasing the amount of dissolved solids in water. Figure 4.7 overleaf illustrates the coordination of this effect, whereby six sets of tests were performed at different charging rates and it has been observed that the higher the charge, the lower the amount of solids left in the water.

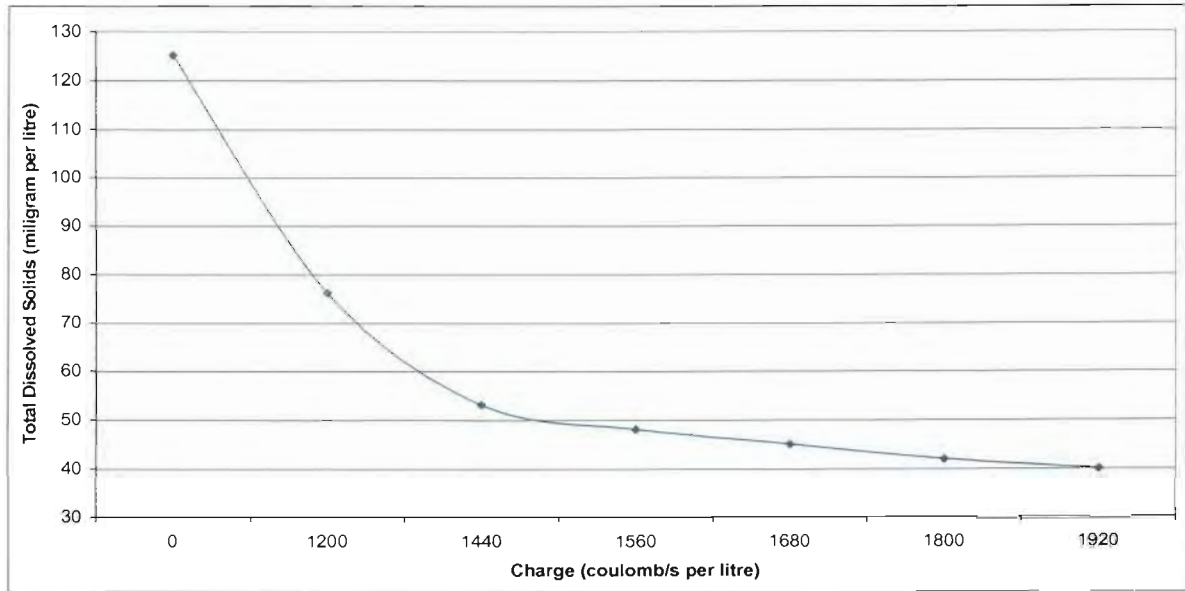


Figure 4.7: The effect of energy charged on the solution total dissolved solids using iron electrodes

4.3.6 The effect of energy charged on phosphate concentration

The iron treatment process reduced the phosphates concentration by up to 75% of the initial concentration. This is illustrated in Figure 4.8 overleaf where 0.36 ppm was lowered to 0.09 ppm with the total energy consumption of about 18720 Coulomb used for every one litre of the water treated.

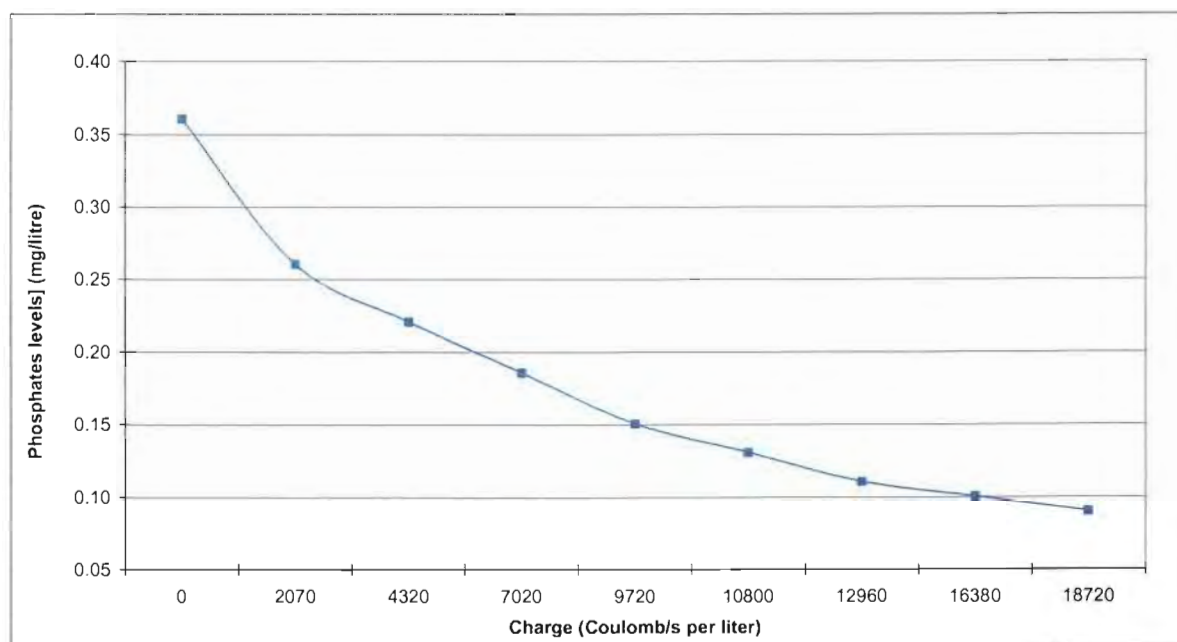


Figure 4.8: The effect of energy charged on the phosphate concentration using iron electrodes

4.4 The Electrochemical Treatment of River Water using Aluminium Electrodes

This method of treatment leaves no residual colour on treated river water. The drawback is the fact that it requires more energy as compared to the iron dosing method. The tabulated results in Appendix A reflect the energy consumption of this process. Aluminium electrode dosing on water indicated an insignificant effect on the change of colour after treatment, thus the colour variation is not indicated in these results.

4.4.1 The effect of energy charged on aluminium dissolution

Similar comparison of pH changes as in iron dissolution was achieved through aluminium dosing to river water. The neutralisation was achieved and the pH reached equilibrium at pH 7.4. Unlike iron dissolution, the measured amount of aluminium dissolved in river water was identified to be less compared to the theoretical values. Figure 4.9 overleaf indicates the variation where an overall error of 5.43% relative to the theoretical values was achieved. The speciation of this behaviour was not determined and no further explanation could be identified.

A dosage of about 700 Coulombs per litre achieved an acceptable pH range which has increased from 6.6 to 7.4 displayed in Figure 4.9. At the start of the treatment, the pH of the water rapidly increased where after the pH gradient decreased. In the last quarter of treatment, there was no significant pH variation (pH was 7.4). Results shown are in accordance with findings from previous studies of MAIC treatments whereafter a particular period of time, the pH of the solution became stable. After neutralisation, Al(III) and OH ions appeared in almost stoichiometrical amounts, because of continual formation of insoluble $\text{Al}(\text{OH})_3$ and pH became constant.

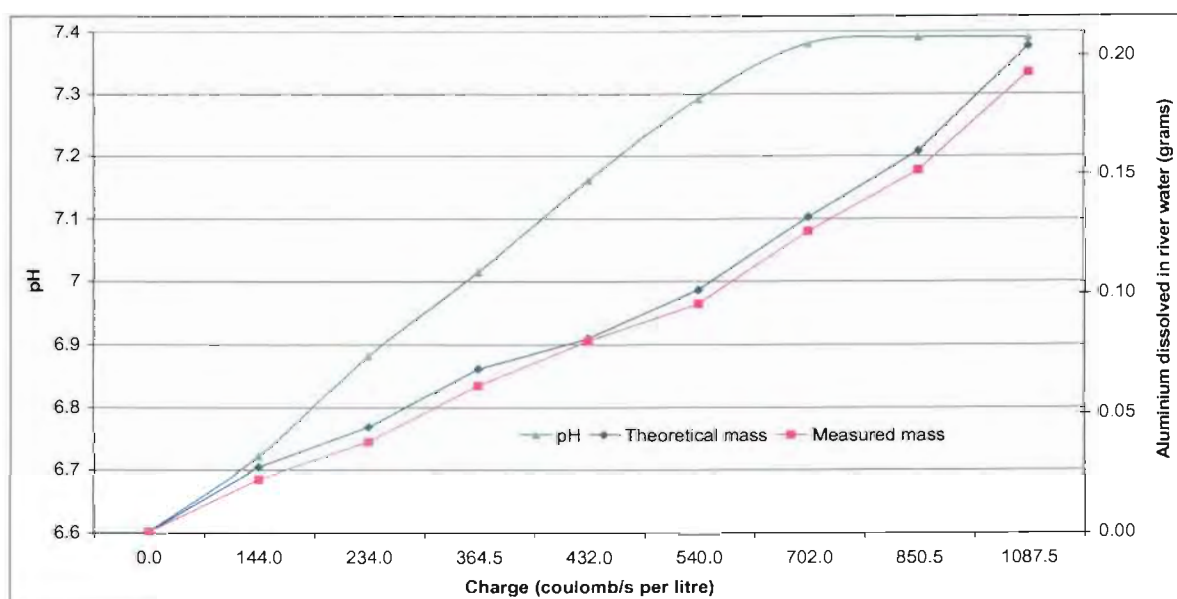


Figure 4.9: The effect of energy charged on the dissolution of aluminium (theoretical and practical) and the pH of the solution

4.4.2 The effect of energy charged on the water colour dissolution

The colour of water is improving as the energy increases; unlike in iron dissolution where there is an increase in colour residuals with an increase in dosing. Aluminium dosing to river water is seen as a remedial solution as compared to the pigmentation caused by iron dissolution.

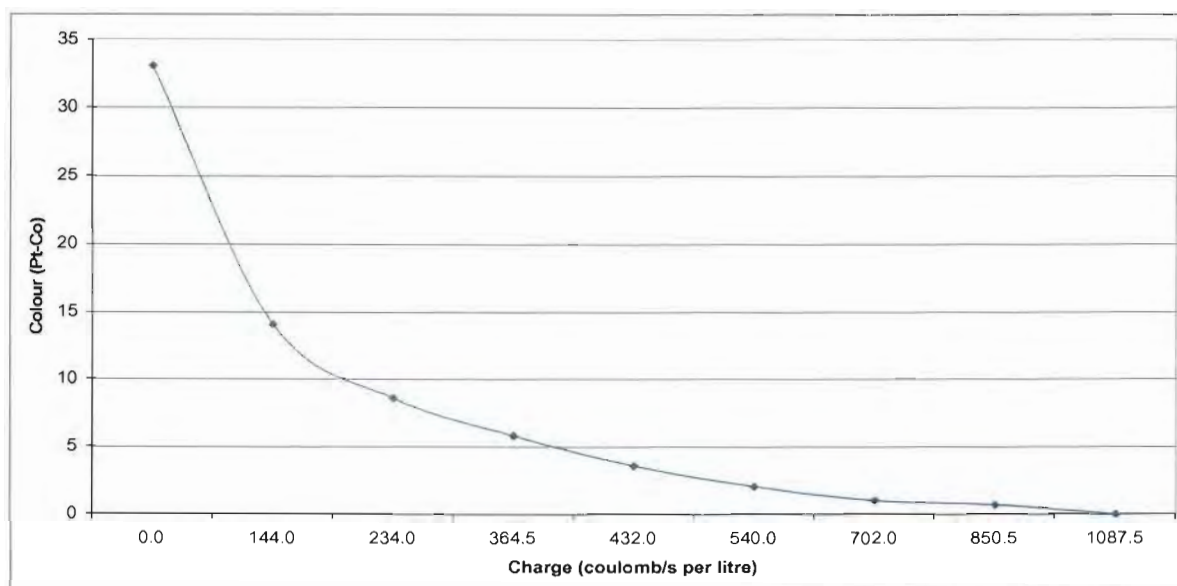


Figure 4.10: The effect of energy charged on the colour of the solution using aluminium electrodes

4.4.3 The effect of energy charged on conductivity

An increased dosing of iron in river water seems to be constantly improving the electric conductance of water. Figure 4.11 illustrates the coordination of this effect, whereby six sets of tests were performed at different charging rates and it has been observed that the higher the charge, the lower the conductance will be.

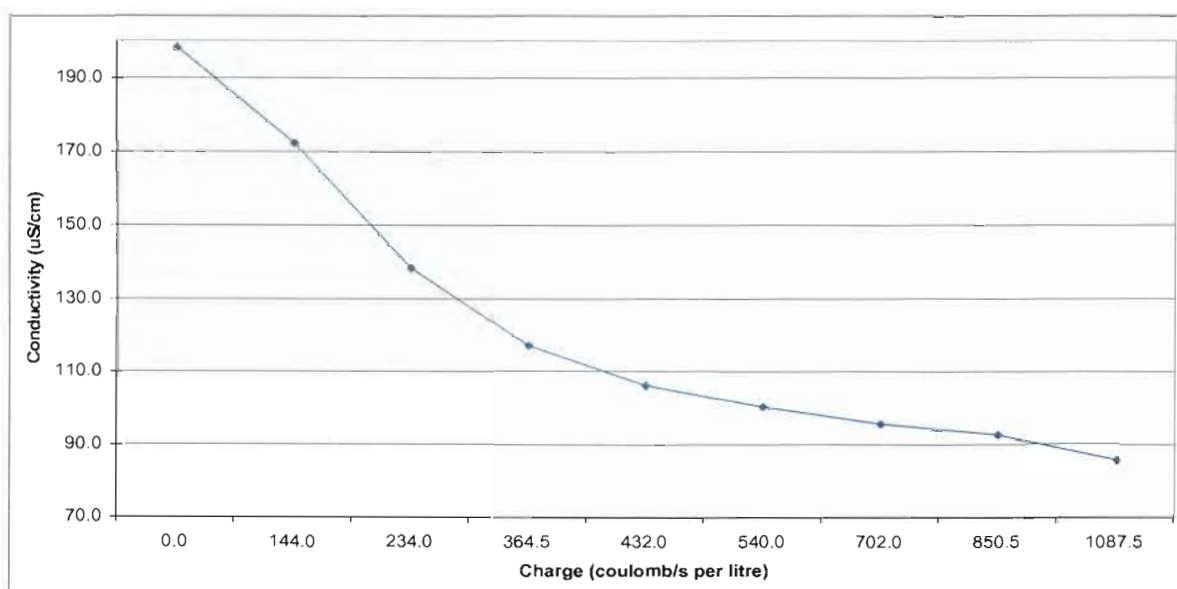


Figure 4.11: The effect of energy charged on the solution conductivity using aluminium electrodes

4.4.4 The effect of energy charged on turbidity

A successful reduction of turbidity was also achieved using aluminium electrodes (below 1 NTU). Eight experiments were run whereby different dosing rates were applied and correlation observed indicates proportionality in terms of the amount of energy used to the amount of turbid materials removed from water. Figure 4.12 displays the results.

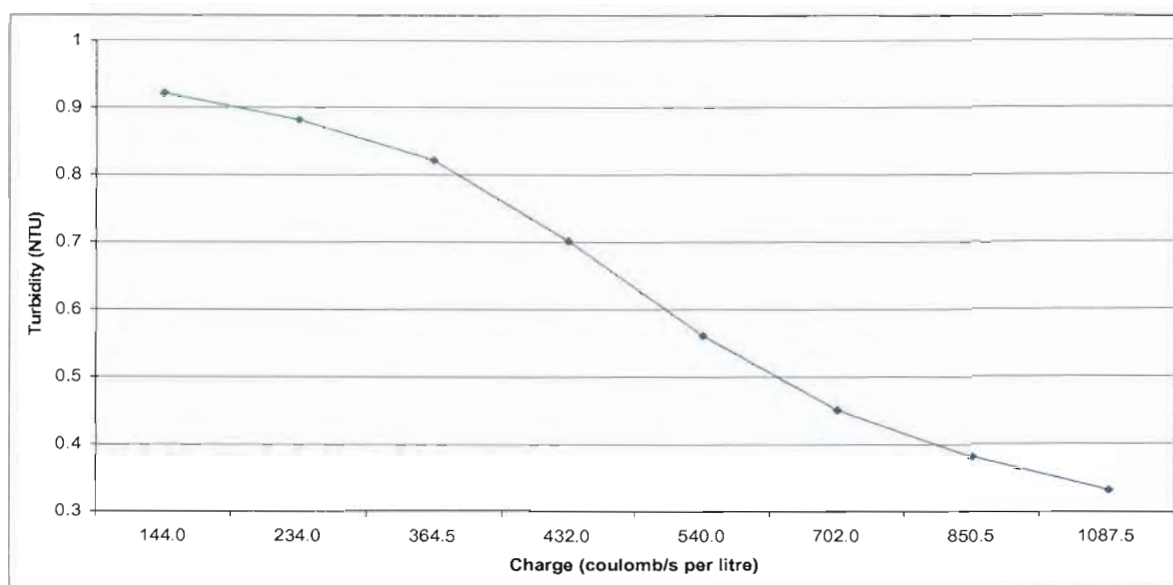


Figure 4.12: The effect of energy charged on the solution turbidity using aluminium electrodes

4.4.5 The effect of energy charged on total dissolved solids

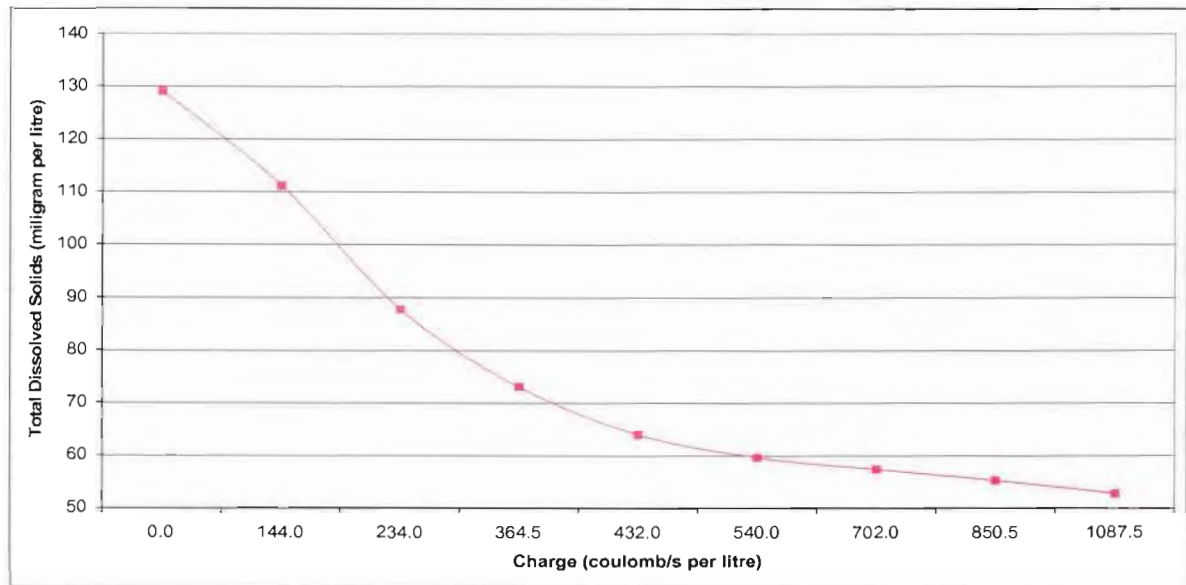


Figure 4.13: The effect of energy charged on the solution total dissolved solids using aluminium electrodes

A successful reduction of dissolved solids was achieved using aluminium electrodes. It is indicated that dissolved solids below 450 mg/L have no negative effect on human consumption. The results on Figure 4.13 indicated correlation observed when varying energy doses of aluminium in water has reduced the amount of solids in river water.

4.4.6 The effect of energy charged on phosphate concentration

The aluminium ion method of treatment achieved at least 50 percent reduction of phosphates. Figure 4.14 illustrates the reduction of phosphates from as high as 0.36 ppm to as low as 0.18 ppm. Figure 4.14 indicates the mole ratio of aluminium consumed compared to the removal of phosphate concentration expressed in percentage.

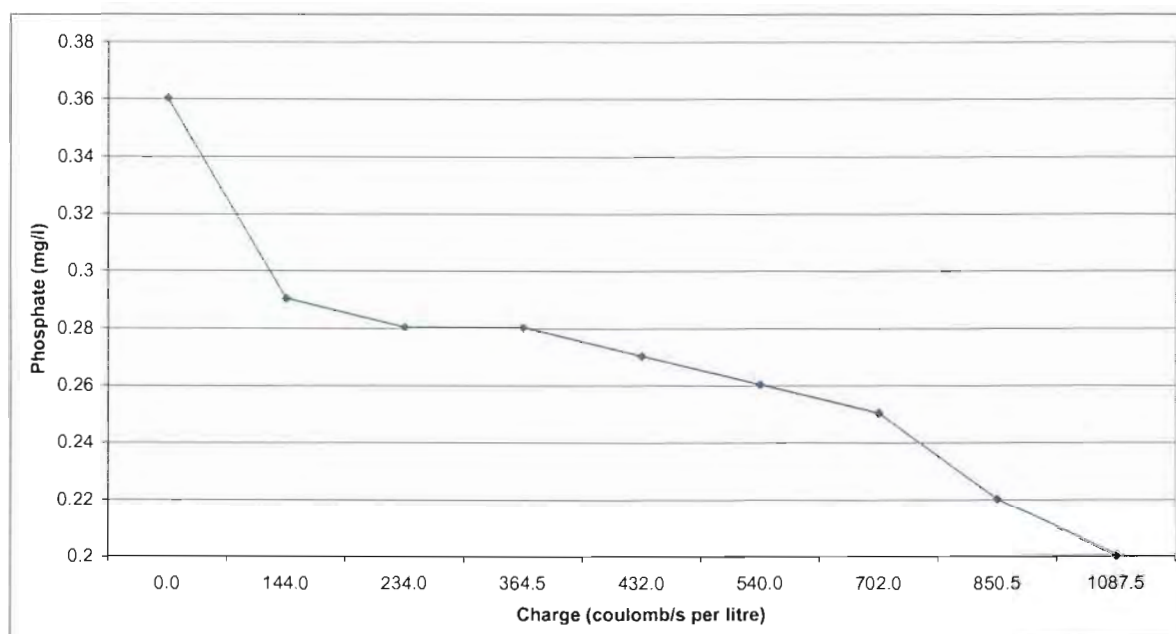


Figure 4.14: The effect of energy charged on the phosphate concentration using aluminium electrodes

4.5 Optimisation

This stage of investigations was aimed to reduce the cost implication of this process, to find the optimal operational conditions, and to achieve best water quality results; in other words at what operating variables will the process yield the optimum results. Although the economical figures do not form part of this report, cost rating was performed mainly focusing on the power consumption. Reduction in energy consumptions was the main objective; achieving best results by reducing the cost of energy employed for this process. During this stage, more operating variables involved in the investigations were studied further. These variables included:

- Alkalinity of raw water,
- Turbidity of raw water,
- Mixing or agitation conditions,
- Levels or concentration of dosing metals (iron and aluminium) in final or treated water, and
- Reduction of energy consumption.

4.5.1 The effect on the colour of treated water using iron electrodes

Agitation or mixing achieved in the form of stirring during experimentation indicated a positive influence in the electroflocculation of river water. The following result was achieved where agitation or stirring was employed. For assisting the alternating current which makes ‘self cleansing’ of electrodes possible, agitation was employed to improve energy consumption during the electrolysis. Stirring reduces the resistance that is formed as a result of film formation on the water-electrode interface. The thicker the film at a point of interface requires more energy. Figure 4.15 indicates the effect of agitation on colour.

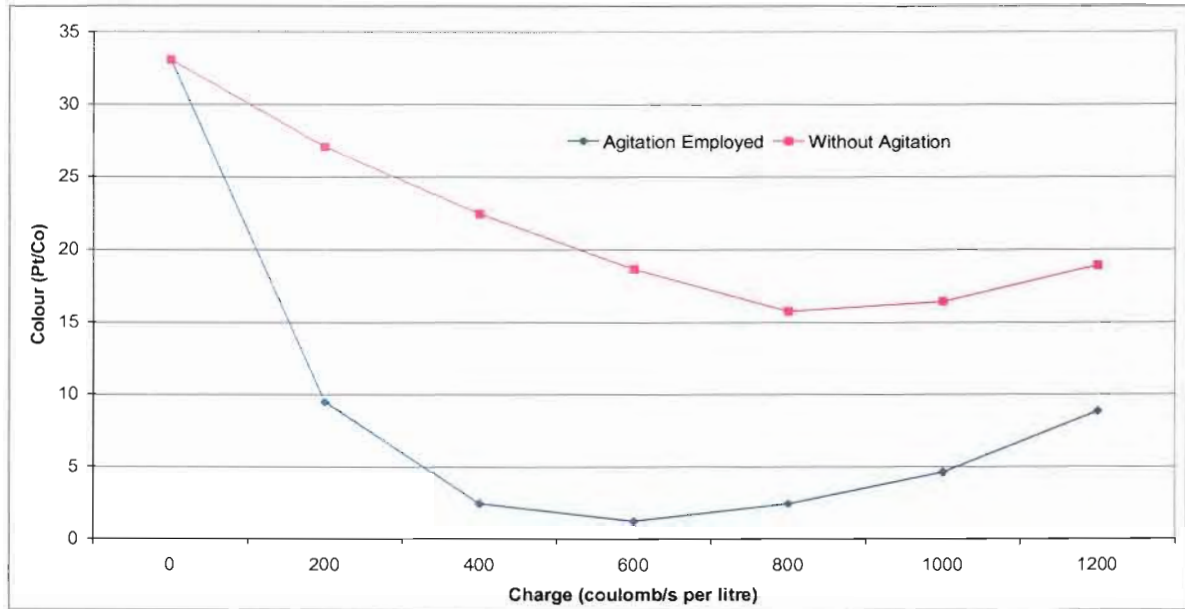


Figure 4.15: The effect of energy charged on the colour of treated water using iron electrodes

4.5.2 The effect on the colour and pH using iron electrodes

After the effect of agitation was evaluated using iron electrodes the challenge was to see if this effect could be improved by reducing the energy utilised. Figure 4.16 above shows how energy could be reduced and still effectively reduce the colour to desired levels (colour of below 15 Pt/Co was aimed). The neutralisation of water was also seen as reaching equilibrium levels where energy consumptions were reduced to a minimum of 17 Coulombs per litre of treated water.

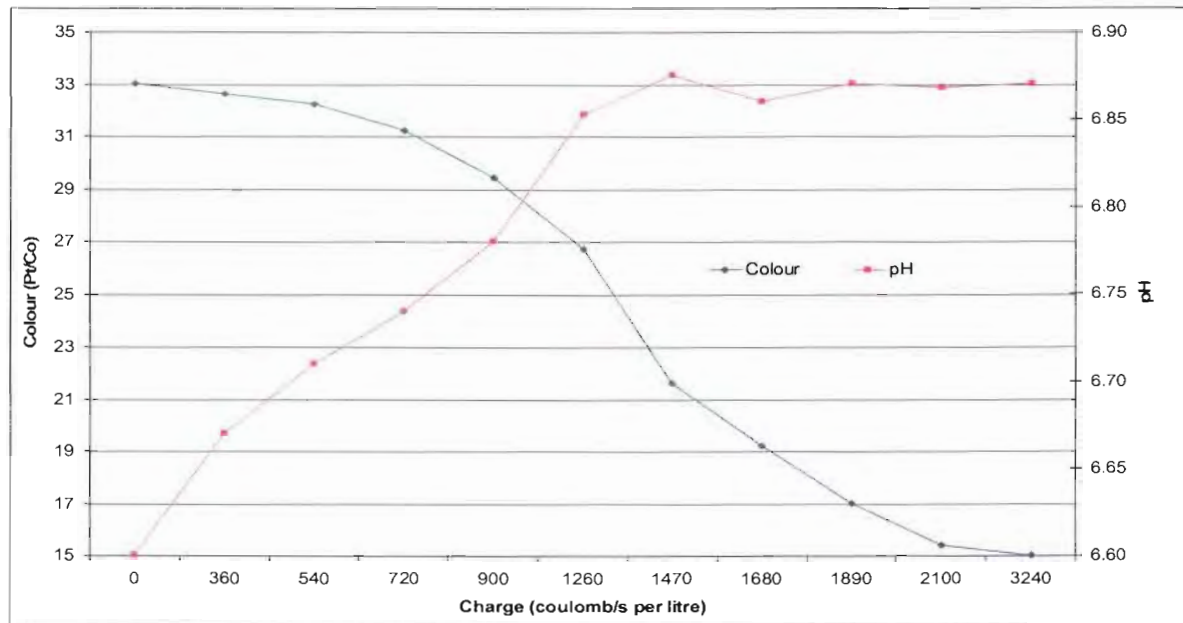


Figure 4.16: The effect of reduced energy charged on the colour of treated water using iron electrodes

4.5.3 The effect on increased iron concentration in water

It was also noted that as the treatment proceeds the level of iron concentration in water increases with an increase in charge. This variation is indicated below (Figure 4.17) with reduced energy levels. The initial variation can be observed in Appendix A where energy optimisations were not considered.

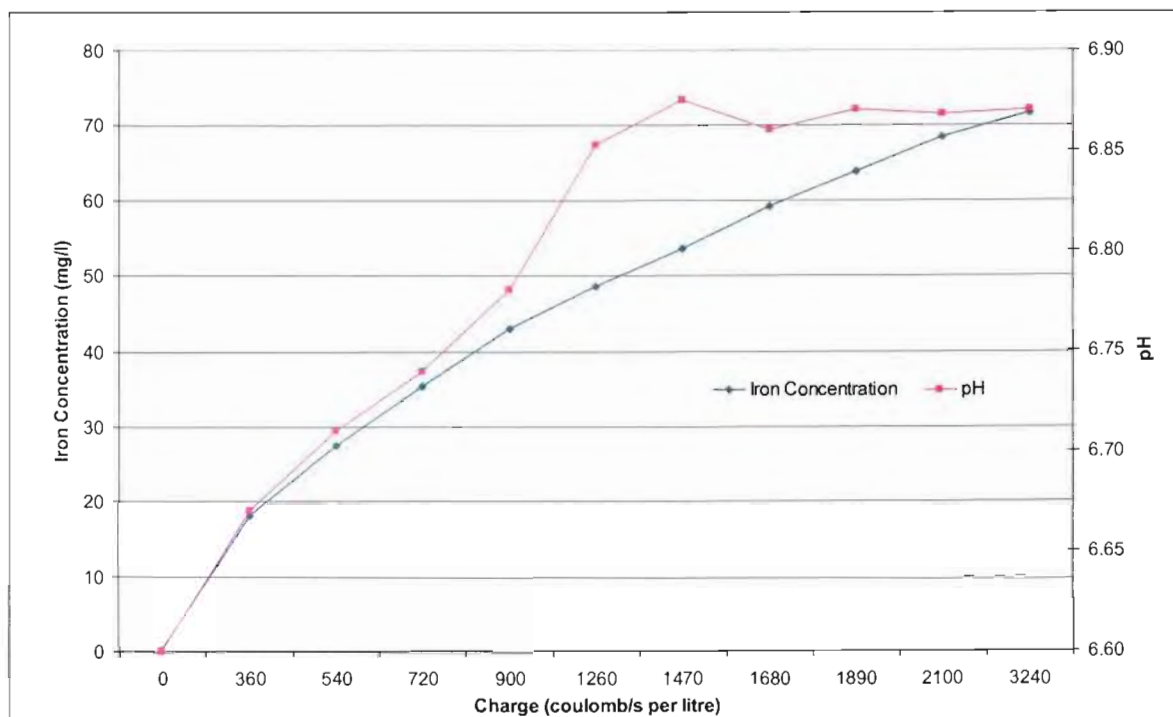


Figure 4.17: The effect of reduced energy charged on increased iron concentration in water

4.5.3 The effect in reduction of phosphates using iron electrodes

Although results overleaf do not indicate maximum removal of phosphates as compared to high energy utilisation, about 40% phosphate removal was achieved and within the required water quality specifications. Figure 4.18 overleaf shows the reduction of phosphate concentrations from 0.36 mg/L to 0.22 mg/L.

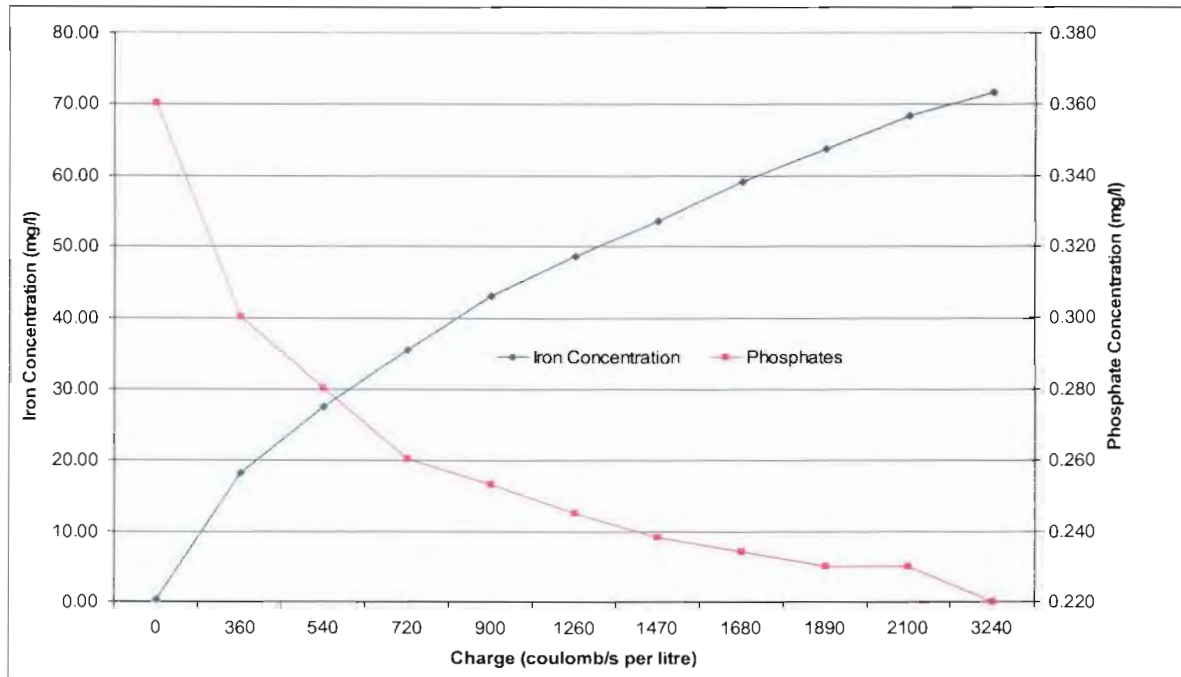


Figure 4.18: The effect of reduced energy charged in reduction of phosphates from water using iron electrodes

4.6 Comparison between Aluminium and Iron Electrodes

The comparison of the performance between iron and aluminium electrodes was based on the stoichiometric calculation of the required mass concentration that should be dosed into river water to achieve optimal results. For both electrodes an equal amount of dosage was projected to be 10 mg/L. This is shown in the comparison Table 4.1 where all characteristics were based on the basis of 10 mg amount of electrode being dosed into one litre of river water. The results achieved were also compared with the water quality limit set by SANS.

Table 4.1: Comparison between aluminium and iron electrodes

Characteristic	Iron Electrode	Aluminium Electrode	Legal limits (SANS 241)
Reaction rate	Faster	Slow	
Energy consumption	Low (34 Coulombs per litre)	High (107 Coulombs per litre)	
Iron	0,09 mg/L	-	0 – 0,1 mg/L
Aluminium	-	0,256 mg/L	0 – 0,15 mg/L
Effect on pH	7.26	6.72	6 – 9
Effect on conductivity	94 μ S/cm achieved	172 μ S/cm achieved	0 – 700 μ S/cm
Effect on colour	Leaves residual colour	No residual colour present	0 – 15 Pt-Co
Effect on turbidity	0,39 NTU achieved	0,92 NTU achieved	0 – 1 NTU
Effect on TDS	53 mg/L achieved	111 mg/L achieved	0 – 450 mg/L
Effect on phosphates	0,24 mg/L achieved	0,29 mg/L achieved	

4.7 Discussion

Apparent current efficiencies for Al and Fe dissolution as aqueous Al(III) and Fe(II) species at pH 6.5 and 7.8 were greater than unity. This was due to additional reactions occurring parallel with Al and Fe dissolution: oxygen reduction at anodes and cathodes, and hydrogen evolution at cathodes, resulting in net (i.e. oxidation plus reduction) currents at both anodes and cathodes. During the investigations, results show that ferric and aluminium ion treatment would be a successful water treatment technique.

The Electrocoagulation process was found to be superior to that of conventional coagulation with aluminium sulphate and iron chloride for treating river water, with 30% more phosphates being removed for the same dose.

Chapter 5: Cost Implications

Besides improving the water quality treatment results, this research also aimed to reduce the cost implications of water treatment process. Before a treatment company can consider changing a treatment technology, cost-saving has to be taken into consideration. Although the economic figures do not form part of this report, cost-rating was performed mainly focusing on the power consumption. Reduction in energy consumption was the main objective; other cost-related issues includes the following:

- Cost of raw materials

Electrodes – cost, performance and lifespan are dependent on current density and electricity consumption when in use

- Electricity cost

This is the cost projected in terms of how much energy will be employed for the treatment- power consumption.

- Maintenance and replacement of materials

During electrolysis, electrodes are ionised because of electrochemical reaction and as a result they need to be replaced on a regular basis; this is the reason why the lifespan of the electrode has to be taken into consideration when making a choice. Metal ion can also be recovered from the sludge after treatment and maintenance costs are minimal due to fewer amounts of raw materials used.

Chapter 6: Conclusion and Recommendations

Electrocoagulation has successfully treated a wide range of waste streams. Previous research has focused on the application of electrocoagulation to a particular situation (plant and waste stream). On-site optimisation and process ‘tuning’ had limited success. Mechanisms are expected to change through the process but the dominant mechanisms and their role are yet to be identified.

The lack of a methodical approach on a mechanistic level is reflected by the lack of similarities in treatment process design. A logical, systematic approach to a fundamental understanding of electrocoagulation is clearly required. The design phase can then proceed on solid scientific and engineering knowledge.

A large number of key mechanisms are dependent on a few operating parameters. Individual ‘optimisations’ exist such as that for pH and speciation of the coagulant ion (Fe^{3+} or Al^{3+}) but this often conflicts with other localised optimal conditions. The electroflotation mechanism, passivation of the electrodes, and economic considerations all have their own operating pH. A trade-off between the competing factors must be evaluated to provide a global optimum operating condition.

Apparent current efficiencies for Al and Fe dissolution as aqueous Al(III) and Fe(III) species at pH 6.5 and 7.8 were greater than unity. This was due to additional reactions occurring parallel with Al and Fe dissolution: oxygen reduction at anodes and cathodes, and hydrogen evolution at cathodes, resulting in net (i.e. oxidation plus reduction) currents at both anodes and cathodes. During these investigations, results show that ferric and aluminium ion treatment would be successful under the following conditions.

- Relatively high raw water alkalinity of greater than 80 mg/l as CaCO_3
- Relatively low raw water turbidity of less than 60 NTU

The electrocoagulation process was found to be superior to that of conventional chemical coagulation with aluminium sulphate and iron chloride for treating river water, with reference to 30% more phosphates removal with equivalent stoichiometrical dosage. Due to high energy consumption which is in low supply in South Africa, the electroflocculation process may be constrained as compared to the conventional chemical coagulation process.

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Appendix A

Experimental Data

Experiment 1

Aim and objective:

To determine the feasibility of phosphate removal using iron electrode on electrochemical technique as a treatment media.

Quantity of river water treated = Two litres

Parameter Recording Table A1:

Time (minutes)	Current (Amp)	Voltage (Volts)	Calculated Mass (g)	Charge (C/L)	Iron Concentration Spec 100-2000 mg/l	Phosphate (mg/l)	Colour (Pt/Co)	pH 6.5 - 8.5
0	1	50	0.0000	0	0.20	0.360	33	6.60
60	1.15	50	0.8027	2070	36.78	0.260	27	6.86
120	1.2	50	1.6753	4320	71.67	0.220	15	6.87
180	1.3	50	2.7223	7020	98.21	0.185	2	6.92
240	1.35	50	3.7694	9720	101.23	0.150	0	6.94
300	1.2	50	4.1882	10800	112.50	0.130	20	6.98
360	1.2	50	5.0259	12960	113.90	0.110	95	6.99
420	1.3	50	6.3521	16380	115.67	0.100	142	7.01
480	1.3	50	7.2596	18720	115.60	0.090	158	7.01

Discussion:

Taking of samples increases conductivity of the solution since the rate of dissolution remain constant throughout the experimentation. This is due to the reduced interface area that restricts the current flow (at constant voltage).

Observations

Solution turns brownish, then greenish

Three suspended layers formed on top of the solution (top-brown, middle-greenish, bottom-white)

Experiment 2

Aim and objective:

To check the effect of neutralisation river water during electro-flocculation process and how it affects change in temperature.

Quantity of river water treated = 1.5 litres

Parameter Recording Table A2:

Time (minutes)	Current (amps)	Voltage (Volts)	pH	Temperature (Degree Celsius)	Calculated Mass (g)	Charge (Coulomb per litre)
0	0.19	30	7.46	26	0.000	0
5	0.19	30	7.44	26	0.017	38
9	0.19	30	7.45	27	0.030	68.4
15	0.19	30	7.47	28	0.050	114
21	0.19	28.4	7.53	28	0.070	159.6
24	0.19	28.6	7.63	29	0.080	182.4
30	0.18	29.4	7.75	30	0.094	216
36	0.18	29.4	7.80	30	0.113	259.2
43	0.18	30.1	7.86	31	0.135	309.6
48	0.18	30.1	7.88	31	0.151	345.6
53	0.18	30.2	7.88	32	0.166	381.6
59	0.18	30.2	7.86	32	0.185	424.8

Observations:

Solution turns brownish green

Experiment 3

Aim and objective:

To test the variation in phosphate removal using different dosing rates of iron in river water

Quantity of river water treated = 1.6 litres

Parameter Recording Table A3:

Time (Minutes)	Current	Voltage	Charge (Coulomb per litre)	pH	Conductivity	Phosphate mg/l
0	0.2	28.1	0	6.85	312	0.370
15	0.2	28.7	1125	7.66	325	0.340
30	0.2	30.0	2250	7.70	342	0.310
45	0.2	27.2	3375	8.01	346	0.270
60	0.2	29.1	4500	8.05	346	0.220
75	0.2	29.5	5625	8.63	345	0.198
90	0.2	31.0	6750	8.89	345	0.181
105	0.2	29.0	7875	6.99	346	0.165
120	0.2	28.2	9000	6.97	346	0.143

Experiment 4

Aim and objective:

To determine change in turbidity after treatment using different dosing rates of metal into water.

Parameter Recording Table A4:

	Dosage rate (g/L)	Turbidity (NTU)
Run 1	0.59	0.45
Run 2	0.72	0.4455
Run 3	0.76	0.48
Run 4	0.85	0.441
Run 5	0.93	0.434
Run 6	0.95	0.3905
Run 7	1.45	0.408
Run 8	1.55	0.405
Run 9	1.62	0.412
Run 10	1.89	0.465
Run 11	2.24	0.48
Run 12	2.48	0.48

Experiment 5

Aim and objective:

To determine the feasibility of phosphate removal using aluminium electrode on electrochemical technique as a treatment media

Quantity of river water treated = Two litres

Parameter Recording Table A5:

time (sec)	Current (amps)	Voltage (volts)	Phosphates (ppm)	pH	Aluminium concentration (ppm)	Charge (Coulombs/L)	Mass dissolved (grams)
0	1.15	50	0.36	6.60	0.200	0	0.0000
2340	1.2	50	0.29	6.72	0.540	1404	0.2631
3600	1.3	50	0.28	6.88	10.200	2340	0.4385
5400	1.35	50	0.28	6.94	26.121	3645	0.6830
7200	1.2	50	0.27	7.16	36.544	4320	0.8094
9060	1.2	50	0.26	7.29	66.145	5436	1.0186
10920	1.3	50	0.25	7.38	99.351	7098	1.3300
12540	1.35	50	0.22	7.39	168.440	8464.5	1.5860
14580	1.45	50	0.2	7.39	258.641	10570.5	1.9806

Observation

A white wax-like layer is formed and suspended from the solution

Experiment 6

Aim and objective:

To determine the feasibility of phosphate removal using aluminium electrode on electrochemical technique as a treatment media

Quantity of river water treated = 500 millilitres

Parameter Recording Table A6:

Time (minutes)	Voltage (volts)	Currents (amps)	pH	Phosphates (ppm)	Mass Dissolved (grams)	Charge (Coulomb/L)
0	50	1.20	6.60	0.36	0	0
10	50	1.15	6.68	0.29	0.064643	1380
20	50	1.20	6.74	0.27	0.134908	2880
30	50	1.20	6.77	0.24	0.202362	4320
40	50	1.20	6.81	0.23	0.269815	5760
50	49	1.20	6.85	0.22	0.337269	7200
60	49	1.20	6.88	0.21	0.404723	8640
70	49	1.30	6.91	0.20	0.511525	10920
80	48	1.20	6.93	0.19	0.539631	11520
90	48	1.20	6.94	0.18	0.607085	12960
100	47	1.20	6.94	0.18	0.674538	14400

Observations

A white wax-like layer is formed and suspended from the solution

Experiment 7

Aim and objective:

To determine concentrations of Turbidity, Phosphate and Colour of treated river water after electrochemical treatment using iron electrode on different electrical currents. The table also indicates percentages removal of Phosphate and Turbidity at varying electrical current supply after 60 minutes reaction time.

Parameter Recording Table A7:

	Time (min)	Current (amps)	Phosphate (mg/L)	Phosphate removal (%)	Turbidity (NTU)	Turbidity removal (%)	Colour (Pt/Co)	Colour removal (%)
River Water	0	0.00	0.3600	0.00	42.32	0.00	33.0	0.00
Run 1	60	0.20	0.2509	30.30	0.48	98.87	27.0	18.18
Run 2	60	0.40	0.1699	52.80	0.45	98.94	15.0	54.55
Run 3	60	0.60	0.1296	64.00	0.44	98.96	2.0	93.94
Run 4	60	0.80	0.1058	70.60	0.39	99.08	1.0	96.97
Run 5	60	1.00	0.1040	71.10	0.32	99.24	20.0	39.39
Run 6	60	1.20	0.0983	72.70	0.29	99.31	95.0	-187.88
Run 7	60	1.40	0.0963	73.25	0.37	99.13	142.0	-330.30
Run 8	60	1.60	0.0900	75.00	0.42	99.01	158.0	-485.19

Observations

At completion of run 6, 7 and 8, colour worsen – become brownish red (apparent colour) and after filtration (true colour) treated water still had colour residue

Experiment 8

Aim and objective:

To determine influence of varied flow of current in one litre of river water using iron electrode on electrochemical technique as a treatment media. Each test was performed within 20 minutes

Quantity of river water treated = One litres

Parameter Recording Table A8:

	Time (seconds)	Current (amps)	Charge (C/L)	theoretical mass mg	actual mass mg	pH	colour	conductivity	tds
River Water						6.60	33	196.00	125
Test 1	1200	1	1200	349.02	474.12	7.00	7	121.20	76
Test 2	1200	1.2	1440	418.82	508.00	7.26	2	94.00	53
Test 3	1200	1.3	1560	453.72	547.92	7.37	5	82.50	48
Test 4	1200	1.4	1680	488.63	549.91	7.40	12	76.60	45
Test 5	1200	1.5	1800	523.53	559.68	7.42	30	71.20	42
Test 6	1200	1.6	1920	558.43	576.00	7.43	95	70.00	40

Experiment 9

Aim and objective:

To determine influence agitation or stirring using iron electrode on electrochemical technique as a treatment media in 750 ml

Quantity of river water treated = 750 millilitres

Parameter Recording Table A9:

Time (seconds)	Current (amps)	Charge (C/L)	Agitation			Without Agitation		
			pH	Colour (Pt/Co)	Phosphates (mg/L)	pH	Colour (Pt/Co)	Phosphates (mg/L)
0	0	0	6.60	33	0.37	6.60	33	0.37
300	0.5	200	7.00	9	0.24	7.77	27	0.34
600	0.5	400	7.26	2	0.17	7.74	22	0.31
900	0.5	600	7.37	1	0.14	7.95	19	0.27
1200	0.5	800	7.40	2	0.12	7.85	16	0.25
1500	0.5	1000	7.42	5	0.12	8.00	16	0.25
1800	0.5	1200	7.43	9	0.11	7.90	19	0.24

Experiment 10

Aim and objective:

To determine influence agitation or stirring using iron electrode on electrochemical technique as a treatment media in 750 ml

Quantity of river water treated = 750 millilitres

Parameter Recording Table A10:

Time	Aluminium	Phosphates	pH	Current	Mass dissolved (g)		Charge	Colour	Conductivity	Turbidity	TDS
(minutes)					theoretical	actual	(C/L)				
0	0.200	0.36	6.6	1.15	0.0000	0.0000	0.0	33	198.0	52	129
4	0.540	0.29	6.72	1.2	0.0270	0.0220	144.0	14	172.0	0.92	111
6	10.200	0.28	6.88	1.3	0.0438	0.0376	234.0	8	138.0	0.88	88
9	26.121	0.28	7.013	1.35	0.0683	0.0615	364.5	6	116.8	0.82	73
12	36.544	0.27	7.16	1.2	0.0809	0.0800	432.0	4	105.8	0.7	64
15	66.145	0.26	7.29	1.2	0.1012	0.0954	540.0	2	99.9	0.56	60
18	99.351	0.25	7.38	1.3	0.1315	0.1257	702.0	1	95.2	0.45	57
21	168.440	0.22	7.39	1.35	0.1594	0.1514	850.5	1	92.3	0.38	55
25	258.641	0.2	7.39	1.45	0.2038	0.1927	1087.5	0	85.5	0.33	53

Experiment 11

Aim and objective:

To determine influence agitation or stirring using iron electrode on electrochemical technique as a treatment media in 2 litres

Quantity of river water treated = two litres

Parameter Recording Table A11:

Time (minutes)	Iron (mg/l)	Phosphate (mg/l)	Colour	pH	Current (amp)	Calc. Mass (g)	Charge (C/L)
0	0.20	0.360	33	6.60	0.6	0.0000	0
20	18.00	0.300	33	6.67	0.6	0.1396	360
30	27.40	0.280	32	6.71	0.6	0.2094	540
40	35.30	0.260	31	6.74	0.6	0.2792	720
50	42.80	0.253	29	6.78	0.6	0.3490	900
60	48.40	0.245	27	6.85	0.7	0.4886	1260
70	53.50	0.238	22	6.88	0.7	0.5701	1470
80	59.10	0.234	19	6.86	0.7	0.6515	1680
90	63.70	0.230	17	6.87	0.7	0.7329	1890
100	68.40	0.230	15	6.87	0.7	0.8144	2100
120	71.67	0.220	15	6.87	0.9	1.2565	3240

Further Results Discussions

Phosphate Levels

Iron treatment process reduced the phosphates concentration by up to 75% of the initial concentration. This is illustrated in Figure A.1 where 3.6 ppm was lowered to 0.09 ppm with the total energy consumption of about 75 coulomb used for every one litre of the water treated.

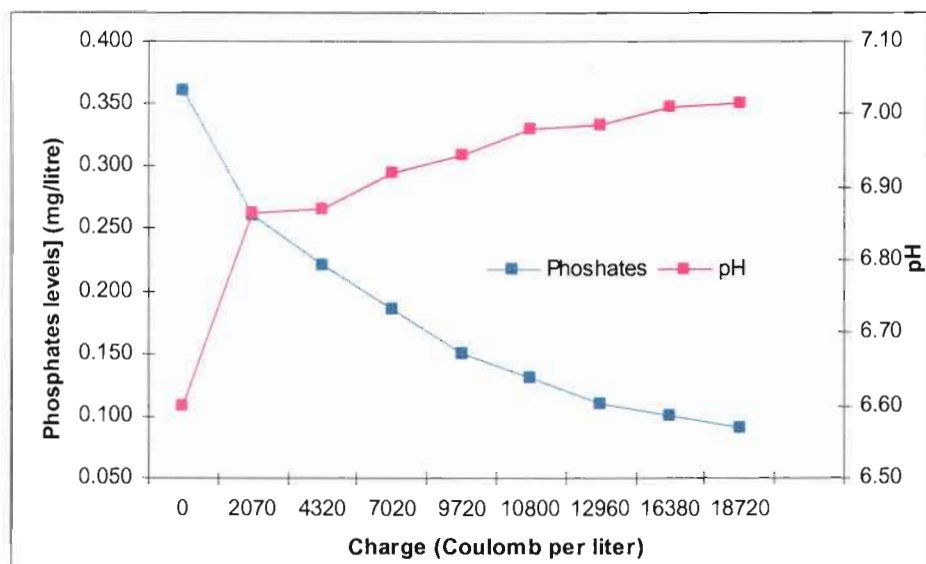


Figure A.1: Phosphate removal by iron dosing

Effect of pH

The removal of phosphate from river water by electrochemistry is highly reliant on the pH of the solution which affects the surface charge of the electrodes, the degree of ionisation, current transfer and the speciation of the electrode species. The electrochemical behaviour of the iron ion was studied in aqueous solution of different pH values using different dosing rates of ions and a fixed/constant amount of phosphate concentration in the solution. The results obtained are presented in Figure A.1 to A.4. It was observed that the maximum removal of phosphates was achieved at pH levels between 6.5 and 7.0, which gradually decreased with further increase in pH.

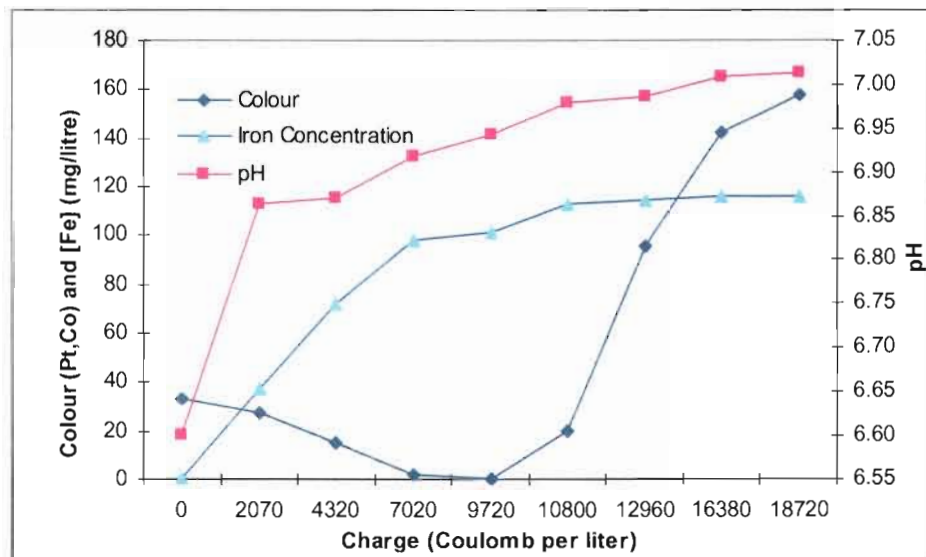


Figure A.2: pH, colour and iron concentration variation

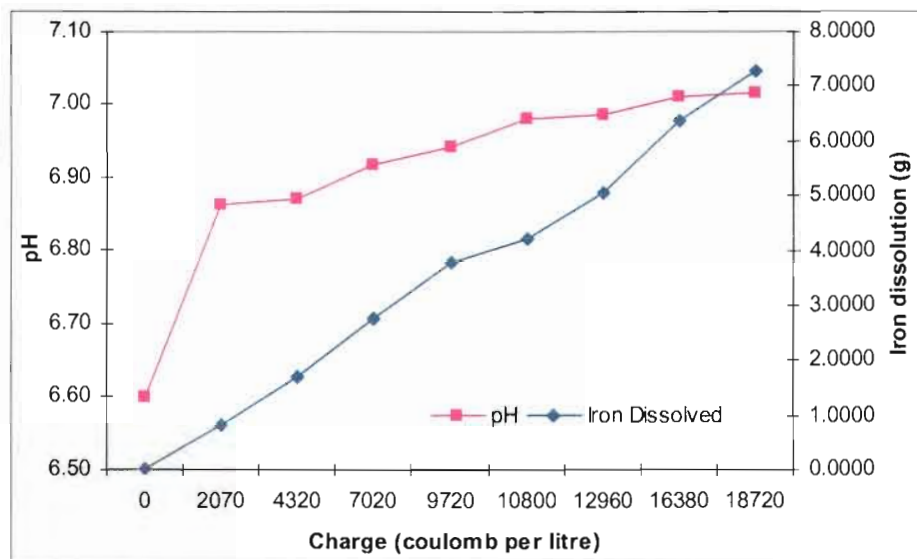


Figure A.3: pH change as an effect of iron dissolution in water

Colour comparability with Iron concentration

Iron electrode as coagulant in water treatment indicated to leave slight residual colour in treated river water, this was also observed in case of ferric chemical treatment (i.e. ferric chloride, ferric sulphate monohydrate). Figure A.2 also indicates that as iron concentration in the water increased to 3.8 ppm, the colour improves and as it goes higher, the colour turns the other way. This marginal change indicates extend at which further experimentation for optimisation purposes could be employed.

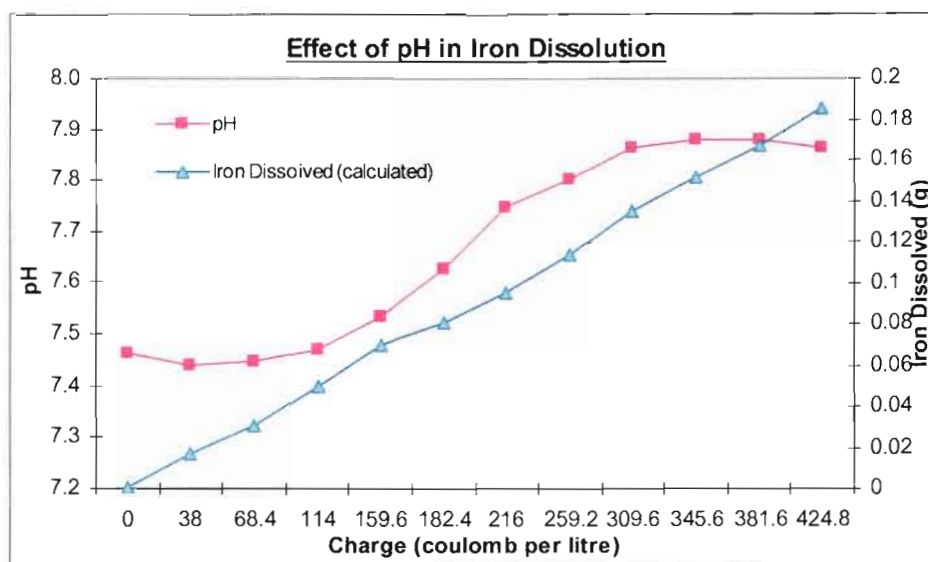


Figure A. 4 Iron Dissolution

Conductivity

The conductance of water increases with increase in metal dosing. Figure A.6 illustrates the extent at which conductivity of water raise because of metal ion increase.

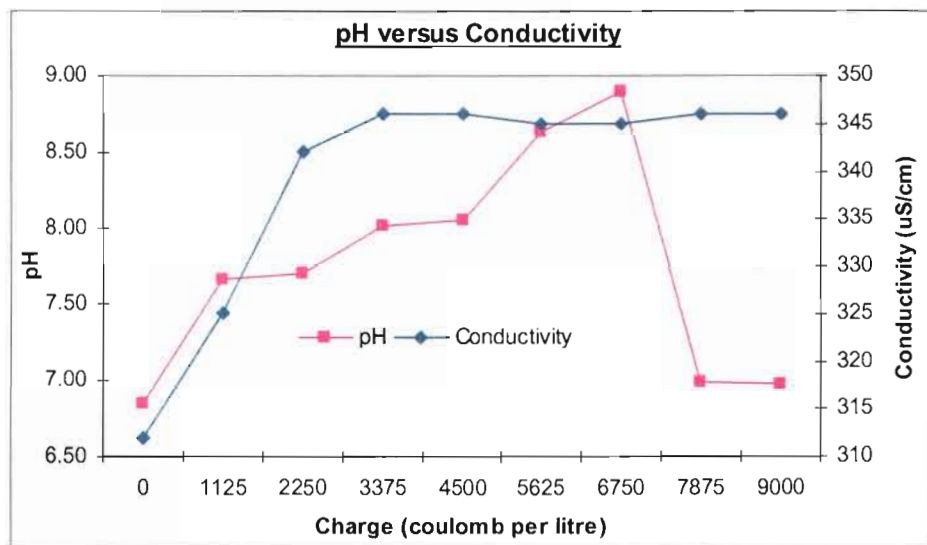


Figure A. 5 Conductance as a result metal dosing

Iron consumption

The amount of iron utilised is directly linked to the amount of energy (expressed as charge). Trial experimentation have been conducted and charge exceeding 75 coulombs per litre have been utilised, about 90 coulombs charge was used per litre of river water and this was reduced to 75 coulombs per litre then to 42.5 coulomb at the optimisation stage. The initial optimisation was aimed to reduce power consumption to below 20 coulombs charge per litre which was calculated theoretically (this is equivalent to 10 mg/L stoichiometric calculation of ferric chloride dosage in chemical treatment). In terms of mass representation the consumption of iron metal was projected theoretically to 3.443 mg per litre of water to be treated and 4.245 mg was achieved.

Figure A.7 below indicates the mole ratio of iron consumed compared to the removal of phosphate concentration expressed in percentage. A removal of 75% phosphates was achieved by a consumption of about 7.3 mg/L iron utilisation.

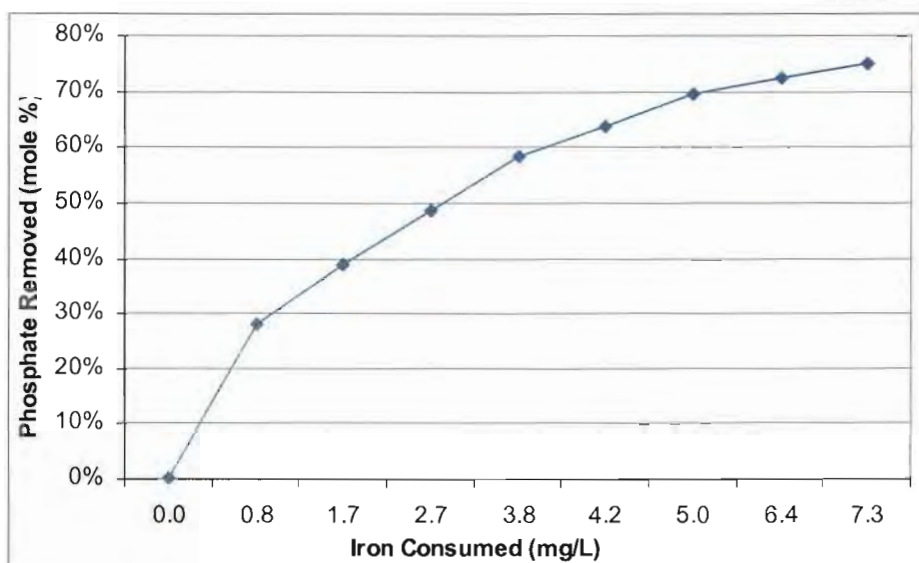


Figure A. 7 – Mole ratio iron consumed to phosphate removed

Aluminium Treatment

This method of treatment leaves no residual colour on treated river water. The drawback is the fact that it requires more energy as compared to the iron dosing method. The tabulated results in the appendix reflect the energy consumption of this process. Aluminium electrode dosing on water indicated an insignificant effect on the change of colour after treatment, thus the colour variation are not indicated on these results

Phosphate Concentration

Aluminium ion method of treatment achieved at least 50 percent reduction of phosphates. Figure A.8 illustrate the reduction of phosphates from as high as 0.36 ppm to as low as 0.18ppm. Although the aluminium concentration indicated gradual increment after 70coulomb per litre of charge dosage, intake from water exceeds 5% of the total daily intake, but no acute health effects are expected except at very high concentrations. The targeted aluminium concentration is 150ppm and maximum is 500ppm

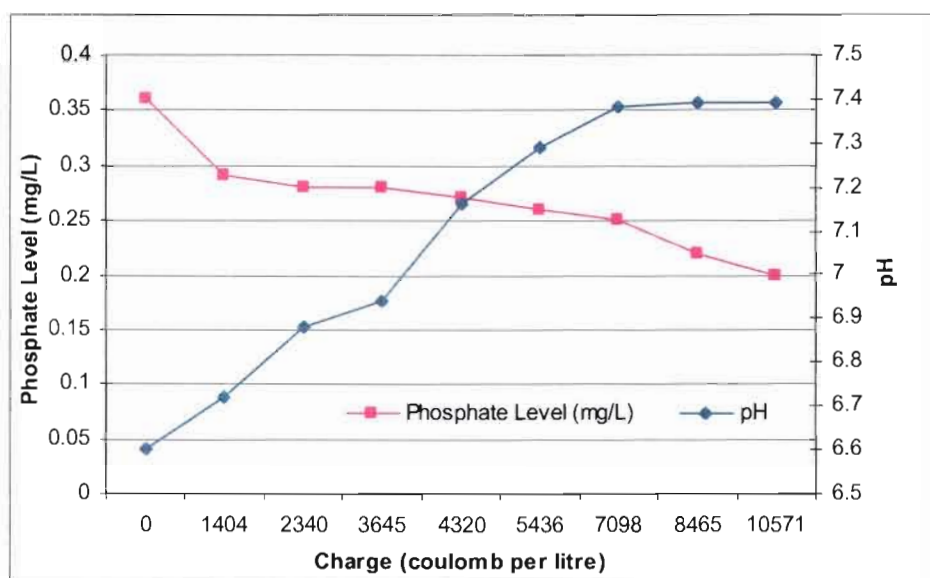


Figure A.8: Phosphates reduction by Aluminium treatment method.

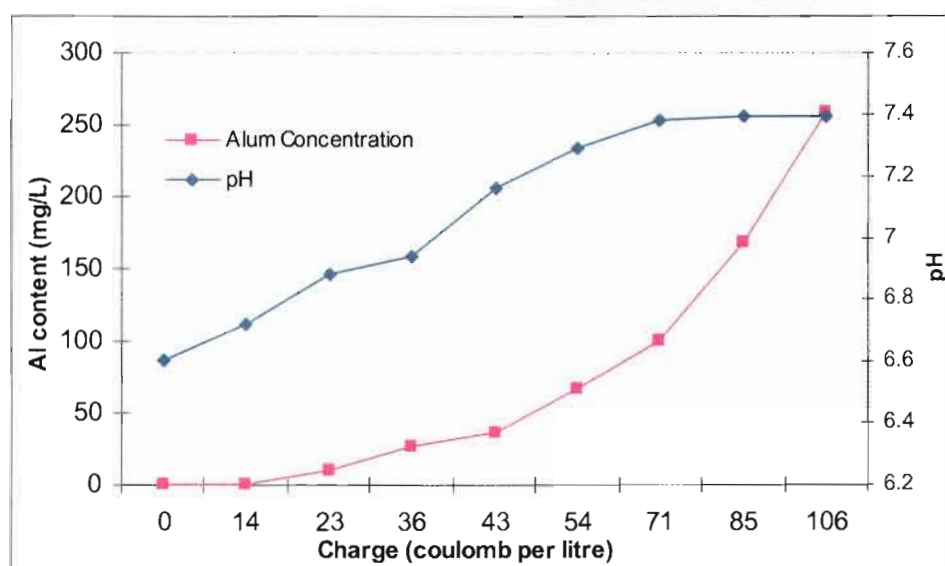


Figure A. 9: pH and Aluminium concentration variation

Aluminium dosage versus pH change

A dosage of about 105 coulomb per litre achieved an acceptable pH range which has increased from 6.6 to 7.4 displayed in Figure 4.9. At the start of the treatment, the pH of the water rapidly and after that the pH gradient decreased. In the last quarter of treatment, there was no significant pH variation (pH was 7.4). Results shown are in accordance with findings from previous studies of MAIC treatments where after particular period of time, the pH of solution became stable. After neutralisation, Al(III) and OH ions appeared in almost stoichiometrical amounts, because of continual formation of insoluble Al(OH)_3 and pH became constant.

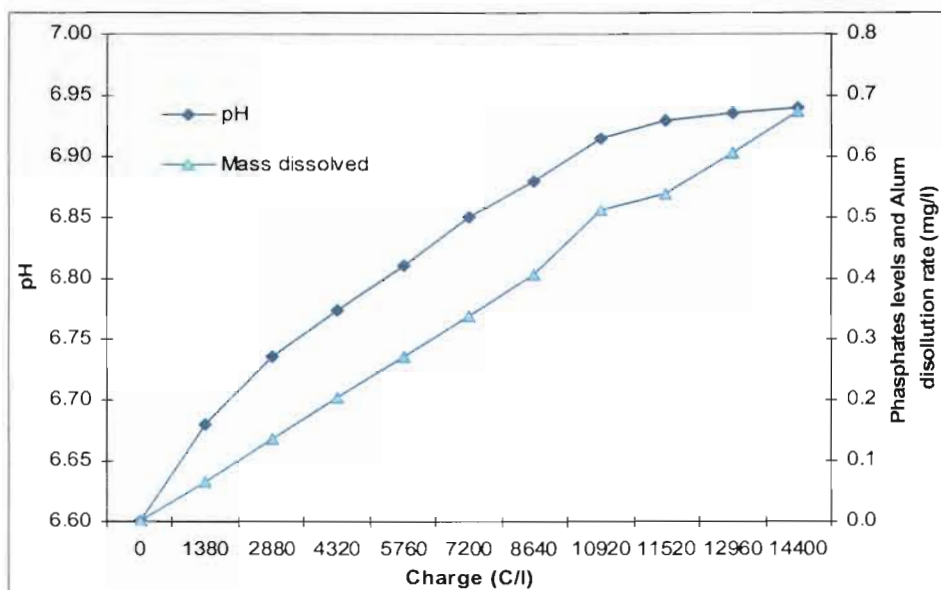


Figure A.10: pH change as an effect of aluminium dosing in river water

Aluminium consumption

Figure 4.11 below indicates the mole ratio of aluminium consumed compared to the removal of phosphate concentration expressed in percentage. A removal of about 45% phosphates was achieved by a minimal consumption of about 2 mg/L aluminium utilisation.

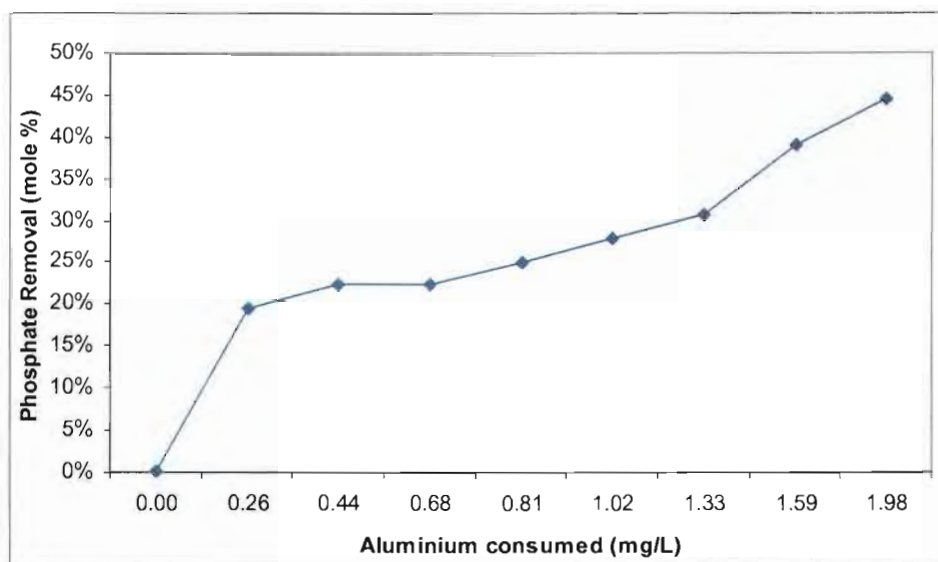


Figure A.11: Mole ratio of aluminium consumed versus phosphate removal

Agitation or mixing achieved in the form of stirring during experimentation indicated to have positive influence in the electro-flocculation of river water. The following result was achieved where agitation or stirring was employed. For assisting the alternating current

which makes 'self cleansing' of electrode possible, agitation was employed to improve energy consumption during the electrolysis. Stirring reduces the resistance that is formed as a result of film formation on the water-electrode interface. The thicker the film at a point of interface requires more energy. A successful application of iron (ferric ion) in water treatment was also indicated in Figure 4.7 by reducing the turbidity of river water to an average of 0.44 NTU. During this period in question the raw water turbidity varied from 60 to 40 NTU. This variation is indicated with different dosage rates of ferric ion on river water.

Combined Iron and Aluminium ions dosing

The combined method of water treatment show better results compared to the individual ion treatment. With this method energy requirements have got a room of optimisation, method of treatment leaves no residual colour on treated river water. The snag is the fact that it requires more energy as compared to the single iron dosing method.

Appendix B

Glossary of Terms and Symbols

A

Symbol and abbreviation of ampere.

absorption

A process "to take in and incorporate." E.g., light can be "absorbed" by a material. In chemistry, a term often used to describe the dissolution of a gas into a liquid or solid. The dissolving gas is said to be "absorbed." Or a liquid substance can be "absorbed" by a solid. This is a bulk process, not to be confused with adsorption.

ac

Abbreviation of alternating current. However this term is also used in connection with ac voltage, that is, an "alternating" voltage that will cause an "ac current" to flow in a conductor, and also in connection with ac power. Contrast with dc.

acid

A compound that dissociates to produce hydrogen (H^+) cations when dissolved in water. See also pH.

active metal

A metal that is easily oxidized (corroded) in air. For example, sodium will violently react with air, aluminium will *always* have an air-formed oxide film on its surface, and iron is easily rusted. These metals have high negative standard electrode potentials and are high the on the electromotive series. Contrast with noble metal.

adsorbate

A material that is adsorbed.

adsorption

An increase of the concentration of a solute in the vicinity of a solid surface, over that in the bulk of the solution, due to the attractive interaction between the solid immersed into the solution and the solute. Adsorption on a solid from a gaseous phase also occurs. It is a surface process, not to be confused with absorption. Opposite: desorption.

aluminium production

Aluminium metal is produced by electrolysis of aluminium oxide dissolved in a high-temperature molten-salt electrolyte. Aluminium is deposited as a liquid metal on the cathode of the electrolytic cell (the aluminium cations are reduced to liquid metal). This is the only large-scale industrial process for the production of aluminium.

ammeter

Instrument used for the measurement of current.

amp

Symbol and abbreviation of ampere.

ampere

Measurement unit of current. Abbreviation: "A" or "amp".

anion

A negatively charged ion.

anode

The electrode where oxidation occurs in an electrochemical cell. It is the positive electrode in an electrolytic cell, while it is the negative electrode in a galvanic cell. The current on the anode is considered a positive current according to international convention; however, in electroanalytical chemistry the anodic current is often considered negative. Contrast with cathode.

anode effect

A condition in an electrolytic cell that produces an abrupt increase in cell voltage and a decrease in current flow. It is usually caused by the temporary formation of an insulating layer on the anode surface. It occurs almost exclusively in molten salt electrolysis, such as in aluminium production.

aqueous solution

A solution with water as the solvent. Contrast with: non-aqueous solution.

atom, atomic structure (proton, neutron, electron)

The smallest physical unit of a chemical element that can still retain all the physical and chemical properties of that element. Atoms combine to form molecules, and they themselves contain several kinds of smaller particles. An atom has a dense central core (the nucleus) consisting of positively charged particles (protons) and uncharged particles (neutrons). Negatively charged particles (electrons) are scattered in a relatively large space around this nucleus and move about it in orbital patterns at extremely high speeds. An atom contains the same number of protons as electrons and thus is electrically neutral (uncharged) and stable under most conditions.

atomic weight

The average relative weight of a chemical element as it occurs in nature referred to some element taken as a standard.

barrier (oxide) film

A thin, continuous, non-porous, electrically insulating film on metal surfaces (usually comprised of oxides).

base

A compound that dissociates to produce hydroxyl (OH^-) anions when dissolved in water (also called "caustic" or "alkali"). See also pH.

bioelectrochemistry

Electrochemistry of biological (living) systems and biological compounds.

buffer solution

A solution with a constant, specified pH. The pH of the solution "resists" any change: addition of small amounts of solvent or even acid or base will not appreciable change the pH. This is called "buffer capacity."

C

Symbol and abbreviation of coulomb.

capacitor

An electrical device which serves to store electricity or electrical energy. It has three essential parts: two electrical conductors, which are usually metal plates, separated and insulated by the third part called the "dielectric." The plates are charged with equal amounts of positive and negative electrical

charges, respectively. This is a "physical" storage of electricity as compared with the "chemical" storage in a battery.

capacity

See capacitance. The term "capacity" is also used in a somewhat different meaning for batteries: it expresses the total amount of electrical charge a battery is able to hold. It is usually expressed in ampere-hours.

cathode

The electrode where reduction occurs in an electrochemical cell. It is the negative electrode in an electrolytic cell, while it is the positive electrode in a galvanic cell. The current on the cathode is considered a negative current according to international convention; however, in electroanalytical chemistry the cathodic current is often considered positive. Contrast with anode.

cation

A positively charged ion.

charge carrier

The particle carrying the electrical charge during the flow of electrical current. In metallic conductors the charge carriers are electrons, while ions carry the charges in electrolyte solutions.

charge density

Charge referred to the unit area of the electrode. Charge divided by electrode area.

charger

An electrical device used to charge a rechargeable battery using household electricity.

charge rate

The current applied to a rechargeable battery to restore its capacity. This rate is commonly expressed as a multiple of the rated capacity.

charge-transfer reaction

A chemical reaction where an electrical charge (usually an electron) is transferred from one reactant to another. See also heterogeneous charge-transfer reaction and homogeneous charge-transfer reaction. In case of an electrode reaction, the electrode itself is considered one of the "reactants." An electrode reaction is a heterogeneous charge-transfer reaction.

charge-transfer resistance

A characteristic quantity for an electrode reaction indicative of its inherent speed: a large charge-transfer resistance indicates a slow reaction. See also non-ohmic resistance.

charging

A process to "fill" a rechargeable battery or a capacitor with electricity by applying a current to its terminals. In a battery, this process will cause electrochemical reactions to occur storing the electricity in chemical form. In contrast, during the charging of a capacitor the electricity is stored as electrical charges, without causing any chemical reactions to occur. Opposite: discharging.

closed-circuit voltage

The voltage of a battery when it is discharging (on-load condition). Abbreviated as "ccv."

coagulation

Coagulation is the process of adding chemicals to water to make dissolved and suspended particles bind together (coagulate) and form larger particles (floculant) that settle out of the water.

concentration

The measure of the amount of dissolved material (solute) in a solution. It can be expressed in a variety of ways. Expressions in weight percent, and grams of solute per litre of solution are common. A more fundamental way to express concentration is used in chemistry: the "molar" concentration. A solution is considered one molar (1 M) if it contains as many grams of solute per litre of solution as is the molecular weight of the solute (the so called gram-mole). This provides an atomistically fundamental expression because one gram-mole of any material will contain the same (and very large) number of molecules. One gram-mole of hydrogen gas contains the exact same number of molecules as one gram-mole of table salt (sodium chloride), even though the latter is much heavier. In this dictionary, the term "concentration" always designates "molarity" unless otherwise specified.

conductivity (electrical)

The measure of a material's capability to carry electrical current. The measurement unit of conductivity (conductance) is the siemens. The reciprocal of resistivity.

conductor (electrical)

A material that is capable to carry an electrical current. See also electronic conductor and ionic conductor. .

corrosion

A chemical (often electrochemical) process that destroys structural materials. Typically it refers to corrosion of metals, but any other material (e.g., plastic or semiconductor) will also corrode. The simplest example of metallic corrosion is the rusting of iron in air. Iron is spontaneously oxidized by the oxygen in air to iron oxides (while the oxygen is being reduced). Metallic corrosion is very often an electrochemical process. It is always electrochemical when the metal is immersed in a solution, but even in atmospheric corrosion a thin film of condensed moisture often covers the surface. The metal in the corrosive solution essentially acts as a short-circuited galvanic cell. Different areas of the surface act as anode and cathode, at the anodic areas the metal is oxidized to an oxide while at the cathodic areas the dissolved oxygen is being reduced. The spontaneous complementary oxidation/reduction processes of "rusting" are spatially separated while an electrical current is flowing "internally" from one part of the corroding metal to another; the current is totally "wasted" as it produces no useful work but only generates heat. (A cell arrangement like this is often called a "local cell.") See corrosion current and corrosion potential.

Corrosion products are typically oxides, but other products (e.g., sulphides) can also form depending on the environment. Corrosion always involves oxidation of the corroding material in the general sense of the term.

corrosion inhibitor

A chemical that stops (or at least decreases the rate of) a corrosion process. The inhibitor can be added to an otherwise corrosive solution (often a very small concentration will accomplish the goal) or it can be incorporated in a coating applied to the metal surface.

corrosion potential

The electrode potential of a corroding metal. It is a "mixed potential" with a value that is in between the equilibrium potentials of the anodic and cathodic corrosion reactions. The corrosion is a spontaneous, dynamic phenomena with electrode reactions taking place and a current flowing. Consequently, both reactions are polarized and their potentials approach each other; as a matter of fact, they must become equal to preserve a single potential for the metal. However, the two reactions

are not necessarily equally polarized. The overpotential of the two electrode reactions will be generally different, and their values will be dictated by the requirement that the electrode potentials be equal (at the "corrosion potential") at one, uniquely defined current (the corrosion current). See the Tafel equation for a relation between overpotential and current. (The i_r drops in the solution and the metal are ignored in the above discussion; this is justified by the close proximity of the anodic and cathodic areas on the corroding metal.)

coulomb

Measurement unit of the electrical charge. Symbol: "C".

The charge passing a given point during one second when the current is one ampere.

current

The movement of electrical charges in a conductor; carried by electrons in an electronic conductor (electronic current) or by ions in an ionic conductor (ionic current). "By definition" the electrical current always flows from the positive potential end of the conductor toward the negative potential end, independent of the actual direction of motion of the differently charged current carrier (or "charge carrier") particles. Two kinds of currents must be distinguished: "direct current (dc)" and "alternating current (ac)." Direct current is the unidirectional continuous flow of current, while alternating current is the oscillating (back and forth) flow of current. In electrochemistry, we almost always use direct current. Consequently, the term "current" always designates "dc" in this dictionary unless specifically stated to be "ac." The normal household current is an alternating current. The measurement unit of current is the ampere.

As mentioned above, the "defined" current flows from the positive terminal of the current source, through the load, to the negative terminal of the source. Consequently, inside the "source" (whether it is electromechanical or electrochemical) the current must flow from the negative terminal to the positive terminal since there must be a complete circuit. This concept is especially important in electrochemistry because an electrochemical cell can be either a current "source" (galvanic cell) or a "load" (electrolytic cell). Furthermore, a rechargeable battery operates as a "source" during discharge and as a "load" during charge. Current flowing through an electrochemical cell is usually the sum of the capacitive current and the faradaic current.

current efficiency

The fraction, usually expressed as a percentage, of the current passing through an electrolytic cell (or an electrode) that accomplishes the desired chemical reaction. Inefficiencies may arise from reactions other than the intended reaction taking place at the electrodes, or side reactions consuming the product. The expected production can be theoretically calculated and compared with the actual production.

current leakage

Current that is bypassing bipolar electrodes in a series coupled cell assembly (due to insufficient sealing or improper piping around the bipolar electrode) and therefore is not producing the required chemical change (electrode reaction).

dc

Abbreviation of direct current. However this term is also used in connection with dc voltage, that is, a steady voltage that will cause a "dc current" to flow in a conductor, and also in connection with dc power. Contrast with ac.

deposition/dissolution

See metal deposition/dissolution reactions.

dissociation

The process that may occur when a chemical compound is dissolved in a solvent (e.g., water). The molecules of the compound will break up ("dissociate") into two or more ions resulting in an ionically conducting electrolyte solution. E.g., the common table salt (sodium chloride) will dissociate into a single charged sodium cation and a single charged chloride anion.

electrical charge

A basic property of matter that gives rise to all electric and magnetic forces and interactions. Matter can be "neutral" (having no electrical charge) or it can have one of two kinds of charges distinguished as "positive" or "negative." The measurement unit of charge is the coulomb.

electrical energy

A form of energy. It expresses the ability of an electrical source to carry out useful work or generate heat. E.g., this energy can be used to drive an electrical motor and carry out some mechanical work, or to generate heat with an electrical heater. The electrical energy is usually expressed in units of watt-hour, symbol: "Wh". See also electrical power.

electrical field

A region of space, associated with a distribution of electric charge, in which forces due to that charge act upon other electric charges.

electrical potential

The electrical potential difference between two point in a circuit is the cause of the flow of a current. It is somewhat analogous to the difference in height in a waterfall that causes the water to fall, or the difference in pressure in a pipeline that causes the gas to flow. In electrochemistry we typically cannot measure "absolute" potentials, only the "difference" of potential between two points. For similar concepts, see electromotive force (emf) and voltage. These terms are sometimes used interchangeably. However, in electrochemistry "emf" usually refers to the potential difference between the two electrodes of an electrochemical cell when there is no current flowing through the cell, "voltage" refers to same with current flowing, and "potential" is usually used in connection with electrodes (see electrode potential). The measurement unit of the potential is the volt.

electrical power

The rate at which an electrical source can supply electrical energy. E.g., a battery may be able to store a large amount of energy, but if it has a small power capability it can provide the energy (do some work) only slowly, and it will take a long time to discharge. Another battery with the same energy storage capability but larger power will provide the energy (do work) faster, but will also be discharged faster. Electrical power is expressed usually in units of watt, symbol: "W". Unfortunately, the terms "power" and "energy" are often used interchangeably in everyday language (and sometimes also in the technical literature) even though they are quite distinct concepts, e.g., when we talk about "energy source" or "power source," we usually mean the same thing. Not only electrical sources but also loads are characterized by a power rating, e.g., an electrical motor or a light bulb is characterized by the power it needs to operate it.

The power of a source (or the power need of a load) can be calculated as the product of the current and voltage ($\text{watt} = \text{ampere} \times \text{volt}$). One watt means that one watt-second ($\text{coulomb} \times \text{volt}$) energy is provided (used) every second. In more practical units, one watt means that one watt-hour ($\text{ampere-hour} \times \text{volt}$) energy is provided (used) every hour.

electrical source (supply)

A source of electrical power (electrical energy), a device that supplies electrical current. It can be electrochemical (battery or fuel cell) or an electromechanical device (dynamo) or a specialized

of the cation of the electrode metal in the solution (see Nernst equation). Contrast with electrode of the second kind and electrode of the third kind.

electrode of the second kind

A metal electrode assembly with the equilibrium potential being a function of the concentration of an anion in the solution. Typical examples are the silver/silver-chloride electrode and the calomel electrode. Contrast with electrode of the first kind and electrode of the third kind.

The assembly consists of a metal, in contact with a slightly soluble salt of this metal, immersed in a solution containing the same anion as that of the metal salt (e.g., silver---silver chloride---potassium chloride solution). The potential of the metal is controlled by the concentration of its cation in the solution, but this, in turn, is controlled by the anion concentration in the solution through the solubility product of the slightly soluble metal salt.

electrode of the third kind

A metal electrode assembly with the equilibrium potential being a function of the concentration of a cation, other than the cation of the electrode metal, in the solution. These have been used, with limited success, in sensors for metal ions for metals that are not stable in aqueous solutions, e.g., calcium and magnesium. Contrast with electrode of the first kind and electrode of the second kind.

The assembly consists of a metal in contact with two slightly soluble salts (one containing the cation of the solid metal, the other the cation to be determined, with both salts having a common anion) immersed in a solution containing a salt of the second metal (e.g., zinc metal---zinc oxalate---calcium oxalate---calcium salt solution). The potential of the metal is controlled by the concentration of its cation in the solution, but this is controlled by the anion concentration in the solution through the solubility product of the slightly soluble metal salt, which, in turn is controlled by the concentration of the cation of the second slightly soluble salt. These electrodes are very sluggish and unstable due to a series of equilibria to be established to produce a stable potential.

electrode potential

The electrical potential difference between an electrode and a reference electrode. We cannot measure the "absolute" potential of an electrode; therefore, the electrode potential must always be referred to an "arbitrary zero point," defined by the potential of the reference electrode. Consequently, it is very important always to note the type of reference electrode used in the measurement of the electrode potential. See also equilibrium electrode potential.

electrode reaction

A chemical "half" (or "partial") reaction occurring at the electrode surface. It is called a "half" (or "partial") reaction because only the oxidation or the reduction part of the overall cell reaction occurs at any one electrode. See also electrochemical reaction. Many electrode reactions can proceed either as oxidation or as reduction, depending on the direction of the current flowing through the electrode/electrolyte interface. See, e.g. metal deposition/dissolution or redox reactions.

An electrode reaction always occurs in several series and parallel elementary reaction steps. Even in the simplest case there are three steps in series: (1) the reactant must be transported to the electrode surface from the bulk of the electrolyte (usually predominantly by diffusion, but it can also occur by electromigration), (2) a charge-transfer reaction occurs, and (3) the product must be transported from the electrode surface to the bulk of the electrolyte.

electrolysis

A process that decomposes a chemical compound into its elements or produces a new compound by the action of an electrical current. The electrical current is passed through an electrolytic cell and

oxidation/reduction reactions occur at the electrodes. E.g., water can be decomposed into hydrogen and oxygen, or a metal can be electroplated by electrolysis.

electrolyte

A chemical compound (salt, acid, or base) that dissociates into electrically charged ions when dissolved in a solvent. The resulting electrolyte (or electrolytic) solution is an ionic conductor of electricity. Very often, the so formed solution itself is simply called an "electrolyte." Also, molten salts and molten salt solutions are often called "electrolyte" when used in electrochemical cells, see ionic liquid. See also solid electrolyte.

electrolytic cell

An electrochemical cell that converts electrical energy into chemical energy. The chemical reactions do not occur "spontaneously" at the electrodes when they are connected through an external circuit. The reaction must be forced by applying an external electrical current. It is used to store electrical energy in chemical form, see rechargeable battery. It is also used to decompose or produce (synthesize) new chemicals by application of electrical power. This process is called electrolysis, e.g., water can be decomposed into hydrogen gas and oxygen gas.

The free energy change of the overall cell reaction is positive.

electromotive force

The cell voltage of a galvanic cell measured when there is no current flowing through the cell. In other words, the equilibrium electrode potential difference between the two electrodes of the cell. Abbreviated as "emf."

electroplating

The process that produces a thin, metallic coating on the surface on another metal (or any other conductor, e.g., graphite). The metal substrate to be coated is made the cathode in an electrolytic cell where the cations of the electrolyte are the positive ions of the metal to be coated on the surface. When a current is applied, the electrode reaction occurring on the cathode is the reduction of the metal ions to metal. E.g., gold ions can be discharged from a gold solution to form a thin gold coating on a less expensive metal to produce "custom" jewellery. Similarly, chromium coating is often applied to steel surfaces to make them more "rust resistant." Electroplating is also used in the production of integrated circuits on computer chips and for other modern electronic instrumentation. The anode material can either be the metal to be deposited (in this case the electrode reaction is electrodisolution that continuously supplies the metal ions) or the anode can be of inert material and the anodic reaction is oxygen evolution (in this case the plating solution is eventually depleted of metal ions). Also called "electrodeposition."

element, chemical

A substance that cannot be decomposed into simpler substances by chemical means.

emf

Stands for electromotive force.

energy

The energy of a system expresses the ability of that system to do some useful work or generate heat. Energy can be in many forms; e.g., mechanical energy, chemical energy, heat energy, electrical energy, etc. The different forms of energy can be converted into each other.

It is a fundamental law of nature that energy can never be converted from one form to another 100%, some of the energy is always converted into heat energy during the conversion. Also, heat can never be converted 100% into any other form of energy.

F

Symbol and abbreviation of farad, and symbol and abbreviation of the Faraday number. (Often a "bold-face" letter is used for the latter, but this is not a general practice.) It is usually obvious from the context which meaning is appropriate.

farad

Measurement unit of capacitance. Symbol: "F," which is the same as the symbol of the Faraday Number. It is usually obvious from the context which meaning is appropriate.

A capacitor has a capacitance of one farad when one coulomb charges it to one volt.

Faraday's Laws

Some of the most fundamental laws of electrochemistry discovered by Faraday in the 1830's. They are usually stated as: (1) In any electrolytic process the amount of chemical change produced is proportional of the total amount of electrical charge passed through the cell. (2) The mass of the chemicals changed is proportional to the chemicals' equivalent weight. The proportionality constant being the Faraday Number.

Faraday Number (Faraday constant)

The Faraday Number (or constant) gives the amount of electrical charge needed to change one gram-equivalent of substance by electrochemical reaction. Its value is 96,485.34 coulombs or 26.80 ampere-hours. This charge is often simply called one "Faraday." Symbol: "F," which is the same as the symbol of the farad. It is usually obvious from the context which meaning is appropriate.

The Faraday number is the product of Avogadro's number and the electrical charge of a single electron.

faradic current (density)

The current (or current density) that is flowing through an electrochemical cell and is causing (or is caused by) chemical reactions (charge transfer) occurring at the electrode surfaces. Contrast with capacitive current.

faradaic reaction

A heterogeneous charge-transfer reaction occurring at the surface of an electrode.

flocculation

Flocculation refers to a process where a solute comes out of solution in the form of floc or "flakes." The term is also used to refer to the process by which fine particulates are caused to clump together into floc. The floc may then float to the top of the liquid, settle to the bottom of the liquid, or can be readily filtered from the liquid.

flow-through electrode

An electrode that permits the electrolyte to flow through it, e.g., a porous electrode or a packed-bed electrode. This type of electrode is especially useful for removing small traces of impurities from the solution by electrolysis (e.g., waste treatment) because the solution contacts a large surface of the electrode material.

frequency

The frequency of an alternating (ac) current is a measure of how many times the direction of the current flow changes, in the same direction, per second. As the direction of flow changes back and forth, the total number of directional changes, per second, is twice the frequency. The frequency of the household current is 60 hertz. The measurement unit of the frequency is the hertz.

half cell

A somewhat archaic term, indicating a structure that contains an electrode and the surrounding electrolyte. Electrochemical cells are often divided, containing two separate electrolytes (one surrounding each electrode, e.g., the Daniell cell). In these cases the electrode and its electrolyte can be considered "half" of the cell. Commercially available reference electrodes can be considered "half cells."

half-cell reaction

A not incorrect, but somewhat archaic term for electrode reaction.

ion

An electrically charged chemical particle (atom, molecule, or molecule fragment). "Anions" are negatively charged (contain excess electron(s), and "cations" are positively charged (deficient in electron(s)).

ionic current

Electrical current with ions as charge carriers.

metal deposition/dissolution

A class of electrode reactions involving oxidation/reduction of a solid metal and its dissolved ion. E.g., if a copper metal rod is immersed in a copper sulfate solution, the copper cations can be cathodically reduced to copper metal, or the copper metal can be anodically oxidized to copper ions. Compare with a redox reaction where both the oxidized and the reduced species are in solution. The terms "electrodeposition" and "electrodissolution" are often used to describe these reactions. These reactions are used in many technologies, such as electroplating, electrowinning, electrorefining, and production of metal powders. And also in electrogravimetry.

mol

The measurement unit and symbol of mole.

molecular weight

The weight of a molecule of a compound that may be calculated as the sum of the atomic weights of its constituent atoms.

molecule

The smallest physical unit of a substance that retains all the physical and chemical properties of that substance. It may consist of a single atom or of a group of atoms bonded together chemically.

Nernst equation

An equation defining the equilibrium potential of an electrode. The potential is the sum of the standard electrode potential and a correction term for the deviation from unit concentrations of the reactant and the product of the electrode reaction in the solution; if the "reduced" form is a metal, a pure metal (not alloyed with other metals) is considered to be at unit concentration.

$$E = E^0 + S \log \frac{C_{ox}}{C_{red}}$$

The correction term is the product of the "Nernst slope" and the logarithm of the ratio of the concentrations (strictly speaking, activities) of the oxidized species and the reduced species. At room temperature, the Nernst slope is 0.05916 volt divided by the number of electrons transferred during the reaction. E.g., for a simple metal deposition/dissolution reaction the slope is 0.05916 for a single charged metal cation, 0.0296 volt for a double charged ion, etc.

normal electrode potential

Alternative name for standard electrode potential.

Ω

Symbol and abbreviation of ohm. (The symbol is the "Greek capital omega" letter, some browsers unfortunately do not support this.)

ohm

Measurement unit of the electrical resistance. Symbol: "Ω". (The symbol is the "Greek capital omega" letter, some browsers unfortunately do not support this.)

Ohm's Law

The relation amongst the current flowing through a resistor and the potential difference between the two ends of the resistor. The potential difference is equal to the product of the current and the resistance (volt = ampere times ohm).

$$V = IR$$

ohmic loss

The total ir drop in an electrochemical cell, including the ir drop in the solution between the electrodes and in any separator.

ohmmeter

Instrument used for the measurement of electrical resistance.

osmotic pressure

The pressure that develops in a solution separated from a solvent by a membrane permeable only to the solvent.

overcharging

During the charging of a rechargeable battery, eventually enough electrical charge is supplied to convert all the active material stored in the electrodes. If charging continues, the battery is said to be "overcharged." It very much depends on the battery system whether overcharging is detrimental to the battery or not.

oxidation/reduction

In a narrow sense, oxidation means the reaction of a substance with oxygen. Hydrogen can react with oxygen to be oxidized to water. Hydrocarbon fuels (gasoline, natural gas, etc) can react with oxygen to be oxidized to carbon dioxide and water. Iron can react with oxygen to be oxidized to "rust." During oxidation, the oxygen itself is being reduced. Oxidation and reduction always occur simultaneously.

During these reactions, electrons are transferred from the substance that is oxidized to the oxygen. In a wider sense, all electron-transfer reactions are considered oxidation/reduction. The substance gaining electrons ("oxidizing agent" or "oxidant") is oxidizing the substance that is losing electrons ("reducing agent" or "reductant"). In the process, the "oxidizing agent" is itself reduced by the "reducing agent." Consequently, the reduction process is sometimes called "electronation," and the oxidation process is called "de-electronation."

oxidation/reduction potential

A measure of the oxidation/reduction capability of a solution. It is a redox potential measured with an inert electrode. An oxidizing solution (e.g., one saturated with oxygen) has a more positive potential than a reducing solution (e.g., one saturated with hydrogen).

passivation

The formation of a thin adherent film or layer on the surface of a metal or mineral that acts as a protective coating to protect the underlying surface from further chemical reaction, such as corrosion, electro-dissolution, or dissolution.

pH

A measure of the acidity/alkalinity (basicity) of a solution. The pH scale extends from 0 to 14 (in aqueous solutions at room temperature). A pH value of 7 indicates a neutral (neither acidic nor basic) solution. A pH value of less than 7 indicates an acidic solution, the acidity increases with decreasing pH value. A pH value of more than 7 indicates a basic solution, the basicity or alkalinity increases with increasing pH value.

The pH of a solution is equal to the negative, ten-based logarithm of the activity of the hydrogen ions in the solution. Neutral water dissociates into equal amounts of hydrogen (H^+) cations and hydroxyl (OH^-) anions. As the product of the concentrations (activities) of the two ions is always a constant 10^{-14} , water has a pH of 7. In acidic solutions the hydrogen ions are in excess, while in basic solutions the hydroxyl ions are in excess.

pH electrode

An electrode assembly with a pH dependent potential. A variety of different electrodes can be used for this purpose, the most common one is the glass electrode.

pH meter

Volt meter that measures the electrical potential difference between a pH electrode and a reference electrode and displays the result in terms of pH value of the sample solution in which they are immersed.

Precipitation

Precipitation is the formation of a solid in a solution during a chemical reaction. This can occur when an insoluble substance is formed in the solution due to a reaction or when the solution has been supersaturated by a compound. In most situations, the solid forms ("falls") out of the solute phase, and sinks to the bottom of the solution (though it will float if it is less dense than the solvent, or form a suspension).

proton

See atomic structure.

Hydrogen ions are often called "protons." Hydrogen is the simplest atom, containing only a proton and an electron. Consequently, a hydrogen cation is indeed a proton. However, this is a simplification because ions are almost always solvated.

(electrode) reaction mechanism

The totality of all the elementary reaction steps occurring in series or parallel that fully defines the overall electrode reaction.

redox reaction

A class of electrode reactions involving oxidation/reduction of two dissolved species. E.g., iron metal can exist in solution as a doubly positively charged ("ferrous") ion or a triply positively charged ("ferric") ion. Such a system is often called a "redox couple," such as the "ferrous/ferric" couple. The ferric ions can be cathodically reduced to ferrous ions, or the ferrous ions can be anodically oxidized to ferric ions. With these reactions, an inert electrode is used that does not take part in any reactions under the conditions of the oxidation/reduction of the ions. This electrode then acts only as a source or sink of electrons; examples are: carbon, graphite, platinum, gold. Compare with a metal deposition/dissolution reaction where one of the reacting species is a solid metal and the other species is in solution.

reducing agent

A substance that is affecting reduction by donating electrons to another substance. See oxidation/reduction. Also called "reductant."

resistor

An electrical circuit element with a fixed resistivity.

under pressure. During discharging, the same cell is used as a fuel cell and the gases are recombined to produce water and electricity.

solubility

The maximum amount of a species that can be dissolved in a given solvent. It is usually expressed as the maximum achievable concentration. A solution is called "saturated" if it contains the maximum dissolvable amount.

standard cell

A non-rechargeable cell (battery) whose emf is accurately known and remains sufficiently constant. It is less and less used nowadays because the availability of electronic voltage standards.

volt

Measurement unit of the electrical potential. Symbol: "V". A term named in honour of Alessandro Volta.

voltage

A term sometimes used interchangeably with electrical potential. See also cell voltage.

voltmeter

Instrument used for the measurement of electrical potential differences.

Appendix C

Drinking water quality guidelines

Colour

Background Information

Introduction	<p><i>True colour</i> is the colour of a water sample from which the turbidity has been removed. <i>Apparent colour</i> includes the colour and appearance of suspended matter. <i>True colour</i> is described by the dominant wavelength or hue together with the degree of brightness or luminance and the saturation or purity of the colour. Colour in domestic water may be due to natural sources of coloured organic matter like humic and fulvic acids. Colour is strongly influenced by the presence of iron, manganese and certain other metals either as natural impurities or corrosion products.</p>
Occurrence	<p>Colour in water can be of natural mineral or origin or it may be as an industrial result of effluents containing soluble coloured materials (discharges from pulp and paper, and textile industries). The presence of iron and manganese can cause a natural brown discolouration in water. Iron and manganese are also found in association with humic acids or lignins. Colloidal matter present in water is often associated with colour. The persistence of colour in water depends on the causative substance(s). The reddish-brown colour from dissolved iron complexes is generally readily removed in conventional water treatment processes. Colour from dissolved organic dyes may be more persistent.</p>
Interactions	<p>The <i>apparent colour</i> of water is strongly related to turbidity. Most natural causes of colour are associated with the presence of dissolved organic matter, and iron and manganese compounds. Other metal ions may on occasion give rise to colour in water.</p>
Measurement	<p>Colour may be measured either in Pt-Co colour units, using the visual colour comparison method, or by spectrophotometric methods, where the colour characteristics are reported as:</p> <ul style="list-style-type: none">• Dominant wavelength (nm)• Hue (colour)• Luminance (%)• Purity (%)
Data Interpretation	<p>Mean values should be used to compare with the criteria given.</p>
Treatment Options	<p>Colour in water supplies is caused by a variety of agents. Different methods may therefore be required to remove colour. These include:</p> <ul style="list-style-type: none">• Filtration of the water through a slow sand filter. The biologically active surface layer on the filter removes colour by metabolising the organic material in the water.• Some forms of colour in water are amenable to removal by coagulation, flocculation, clarification (by settlement or flotation) and filtration. A further activated carbon filtration step may be beneficial.

- Some forms of colour in water are readily removed by strong oxidising agents such as ozone.

In many cases a combination of treatment processes will be required to achieve the water quality required. Some improvement in the colour of household water can be achieved by filtering it through a disposable activated carbon cartridge.

The Effects of Colour

Norms	The norm used in the guideline for colour is aesthetic effects.
Effects	No direct health effects result from the presence of colour in drinking water except when colourants are toxic. Aesthetic effects are mainly visual but some colourants may stain or otherwise affect household appliances, for example, iron or manganese.
Mitigation	For drinking purposes, small amounts of water can be treated using domestic water purifiers / filters.
Criteria	A Target Water Quality Range 15 Pt-Co units is recommended for drinking water.

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Iron

Background Information

Introduction Pure iron is silvery in colour but usually appears as greyish black or brown deposits as a result of oxidation. Iron is found in three oxidation states, namely, 0, II and III of which the III oxidation state is the most common. In water, iron can be present as dissolved ferric iron, Fe(III), as ferrous iron, Fe(II) or as suspended iron hydroxides. Biologically iron is an essential micronutrient required by all living organisms. High concentrations of iron are predominantly an aesthetic concern since ferrous salts are unstable under the pH conditions prevailing in drinking water and precipitate as insoluble ferric hydroxide, which settles out as a rust-coloured silt.

Occurrence Iron is the fourth most abundant element and constitutes five percent of the earth's crust. It is found in many minerals, the most common of which is haematite (Fe_2O_3), widely used as an iron ore for metallurgical purposes. Other important iron minerals are pyrite (FeS_2), siderite (FeCO_3), magnetite (Fe_3O_4), goethite ($\text{FeO} \cdot \frac{1}{2}\text{H}_2\text{O}$) and limonite ($2\text{FeO} \cdot 3\text{H}_2\text{O}$), as well as a number of mixed ores, such as chalcopyrite (CuFeS_2) and arsenopyrite (FeAsS). Pyrite is often associated with coal formations and iron may occasionally also be found in the elemental form, either as terrestrial iron or as meteoric iron. The reddish colour of soil is due to iron, the median concentration in soil being 4.0 % (m/m). Typically, the concentration of dissolved iron in:

- unpolluted surface water, is in the range of 0.001 - 0.5 mg/°; and
- sea water, is approximately 0.002 mg/°.

The speciation of iron is strongly related to the pH and the redox potential of the water. At neutral or alkaline pH, under oxidising conditions, the dissolved iron concentration is usually in the $\mu\text{g}/^\circ$ range but under reducing conditions, soluble ferrous iron may be formed and substantially higher concentrations in the $\text{mg}/^\circ$ range may be encountered. Where marked acidification of the water occurs and the pH is less than 3.5, the dissolved iron concentration can be several hundred $\text{mg}/^\circ$, as may be the case with acid mine drainage.

There is a natural cycling of iron between the dissolved and precipitated phases at the water sediment interface, in which micro-organisms, particularly iron bacteria such as *Gallionella spp.* play a significant role.

Interactions The concentration of dissolved iron in water is dependent on the **pH**, redox potential, **turbidity**, **suspended matter**, the concentration of **aluminium** and the occurrence of several heavy metals, notably **manganese**. The natural cycling of iron may also result in the coprecipitation of trace metals such as **arsenic**, **copper**, **cadmium** and **lead**.

Measurement The criteria are given in terms of the total iron concentration, expressed in units of $\text{mg}/^\circ$. The reference method for the determination of iron is by atomic absorption spectrometry (AAS), using an air-acetylene flame. Measurement of the total iron concentration requires acidification followed by filtration prior to AAS analysis. Where other methods are used, their characteristics relative to the reference method should be known.

Data Interpretation Mean values should be used to compare with the criteria given. Turbidity and pH must also be taken into account in the interpretation of iron concentrations.

Treatment Options Iron in water supplies is most conveniently removed by applying conventional water treatment processes of coagulation with lime or alum, followed by settlement and filtration. Iron can also be removed from water using an oxidising process which will convert the iron into an insoluble hydroxide or hydrated oxide, removable by filtration. The following treatment approaches are used:

- The water can be **aerated** by devices such as fountains, cascades or mechanical aeration;
- The addition of lime to the water will raise the pH and facilitate the oxidation of iron by air in the water, followed by settlement of the iron oxide;
- The water can also be **chemically oxidised** by dosing with chlorine, hydrogen peroxide, ozone or other strong oxidants. On an industrial scale chlorine is commonly used as the chemical oxidant. Post-treatment, high levels of residual chlorine should be avoided since this may interfere with the quality of the water.

Removal of iron can be achieved on a household scale by cascading the water through the air and allowing the iron oxide particles to settle. On an industrial scale the process usually needs to be more closely controlled and monitored because the consequences of incomplete treatment may be severe.

For the optimisation of treatment processes it is important to determine both the total and dissolved iron species and their relative concentrations.

The Effects of Iron

Norms The norms used in the guideline are based on aesthetic and health effects. The major effects of the presence of iron in domestic water are aesthetic, but in some cases distribution systems may also be affected. Health effects may occur at extremely high concentrations.

Effects Excessive ingestion of iron may result in haemochromatosis, wherein tissue damage occurs as a consequence of iron accumulation. Haemochromatosis generally results from prolonged consumption of acid foodstuffs cooked in kitchenware made of iron. Poisoning is rare since excessively high concentrations of iron do not occur naturally in water. The extreme unpalatability of such water would probably prevent consumption. Further, iron in the distribution system promotes proliferation of iron-oxidising bacteria which oxidise ferrous iron to ferric iron, and manifest as slimy coatings in plumbing when the iron concentration of the water in the distribution system approaches 0.3 mg/•. Effects are predominantly aesthetic, such as the staining of enamelled surfaces of baths, hand basins and lavatory cisterns/bowls and laundry. Iron causes discolouration of water supplies when present at low concentrations in association with aluminium. Iron that settles out in distribution systems gradually reduces the flow rate of water. The only associated health effects are those that could arise from the presence of microbial deposits on internal surfaces of plumbing.

Iron complexed with humic acid, a natural water constituent in certain regions, causes a brown discolouration of water at high concentrations. This may be aesthetically unacceptable, but has no adverse health implications.

Mitigation

Mitigation against aesthetic effects of the presence of iron in domestic water involves regularly cleaning of bathroom and sanitaryware to prevent the buildup of permanent stains. Mitigation of the effects of ingesting excessive concentrations of iron is not normally an issue, since poisoning from water is rare. However, iron poisoning in children from accidental consumption of anaemia-treatment iron supplement tablets, is not that rare. If iron poisoning, acute or chronic, is suspected, medical advice should be sought.

Criteria

Effects of Iron on Aesthetics, Human Health and Household Distribution Systems

Iron Range (mg/•)	Effects
Water Quality Target Range 0 - 0.1	No taste, other aesthetic or health effects associated with consumption and use
0.1 - 0.3	Very slight effects on taste and marginal other aesthetic effects. Deposits in plumbing with associated problems may begin to occur. No health effects; the water is generally well tolerated.
0.3 - 1.0	Adverse aesthetic effects (taste) gradually increase as do possible problems with plumbing. No health effects.
1 - 10	Pronounced aesthetic effects (taste) along with problems with plumbing. Slight health effects expected in young children, and sensitive individuals.
10 - 30	Severe aesthetic effects (taste) and effects on the plumbing (slimy coatings). Slight iron overload possible in some individuals. Chronic health effects in young children and sensitive individuals in the range 10 - 20 mg/•, and occasional acute effects toward the upper end of this range.
30 - 100	As above Long-term health effects gradually increase.
100 - 300	As above Chronic health effects. Acute toxicity may begin to appear.
300 - 3 000	As above Chronic and acute health effects. Accidental iron poisoning from water is rare.
3 000 - 30 000	As above Lethal toxicity occurs.

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pH

Tentative guideline

Background Information

Introduction The pH of a solution is the negative logarithm to the base ten of the hydrogen ion concentration, given by the expression:

$$\text{pH} = -\log_{10}[\text{H}^+]$$

where $[\text{H}^+]$ is the hydrogen ion concentration.

At pH less than 7 water is acidic, while at pH greater than 7 water is alkaline.

The pH of natural waters is the result of complex acid-base equilibria of various dissolved compounds, mainly the carbon dioxide-bicarbonate-carbonate equilibrium system, which is also affected by temperature. Conditions which favour production of hydrogen ions result in a lowering of pH, referred to as an acidification process. Alternatively, conditions which favour neutralisation of hydrogen ions result in an increase in pH, referred to as an alkalization process. The pH of water does not indicate the ability to neutralise additions of acids or bases without appreciable change. This characteristic, termed buffering capacity, is controlled by the amounts of acidity and alkalinity present.

The pH of a water does not have direct health consequences except at extremes. The adverse effects of pH result from the solubilisation of toxic heavy metals and the protonation or deprotonation of other ions. The pH of most raw water sources lies within the range of 6.5 - 8.5. The main significance of pH in domestic water supplies relates to its effects on water treatment.

Occurrence The geology and geochemistry of the rocks and soils of a particular catchment area affect the pH and alkalinity of the water. The pH of most raw waters lies in the range of 6.5 - 8.5. Biological and anthropogenic activities such as nutrient cycling and industrial effluent discharge respectively can give rise to pH fluctuations. Notably, acid mine drainage can have a marked effect on the pH. Further, acid-forming substances, such as oxides of sulphur and nitrogen released into the atmosphere may ultimately alter the acid-base equilibria in natural waters and result in a reduced acid-neutralising capacity and hence lowering the pH.

Interactions The pH of natural waters is influenced by various factors and processes, including temperature, discharge of effluents, acid mine drainage, acidic precipitation, runoff, microbial activity and decay processes.

Measurement Water pH is measured electrometrically using a pH meter. The pH meter should be calibrated against standard buffer solutions of known pH prior to measurement of a sample. Fresh samples should be used to determine pH. The temperature at which measurements are made should always be reported, since pH measurement is influenced by temperature. Errors may be caused by the presence of sodium at pH values greater than 10.

Data Interpretation	Use of individual or mean values to compare with the criteria given depends on the application. Normally, individual values are used but the pH should always be interpreted in relation to the full analysis of the water sample and its use. For example, if the pH is acidic, the water should be analysed for metal constituents, which may have dissolved from the distribution system.
Treatment Options	<p>The main significance of pH in domestic water supplies relates to its effects on water treatment processes. The pH of water can be adjusted up or down by the addition of an alkali or an acid.</p> <p>Commonly used alkaline reagents are sodium carbonate, sodium hydroxide and lime. Acidic reagents commonly used are carbon dioxide (a gas which forms carbonic acid in water), hydrochloric acid or sulphuric acid. The reagent is usually added in dilute form using a dosing pump controlled by a pH monitor.</p> <p>The adjustment of pH in water will inevitably increase the salinity of the water by adding ions such as sodium, carbonate, hydroxyl, sulphate or chloride. Reagents should be chosen to minimise secondary effects. For certain purposes the pH of the water will need to be stabilised to within a chosen range by the addition of buffering reagents.</p> <p>The handling of acids and alkalis is often hazardous requiring special precautions in the form of protective clothing and in materials used in the manufacture of the dosing equipment.</p>

The Effects of pH

Norms	The norms used in the guideline for pH are based on human health and aesthetic effects.
Effects	<p>The selection of raw water as a drinking water source is never based solely on pH. Danger to health would result primarily from the presence of metal ions, which are more likely to influence selection than the pH value. A direct relationship between the pH of drinking water and human health effects is difficult, if not impossible to establish since pH is very closely associated with other aspects of water quality.</p> <p>The taste of water, its corrosivity and the solubility and speciation of metal ions are all influenced by pH. At low pH water may taste sour, while at high pH water tastes bitter or soapy. The potential toxicity of metal ions and chemicals which can be protonated, for example ammonia, is influenced by pH. Changes in pH affect the degree of dissociation of weak acids and bases. This effect is of special importance because the toxicity of many compounds is affected by their degree of dissociation.</p> <p>Corrosion in the water supply system is a major source of metal contamination in drinking water. Metals that have the potential for causing such contamination are lead, copper and zinc. Lead is subject to corrosion at a pH higher than 12. Corrosion of cadmium is only significant below pH 6. Other metals which are frequently used in household plumbing and that may be affected by pH are copper and zinc.</p>
Mitigation	See Treatment Options .

Criteria

Effects of pH on Aesthetics and Human Health

pH Range (pH units)	Effects
< 4.0	Severe danger of health effects due to dissolved toxic metal ions. Water tastes sour
4.0 - 6.0	Toxic effects associated with dissolved metals, including lead, are likely to occur at a pH of less than 6 Water tastes slightly sour
Target Water Quality Range 6.0 - 9.0	<i>No significant effects on health due to toxicity of dissolved metal ions and protonated species, or on taste are expected. Metal ions (except manganese) are unlikely to dissolve readily unless complexing ions or agents are present. Slight metal solubility may occur at the extremes of this range. Aluminium solubility begins to increase at pH 6, and amphoteric oxides may begin to dissolve at a pH of greater than 8.5. Very slight effects on taste may be noticed on occasion</i>
9.0 - 11.0	Probability of toxic effects associated with deprotonated species (for example, ammonium deprotonating to form ammonia) increases sharply. Water tastes bitter at a pH of greater than 9
> 11.0	Severe danger of health effects due to deprotonated species Water tastes soapy at a pH of greater than 11

Note:

The above criteria indicate possible health effects in the general population and the descriptions given for health effects should be considered tentative. The criteria are tentative since pH does not exert direct health effects, but may exert indirect health effects via metal solubility.

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Total Dissolved Solids

Background Information

Introduction The total dissolved solids (TDS) is a measure of the amount of various inorganic salts dissolved in water. The TDS concentration is directly proportional to the electrical conductivity (EC) of water. Since EC is much easier to measure than TDS, it is routinely used as an estimate of the TDS concentration.

Electrical conductivity (EC) is a measure of the ability of water to conduct an electrical current. This ability is a result of the presence of ions in water such as carbonate, bicarbonate, chloride, sulphate, nitrate, sodium, potassium, calcium and magnesium, all of which carry an electrical charge. Most organic compounds dissolved in water do not dissociate into ions, consequently they do not affect the EC.

Occurrence Virtually all natural waters contain varying concentrations of TDS as a consequence of the dissolution of minerals in rocks, soils and decomposing plant material and the TDS of natural waters is therefore often dependent on the characteristics of the geological formations the water was, or is, in contact with.

Typically, the concentration of the TDS in

- rainwater is low, generally less than 1 mg TDS/•;
- water in contact with granite, siliceous sand and well-leached soils is generally low, less than 30 mg TDS/•;
- water in contact with precambrian shield areas is generally below 65 mg TDS/•; and
- water in contact with palaeozoic and mesozoic sedimentary rock formations is generally in the range of 195 - 1 100 mg TDS/•.

TDS are likely to accumulate in water moving downstream because salts are continuously being added through natural and manmade processes while very little of it is removed by precipitation or natural processes. Domestic and industrial effluent discharges and surface runoff from urban, industrial and cultivated areas are examples of the types of return flows that may contribute to increased TDS concentrations .

High TDS concentrations in surface water are also caused by evaporation in water bodies which are isolated from natural drainage systems. The saline pans in the central parts of South Africa are such water bodies.

Interactions The properties of the TDS are governed by the characteristics of the constituent inorganic salts dissolved in the water. As such, TDS is also closely related to other water quality constituents such as the **total hardness** and the **corrosion** and scaling potential of water.

Measurement The criteria are given in terms of TDS concentration in mg/•, as well as the equivalent EC, expressed in milli-Siemens per metre (mS/m), measured at, or corrected to a temperature of 25 •C.

The TDS concentration can be measured as

- an estimate of the EC value (see below);
- the dry weight of the salts after evaporation of a known volume of filtered water;
- the sum of the concentrations of the constituent cations and anions.

For most natural waters electrical conductivity is related to the dissolved salt concentration by a conversion factor ranging from 5.5 - 7.5. The average conversion factor for most waters is 6.5. The conversion equation is as follows:

$$\text{EC}(\text{mS/m at } 25^{\circ}\text{C}) \times 6.5 = \text{TDS}(\text{mg/}^{\circ})$$

The exact value of the conversion factor depends on the ionic composition of the water, especially the pH and bicarbonate concentration. Should very accurate measures of TDS be required, the conversion factor should be determined for specific sites and runoff events.

Data Interpretation

The TDS concentrations in water prevailing for long periods of time rather than a few extreme events, is important. Therefore annual, seasonal mean or mean values for TDS concentrations should be used to compare with the criteria for TDS.

Treatment Options

Although some salts, such as those of calcium, magnesium and certain heavy metals can be removed by chemical precipitation, most of the inorganic salts dissolved in water can only be removed by distillation or by highly sophisticated physical-chemical separation technologies. All these technologies are characterised by their high cost and/or their high energy requirements.

The technologies available for reducing the concentration of TDS in water are:

- **Demineralisation** in a mixed-bed ion exchange column, usually where the feed TDS concentration is approximately 2 000 mg/°. Disposable ion exchange canisters can be used to produce potable water for domestic consumption whereas large banks of ion exchange filter beds, which are capable of being regenerated, are used on an industrial scale. Ion exchange processes are also used for the production of ultrapure water.
- Treatment by membrane processes such as **reverse osmosis** or **electrodialysis** where the TDS concentration is in the range of 2 000 - 3 500 mg/°. Small low-pressure reverse osmosis modules fed from a domestic supply line reliably produce potable water for household consumption and are easily replaced after one to three years if the membrane becomes fouled through scaling. Large-scale treatment is achieved with banks of reverse osmosis modules in parallel.
- **Distillation**, in cases where the TDS concentration is approximately 10 000 mg/°.

All the process alternatives are usually fouled by suspended matter and may also be impeded by severe scaling from hard waters. All large-scale processes require high levels of design, operator and maintenance skills. Furthermore, all processes produce a concentrated waste stream of the salts removed from the water and may cause disposal difficulties.

The Effects of Total Dissolved Solids

Norms

The norms used in the guideline for TDS are aesthetic and human health effects and economic impacts.

Effects

Low concentrations of particularly calcium and magnesium salts have nutritional value, although water with an extremely low TDS concentration may be objectionable because of its flat, insipid taste. Health effects related to TDS are minimal at concentrations below 2 000 - 3 000 mg/• TDS. In contrast, high concentrations of salts impart an unpleasant taste to water and may also adversely affect the kidneys.

Some of the physiological effects which may be directly related to high concentrations of dissolved salts include:

- laxative effects, mainly from sodium sulphate and magnesium sulphate, see **sulphate**;
- adverse effects of sodium on certain cardiac patients and hypertension sufferers;
- effects of sodium on women with toxæmia associated with pregnancy; and
- some effects on kidney function.

Bathing and washing in water with excessively high concentrations of TDS may give rise to excessive skin dryness and hence discomfort. Soap may lather poorly or with difficulty, see **calcium** and **magnesium**.

Chemical corrosion may occur when the alkalinity, i.e. the concentrations of carbonate, bicarbonate and hydroxide are low, the TDS concentration is high, particularly the concentrations of chloride and sulphate, and the pH is low. Scaling may also occur, see **corrosion**, **calcium**, **magnesium** and **total hardness**. Excessively high concentrations of TDS may adversely affect plumbing and appliances and hence the maintenance and replacement requirements.

Mitigation

Measures to mitigate the effects of having consumed water containing a high TDS concentration are unnecessary since salts are rapidly eliminated in the urine once consumption of such water has been discontinued. Any electrolyte imbalances that may result can be restored by consuming water with more acceptable levels of dissolved salts.

Water with high concentrations of TDS may be diluted with other sources, e.g. rain water.

Modifications EC is usually measured at 20 •C for domestic water use, but in view of the climate of South Africa, EC values should be measured at 25 •C. Since measurement of EC is quick and simple, it is suggested that the standard measurement of EC with the application of a conversion factor to a TDS measurement be adopted.

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Turbidity

Background Information

Introduction	<p>Turbidity is a measure of the light-scattering ability of water and is indicative of the concentration of suspended matter in water. The turbidity of water is also related to clarity, a measure of the transparency of water and settleable material, which refers to suspended matter which settles after a defined time period as opposed to that which remains in suspension.</p> <p>Micro-organisms are often associated with turbidity, hence low turbidity minimises the potential for transmission of infectious diseases. The probability of the presence of carcinogenic asbestos fibres is also reduced under conditions of low turbidity. Turbidity also affects the aesthetic quality of water.</p>
Occurrence	<p>Turbidity in water is caused by the presence of suspended matter which usually consists of a mixture of inorganic matter, such as clay and soil particles, and organic matter. The latter can be both living matter such as micro-organisms and non-living matter such as dead algal cells. The turbidity of raw water can range from less than one nephelometric turbidity unit (NTU) in very clear water, to over 1 000 NTU in turbid, muddy water.</p> <p>Soil particles constitute the major part of the suspended matter contributing to the turbidity in most natural waters. Discharge of sewage and other wastes can contribute significantly to turbidity.</p>
Interactions	<p>Turbidity is strongly associated with apparent water colour. The relationship between turbidity, taste and odour of raw and treated water has long been recognised. However, all these constituents may also be present in the absence of excessive turbidity.</p>
Measurement	<p>The criteria refer to turbidity measured in nephelometric turbidity units (NTU). A nephelometric turbidimeter is used for the measurement of turbidity. Turbidity should be determined on the day of sample collection. If necessary, samples may be stored in the dark for 24 hours, after which irreversible changes in turbidity occur. Samples must be shaken vigorously before examination.</p>
Data Interpretation	<p>Single-sample values should be used to compare with the criteria given and should be interpreted as maximal values, not to be exceeded. Turbidity should also be interpreted in conjunction with the suspended solids concentration and content.</p>
Treatment Options	<p>The settleable fraction of the suspended matter in water will tend to gradually settle to the bottom where the water is not disturbed. However, the smaller particles and colloidal fraction do not settle out and are kept in suspension by Brownian motion, as well as by mutual repulsion of the like-electrical charges which are often present on the surfaces of the suspended matter. When a flocculant is added to a water, the electrical charges are neutralised and the particles cohere and settle out.</p> <p>Removal of turbidity from domestic or industrial water normally requires an effective coagulation and flocculation process following settlement or deep-bed or multimedia filtration, if the particles involved are colloidal in nature.</p>

Coagulants like aluminium sulphate or ferric chloride are conventionally used, with small doses of polyelectrolytes added to assist in flocculation. With many waters, small doses of polyelectrolytes alone may be sufficient to promote flocculation of the particles for removal by settlement and filtration.

Silica sand filters are most commonly used in large-scale treatment plants. Multimedia filters of anthracite and garnet are also used, even though there is a growing tendency to use membrane processes such as microfiltration or ultrafiltration in more critical applications. Filter backwash water may cause disposal difficulties. The processes require careful design and skilled monitoring and control. They are generally not suited to application on a household scale.

As the turbidity of water increases, the amount of chlorine required for disinfection of the water increases. Low turbidity therefore minimises the required chlorine dose and reduces the formation of chloro-organics that often give rise to taste and odour problems and trihalomethanes. Due to the many advantages associated with water of low turbidity and the relative ease of monitoring, it is often used as an indicator of potential water quality problems during treatment.

The Effects of Turbidity

Norms	The norms used in the guideline are based on human health and aesthetic effects.
Effects	<p>The consumption of turbid water <i>per se</i> does not have any direct health effects, but associated effects due to microbial contamination or the ingestion of substances bound to particulate matter, do. Turbidity can have a significant effect on the microbiological quality of water. Microbial growth in water is most extensive on the surface of particulates and inside loose, naturally-occurring flocs. River silt also readily adsorbs viruses and bacteria. During treatment, micro-organisms become entrapped in the floc formed during coagulation and breakthrough of the floc may represent significant microbial contamination. Consumption of highly turbid, chlorinated water may therefore pose a health risk. Particulate matter can also protect bacteria and viruses against disinfection. The adsorptive properties of some suspended particles can lead to the entrapment of undesirable inorganic and organic compounds in water, including metal-humate complexes and herbicides (e.g. 2,4-D, Paraquat, Diquat). This may interfere with the detection of such compounds, and could be an indirect health risk.</p> <p>Turbidity may also be associated with the presence of inorganic ions such as manganese(II). For example, when water containing manganese(II) ions is treated with chlorine and left to stand, slow reaction kinetics indicate that colloidal manganese(IV) oxide is formed, leading eventually to the formation of a fine precipitate.</p>
Mitigation	<p>Any adverse effects thought to be due to microbial contamination or adsorbed substances should be referred to a medical practitioner.</p> <p>Aesthetic effects (appearance, taste, odour) of turbidity can be mitigated or removed by filtration using household water filters if relatively small amounts of water are involved such as for food preparation and drinking.</p>

Criteria

Effects of Turbidity on Aesthetics and Human Health

Turbidity Range (NTU)	Effects
<i>Target Water Quality Range</i> 0 - 1	<i>No turbidity visible No adverse aesthetic effects regarding appearance, taste or odour and no significant risks of associated transmission of infectious micro-organisms. No adverse health effects due to suspended matter expected</i>
1 - 5	No turbidity visible A slight chance of adverse aesthetic effects and infectious disease transmission exists
5 - 10	Turbidity is visible and may be objectionable to users at levels above 5 NTU. Some chance of transmission of disease by micro-organisms associated with particulate matter, particularly for agents with a low infective dose such as viruses and protozoan parasites
> 10	Severe aesthetic effects (appearance, taste and odour). Water carries an associated risk of disease due to infectious disease agents and chemicals adsorbed onto particulate matter. A chance of disease transmission at epidemic level exists at high turbidity

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