

Optimisation of reaction conditions of particle aggregation in water purification – back to basics

P Polasek^{1*} and S Mutl^{2#}

¹ Water and Wastewater Treatment Specialist Consultant, PO Box 61965, Marshalltown 2107, South Africa

² Institute of Hydrodynamics, Academy of Sciences of the Czech Republic, Pod Patankou 5, 166 12 Praha 6, Czech Republic

Abstract

Basic types of pollutants in surface waters and methods for their removal are reviewed. Guidelines are provided for selecting the most effective hydrolysing destabilisation reagent (coagulant) for a particular quality surface water, which is polluted with different types of impurities, and optimising the reaction conditions under which its purification takes place.

Keywords: mineral impurities, natural organic matter (NOM), natural biological materials (NBM), aggregation stability, aggregation destabilisation, optimum dosage, optimised reaction conditions, optimised dosage and optimised reaction pH

Introduction

Until recently, in most English speaking countries, turbidity was considered to be the indicator of major pollutants used for monitoring the quality of purified water. In South Africa, turbidity is still considered to be the most important pollution indicator, which is used exclusively in most waterworks for monitoring their performance and for control of the required dosing rate of destabilisation reagent. Only very recently has the technological significance of organic pollution finally been recognised also in South Africa (Anonymous, 2000; Pryor and Freese, 1998), although not yet fully accepted as one of the most significant pollutants determining the quality drinking water. In contrast, Continental Europe has always considered natural organic matter (NOM) and other pollutants such as anion of destabilisation reagent (Me) and natural biological materials (NBM) to be equally or even more undesirable than turbidity alone. The aim in the purification of water in Continental Europe was always directed at the removal of all these pollutants to the highest possible extent by a simple coagulation process, which takes place under optimised reaction conditions.

The purification process by which dissolved natural organic matter (NOM), in addition to turbidity, is effectively removed is now being referred to as enhanced coagulation. Although this term cannot be substantiated in a physical chemistry meaning (Polasek and Mutl, 2000), it is now also adopted in South Africa (Pryor and Freese, 1998). It is claimed that NOM is effectively removed by the enhanced coagulation process at a dosage of destabilisation reagent by as much as eight times greater than that required for the removal of turbidity (Pryor and Freese, 1998). In this regard it should be pointed out that dosage of destabilisation reagent is a very important factor influencing the overall quality of the purified water as well as the economy of the purification process. Therefore, the dosage must be kept as low as possible but be sufficient to purify water to wholesome potable quality at all times. It will be evident from

practical examples of different waterworks shown in this paper that the dosage of destabilisation reagent is not eight times that required for turbidity removal as claimed, when purifying surface water from a source suitable for drinking water supply.

Due to the variety of mechanisms that may be engaged in the transformation of water impurities into separable suspensions, the term coagulation does not reflect the basis of all partial processes taking place during transformation of all kinds of colloidal impurities into readily separable flocs. It is more accurate to call this process aggregation and the flocs formed aggregates (Polasek and Mutl, 1995a; Polasek, 2003). In this context both terms, i.e. aggregation and aggregates are used in this paper.

The purpose of this paper is to review the basic types of impurities polluting surface waters and their influence on the determination of optimised reaction conditions under which water purification should take place, if all types of impurities are to be removed most effectively. It also introduces guidelines for selecting the most effective destabilisation reagent (coagulant). Furthermore, by using simplified models it explains how to determine the optimum dosage of destabilisation reagent for the removal of a single impurity and the optimised reaction conditions for the removal of a mixture of different types of impurities contained in surface waters.

Types of impurities in surface waters

Surface waters are dispersive systems containing particles of impurities of varying character with different degrees of dispersion. They are polluted by impurities which can be mineral, organic and biological by nature. According to their affinity to water the particles of impurities are either hydrophobic (turbidity producing dispersions and the anion of destabilisation reagent) or hydrophilic (dissolved organic matter of various types and nature). In some instances a hydrophobic colloid is surrounded by a hydrophilic colloid, which produces a protective colloid. The protective colloidal particles carry negative charges and are strongly hydrated. They appear as hydrophobic but behave as hydrophilic colloids and are the most difficult to aggregate. The quantities and the proportional presence of different types of impurities in water are determined by

e-mail: mutl@ih.cas.cz

* To whom all correspondence should be addressed.

☎ +2712 347-7537; fax: +2712 347-4969; e-mail: polasek@mweb.co.za

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the nature of the water source and can vary over a relatively wide range not only between different water sources but also within the same water source throughout the year depending on climatic conditions, composition of the catchment, etc.

The kind, character and quantity of the mineral impurities, dissolved organic matter and biological materials and their concentrations are important parameters governing the selection of the most suitable water purification processes. The total content of suspended and dissolved solids, alkalinity, pH and ionic strength of the water are also very important process parameters.

Mineral impurities

As a rule, the mineral impurities are formed by clay particles and inorganic precipitates resulting from chemical reactions taking place in surface waters. Furthermore, frequently occurring natural pollutants in surface water are also iron, manganese and, in some cases, aluminium. Other mineral impurities originate from industrial effluents.

Organic matter

The most important and abundant water pollution is produced by dissolved organic matter. The organic impurities comprise a broad spectrum of substances of natural and synthetic origin of different structures and molecular weights. The composition and structure of organic matter is diverse (Collins et al., 1985; Collins et al., 1986; Gregor et al., 1997; Korshin et al., 1997; Gregor et al., 1997; Volk and LeChevalier, 2000).

Technologically, dissolved organic matter is the most significant pollutant in surface waters. It can be of natural and anthropogenic origin. The natural organic matter (humic substances and proteins) sources are soil and sediment extracts, products of vital activities and decaying plants and animals. The sources of anthropogenic organic matter are sewage and industrial wastewaters, effluents and runoff from agriculture, etc. Both types can be present in the form of analytical and colloidal dispersions or in the form of suspensions, and all constitute an important group of substances, which must be removed from the water in order to minimise health risk.

The presence of organic matter influences the chemical, biological and hygienic properties of water. Some of them have toxicogenic, mutagenic, allergenic and teratogenic effects (Hocman, 1986). Others are not toxic on their own, but can influence the taste and odour of water and may become toxic during the water purification process, for instance, after chlorination. Some organic matter is capable of forming complexes with metals (humic matter, amino acids, polysaccharides), which then prevent their removal from water. From a hygienic point of view, the products of life and decay of organisms such as actinomycetes, algae, etc. also represent an undesirable group of organic matter. Furthermore, most organic matter can become a source of secondary pollution because, due to their nature, they are a source of carbon facilitating development of micro-organisms in the reticulation systems.

Biological materials

Biological materials are algae, bacteria and viruses. They behave like hydrophobic dispersions and usually carry a negative charge.

Water purification

The main purpose of the purification of surface waters is the removal of colloidal dispersions, which are characterised by a high degree of

dispersion, all of which are aggregationally and kinetically stable. The aggregation stability, defined as the resistance of particles to mutual bonding, is dependent on the composition and structure of individual particles. The prerequisite for the removal of these particles is their aggregation destabilisation and subsequent aggregation into the aggregates separable by common separation processes such as sedimentation, flotation and filtration.

The hydrophobic impurities are mainly stabilised by surface, usually negative charge (the electric double layer). The hydrophilic impurities are stabilised by a hydration layer and their negative charge is caused by ionisation of the carboxyl and phenol functional groups. The stabilisation energy is concentrated only in certain places, the so-called active centres, which are located on the surface of hydrophobic particles, such as corners and edges, and in the functional groups of hydrophilic particles (organic molecules).

The chemical structure of the particles of impurities determines the distribution of the active centres on their surface and for a given impurity it remains unchangeable. Physical configuration of the particles of impurities determines the accessibility of their active centres to the particles of the destabilisation reagent. The products of hydrolysis, the hydroxocomplexes, bind themselves onto the particles of impurities only in these active centres and neutralise their charge with the charge they carry, thus destabilising them.

The particles of impurities of different compositions have their active centres accessible at different pH values. Their configuration changes, depending on reaction conditions. Open configurations predominate at low pH and closed configurations prevail at high pH values. The active centres are more accessible in the open configurations than in the closed ones. Therefore, particle aggregation proceeds easily when the hydrophilic particles are of an open, chain type, or where the macromolecule chains unravel due to the optimised reaction conditions and the functional groups become accessible. In contrast, it progresses with difficulty when the hydrophilic particles are of a coil-like configuration and the functional groups are closed within the molecule.

Formation of aggregates can be effected by two mechanisms:

- **Destabilisation of particles** attained by suppression or removal of energetic or steric barrier, which is achieved by means of addition of a destabilisation reagent, commonly Al or Fe salt, that hydrolyse after addition to water and form hydroxopolymers capable of adsorption onto the surface of the particles of impurities. The adsorbed hydroxopolymers suppress the extent of the barrier totally, or only partially, by the charge they carry and thereby enable their mutual contacts and subsequent combining.
- **Inter-particle bridges** produced by added cationic polyelectrolyte (CPE), which directly combine the particles of impurities in the aggregates.

Purification of turbid waters

Purification of turbid waters is technologically simple and relatively undemanding. The removal of these dispersions is usually accomplished by particle destabilisation, particle bridging (when CPE is used), or by their interception in a precipitate.

Purification of waters laden with dissolved organic matter

The removal of organic matter is best affected by the addition of trivalent Fe or Al salt, which hydrolyses in water and forms hydroxocomplexes (Robinson, 1979; Polasek and Mutl, 1995a;

Polasek and Mutl, 2002). The formation of coordination compounds takes place between the metal ions of hydroxocomplexes and the hydrophilic particles, with the hydrophilic particles acting as ligands determining the magnitude of the charge of the formed compounds and thereby also the extent of their destabilisation. Sometimes, but to a limited extent only, the removal of organic matter also takes place by its adsorption onto the formed aggregates and when organic pollution is produced by fine suspensions, also by the mechanical interception of these suspensions into the formed aggregates (sweep coagulation).

The efficiency of the removal of organic matter is influenced primarily by the reaction conditions under which their aggregation takes place, the dosage of destabilisation reagent and the reaction pH value. The reaction pH at which organic matter is most efficiently removed is determined by the predominant type of organic matter. Therefore, the beneficial reaction pH is dependent on the presence of individual types of organic matter, as characterised by their functional groups. Extensive research has shown that, for instance, colour-producing organic matter is most effectively separated in a pH range of 5.0 to 6.5 (Packham, 1962; Packham, 1964; Hall and Packham, 1965a; Hall and Packham, 1965b; Anonymous, 1967; Cizek et al., 1970; Mangravite et al., 1975; Podhorsky and Zacek, 1975; Schnitzer, 1976; Edzwald et al., 1977; Tucek et al., 1977; Glazer and Edzwald 1979; Anonymous, 1979; Edzwald, 1978; Edzwald, 1981; Edzwald et al., 1982; Edwards and Amirtharajah, 1985).

It should be pointed out that when coloured waters are purified they can, in some cases, be decolourised even at a suboptimum dosage of the destabilisation reagent - the reason being that a drop in the pH value caused by hydrolysis of the destabilisation reagent results in the shifting of the double bonds responsible for colour in the colour-producing molecules, thus decolorising them without actually removing them from the water.

No direct removal of the organic matter can be effected by CPE. The efficiency of CPE for the removal of hydrophilic impurities is almost insignificant and, therefore, CPE should not be used for purification of waters containing organic matter in technologically significant concentrations, i.e. concentration of COD_{Mn} in raw water is higher than its permissible limit in the purified water (Figs. 6 to 9) (Polasek and Mutl, 2002).

Purification of waters laden with biological materials

Biological materials behave like hydrophobic dispersions and usually carry a negative charge. Therefore, the removal of biological pollution is effected by the methods commonly used for the purification of turbid waters. High separation efficiencies of the bio-materials are achieved when the aggregation process takes place under optimised reaction conditions.

At lower concentrations algae can be removed by interception into the precipitate produced by the destabilisation reagent. In such cases the destabilisation reagent is usually applied at a dosage higher than the optimised dosage for the removal of *Me*, *Tu* and *COD_{Mn}* (Kubel, 1866; Polasek and Mutl, 1995a), thus enabling algae to be removed quantitatively by the mechanism of particle enmeshment. At higher concentrations, the prerequisite for the removal of algae is their immobilisation and even destruction by means of a suitable oxidant applied for water pretreatment. The destruction of algae is usually accompanied by the development of an unpleasant taste and odour, both of which are removable by activated carbon adsorption.

The purification of algae-laden waters can lead to certain operational problems, for instance, considerable shortening of filter

runs. The latest research proved that the true source of the technological difficulties is not so much algae themselves but products of their decay, which act as polyelectrolytes, limiting duration of the filter runs (Kavalir, 1995).

Non-separable particles

The process of aggregation-destabilisation is the process that determines the efficiency of water purification at large. When the process is aimed at removing all types of impurities of different composition, their respective residual minima are usually achieved at different dosages of destabilisation reagent. Because each of the impurities behaves differently under different reaction conditions, there is always a certain quantity of impurities that cannot be destabilised at all and, therefore, cannot aggregate into kinetically unstable, separable aggregates. These particles constitute the non-separable particles of impurities, which cannot be removed from the water under the reaction conditions applied.

Assuming that the destabilisation reagent is effectively dispersed throughout the volume of purified water, then the non-separable portion of particles will not change too much during the purification process because the removal of the destabilised particles can take place only by means of additional mechanisms such as sorption on the surface of aggregates, particle enmeshment, aggregation by forceful overcoming of the remaining energy barrier, etc.

In view of the above, optimisation of the reaction conditions requires the establishment of minimum compromised dosage and reaction pH value at which the greatest portion of impurities of all kinds is removed.

Dependence of destabilisation efficiency on dosage of destabilisation reagent

Aggregation of hydrophobic particles can be expected to proceed quantitatively when the particles of the destabilisation reagent are adsorbed onto the surface of the particles of impurities in such quantities that the charge they carry is sufficient to suppress the energy barrier of all particles of impurities to such an extent that their aggregation may proceed. Similarly, the quantitative aggregation of hydrophilic particles can be expected to take place when the destabilisation reagent is dosed into the system at a stoichiometric quantity with respect to the ligands which are capable of forming co-ordination compounds.

The course of the formation of separable suspension on dosage of destabilisation reagent can be illustrated by simplified models described below (Polasek and Mutl, 1995a). The validity of these models is limited by the following assumptions:

- The unit quantity of the destabilisation reagent always contains the same quantity of particles capable of destabilisation
- The quantitative homogenisation of added destabilisation reagent with water takes place immediately after addition of the destabilisation reagent
- The chemical and physical conditions of aggregation are optimal.

The course of the aggregation process is illustrated by the changes in the content of anion of the added destabilisation reagent (*Me*), turbidity (*Tu*) (both characterising hydrophobic particles) and *COD_{Mn}* value (characterising hydrophilic particles) on dosage of the destabilisation reagent.

The simplest model shown in Figs. 1 and 2 illustrates the situation when the raw water contains only a single type of

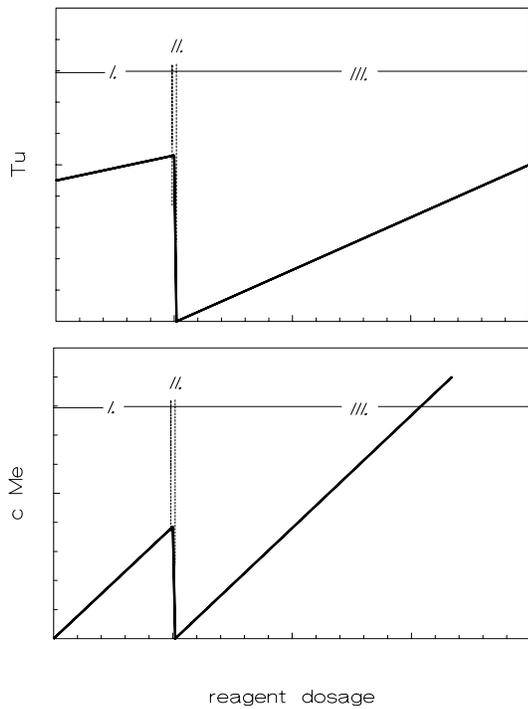


Figure 1

Removal of a hydrophobic impurity (turbidity - Tu)

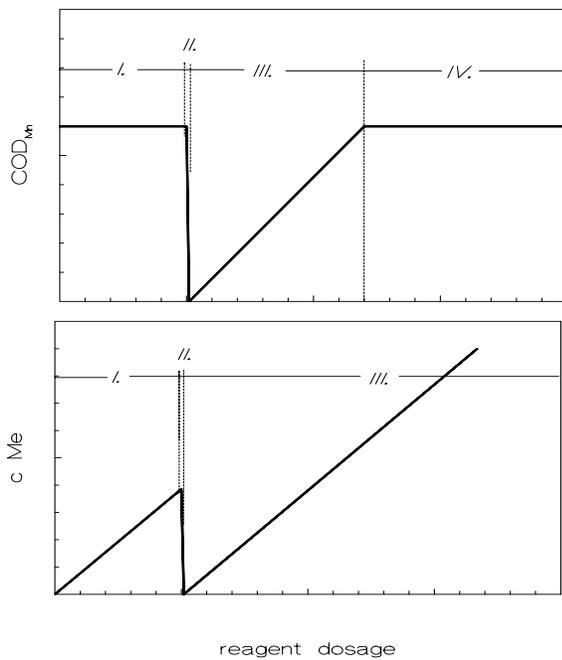


Figure 2

Removal of a hydrophilic impurity (organic matter - COD_{Mn})

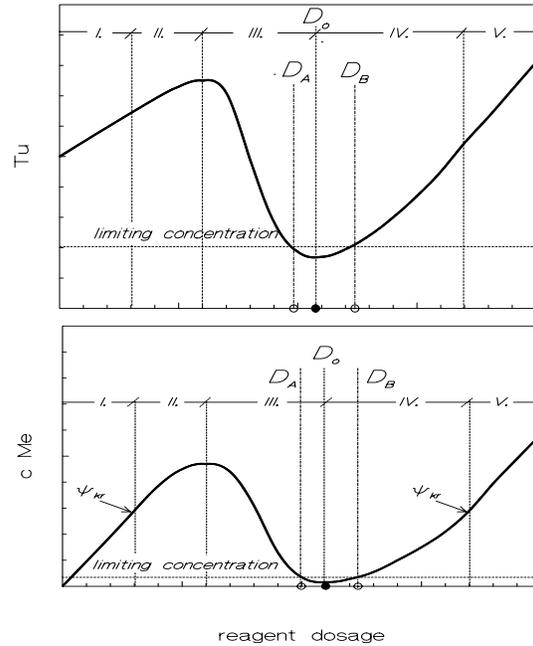


Figure 3

Removal of hydrophobic impurities (turbidity - Tu)

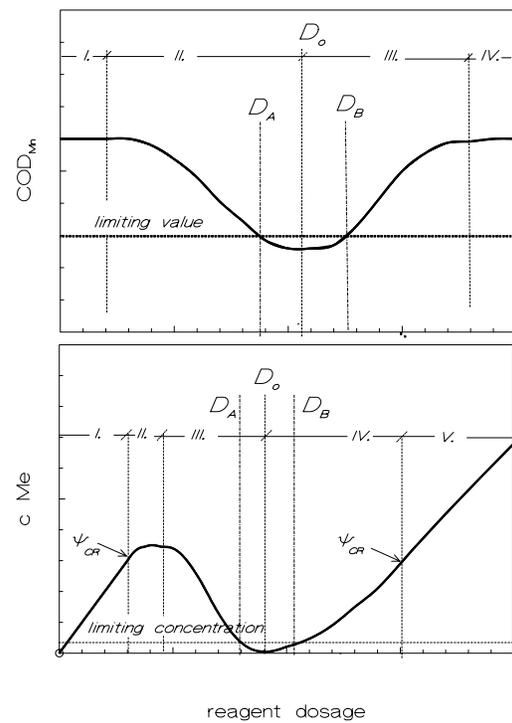


Figure 4

Removal of hydrophilic impurities (organic matter - COD_{Mn})

hydrophobic or hydrophilic impurity, the number of active centres is small, all centres are accessible to the particles of destabilisation reagent and all particles of the impurity are stabilised by the same mechanism.

When a gradually increasing quantity of destabilisation reagent is added to such a system, gradual occupation of the active centres by the particles of hydroxocomplexes takes place. At low dosages,

when only a few of the active centres are occupied, both Me and Tu gradually increase while COD_{Mn} remains unchanged (Region I). At a dosage at which as many active centres are occupied as required for total aggregation-destabilisation, immediate destabilisation of all particles of impurities is achieved and particle aggregation takes place; such a dosage is called the equilibrium dosage (D_{eq}). This is evidenced by a sharp drop to zero of Me , Tu and COD_{Mn} (Region

II). Any further increase in reagent dosage leads to the adsorption of hydroxocomplexes onto the surface of particles already destabilised, thus restabilising them with the result that Me , Tu as well as COD_{Mn} increases with increasing dosage (Region III). After COD_{Mn} reaches its original value it remains constant in spite of any further increase in reagent dosage (Region IV).

The models described above are basic in character since, even with the most simplified assumptions, important differences in the partial phases of the aggregation-destabilisation process exist between the hydrophobic and hydrophilic impurities as is evident from Figs. 3 and 4.

Figure 3 shows the purification of water containing only hydrophobic colloids. The main mechanism of aggregation-destabilisation is that of the specific adsorption of the products of hydrolysis of Al or Fe salt accompanied by charge neutralisation. In the region of the lowest dosages the products of hydrolysis are adsorbed onto the surface of the hydrophobic particles, thus causing reduction in their energy barrier. Since none of the particles is sufficiently destabilised and, therefore, capable of aggregation, concentration of Me in the system increases proportionately with dosage. This increase is also accompanied by an increase in Tu which is a result of the increasing number of particles in the system (Region I).

After exceeding the critical value of the energy barrier Ψ_{CR} of the particles with the lowest number of active centres, destabilisation takes place by forcibly overcoming the remaining barrier. The effect of destabilisation is enhanced by an increasing reagent dosage because with any increase in dosage the critical value Ψ_{CR} of the particles having a greater number of active centres is exceeded. At the same time, the energy barrier of the particles having a lower number of active centres is further reduced. This results in enhancing both the destabilisation of particles and subsequently their aggregation. The velocity and efficiency of both processes are dependent on the proportional presence of all different types of the particles of impurities in the system. An increase in dosage results in gradually slowing the rate of increase in the content of Me and Tu until their respective peaks are reached; it is, however, smaller than that corresponding to the added quantity of reagent because a portion thereof takes part in the destabilisation and aggregation reactions (Region II).

As soon as the respective peaks are reached, a further increase in reagent dosage is accompanied by a rapid drop of Me and Tu until their respective minima are reached. A dosage at which this minimum is reached is called the optimum dosage D_o for the particular pollutant and marked D_o^{Me} , D_o^{Tu} , etc. (Region III). This is the region where the most efficient and the fastest progress in destabilisation of particles of impurities takes place.

With a further increase in dosages above the optimum dosage (D_o), a portion of the particles of the destabilisation reagent is engaged in destabilisation reactions, another portion binds itself onto the particles of impurities already destabilised and thus restabilising them, and the remainder are mutually bound together and produce a hydroxide precipitate. As restabilisation progresses, aggregation-destabilisation proceeds with diminishing efficiency, which is evident by increasing concentrations of residual Me and Tu . Initially, at a dosage close to optimum, the rate of increase in Me and Tu is much slower than that corresponding to the reagent dosage and it gradually increases with dosage until the critical value Ψ_{CR} is reached (Region IV). When the critical Ψ_{CR} value is reached destabilisation of particles and their aggregation ceases completely. A further increase in dosage above that corresponding to Ψ_{CR} results in Me as well as Tu increasing proportionally with increasing dosage (Region V).

The region between the respective dosages $D_A^{Me,Tu}$ and $D_B^{Me,Tu}$ determines the region in which the most efficient aggregation-destabilisation of the particles of impurities takes place, Me and Tu respectively are minimal and within the limits allowed for in the relevant standard for the quality of purified water. It is called the range of optimum; its width is dependent on properties and variability in composition of the particles of impurities.

Figure 4 shows that the process of removal of hydrophilic particles, characterised by the COD_{Mn} , differs from the process of removal of the hydrophobic impurities such as Me and Tu . The main mechanism for aggregation-destabilisation of hydrophilic particles is that of co-ordination reactions between the particles of impurities and the metal ions of hydroxocomplexes accompanied by changes in the charge of the particles of impurities (Stumm and Hahn, 1967; Stumm and Morgan, 1981; Stumm, 1987). At first, the destabilisation reagent particles bind themselves to suitable functional groups of the particles of impurities up to a dosage at which all particles having the lowest number of functional groups are capable of forming hydroxocomplexes. Therefore, at low dosages particle aggregation does not take place and COD_{Mn} remains practically unchanged (Region I), while Me increases proportionately with dosage.

From a dosage at which a substantial portion of the hydrophilic particles is destabilised, gradual formation of the co-ordination compounds takes place between the products of hydrolysis and hydrophilic particles and, as a result, the hydrophilic particles begin to aggregate. The hydrophilic particles that aggregate first are those having the lowest number of functional groups. As reagent dosage increases more particles with a higher number of functional groups gradually become accessible to the particles of the destabilisation reagent and these particles begin to aggregate, too. Therefore, COD_{Mn} slowly decreases with dosage and its lowest value is obtained in the dosage range (and at a pH value) enabling the macromolecule chains to unravel. A dosage at which most of the accessible functional groups are occupied, the efficiency of aggregation reaches its maximum and COD_{Mn} its minimum (Region II). The dosage at which this minimum is reached is the optimum dosage D_o^{COD} for the removal of organic matter. Purifying waters containing dissolved organic matter at a concentration of technological significance, the lowest residual COD_{Mn} is often obtained at a dosage higher (and a pH value lower) than that at which the lowest Me is obtained.

With a further increase in dosage above the optimum (D_o^{COD}), several processes take place simultaneously, namely a portion of the particles of impurities in the form of macromolecular chains unravel and their functional groups become accessible to the particles of the destabilisation reagent owing to a drop in the pH value caused by hydrolysis of the reagent, another portion of the particles is adsorbed onto the surface of the formed aggregates, yet another portion of the particles is bound onto the particles already destabilised thus restabilising them, and the remaining particles are entrapped in the aggregates. The efficiency of particle aggregation gradually decreases until it ceases completely and the decrease is influenced by the prevailing process. In most cases, the initial process enabling aggregation of the impurities prevails. Cessation of aggregation of hydrophilic impurities often begins at a dosage considerably higher than that corresponding to the cessation of aggregation of hydrophobic impurities.

With a further increase in dosage above the optimum (D_o), restabilisation of particles begins and aggregation gradually decreases until COD_{Mn} reaches its initial value in the raw water (Region III). With a further increase in reagent dosage, COD_{Mn} value remains unchanged (Region IV).

For the destabilisation of hydrophilic impurities, the range of optimum dosage is between the dosages D_A^{COD} and D_B^{COD} (Fig. 4).

The width of this optimum range together with rate and efficiency of particle aggregation are influenced by the variability of the chemical composition of the impurities (each type of impurity requires a stoichiometric quantity of destabilisation reagent for the formation of complexes). Composition of the particles of impurities determine the accessibility of the functional groups capable of reactions with the hydroxocomplexes.

Selection of the most effective destabilisation reagent

Hydrolysing salts of Fe and Al, such as ferric chloride, aluminium sulphate and polyaluminium chloride (PACl), are used as the destabilisation reagents. Substituting the hydrolysing destabilisation reagent with cationic polymer (CPE) has become widely used during the past 20 years in South Africa (Polasek and Mutl, 2002).

Selection of the most effective hydrolysing destabilisation reagent is dependent, among other factors, on the ionic strength μ of the raw water. The ionic strength μ of water can be calculated with sufficient accuracy from the relationship (Podhorsky and Zacek, 1975)

$$\mu = (0,01 H_t + \frac{1,5}{48} X + \frac{Y}{35,5} + Alk_{4,5}) 10^{-3} \quad (1)$$

where:

- H_t - total hardness (mg $\text{CaCO}_3 \cdot \ell^{-1}$); $\cdot \ell$
- X - content of sulphates (mg $\cdot \ell^{-1}$)
- Y - content of chlorides (mg $\cdot \ell^{-1}$)
- $Alk_{4,5}$ - alkalinity (meq $\text{CaCO}_3 \cdot \ell^{-1}$).

When selecting the most suitable destabilisation reagent, the following values of the ionic strength of raw water can be used as a guide as is evident from the illustration of Eq. 1 in Fig. 5:

- Aluminium sulphate for waters having $\mu \leq 4 \cdot 10^{-3}$
- Ferric chloride for waters having $\mu \geq 4 \cdot 10^{-3}$

In Fig. 5, K is a separation constant, the value of which is dependent on ionic strength of water. The higher the K the more efficient is the reagent for particle aggregation at the given ionic strength of water (Zacek, 1981). The most effective destabilisation reagent can only be determined by jar tests.

Choice between destabilisation reagent and CPE is water quality dependent. This is clearly evident from comparison of the process efficiency achieved with different reagents at Saulspoort Waterworks and illustrated in Figs. 6 to 9. For this particular waterworks the most effective destabilisation reagent is ferric chloride, aluminium sulphate is more efficient than PACl, and CPE is totally unsuitable (Polasek and Mutl, 2002).

Dosage of destabilisation reagent

The attainable purification of water and the efficiency of the purification process are dependent, among other factors, on the reagent dosage applied. From a technological point of view, two different dosages are distinguished:

- Optimum dosage D_o ,
- Optimised operational dosage D_p .

The best attainable purification of water together with the optimum and optimised reagent dosages (D_o and D_p) and reaction pH are commonly determined by jar tests. The recommended jar test procedure is more fully described in Polasek and Mutl, 1995a.

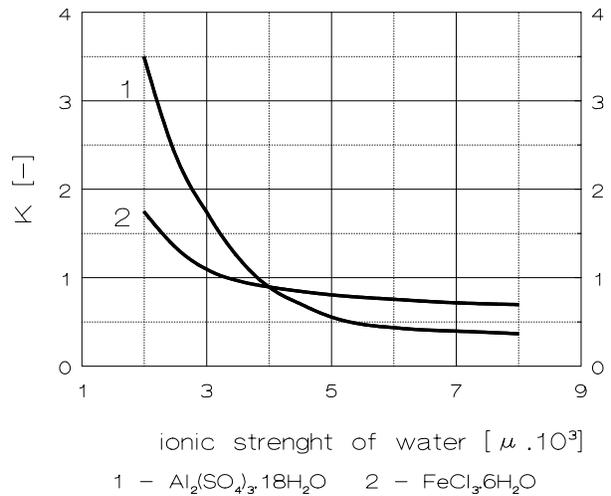


Figure 5
Dependence of separation efficiency constant K on ionic strength

Optimum dosage

The optimum dosage for the removal of a monitored determinant is defined as a dosage at which its maximum attainable removal is achieved. The individual optimum dosages D_o^{Me} , D_o^{Tu} , D_o^{COD} , D_o^{BIO} , etc., usually differ one from another, depending on the composition of their impurities.

Optimised operational dosage

The optimised operational dosage (D_p) is defined as a dosage at which all monitored determinants are removed to within their permissible limits. The optimised dosage is proportional to the extent of water pollution. From an economic point of view it is required that the optimised dosage of destabilisation reagent is as small as possible, but large enough to purify the water to its required quality.

When selecting the optimised operational dosage it is advisable to proceed using graphical illustration of dependence of changes in the residual concentration of each determinant on dosage, in order to select such a dosage at which all types of impurities are removed to below their maximum permissible limits. The range of optimum between dosages D_A and D_B is the range of dosages where the residual concentration of the respective determinant is within the maximum limits allowed for by the relevant standard for the quality of purified water. The optimised operational dosage is a dosage within the range of optima (between dosages D_A and D_B - for individual determinants), which is coincident to all determinants monitored (Figs. 3 and 4). The extent of the range of the optimised operational dosage is dependent on a number of physical and chemical factors such as the variability of impurities, ionic strength and the pH of water and it can vary from narrow to wide.

Figure 3 illustrates the typical course of the process for the removal of hydrophobic particles. It shows that the optimum ranges for Me and Tu are almost identical. Any dosage from within the range of dosages D_A^{Me} and D_B^{Me} can be selected as the optimised operational dosage (D_p). Figure 4 compares the typical course of the processes for the removal of hydrophobic (Me) and hydrophilic (COD_{Mn}) impurities. It illustrates the situation when their respective optimum ranges differ. The optimised operational dosage is selected from within the optimum range where both optimum ranges are

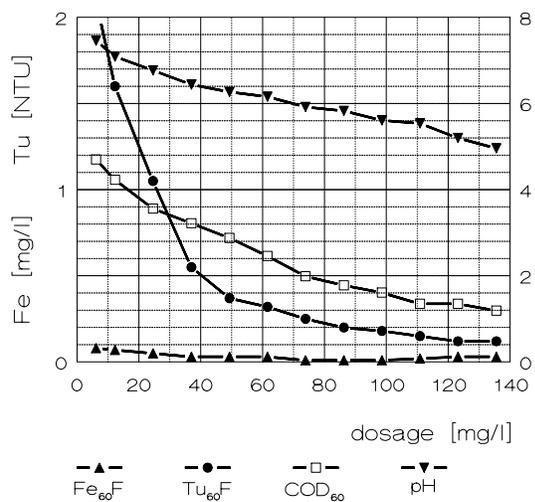


Figure 6

Treatment process efficiency attainable with FeCl_3

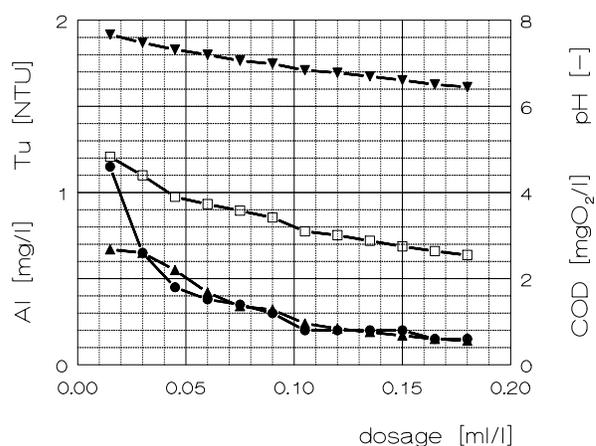


Figure 8

Treatment process efficiency attainable with PACI (Product M-30)

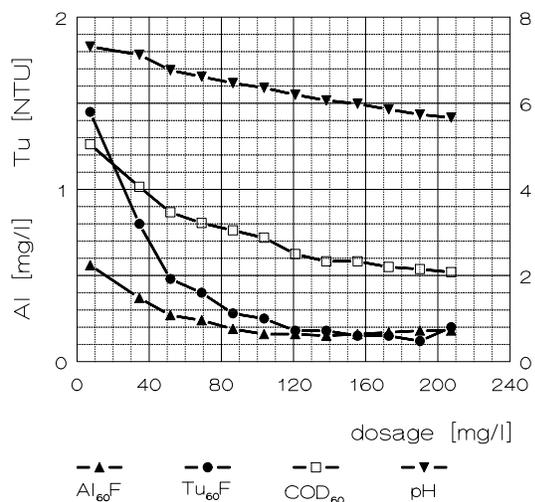


Figure 7

Treatment process efficiency attainable with $\text{Al}_2(\text{SO}_4)_3$

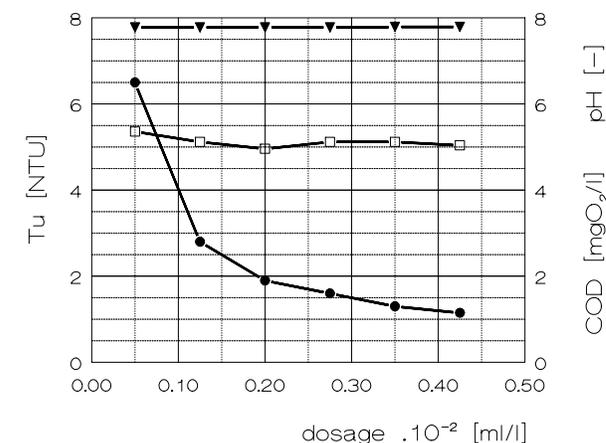


Figure 9

Treatment process efficiency attainable with CPE (Product L-100)

coincident, i.e. between dosages D_A for COD_{Mn} and D_B for Me. Should there be no coincident optimum range, a selection from outside the optimum ranges is made in such a way that the best possible removal of organic matter is obtained at a dosage at which the residual Me does not exceed its maximum permissible value. If the water is not purifiable to within the permissible limits, or if the desired quality of the purified water cannot be produced economically by the simple destabilisation-aggregation process, then multi-stage purification process and/or additional more advanced processes would have to be considered.

When the optimum ranges of the individual pollutants are narrow and coincident, then optimisation of the reagent dosage is relatively simple as illustrated in Fig. 10 (Blackheath Waterworks supplying Cape Town) (Polasek and Mutl, 1995b). The optimum dosages D_o^{Al} and D_o^{COD} do not differ much from one another and both are within the range defined by the reagent dosages D_A^{Al} and D_B^{Al} when the permissible limit for residual Al content is $c = 0,2 \text{ mg Al} \cdot \text{L}^{-1}$ and even by dosages D_A^{Al} and D_B^{Al} when the permissible limit

for residual Al content is $c = 0,1 \text{ mg Al} \cdot \text{L}^{-1}$. Any dosage from within this range can be used as the optimised operational dosage D_p .

Figure 11 illustrates the situation when optimum dosages D_o^{Al} , D_o^{Tu} and D_o^{COD} differ considerably and the range of their optimum dosages is broad (Saulspoor Waterworks supplying City of Bethlehem, Free State) (Polasek and Mutl, 1995b). In such a case, the operational dosage D_p^{Al} has to be selected from the dosages considerably greater than that of D_A^{Al} in such a way that satisfactory reductions in both COD_{Mn} and Tu are also obtained - dosage D_A^{COD} becomes the operational dosage.

When algae (BIO) are present in the raw water in technologically significant concentration, it is not always easy to determine the optimised operational dosage as is evident from Figs. 12 and 13. These figures illustrate optimisation of dosage at the Podoli Waterworks purifying Vltava (Moldau) River water and supplying Prague (Czech Republic) (Polasek and Mutl, 1995a). Figure 12 shows the attainable purification of the water using aluminium sulphate and Fig. 13 shows the attainable purification when using ferric chloride.

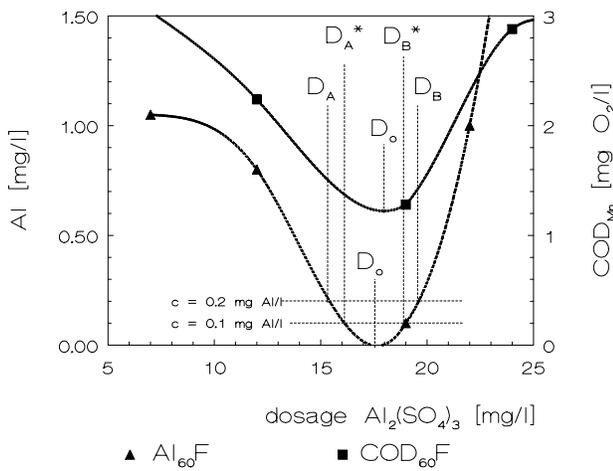


Figure 10

Optimisation of dosage - Narrow range of optimum dosage

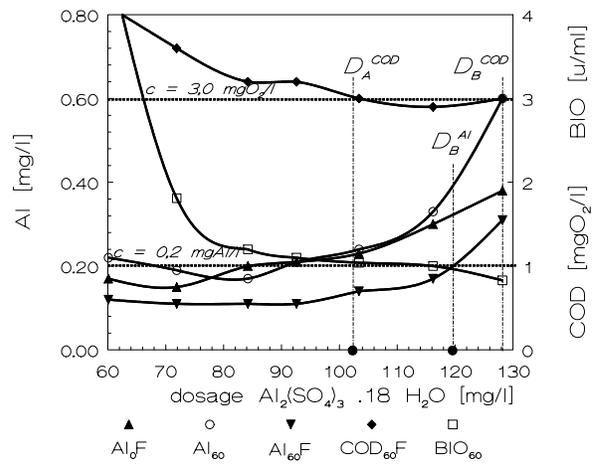


Figure 12

Optimisation of dosage
Prague - Podolf Waterworks

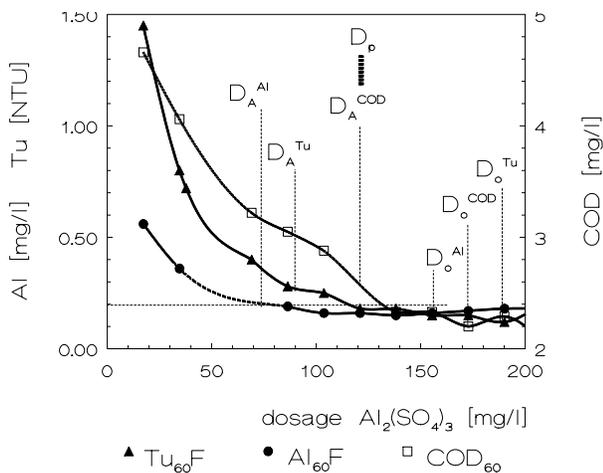


Figure 11

Optimisation of dosage
Wide range of optimum dosage

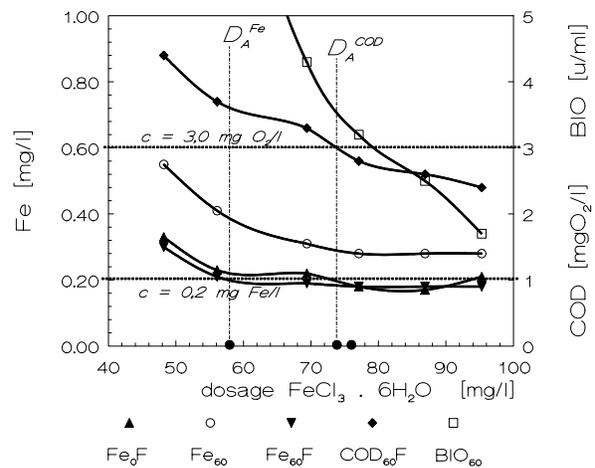


Figure 13

Optimisation of dosage
Prague - Podolf Waterworks

Figure 12 shows that the optimum dosage of aluminium sulphate for the removal of both Al and COD_{Mn} value is coincident within the range of $D = 100$ to 120 $mg\ Al_2(SO_4)_3 \cdot 18H_2O \cdot l^{-1}$. The BIO value drops sharply up to a dosage of around $D = 75$ $mg\ Al_2(SO_4)_3 \cdot 18H_2O \cdot l^{-1}$ and thereafter decreases very slowly with increasing dosage. The optimum dosages were determined by jar tests from the samples taken after completion of sedimentation and subsequently purified by centrifugation ($SE_{60}F-Al$ and $SE_{60}F-COD$) which simulates filtration. In contrast, the residual BIO value was determined by jar tests from the samples of water taken after sedimentation ($SE_{60}-BIO$). It characterises the expected residual content of algae entering filters. Therefore, dosage D_A^{COD} becomes the operational dosage.

Figure 13 shows that Fe drops to below its permissible residual value at a dosage of around $D = 58$ $mg\ FeCl_3 \cdot 6H_2O \cdot l^{-1}$ and at higher dosages it remains almost unchanged. Further, COD_{Mn} drops to below its permissible residual value at a dosage around $D = 75$ $mg\ FeCl_3 \cdot 6H_2O \cdot l^{-1}$ and with higher dosages it continues to gradually decrease. Its removal is more efficient than that obtained with aluminium sulphate. At a dosage $D = 75$ $mg\ FeCl_3 \cdot 6H_2O \cdot l^{-1}$ the

residual BIO value is still high, considerably higher than that obtained with aluminium sulphate with the same dosage, but drops fast with increasing dosage. Due to a wider range of optimum in respect of residual Fe , the optimised operational dosage can be selected at $D_p \approx 95$ $mg\ FeCl_3 \cdot 6H_2O \cdot l^{-1}$, at which residual COD_{Mn} is considerably lower and the residual BIO value approaching that obtained with aluminium sulphate.

It should be emphasised that any deviation from the optimised operational dosage results in decreased overall efficiency of the purification process. The decrease in efficiency may also be experienced even when the optimised operational dosage is applied; this is usually the consequence of ineffective homogenisation of the destabilisation reagent with water, which produces over- and under-dosed zones in the water being purified.

Optimisation of reaction pH

The effective purification of water takes place at a particular pH value. In pure water the ferric hydroxide flocs are formed over a wide pH range varying between 4 and 11. In contrast, aluminium hydrox-

ide flocs are formed over a much narrower pH range because it is more soluble in the acidic pH range than ferric hydroxide and in an alkaline environment it forms aluminates.

The optimum reaction pH for the removal of a pure substance corresponds to that of its isoelectric point. However, surface waters contain a mix of different kinds of hydrophobic and hydrophilic colloids, the isoelectric points of which are at different pH values. The reaction pH is dependent on the presence of individual types of organic matter characterised by their functional groups and determined by their ratio. Consequently, water purification should always be carried out at a compromised reaction pH at which all of the pollutants monitored are removed to below their respective maximum permissible limits. Therefore, it is necessary to establish (by jar tests) an optimised reaction pH. The optimised pH represents such a pH value at which all kinds of impurities present in the water are removed with the highest attainable efficiency. Since most organic substances present in surface waters are of an acidic character, the surface waters, as a rule, should be purified to potable quality by aggregation process taking place in the acidic pH range, usually at a pH of between 6.5 and 4.0.

The addition of hydrolysing destabilisation reagent reduces alkalinity and thereby also pH of the water, usually approaching optimised reaction pH. For slightly polluted water the required destabilisation reagent dosage is small and therefore the optimised pH is not achieved in the waters with higher alkalinity. In such a case alkalinity can be reduced by a higher dosage of destabilisation reagent or by dosing acid. The choice between the two is determined by economic and operation considerations.

When the alkalinity of raw water is too high, an excessive dosage of the hydrolysing destabilisation reagent is required for the adjustment of pH to its optimised reaction value. In such a case only a portion of the reagent dosage is utilised for aggregation-destabilisation and the remaining portion of reagent dosage is consumed for alkalinity and pH adjustment. Therefore, it is often more economical to pretreat the raw water with acid in order to reduce natural alkalinity to a level at which the optimised operational dosage of destabilisation reagent can be fully utilised for the aggregation-destabilisation of the impurity particles.

In contrast, when higher pollution of the water requires greater dosages of destabilisation reagent and the natural alkalinity of the water is low, or when the optimised reaction pH is in the alkaline region, then it is necessary to increase alkalinity by adding calcium hydroxide, caustic soda or soda ash. The low alkalinity waters sometimes also require that their ionic strength is increased in order to improve the overall process efficiency. These adjustments result in changes of pH and ionic strength of water which, in turn, result in changes of charge ratios of the particles of impurities. Therefore, the changes in alkalinity must take place sufficiently in advance to the point of addition of the destabilisation reagent. The correct location of the dosing point for the pre-alkalisation reagent is very important from the destabilisation process point of view. Its location is determined by the form and the manner in which this reagent is dosed and the time required for its complete dissolution. Furthermore, its homogenisation with water and all relevant reactions must also be completed prior to the addition of the destabilisation reagent, because no dissolution of pre-alkalisation reagent (lime) can be allowed to continue after addition of the destabilisation reagent.

Pre-alkalisation of raw water is determined by jar tests carried out with raw water pre-alkalised to different pH values. Figures 14 to 17 compare the effect of pre-alkalisation of raw water to different pH values at George New Waterworks (Cape type coloured soft water characterised by colour $Co = 500$ HU and $COD_{Mn} = 52.5$ mg $O_2 \cdot L^{-1}$) and its effect on the removal of various

determinants (Polasek and Mutl, 1995b). At pre-alkalisation to pH = 10.0 the optimum dosages D_o^{Fe} , D_o^{Co} and D_o^{COD} are in the range of 68 to 74 mg $FeCl_3 \cdot L^{-1}$. At pre-alkalisation to pH = 10.2 (Fig. 16) there is a sharp optimum for all these determinants at $D_p = 110$ mg $FeCl_3 \cdot L^{-1}$. The residual values of individual determinants are slightly higher than those obtained at the pre-alkalisation to pH = 10.0 and thus the pH = 10.0 can be considered to be the operational pre-alkalisation pH. The optimised operational reaction pH = 4.8.

General notes

It should be emphasised that the sole purpose of pre-alkalisation is the adjustment of the natural alkalinity and pH of raw water in order to create optimised reaction conditions for the aggregation-destabilisation of the impurity particles and not to take care of final pH of the purified water, as is commonly practised in South Africa. This is bad engineering practice because the aggregation-destabilisation of the impurity particles takes place very much outside of the optimised reaction conditions. Such practice produces drinking water of a quality which is well below that attainable when the aggregation process takes place under the optimised reaction conditions. Therefore, the final pH adjustment of the purified water, as the word *final* clearly describes, must be carried out in the purified water and not in the raw water, or water undergoing purification.

Quite often, even when the purification process takes place under optimised reaction conditions as determined by jar tests, the quality of purified water is poorer than that predetermined by the jar tests. The reasons for that is functional shifting of individual unit processes into subsequent unit operations, where optimum conditions for such process do not exist. For instance, the dispersion of destabilisation reagent and its homogenisation shifts into the flocculator, the process of aggregation shifts into the sedimentation tanks and filters and sometimes even into the reticulation system. Consequently, a greater quantity of non-separable impurity particles remains in the purified water. Furthermore, non-homogeneous flocs of a wide range of sizes and densities are formed. Hence, the flocs unsuitably prepared from a separation point of view enter the sedimentation plant. This unfavourably influences the sedimentation velocity for which the sedimentation plant must be designed because the sedimentation velocity must be designed with due consideration for the smallest-size-fraction of flocs that have to settle. Therefore, in order to compensate for incorrect functioning of the preceding unit operations, either lower performance efficiency of the sedimentation plants have to be accepted, or they have to be oversized resulting in the design of larger and more costly sedimentation systems.

The correct functioning of each individual unit operation for the formation of flocculent suspension and its separation has a decisive effect on the optimisation of the waterworks performance as a whole. Therefore, every effort should be made to minimise functional shifting of the individual processes into subsequent unit operations.

When the quality of purified water is worse than that predicted by jar tests, the hydrodynamic conditions under which the formation of flocculent suspension and of their separation take place, may also require optimisation.

Conclusions

It should be the aim of every waterworks operator to operate the works under optimised reaction conditions in order to ensure that water is purified to its overall best attainable quality at all times.

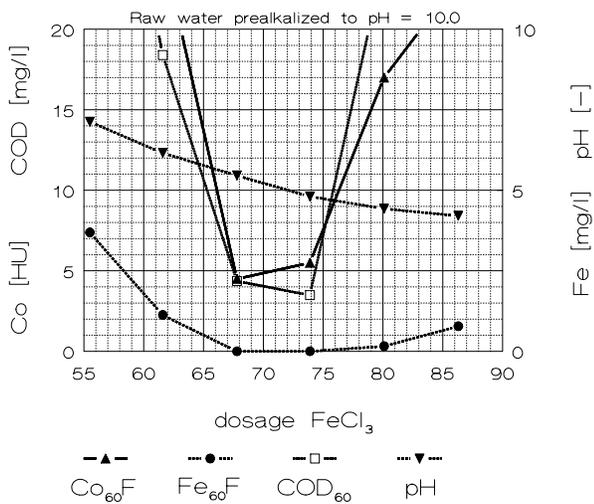


Figure 14
Optimisation of dosage FeCl₃

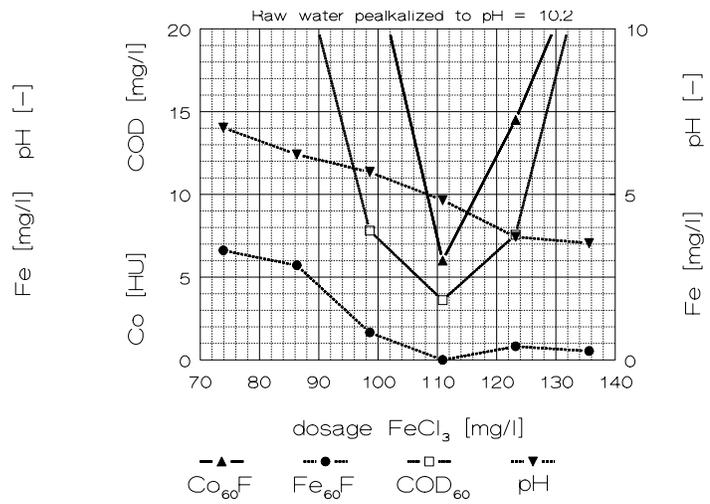


Figure 16
Optimisation of dosage FeCl₃

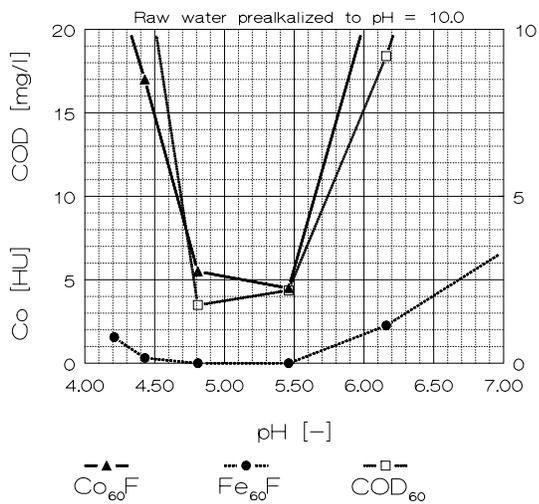


Figure 15
Optimisation of dosage FeCl₃

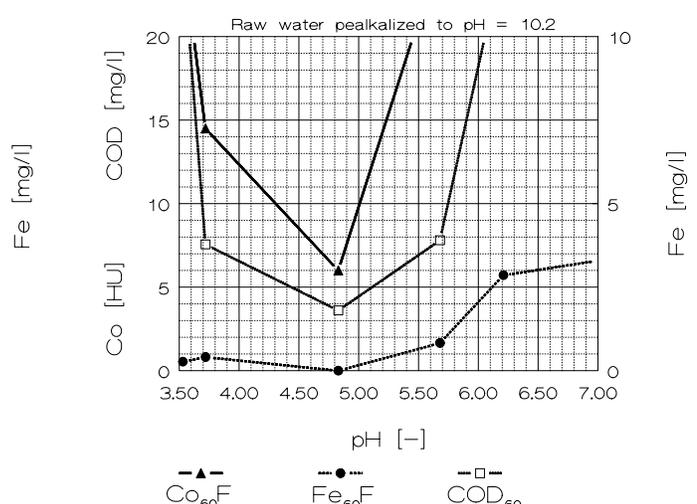


Figure 17
Optimisation of dosage FeCl₃

A factor significantly influencing the selection of the most effective destabilisation reagent is the ionic strength μ of water. An Al³⁺ salt is a more efficient destabilisation reagent up to $\mu = 4 \cdot 10^{-3}$ and Fe³⁺ salt from $\mu \geq 4 \cdot 10^{-3}$.

Two factors significantly influencing the overall efficiency of water purification are dosage of destabilisation reagent and reaction pH. When the purification process is aimed at removing a single pollutant only, for instance impurities exhibiting turbidity (South African practice), then a dosage at which maximum reduction, i.e. minimum attainable residual concentration of such a pollutant is achieved, is the optimum dosage for such a pollutant. When the purification process is aimed at removing a mixture of different impurities (Me, organic matter, algae, turbidity, etc.), then the purification process must take place under optimised reaction conditions at which residual concentration of each pollutant monitored is below its permissible limit. The optimum range for individual pollutants is usually achieved at different dosages and different reaction pH values. Therefore, the optimised operational dosage is a compromised dosage which is selected from within those

parts of the ranges of optimum, where these are coincident for all individual pollutants monitored. The optimised reaction pH is selected in a similar way.

It is evident from Figs. 11 to 13 that the removal of organic matter from natural surface waters could require a higher dosage of destabilisation reagent than that required for the removal of turbidity only, but it is nowhere near to eight times as claimed in Pryor and Freese, 1998.

Pre-alkalisation of raw water, when necessary, is required for the optimisation of reaction pH only. It should never be combined with the final pH adjustment of the purified water (as is the current South African practice), i.e. pre-alkalisation being carried out to a level which after a drop in alkalinity caused by hydrolysis of the added destabilisation reagent becomes the final pH value of the purified water supplied to consumers (usually pH > 8). This is because under such practice the operational reaction pH is very much outside of the optimised reaction pH, which is required for the most effective removal of all kinds of impurities contained in the water. As a result, purified water of considerably poorer quality is

produced in comparison to that attainable under optimised reaction conditions.

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Notations

Legend to Figures 1 to 4

Me	Concentration of anion of destabilisation reagent (Al^{3+} or Fe^{3+})
Tu	Turbidity
COD_{60}	NOM expressed as chemical oxygen demand (oxidisability) of water determined by Kubel method (oxidation of the organic matter in a boiling mixture of potassium permanganate (KMnO_4) and sulphuric acid).

Legend to Figures 6 to 17

Tu_{60}	Total content of residual Tu-particles in a sample of water after 60 min sedimentation corresponding to the total quantity of Tu-particles at the outlet from the sedimentation separation stage.
Al_0F , Fe_0F	Content of residual Al or Fe in centrate of a sample of water at the beginning of sedimentation corresponding to the inlet to sedimentation separation stage.
Al_{60} , Fe_{60}	Content of residual Al or Fe in a sample of water after 60 min sedimentation corresponding to the total quantity of residual Al/Fe at the outlet from the sedimentation separation stage.
Al_{60}F , Fe_{60}F	Content of residual Al or Fe in centrate (supernatant from a batch type centrifugation) of a sample of water after 60 min sedimentation corresponding to a non-separable portion of Al/Fe at the outlet from the sedimentation separation stage.
Tu_{60}F	Content of residual turbidity in centrate of a sample of water after 60 min sedimentation corresponding to a non-separable portion of Tu particles at the outlet from the sedimentation separation stage.
COD_{60}	Total COD_{Mn} value in a sample of water after 60 min sedimentation corresponding to the total quantity of NOM at the outlet from the sedimentation separation stage.
COD_{60}F	Residual NOM in centrate of a sample of water after 60 min sedimentation corresponding to a non-separable portion of NOM at the outlet from the sedimentation separation stage.
BIO_{60}	Total number of algae in a sample of water after 60 min sedimentation corresponding to the total number of algae at the outlet from the sedimentation separation stage.
BIO_{60}F	Residual algae in centrate of a sample of water after 60 min sedimentation corresponding to a non-separable portion of algae at the outlet from the sedimentation separation stage.

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