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PHYSICAL-CHEMICAL TREATMENT
OF TMP-NEWSPRINT MILL EFFLUENT
AS A CLOSED CYCLE TECHNOLOGY

A Thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfilment of the requirements of the degree of
Master of Engineering

by

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July 1993

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PHYSICAL-CHEMICAL TREATMENT OF TMP-NEWSPRINT MILL EFFLUENT AS A CLOSED CYCLE TECHNOLOGY

ABSTRACT

Pulp and paper mills have to comply to increasingly more stringent environmental regulations. Only one solution can satisfy all present and future effluent regulations, and eliminate all impact on receiving waters. This solution is to recycle the whole effluent back to the mill, after treatment.

The subject of this research was to develop a physical-chemical process that would be suitable for the treatment of TMP-Newsprint effluent as a closed cycle technology.

A mixture composed of 80% TMP cleaner rejects, 10% contaminated condensate from the heat recovery and 10% chip wash water was used to approximate the effluent from a very low water usage mill.

Preliminary experiments were performed using lime, magnesium oxide, activated carbon, potassium phosphate and alum. The most promising treatment identified was using a combination of magnesium oxide, lime and potassium phosphate. It was found that 300 mg/L of MgO, 1000 mg/L of CaO and 500 mg/L of KH_2PO_4 gave over 90 % extractives removal, a reduction of 60 % in colour and 75 % in turbidity, while maintaining a low water hardness. It was also found that MgO addition was not required at the dosages used.

Test were also performed on effluent with an elevated level of inorganic dissolved solids that would be typical of a closed cycle mill. It was found that higher dosages of lime would be required, and that potassium phosphate would no longer be necessary.

The results of this study have shown that there is great promise in using a physical-chemical process as part of a closed cycle treatment scheme.

RÉSUMÉ

Les usines de pâtes et papiers doivent se soumettre à des réglementations environnementales de plus en plus sévères. Une seule solution leur permettrait de satisfaire toutes les normes existantes et futures, et d'éliminer tout impact sur le cours d'eau récepteur. Cette solution est de recycler tout l'effluent à l'usine, pour le réutiliser après traitement.

L'objectif de ce travail était de développer un procédé physico-chimique pouvant être utilisé comme technologie principale en circuit fermé pour le traitement de l'effluent d'une usine PTM de papier journal.

Un mélange composé de 80% de rejets des cyclones du PTM, de 10% du condensat contaminé provenant de la récupération de chaleur et de 10% d'eau de lavage des copeaux a été utilisé pour simuler l'effluent d'une usine à très faible consommation d'eau.

Des expériences préliminaires ont été effectuées à l'aide de chaux, d'oxide de magnésium, de charbon activé, de phosphate de potassium et d'alum. Le traitement le plus prometteur a été identifié comme étant une combinaison d'oxide de magnésium, de chaux et de phosphate de potassium. Il a été découvert qu'à un dosage de 300 mg/L de MgO, 1000 mg/L de CaO et 500 mg/L de KH_2PO_4, plus de 90 % des acides gras et résiniques sont enlevés, la couleur est réduite de 50 % et la turbidité de 75%, tout en maintenant une faible dureté de l'eau. Il a aussi été trouvé qu'au dosage de chaux requis, l'addition de MgO n'était plus nécessaire.

Des essais ont aussi été effectués sur l'effluent simulé additionné de contaminants inorganiques typiques d'une usine en circuit fermé. Il a été trouvé qu'un dosage plus

élevé de chaux est requis, et que l'addition de phosphate de potassium n'est plus nécessaire.

Les résultats obtenus au cours de cette étude ont démontrés qu'un traitement physico-chimique à la chaux est très prometteur comme procédé de traitement en circuit fermé.

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1.0 INTRODUCTION

Pulp and paper mills are affected by many environmental regulations. These regulations are set and modified by governments, in response to advances in technology and to pressure from the population. The pulp and paper mills must install new sophisticated treatment systems to meet these regulations. These installations must be modified and expanded, as more stringent rules are added.

The effluent treatment systems are usually very expensive. Most of the time they do not benefit the product, but they add to the cost for the production of this product.

The ideal treatment system would satisfy all future effluent regulations. The only way to meet this objective is to eliminate the effluent altogether, by recycling it back to the mill, after treatment.

1.1 Closed cycle technology

The term "closed cycle technology" in the Pulp and Paper industry, refers to processes that treat the contaminated effluent from a mill so that it can be recycled back into the process. The final result is that no effluent is discharged into the receiving waters. It is of primary importance that the treatment removes the contaminants in the effluent that would impact either the quality and properties of the paper produced or the operation of the pulp and paper processes.

Some mills in Canada are actually operating with a closed water cycle (Millar Western in Meadow Lake, Louisiana-Pacific in British Columbia). These mills are new and were designed to be effluent-free with a low water usage. The closed cycle technologies used in those mills (evaporation, freeze crystallisation), bring the quality of the effluent close to that of drinking water. However those technologies are very expensive to install and to operate, and such a good quality water is not required for most mill usages.

It is a very different challenge if the goal is to transform an existing mill, designed with a high water consumption and no effluent treatment, in order to lower the fresh water required in the process, and to design a treatment process that would be simple and cheap. Ideally, the water treatment plant would treat the water just enough for the needs so that money is not spent on the extra cleaning that is not really required. This is the perspective in which this work was carried out.

1.2 Objectives of this study

The main objective of this thesis was to develop a physical-chemical process that could treat the effluent of a TMP-newsprint mill, and give a water of quality suitable for its recycle into the process.

The specific objectives of this study were:

1. To evaluate the future TMP-newsprint effluent characteristics after reduction of the water consumption.
2. To study lime treatment as a potential physical-chemical treatment for closed cycle technology.
3. To assess the quality of water produced from this process and establish the need for a "polishing" treatment.
4. To examine the options for the disposal of the sludge produced by the treatment process.
5. To recommend a closed cycle process for the TMP-newsprint mill.

1.3 Organisation of the thesis

Chapter 2 reviews the background that is necessary for a better understanding of the following sections of this work. It includes an introduction on closed cycle technology, a review of the possible water treatment alternatives, a description of the TMP-newsprint mill studied and its effluent, and the potential effects of water contaminants on the papermaking process. The case of the Kimberly-Clark mill in Huntsville is then presented. Finally, the chemistry of the physical-chemical process and the experimental designs used are explained.

Chapter 3 describes the equipment and the experimental proceduresthat have been used for the experimental part of this work. It includes a description of the effluent mixture that has been used.

The results are presented and discussed in the nest three chapters. Chapter 4 presents the screening experiments, Chapter 5, the formal experimental part, and Chapter 6, the additional experiments.

The suggested closed cycle treatment scheme is presented in Chapter 7.

Chapter 8 summarizes the conclusions that were reached and gives some recommendations for future work.

2.0 BACKGROUND

2.1 An introduction to closed cycle technologies

2.1.1 The global closed cycle scheme

A closed cycle treatment process is generally comprised of three separate components as shown in Figure 2.1.

Primary Closed Cycle Technology

The primary closed cycle technology is the coarse treatment of the mill effluent. The general intent is to remove the bulk of dissolved contaminants from the stream being recycled. In general, suspended solids have been removed by primary clarification prior to this step.

Polishing Technology

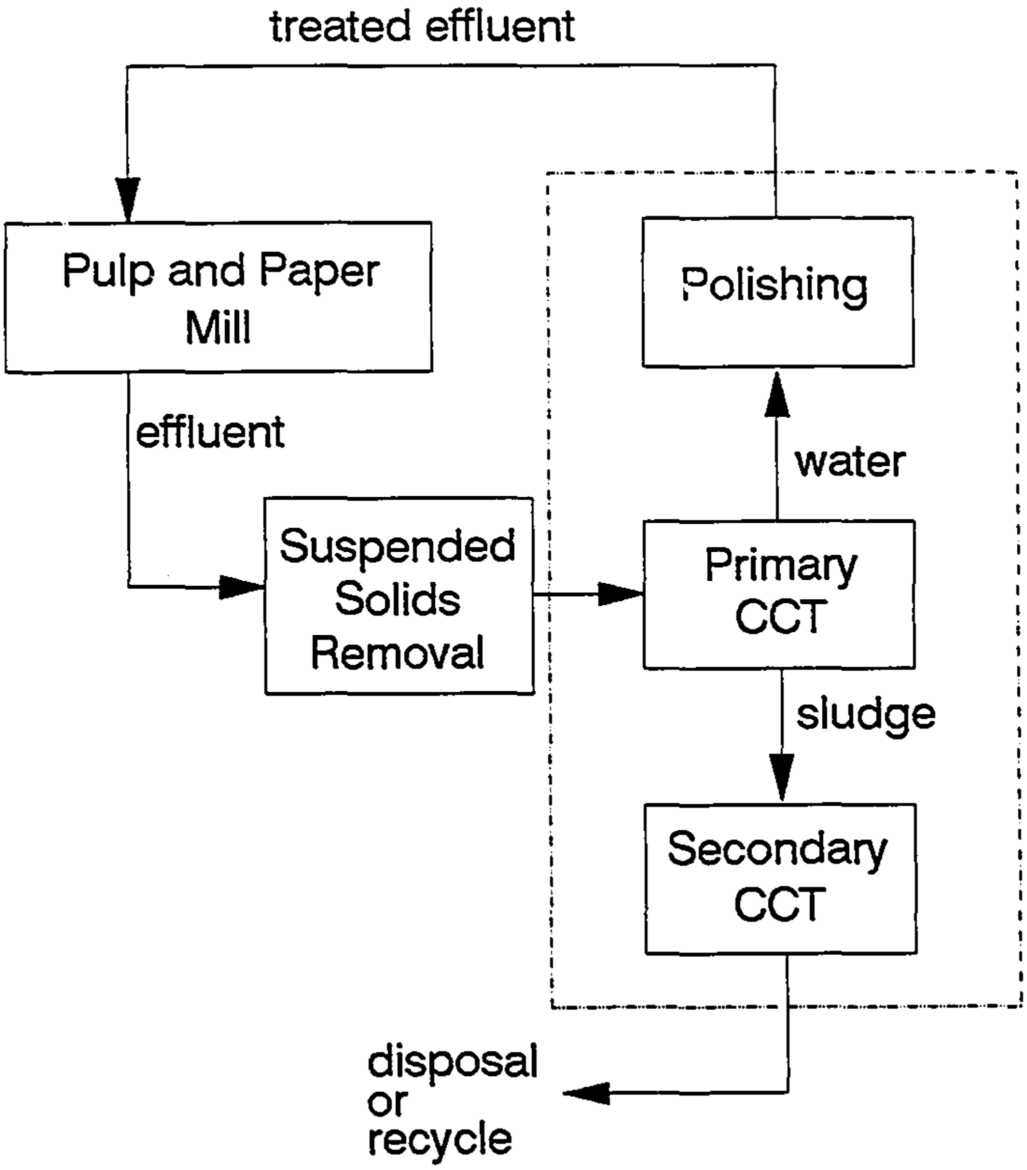
Polishing treatment refers to the additional treatment that might be required after the primary closed cycle technology. The need for this technology will depend on the primary closed cycle technology selected and the end usage of the treated water.

Secondary Closed Cycle Technology

The secondary closed cycle technology treats the concentrated liquid or solid byproduct produced in the primary closed cycle technology, in order to minimize it for disposal or recycle. This step could include a combination of technologies, and may involve the recycle of a stream to the primary closed cycle treatment for re-processing. Generally,

FIGURE 2.1

CLOSED CYCLE TREATMENT SCHEME



secondary closed cycle technologies must handle a much lower flow rate than the primary closed cycle treatment or polishing treatment processes. This implies that processes too expensive for the treatment of the total mill flow can be considered.

2.1.2 Closed cycle technologies: the options

Many options are available for each of the three treatment steps of the closed cycle scheme. Some treatment alternatives can be included in more than one category. Table 2.1 lists the different options available for each treatment step. A summary of each of these technologies follows.

TABLE 2.1

CLOSED CYCLE SCHEME TREATMENT OPTIONS

Primary closed cycle technology	Biological Treatment Evaporation Freeze crystallisation Physical-chemical treatment
Polishing technology	Activated carbon Biological treatment Membranes Ion exchange Physical-chemical treatment
Secondary closed cycle technology	Combustion Dewatering Evaporation Land application Landfill Regeneration Wet air oxidation

PRIMARY CLOSED CYCLE TECHNOLOGIES

Biological treatment

The biological treatment of effluents is a process which uses microorganisms, primarily bacteria, to degrade the organic content of waste waters. Its purpose is to reduce the biochemical oxygen demand (BOD) and to remove toxicity. In general, it is sensitive to changes in temperature, pH, quality of the feed to the system (nutrients and toxic materials) and oxygen concentration.

Biological treatments can be classified into two main categories: aerobic and anaerobic processes.

In the aerobic process, microorganisms consume BOD in the presence of oxygen to convert the wastes into CO_2 and H_2O (36, 38). The process can use either air or pure oxygen. It is important to insure a sufficient and even distribution of the oxygen throughout the waste water. It is usually necessary to add nitrogen and phosphorous, which are nutrients required for the metabolic activity of the microorganisms.

Many types of aerobic treatment have been developed:

Activated sludge treatment:

> In an activated sludge treatment, the waste water is treated biologically and is then sent to a clarification unit. A portion of the settled sludge is recycled to the process to ensure a high biomass density. The retention time for this process is usually short, typically between 3 and 24 hours, and over 95 % BOD_5 removal is achieved. The process is sensitive to changes in pH and in the composition of the waste fed to the system. Settling aids can be required, and the operating

manpower required is high compared to the other types of biological treatments. The sludge generated is abundant and hard to dewater.

Aerated stabilisation basins:

This process uses aerators to diffuse air into the effluent to be treated. It requires basins covering large areas. Long retention times are necessary to achieve a high efficiency. Typically, 5 to 15 days are required for about 90 % BOD_5 removal. This process is more tolerant of BOD load variations and produces a minimal amount of sludge. The majority of the excess biomass is degraded at the bottom of the basin, which is characterised by the anaerobic conditions that are prevailing due to the stagnant conditions in this zone. The operating costs are low because this process needs little manpower and there is no sludge to handle.

Biological filter:

In this process, a biological filter is used to bring a continuous flow of effluent in contact with the micro-organisms that are fixed to the filtering medium, in the presence of atmospheric air. The two kinds of filter used are the trickling filter and the rotary disc filter. In the trickling filter, effluent is distributed over a fixed bed of media. Many types of media are available, from different packing materials to vertical strips of plastic. In the rotary disc, a series of equally spaced discs are attached vertically to a rotating shaft. The discs are partially immersed in a channel where the effluent is drawn into the discs on which the micro-organisms are fixed. This section of the disc is then exposed to air by the rotation of the shaft.

In anaerobic digestion, the micro-organisms utilize chemically bound oxygen in the absence of free oxygen to form methane, carbon dioxide and hydrogen sulphide (1). This process is not recommended for effluents that contain a high sulphur concentration and is better suited for highly concentrated effluents. This process minimizes the quantity of solid waste produced and the methane produced can be burned for its calorific value.

Evaporation

With this technology, the mill effluent is evaporated and the distillate is collected for recycle. The remaining concentrated liquor contains the organic and inorganic compounds that were present in the untreated effluent. It must then be treated in a secondary treatment process. The distillate is saturated with volatile organics, which must be removed in a polishing step. Evaporation requires large quantities of energy and therefore is expensive to operate.

Evaporation could also be used as a secondary closed cycle technology, to raise the solids content of the byproduct stream from the primary closed cycle technology.

The Millar Western BCTMP mill in Meadow Lake, is a closed cycle mill. It uses evaporation as primary closed cycle technology (29, 40, 41).

Freeze Crystallization

Freeze crystallization technology has recently been adapted for the treatment of pulp and paper industry by HDP Inc. (24).

In the freeze crystallisation process, raw effluent is first filtered and its temperature is lowered until crystals of pure water are formed. The total dissolved solids are concentrated to about 15%. Since the crystals have a lower density than the concentrated solution, they float to the top of the unit, where they are separated. They are then washed with a spray of clean melted water, and melted to recover the water. The mother liquor can be further concentrated by evaporation to between 50% and 70% total dissolved solids for combustion.

This water treatment process operates at low temperature, which eliminates corrosion problems and keeps volatile organic contaminants in the concentrate. However, in order to obtain crystals of a good purity, the process needs to be very well controlled.

Freeze crystallization was installed as a primary closed cycle technology at the Louisiana-Pacific mill in British Columbia. The mill is a bleached chemi-thermomechanical pulp mill using 100% aspen as furnish. Problems were encountered in the water-ice separation process, and consequently, the freeze crystallization treatment was changed for an evaporation process.

Physical-Chemical Treatment

Physical-chemical treatment is a complex treatment process that uses combinations of the following processes: precipitation, coagulation and flocculation. The reactions are obtained by the addition of one or a combination of chemicals. The most frequently used chemicals are lime, ferric chloride, alum, etc.

The main historical application of lime in the pulp and paper industry has been to remove colour from kraft bleach plant effluents. This type of effluent has a high concentration of long chain organic colloids such as lignin. A fair amount of information is available from the literature published since the 1950's.

Many chemicals such as alum, ferric chloride, activated carbon and others have also been tested for colour removal. However lime was always found to be the best alternative because of its low cost. It was also very attractive that the lime used for decolorization could be recovered in the kraft recovery system. At the same time, the colour bodies removed would be destroyed in the lime kiln. The main disadvantage of the lime process is the abundant and gelatinous sludge produced, which is difficult to dewater using conventional means such as centrifuges and belt presses.

Many variations of this process have been tested, including the massive lime process, the minimum lime process, and the magnesium and lime process.

Massive lime process (7, 22, 30, 37, 38):

> Initially, the main problem encountered with lime treatment was the production of a difficult to dewater sludge. In an attempt to solve this problem, the amount of lime added was increased to about 10 000 - 30 000 mg/L. The colour removal is then about 94 - 95% and a reduction in BOD_5 of 50% is achieved. About 200 - 700 mg/L of calcium remain in the treated water, causing hardness. Because of the high lime dosage, the gelatinous colour bodies account for only a small fraction of the total sludge volume. The sludge obtained with this process can easily be dewatered and sent to the lime kiln for lime recovery. The capacity of the recovery and chemical preparation equipment often needs to be increased to handle the large amount of lime required for the massive lime process. If the lime is not recovered, the cost for chemical addition is very high. For this reason, massive lime treatment is usually applied to selected streams only.

Minimum lime process (6, 20, 22, 25, 30, 34, 38, 39):

> The minimum lime process is an improved version of the massive lime process. It uses lime concentrations of about 1000-3000 mg/L to treat bleach plant effluent. 85-93% colour removal and about 45% BOD_5 reduction are achieved. To enhance the settling and dewatering of the sludge, lime is added prior to the primary clarifier where the primary sludge settles with the lime-organic sludge. This combined sludge is removed, thickened by centrifugation and burned in the lime kiln. Therefore, in only one step, the lime is recovered and the organic solids are combusted. The overflow from the clarifier is treated with CO_2 to convert soluble lime into insoluble carbonate.

Magnesium and lime (34, 38):

> As a way to decrease the quantity of lime required in the colour removal treatment, magnesium sulphate or magnesium hydroxide can be added prior to the lime addition. Typical concentrations used are 30-100 mg/L of magnesium hydroxide with 500-800 mg/L of lime. 90% colour removal is achieved using a process similar to the minimum lime process.

POLISHING TECHNOLOGY

Activated Carbon

In the activated carbon treatment process, the mill effluent is passed through columns of activated carbon, where dissolved organics are adsorbed (38). Filtering of the effluent is required before and after the activated carbon treatment.

The performance of the process depends on the effluent pH, the carbon particle size and pore size and on the molecular weight of the adsorbed component. The activated carbon needs to be regularly regenerated. This process is characterized by a high cost.

One commercial application of this process is the PACT system licensed by Zimpro Inc. This treatment system involves a combination of biological treatment and adsorption with activated carbon. Both actions occur simultaneously, as activated carbon is added to the effluent prior to the mixed and aerated basins. This system is in operation at El Paso in Texas (United States), on a municipal effluent (46). It is used in combination with a lime treatment, and ozonation.

Biological Treatment

Biological treatment can also be used as polishing technology. This process was discussed in the primary closed cycle technology section.

Membrane Technologies

In this technology, a pressure differential is applied across a semipermeable membrane between the effluent water to be treated and the treated water (3, 44). If this pressure difference is higher than the osmotic pressure, water is forced through the membrane, leaving the impurities behind. The selection is based mainly on molecular weight, and can be adjusted by proper selection of the membrane itself. Two streams are generated by this process, a purified water and a concentrated solution.

Reverse osmosis separates both organic and inorganic matter from the main stream (31). However, reverse osmosis has a low flux rate, and poor economies of scale. The maximum flux through the membrane is typically 0.2 m^3/m^2/day. The flux rate is temperature, pressure and pH dependent. The fouling of the membranes, reduces the flux rate and the membrane life. Frequent cleaning of the membranes is therefore required.

Ion Exchange

In the ion exchange process, the mill effluent is passed through a bed of resin particles, where dissolved ionic species in the stream such as calcium, sodium and magnesium ions are exchanged for hydrogen or hydroxide ions (7, 22, 31). This technique removes the contaminant to very low concentrations. However, the resin bed needs to be regenerated regularly, and is easily contaminated with organics.

Physical-chemical Treatment

Physical-chemical treatment can also be used as polishing technology. This process was discussed in the primary closed cycle technology section.

SECONDARY CLOSED CYCLE TECHNOLOGY

Combustion

The sludge produced by the primary closed cycle technology and the polishing technology can be first dewatered and then burned for power generation. These sludges could be mixed with primary sludge to make dewatering easier.

For a sludge to be suitable for incineration, some requirements must be met to insure a self-sustaining combustion (38):

1. The sludge must contain a minimum of 30 % dry solids.
2. The heating value of the dry sludge must be at least 1400 J/g.
3. The sludge must have an organic content of at least 67 %.

Dewatering

Dewatering of the sludge is required as a pre-treatment for most secondary closed cycle technology schemes. Many techniques are available, and a combination of more than one of these is often required to reach the higher dryness required for certain uses.

The different types of sludge have varying resistances to dewatering. Primary sludge is usually easier to dewater than sludge from secondary treatment. Polymers can be required as a dewatering aid.

The technologies that are most frequently used for dewatering in the pulp and paper industry and the dryness of the cake they typically produce are as follows (13, 38):

- gravity thickeners: 2 %
- flotation thickeners: 4 %
- vacuum filters: 20-30 %
- belt presses: 10-50 %
- centrifuges: 20-40 %
- screw presses: 50-55 %
- V presses: 30-45 %

Evaporation

Evaporation can also be used as secondary closed cycle technology, to increase the concentration of the reject stream from the primary or polishing technology. This process was discussed in the primary closed cycle technology section.

Land Application

Land application could be used as a secondary closed cycle technology. In this case, the wet sludge or the concentrated liquid byproduct from the primary closed cycle technology or polishing technology can be used for soil amendment or as fertilizer. A dry solids content of 3 to 8 % is typical for land application. A much drier sludge is required for use as a soil amendment.

For use as soil amendment, the following criteria must be met (38):

1. The carbon / nitrogen ratio must be between 20:1 to 30:1.
2. The calcium / magnesium ratio must be higher than 6:1.

A survey of sludge from different paper mills(38), showed that the first criterion was usually met and that the second one usually implied that addition of lime was required. This last fact suggests that this option would be well suited for sludge from a physical-chemical treatment using lime.

If sludge is used as fertiliser, the following guidelines should be met:

1. The sludge must not have a high content of heavy metals.
2. pH of the sludge should be 6.5 or higher.
3. Nitrogen content should not exceed that normally taken up by the crop in one season.
4. The sludge should be free of living pathogenic organisms.
5. The sludge should be applied in a way that it is not available for direct ingestion by domestic animals or humans.

This method of disposal would be especially well suited for sludges generated by a chemical treatment using lime and phosphate. In Europe it is a well known practice to add lime to municipal sludges to reach a pH of 12 and above (13). At this pH, it is considered that there is no bacterial activity. This high pH is also very well suited for soils that are acidic due to the addition of chemical fertilisers.

Landfill

As a secondary closed cycle process, dewatered sludge or ash from combustion could be sent to landfill. The cost of this option is very site specific and depends on the availability of a local suitable and affordable landfill site. As more landfill sites fill and because of increasingly stringent regulations and pressure from the public, this option is becoming less attractive. Sludge is usually sent to landfill at solids concentrations above 15 % (38).

Regeneration

Dewatered sludge or concentrated liquid from the primary closed cycle technology could be treated to regenerate the chemicals that were used in the water treatment. The treated byproduct could then be recycled to the primary closed cycle process (18, 22, 27, 39), e.g. calcination of lime mud to lime, and its subsequent recycle to the primary closed cycle process. This technology would be useful in combination with a physical-chemical treatment used as primary closed cycle technology.

Wet Air Oxidation

The wet air oxidation process uses high temperatures and pressures to oxidize organic materials present in the stream to be treated. Because of the high operating costs due to the extreme conditions used, wet air oxidation shows most promise as a secondary closed cycle technology.

This process is attractive for sludge that is difficult to dewater, such as biological sludge or that generated by lime treatment. The gases generated consists mainly of air and carbon dioxide, and the inorganic contaminants end up in their highest oxidation states. One of the disadvantages is that some organic material is converted to acetic acid which is very corrosive.

In this process, the liquid waste is mixed with compressed air or oxygen and the pressure and temperature of the mixture are raised until the oxidation reactions take place (26). Typical operating temperatures and pressures are above 250 °C and 15200 kPa. The reaction products are water, carbon dioxide and oxidized inorganics. Reductions of up to 88 % in COD and of close to 100 % for suspended solids have been obtained in laboratory experiments (26). Colour and turbidity reductions were also very high.

The wet air oxidation process is used on sludge from pulp and paper effluent treatment at some mills in Europe and in the United States.

2.2 The TMP-newsprint mill and its effluent

The closed cycle technologies discussed in the previous section, were considered for the closed cycle process scheme suitable for a TMP-newsprint mill. The actual mill studied in this work and its effluent are described in the following pages.

This pulp and paper mill produces 550 ADt/d of newsprint from TMP pulp. At the time the experimental testing was done, the effluent flow was 28 m^3/ton of paper produced.

Four main processes are involved in the making of newsprint at this mill (11):

- Wood handling and preparation
- Pulping using the TMP process
- Paper making
- Effluent treatment

2.2.1 Wood handling and preparation

The wood used by the mill arrives in the form of chips (70%) and logs (30%) coming from two species, balsam fir (60%) and spruce (white, black and red) (40%).

Logs undergo dry debarking, are cut into chips and then screened to remove saw dust. Chips, upon their arrival at the mill, are screened and sent to the chip storage pile. Wood handling and preparation do not use water.

As needed, chips are recalled, blown to the pulping area, and washed with warm water (45-65°C) to remove contaminants such as sand, saw dust and bark.

The chip wash water is a major contributor to the effluent. This stream is rich in suspended solids, mainly large particles such as pieces of wood and bark. Also, organics from the chips such as extractives, dissolve in the warm water. Dissolved inorganics are also present.

2.2.2 Pulping using the TMP process

After the wood preparation, chips are sent to a pre-steamer. They are than pressurized and directed to the primary and secondary refiners. Sodium sulphite is added to the refiners to aid in the pulping process. Pulp goes to pressurized cleaners where steam is separated and sent to the heat recovery. The pulp goes to a latency chest. Condensate from the heat recovery contributes to the effluent. It contains few suspended solids but is rich in extractives.

From the latency chest, pulp is screened. Pulp is then cleaned in a four stage process.

Screen rejects are refined and screened in the rejects refining system. Rejects from the fourth stage of cleaners are sent to the effluent. They contain a high concentration of suspended solids, mainly fibres. It is also rich in dissolved organics.

Pulp is thickened in two discs filters, and clear and cloudy waters produced are used for dilution in the TMP screens and cleaners.

The pulp is bleached with sodium hydrosulphite for the production of standard newsprint and with hydrogen peroxide for the production of a high brightness paper.

The pulp preparation process is the main contributor of contaminants to the effluent. This is where most of the chemicals are added, either for pulping or for bleaching. These chemicals are the main sources of inorganic contaminants, mainly sodium and sulphur compounds. Pulping is also the process where most of the dissolved organics are extracted from the wood.

2.2.3 Papermaking

The bleached pulp is fed to two paper machines. Broke from the two paper machines is recycled and white water surplus is reused.

The paper making process does not contribute significantly to the effluent because the major portion of the white water is reused in the process.

2.2.4 Effluent treatment

The effluent treatment consists of a primary clarifier and a sludge dewatering system. Dewatered primary sludge is mixed with bark and burned in the hog fuel boiler.

2.2.5 Chemicals used in the process

Some of the chemicals used in the process will eventually go into the effluent. These can be divided into two different categories:

1. Chemicals used continuously in the process, for example, bleaching chemicals.

2. Chemicals that would not usually go to the effluent but that can sometimes be found in it because of an accidental spill, the cleaning and purging of

a tank, or an occasional use (slimicide, etc.). The quantities involved are usually small.

Table 2.2 lists the main chemicals in the first category. The table shows that the main chemicals added contain sodium and sulphur, which are the two major inorganic contaminants.

TABLE 2.2

MAIN CHEMICALS USED IN THE TMP PAPERMAKING PROCESS

CHEMICAL	Quantity	USAGE
Sodium hydrosulphite	1300 kg/day	Bleaching
Hydrogen peroxide 70%	800 kg/day	Bleaching
Silicate de sodium	1100 kg/day	Bleaching
Caustic soda	700 kg/day	Bleaching
Caustic soda 50 %	900 L/day	Effluent neutralization
Sodium sulphite	4400 kg/day	Pulping

2.3 Potential effects of water contaminants on the papermaking process

In a closed cycle scheme, the effluent from the TMP-newsprint mill described in the previous section would be treated, and recycled to the mill to be used in the process.

If the water is to be recycled to the papermaking process, there are no defined criterion for quality. As the proportion of water recycled to the process increases, the concentration of contaminants will rise. Above a certain level, some contaminants can create operating problems and lower the quality of the paper produced. The risk attached to water recycling lies in the fact that this level is not known, and can only be roughly estimated.

Because of the great variety in the products and fabrication processes, and because of the lack of experience in water recycling, the water quality that is required is unknown.

In this section, the potential problems are reviewed, and their most probable causes are identified.

2.3.1 Corrosion

Corrosion is caused by dissolved contaminants, both organic and inorganic (8, 9, 19, 32, 38, 45). Corrosion due to biological activity can be controlled by the use of biocides and slimicides. The most problematic population is the sulphate reducing anaerobic bacteria. In highly closed processes, these are an important cause for corrosion.

Corrosion due to dissolved solids is caused mainly by chlorides, sulphates, lignin related sulphur compounds, organic acids, carbonates, iron, manganese, calcium, magnesium and barium ions. A higher concentration of dissolved solids leads to an increase in the electrical conductivity of the water, which increases the rate of corrosion. The effect of the dissolved inorganics is more critical at high temperatures, high velocities and low pH.

2.3.2 Brightness reversion

The brightness reversion of paper is its rate of yellowing. It is caused by storage, heat and exposure to light. The main mechanism causing colour reversion is the photochemical oxidation of the lignin (21, 38). A decrease in the stability of colour is known to be caused by some metal ions (iron, copper, manganese and aluminium). Some studies have shown that the concentration of these ions in the white water was well above that allowed by the theoretical solubility, and that they are strongly adsorbed onto the pulp fibres. As a result, brightness reversion would probably be a critical problem in a closed water cycle.

2.3.3 Temperature increase

As the water cycle is closed, the temperature of the process water will increase. Temperatures up to 66 °C have been reported (21). Higher temperatures increase the rate of corrosion.

Another challenge associated with zero discharge operation is thermal build-up, and the availability of adequate cooling water. For this reason, a cooling system could be necessary to treat a portion of the water.

A higher temperature also has benefits. It can brings energy savings by lowering the steam requirement, and improves pulp drainage.

2.3.4 Lower physical properties

An increase in dissolved salt concentrations should not have a detrimental effect on the physical properties of the paper (19, 10). In previous work, concentrations of 20 000 mg/L were observed before an impact could be seen on the paper properties (21).

An accumulation of fines could have a detrimental effect on the quality of the paper.

When present in high concentrations in the process water, extractives can have a negative effect on the burst and tensile strength of the paper (43).

2.3.5 Microbial contamination

With an increase in the organic and nutrient (K, N and P) content of the process water, biological growth can become a problem. In closed water systems, the concentration of dissolved oxygen rarely exceeds 1 mg/L, especially in stagnant areas. This will result in growth of anaerobic bacteria. These can cause slime, odour, foam as well as corrosion (45).

Aeration of the process water is usually a good solution as the aerobic bacteria are less troublesome than the anaerobic ones because their activity produces less aggressive compounds (CO_2, water and nonvolatile organic acids) than the byproducts of anaerobic decomposition (volatile organic acids, hydrogen, CO_2, sulphides and methane).

Biological activity can also produce discoloration and spots on the paper.

The high temperature encountered with the water cycle closure will cause a shift in the population of bacteria present in the process water. Thermophilic organisms are those that are present at temperatures above 50 °C. They tend to form spores and are more difficult to control. However, if the water temperature goes over 70 °C, bacterial growth will be inhibited.

2.3.6 Build-up of fines

A higher content of fines in the process water decreases the drainage of the pulp. This problem could be solved by removing them with filters or by increasing the first-pass retention of fines on the machine. However, this is likely to require the use of retention aids because a high concentration of dissolved ions changes the normal ionic forces and leads to a decreases in the retention on the machine (21).

A high concentration of fines also causes felt and wire plugging, which decreases felt and wire lives. It can cause shower plugging.

2.3.7 Pitch deposition

Pitch deposition on the paper can be caused by extractives, including resin and fatty acids. This is of particular concern in the present study, as a high concentration of resin and fatty acids are extracted in the TMP process. The pitch could be dispersed on the sheet and sold with the paper, but this is dangerous because it could cause a decrease in the quality of the paper (45).

2.3.8 Scaling

Scaling is the result of crystallization or precipitation of carbonates, silicates, sulphates, and oxylates with calcium, magnesium, manganese, iron, aluminium and barium ions. Usually, to control scaling, the hardness of the water is controlled (32, 38). It can also be controlled with the use of sequestering agents such as EDTA. Water hardness of over 900 mg/L has been observed without adverse effects on the system.

2.4 Closed cycle scheme investigated

The closed cycle treatment scheme investigated, will have to give a water of sufficient quality so that the detrimental effects described in the previous section do not occur, or can be kept under control.

The main purpose of this work was to study if a physical-chemical treatment using lime as the main treatment chemical could be used as a primary closed cycle technology. The need for a polishing and for a secondary closed cycle technology were also investigated.

The challenge of the study is the difficult application for the recycled water: the making of newsprint paper. Many recycled fibres board mills have closed water cycles. However, board is much less sensitive to impurities in process water than newsprint.

One tissue mill in Ontario, is almost effluent free, and is using a physical-chemical process to treat its effluent before recycling it. The mill and its treatment process are discussed in the following section.

2.5 The case of Kimberly Clark, in Huntsville, Ontario

The Kimberly-Clark tissue mill situated at Huntsville, Ontario, treats the mill effluent in a lime and magnesium process, shown in Figure 2.2, and recycles most of the treated water. The treatment process provides a recycled effluent of high quality which is more than adequate for the needs of the tissue process.

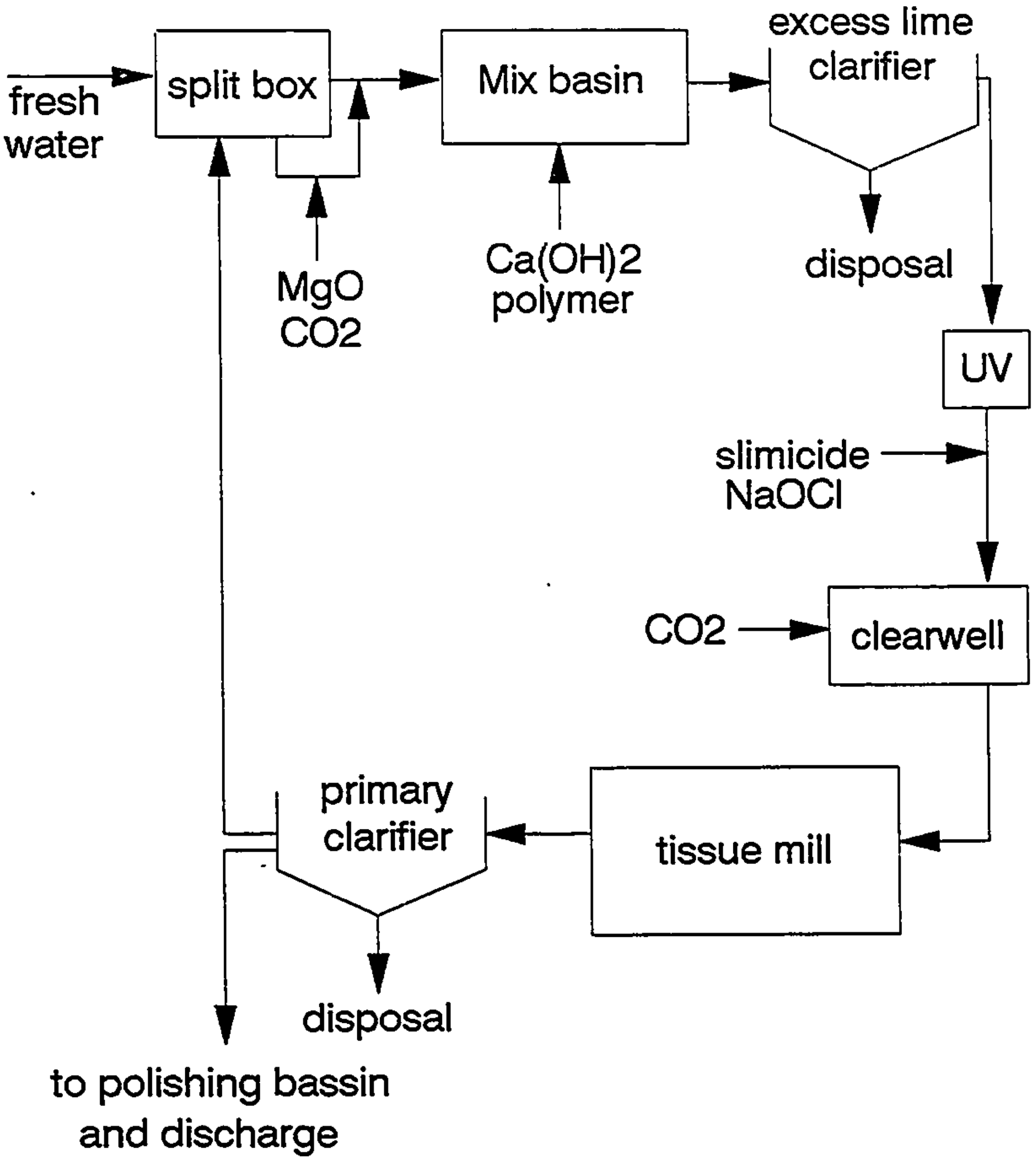
One tissue machine produces about 95 t/day of finished product. The mill furnish is 100% virgin pulp, mainly hardwood kraft and Brazilian Eucalyptus.

There are essentially no fillers or additives used in the manufacturing process, and the virgin pulp furnish contains little dissolved organic contaminants. Therefore the effluent discharge prior to any treatment has relatively low dissolved solids and contains only 116 mg/L of suspended solids, mainly fibre fines. The fresh water consumption at the mill is only about 16 m^3/t on a year-round basis.

The Kimberly-Clark effluent is significantly different from the TMP-newsprint process effluent being considered in this study. However, the type of contaminants present in the water at Huntsville are similar, but lower in concentration. The fact that this process is technically and economically feasible shows that this process, is worth investigating.

FIGURE 2.2

TREATMENT SCHEME
KIMBERLY-CLARK, HUNTSVILLE



2.5.1 Water treatment process

The mill effluent is first treated in a primary clarifier where most suspended solids are removed by settling. The clarified effluent is separated into two flows: the bulk is treated for recycle by the physical-chemical process, and a smaller quantity is discharged from process (about 15% of total flow), to maintain low temperature and chloride concentration in the recycled water.

The discharged effluent is treated in two polishing aerated basins to reduce temperature and increase the oxygen level. The effluent from the polishing basins is used for irrigation during most of the year. During the winter months, the effluent is treated in 3 one-acre sand-filled percolating beds before being discharged to the Big East River.

The main flow out of the primary clarifier is mixed with make-up raw water from the Big East River, and this combined flow is treated for use in the mill.

A 20 L/min. flow of effluent is withdrawn from the main flow and mixed with 7 mg/L of MgO in the MgO reactor. CO_2 from the natural gas boiler off-gases is added at a rate to maintain the outlet pH of the MgO reactor at 8.3.

The primary function of the MgO reactor is to ensure complete dissolution of the MgO and to raise pH. The primary function of MgO, later in the process, is as a coagulant after hydrated lime has been added.

The solution from the MgO reactor is combined with the main flow, which is fed into the lime mix basin. In this basin, 125 mg/L of $Ca(OH)_2$ is added and the pH rises to 10.7.

A polyelectrolyte is added in the next well-mixed basin at a concentration of about 1.5 mg/L. $Mg(OH)_2$ formed by the above reaction has limited solubility, and serves as a gelatinous floc, whereas the polymer serves to increase the floc size by aiding in the flocculation of the suspended and colloid particles. This mixture is agitated in a 40 minutes flocculating basin.

The mixture from the flocculating basin is sent to the excess lime clarifier where the solids settle.

pH is lowered near the clearwell outlet from 10.7 to 7.0 by the addition of CO_2 contained in the natural gas boiler flue gas, to reduce the potential for scale formation by lowering the carbonate concentration.

Sludge is collected from the primary settling and excess lime clarifiers, mixed in a sludge blending chest, dewatered on a vacuum belt filter and sent to landfill at approximately 30-35% solids. Even though lime/MgO sludge is known to have a low drainage and be difficult to dewater, no problems have been encountered at the mill.

2.5.2 Treatment efficiency

Samples of effluent were taken and analyzed before and after the effluent treatment. Table 2.3 summarizes the results obtained.

TABLE 2.3

TREATMENT EFFICIENCY AT KIMBERLY-CLARK, HUNTSVILLE

Parameter	Units	Clarified mill effluent	Treated effluent
pH		6.7	6.9
Conductivity	μS/cm^2	423	450
Total suspended solids	mg/L	1	8
Total dissolved solids	mg/L	548	460
Extractives	mg/L	12	6
Sulphate	mg/L	21.33	22.34
Carbonate	mg/L	134.4	139.2
Sodium	mg/L	89.76	88.29
Calcium	mg/L	15.9	16.46
Magnesium	mg/L	4.95	4.03
Total organic carbon	mg/L	45	43

The level of contaminants is very low, even before treatment. This means that it is very hard for the treatment to have a good efficiency since most contaminants will be at their residual level.

As expected, the treatment has little effect on most of the contaminants that were analyzed.

2.6 Some Chemistry

But how does this process work? This section gives an overview of the chemical mechanisms and the physics under this treatment process.

2.6.1 Magnesium oxide and lime

The removal of contaminants with magnesium oxide and lime is due to a series of complex physical and chemical reactions. Lime has the most important role. However, magnesium oxide is used to aid the reaction.

Many chemical reactions occur between the treatment chemicals and the different types of contaminants. The reactive contaminants can be divided into three categories:

- Organics
- Hardness
- Heavy metals

The removal of all contaminants is improved at higher temperatures. This is because the reaction rates are higher and the solubility of calcium and magnesium salts are lower at elevated temperatures. Settling of precipitated materials is also improved because the density and viscosity of hot water is less than that of cold water.

Organics

The reaction of the organic contaminants with lime depends on the following variables:

1. The dosage of lime.
2. The alkalinity of the water being treated.
3. The pH of the solution.

The enolic and phenolic hydroxyls form calcium-organic insoluble salts as they react with calcium (5, 22). The general reactions are as follow:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$2R\text{-}COOH + Ca(OH)_2 \rightarrow (R\text{-}COO)_2Ca\downarrow + 2H_2O$$

A similar reaction occurs with the resin and fatty acids. These acids react to form insoluble calcium resin and fatty acid salts which precipitate (6, 15).

The molecular weight distribution of the colour bodies is also an important variable in the reaction. Organics of molecular weight (MW) over 5000 are completely removed with lime treatment. Those with MW in the range 400-5000 undergo partial removal. Finally, those with MW less than 400 are not removed (5, 16, 22).

One hypothesis is that lime reacts with the longer chain organics to break them into smaller units. This implies that analysis for a specific long chain molecule before and after lime addition would show a high removal whereas analysis for total organic carbon would show no change, because the removal was in fact a transformation, a shift of the larger units into smaller units.

Hardness

Lime and magnesium are commonly used to soften water, i.e. to reduce the concentration of calcium and magnesium (4, 23). The reactions are as follows:

MgO is added first. It reacts according to:

$$MgO + CO_2 \longrightarrow MgCO_3$$
$$MgO + Ca(HCO_3)_2 \rightarrow MgCO_3 + CaCO_3 + H_2O$$
$$MgCO_3 + CaSO_4 \rightarrow MgSO_4 + CaCO_3$$

Lime is then added to the mixture. The first reaction is the slaking of lime according to the following reaction:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Then, lime forces magnesium to precipitate as a gelatinous $Mg(OH)_2$ floc which coagulates the suspended and colloidal solids (4). The colloidal materials can also serve as condensation nuclei.

$$Mg^{2+} + Ca(OH)_2 \text{ --> } Mg(OH)_2\downarrow + Ca^{2+}$$

The following reactions also take place:

$$Ca(OH)_2 + 2CO_2 \text{ ---> } Ca(HCO_3)_2$$
$$Ca(OH)_2 + Ca(HCO_3)_2 \text{ ---> } 2CaCO_3\downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 \text{ ---> } Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O$$
$$MgSO_4 + Ca(OH)_2 \text{ ---> } Mg(OH)_2\downarrow + CaSO_4$$
$$MgCO_3 + Ca(OH)_2 \text{ ---> } Mg(OH)_2\downarrow + CaCO_3\downarrow$$

CO_2 can be added to complete the reactions and to neutralize pH according to:

$$Ca(OH)_2 + H_2O + CO_2 \text{ --> } CaCO_3\downarrow + 2H_2O$$
$$MgCO_3 + H_2O + CO_2 \text{ --> } Mg(HCO_3)_2$$

At high temperatures, hardness removal is very high, approaching an optimum at a temperature of 65 °C.

Heavy metals

Heavy metal compounds will react in a similar way to form hydroxides, which usually have very low solubilities (17, 23, 5), and will precipitate. The following metals should be removed to very low levels:

- Manganese
- Zinc
- Copper
- Cadmium

- Lead
- Chromium
- Radium
- Barium
- Silver

SiO_2 is also removed by adsorbtion on the magnesium precipitate. At pH above 10, phosphates are precipitated to very low levels.

Two contaminants, potassium and sodium, are not removed by lime treatment. However, they are not expected to have negative effect unless found at very high concentrations. These can be eliminated only by ion exchange, evaporation and reverse osmosis.

2.6.2 Potassium phosphate

Phosphate can be used to remove the permanent hardness of the treated water. Sodium phosphate is usually used but potassium phosphate can also be used to obtain the same results.

Sodium and potassium associate preferentially with Cl^- and SO_4^{2-} which are causing permanent hardness. Phosphate then associates with calcium, magnesium and iron to form insoluble phosphate compounds that precipitates.

The reactions work best at pH above 9. They are as follow (14, 42):

$$3CaCO_3 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2\downarrow + 3Na_2CO_3$$

$$3MgSO_4 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2\downarrow + 3Na_2SO_4$$

$$FeCl_3 + Na_3PO_4 \rightarrow FePO_4\downarrow + 3NaCl$$

$$3CaH_2(CO_3)_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2\downarrow + 6NaHCO_3$$

$$CaH_2(CO_3)_2 + Na_2HPO_4 \rightarrow CaHPO_4\downarrow + 2NaHCO_3$$

$$CaSO_4 + Na_2HPO_4 \rightarrow CaHPO_4\downarrow + Na_2SO_4$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

2.6.3 Polymers

Polymers are usually used for two main purposes:

1. To prevent the fragmentation of fragile flocs under the effect of hydraulic forces.
2. To increase the size of the small and slow settling flocs.

Polymers are synthetic organic compounds of high molecular weight, composed of a chain of monomers. Their natural form is condensed. Before they can be used, they have to be activated by bringing them into solution. This has the effect of unfolding the polymer chain, freeing the active sites (12, 17, 35).

Polymers can be divided according to their ionic charge: anionic, cationic, and non-ionic. For flocculation of suspended particles, anionic and non-ionic polymers are usually used, because almost all naturally occurring particles, both organic and inorganic, are negatively charged.

Polymers work by flocculating colloidal and fine suspended particles by the adsorption of polymers on the colloidal surface, and from bridging of polymer chains between solid particles. The functional group of the polymer adsorbs at the particle surface, leaving the rest of the molecule free to attach with another particle having some vacant adsorption sites. These form particle/polymer complexes.

The bonding mechanism between a functional group on the polymer and a site on the colloid's surface is very specific and depends on the molecular weight and degree of branching of the polymer. The following variables also have a strong influence:

Agitation:	If the agitation is strong, creating high shear forces, the flocculated or coagulated colloids will tend to redisperse.

Zeta potential: The zeta potential is a measure of the electrokinetic charge which exists at the solid-liquid interface of the particles in suspension. It is a measure of the stability of the colloidal particle. A high zeta potential means that these forces of separation are high and that the particles interact strongly. These forces tend to keep the particles in suspension. The zeta potential varies with pH, and temperature, and this variation is material dependent.

Conductivity: The conductivity of the water being treated is important. It is a measure of the concentration of organic and inorganic dissolved salts in the system. These salts compete with polyelectrolytes, and decreases their efficiency by being adsorbed on the active sites of the colloidal surface.

The most common way to find the appropriate polymer is to perform beaker tests. The concentration of polymer added is also very critical, because over a certain dosage, a reversal occurs, and the particles are restabilized with an opposite charge.

Two polymers were used during the trials, non-ionic polyethylene oxide (Alkox E-300 Q640 from Quadra Chemicals) and anionic polyacrylamide (Superfloc^{+} A-130 PWG from Cyanamid).

The first one was used to help the settling of the fine suspended fibres to reach a low level of suspended solids before the physical-chemical treatment. The second one was used to increase the floc size after the addition of the treatment chemicals.

2.7 Experimental design

2.7.1 General

Statistical experimental design is a useful tool that helps in obtaining the maximum knowledge from a limited amount of information.

The first step is the formulation of a hypothesis that must be confirmed or invalidated by the experimental program. The null hypothesis, H_o, is assumed to be true until the results of the experiments show otherwise. The alternative hypothesis H_a is usually the one of interest. It takes into account all cases not covered by H_o (28).

Even if experimental design and statistical analysis are used, there is still a risk of drawing the wrong conclusion. However, this risk is known and selected at an acceptable level. Two types of risks can be identified:

-	α risk:	Probability of accepting H_a when H_o is true
-	β risk:	Probability of accepting H_o when H_a is true

Once the hypothesis have been formulated and the acceptable risk identified, the next step is to select a specific design of experiments. This design will determine which experiments will actually be required so that the hypothesis can be confirmed or invalidated with the risk that [illegible] accepted.

The selection of the design depends on many factor. The two main ones are time and resources that are available, and that will determine the number of experiments that can be performed.

Another important factor to consider is the presence of interactions. An interaction exists between two variables, if the effect of one of the variable on a measured parameter is different when the second variable is at a low, or high level. For example if pH rises with an increase in variable A when variable B is at a low level, but increases when B is at a high level, it means that there is an interaction between A and B. When interactions exists, they must be taken into account or else they will distort the results.

When designing an experiment, the amount of information that can be collected with a certain number of experiment is fixed. It is referred to as degree of freedom. One degree of freedom equals one information that can be obtained. Examples of information are the response of a variable, or an interaction, or an evaluation of the error.

The results obtained from the experimental designs can be studied using the ANOVA (ANalysis Of VAriance) table. In an ANOVA, the variance within the means (noise) is compared to the variance between the means (signal). If the signal to noise ratio exceeds that which is expected by chance, then there is a difference between the means. The null hypothesis considered here is that all means are the same: H_o: $\mu_1 = \mu_2 = ...$

This ANOVA table is a way to put the information into the form of summary tables and graphs, that will help to identify the most important variables and interactions, with regard to their effect on the response. It is also possible to study the polynomial functional nature of the data, to find the shape of the curve represented. It is also possible to plot the interactions, to be able to quickly identify the weak and strong interactions.

2.7.2 Central composite design

The central composite design was selected to study the effect of the variation in chemicals addition on process efficiency.

One of the simplest design is a full factorial design with two levels. This design allows the study of both variables and interactions. It can be represented by a cube (Figure 2.3). Each axis is a variable being studied and there are two levels for each variable.

The central composite design (CCD) is an extension on this full factorial design (2). In addition to the 8 points required for the three variable full factorial design, it includes a central point, and a low and a high extreme point for each variable, centred at the zero. The CCD can be represented as shown in Figure 2.4. The circles represent the points for the full factorial design, and the stars represent the additional points. The location of the star points is not free. Their distance from the centre point is fixed. Tables are available for many different cases, taking into account the number of variables, if the design is a full or partial factorial, etc.

The central composite design allows the evaluation of the effect of the main variables, and the effect of the simple interactions.

In this work, a central composite design with a full factorial was used, with three variables. The number of experiments required was 15: 8 for the factorial design, 1 for the centre point and 6 for the star points. Replicates were also required for a better measure of the error.

2.7.3 TAGUCHI

A full factorial design allows the study of the main variables, the main interactions between the variables, and a complex interaction taking the three variables into account. However, such complex interactions are extremely rare. The degree of freedom allocated for the study of this complex interaction could be used to obtain more valuable information.

FIGURE 2.3
FULL FACTORIAL DESIGN
3 VARIABLES - 2 LEVELS

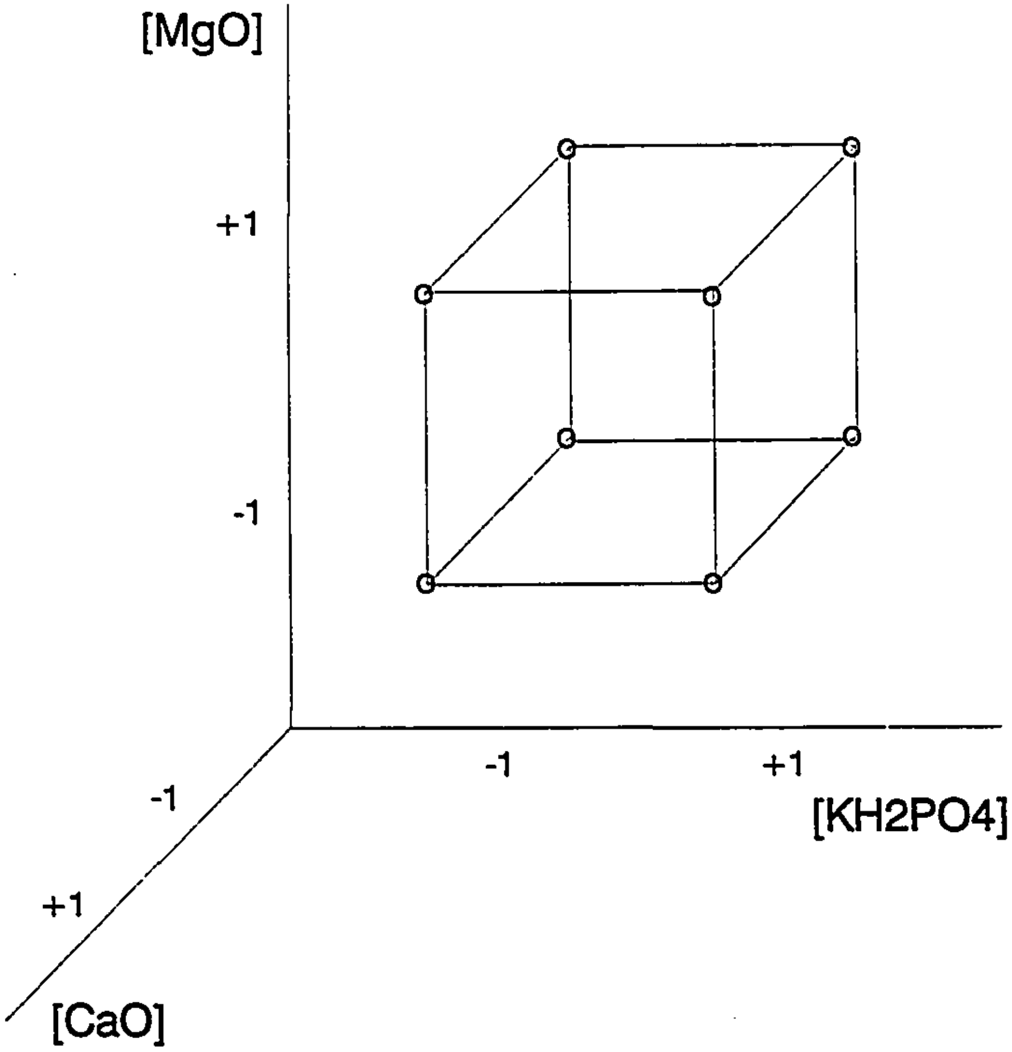
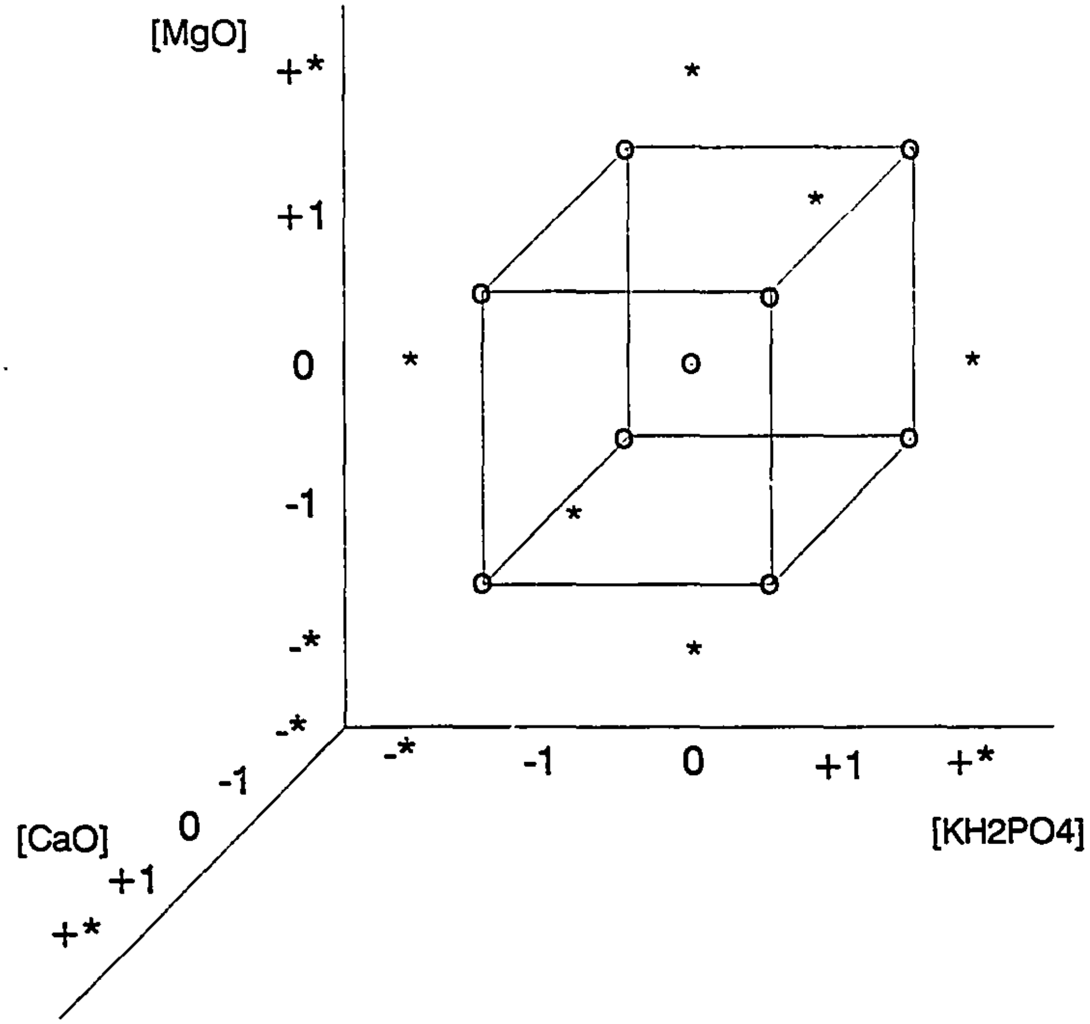


FIGURE 2.4

CENTRAL COMPOSITE DESIGN (CCD)
3 VARIABLES - 5 LEVELS



One type of modified design, that provides a more efficient use of the time and resources, was originally proposed by Taguchi (28). This technique allows the use of the degrees of freedom associated with interactions that are known to be negligible to study additional variables or the error associated with the experiments.

For this work, a design called L16 from Taguchi was used and can be represented as shown in Figure 2.5. This design allows to study the effect of five variables at two levels, as well as all main two variables interactions. Its main objective was to identify changes in treatment efficiency due to higher concentrations of inorganic dissolved solids in the effluent, or due the a pre-treatment process.

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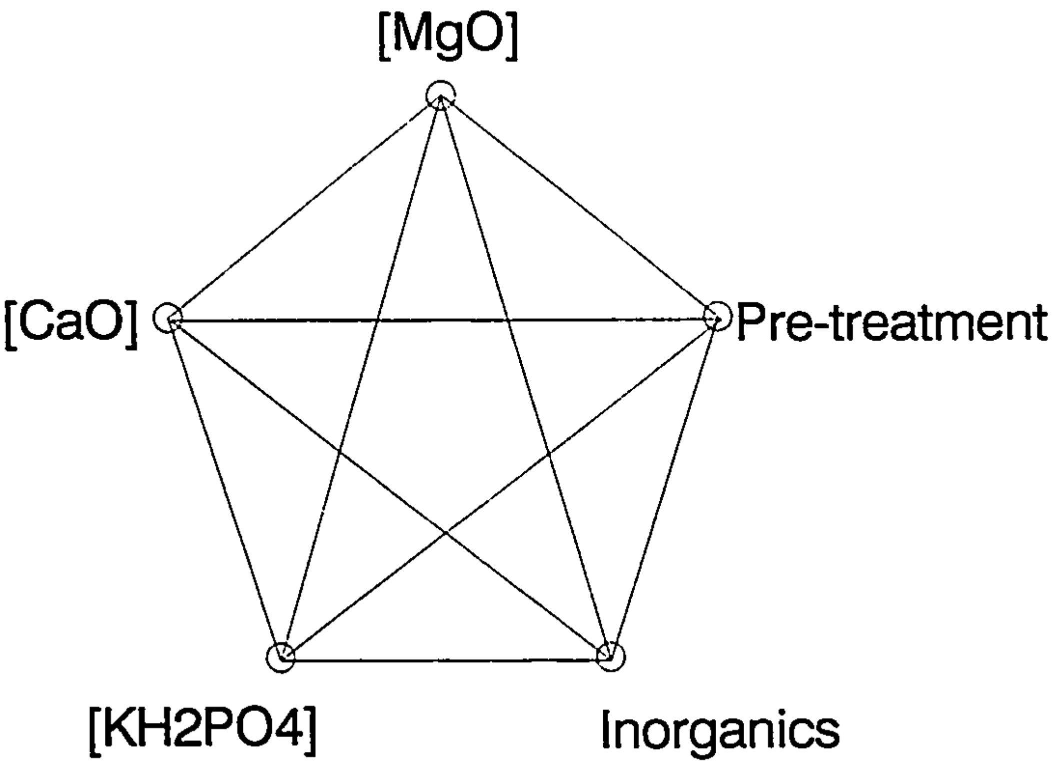
FIGURE 2.5

TAGUCHI L16 DESIGN

5 VARIABLES - 2 LEVELS



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3.0 EXPERIMENTAL PROCEDURES

3.1 Experimental Set-up and procedure

The experimental set-up consisted of a constant temperature water bath, 1 L beakers and a stirrer.

The sample to be treated was heated and kept at a constant temperature of 60°C in the water bath. This temperature was selected because it is the most likely temperature of the effluent after reduction of the water consumption.

Chemicals were added sequentially and mixed with a strong agitation, leaving 2 minutes between each addition, for reaction to take place. A polymer was added at the end of the experiment, to help flocculation. Conductivity and pH were measured, and the sample was left to settle for an hour. The supernatant was decanted and saved for further analysis. The sludge was kept for suspended solids measurement to perform mass balances.

All samples were refrigerated at 4 °C until analyzed.

3.2 Methods and equipments used for analyses

3.2.1 Suspended and dissolved solids

Suspended and dissolved solids were measured according to CPPA Standard H.1 (2). This technique involves filtering a known volume of sample using a 1.5µm pore filter. The filter is dried at 105 °C and suspended solids are then determined gravimetrically.

The filtrate is used for dissolved solids determination. A known volume is evaporated and dried at 105 °C in a crucible and the dissolved solids concentration is also found by gravimetry. To determine volatile solids, either suspended or dissolved, the total solids are ignited in a muffle furnace at 550 °C.

3.2.2 Dissolved organic carbon

Dissolved organic carbon was measured using a Technicon AutoAnalyzer (4). A filtered sample is automatically introduced into the Technicon Autoanalyzer. The sample is acidified and sparged to remove inorganic carbon. Then, the sample is oxidised with a UV digester in an acid-persulphate mixture. The CO_2 that is liberated passes through a semi-permeable membrane and reacts with a phenolphtalein reagent. The intensity of the colour is measured with a colorimeter and the organic carbon concentration is automatically calculated using a computerized data management system.

3.2.3 DCM extractives

DCM extractives were analyzed at the Pulp and Paper Research Institute of Canada (Pointe-Claire) according to Tappi procedure T204om-88 (5). It involves adjusting the pH of the sample to 2, extracting with dichloromethane, evaporating the extractives and then using a gravimetric method to calculate the concentration. The extractives obtained include fats, resins, waxes and non-volatile hydrocarbons.

3.2.4 Colour

Colour was measured using CPPA standard H.5 (3). This technique involves the comparison of the absorbance of the filtered sample with that of a platinum-cobalt standard solution. The absorbance is measured at a wavelength of 465 nm on a spectrophotometer. Colour is expressed in arbitrary colour units (c.u.). One c.u. is equivalent to the absorption of light at 465 nm by 1 mg/L platinum in the platinum-cobalt standard solution.

3.2.5 Turbidity

Turbidity was measured according to standard 2130B of Standard Methods for the Examination of Water and Wastewater (1). Turbidity is a measure of light diffraction when it passes through the sample. It is expressed in nephelometric turbidity units (NTU).

3.2.6 Ca^{2+}, Mg^{2+} and Na^{+} ions

The concentration of Ca^{2+}, Mg^{2+} and Na^{+} ions were found using atomic absorption spectrometry (6). In this technique, a sample is vaporized and dissociated into free atoms by the heat of a flame. A radiation source emits incident energy of a known wavelength. The energy absorbed by the element in the sample is then measured. The concentration of the element can be read from a calibration curve made with the readings obtained with standard solutions.

3.2.7 PO_4^{2-}, SO_4^{2-} and CO_3^{2-} ions

PO_4^{2-}, SO_4^{2-} and CO_3^{2-} ions were analyzed using ion chromatography (7). The sample is injected into a stream of eluent, and passed through a series of ion exchangers. The anions of interest are separated and then measured by conductivity. They are identified on the basis of their retention time as compared to standards, and the quantity is measured by peak area or peak height.

3.3 Characteristics and choice of mixture

At the time the experimental testing was done, the effluent flow was 28 m^3/ton of paper produced. However, the experimental water treatment process would not be used on the TMP-newsprint effluent as it is presently, but instead it would be implemented after a number of process modifications, done in order to bring the fresh water consumption down from 28 m^3/ton to about 10 m^3/ton. The resulting effluent would be more concentrated than the present one.

The detailed characteristics of the future concentrated effluent are not known. However, it was desirable to approximate the concentrated effluent for the testing program.

It was identified that after implementation of the water reduction program, three of the existing effluent sources would form the majority of the future effluent. It was assumed that by combining these three sources in the appropriate proportions, a reasonable approximation of the future effluent would be obtained. This mixture would give an approximation of the effluent, at a 10 m^3/ton water usage, and with discharge of the effluent to the river after treatment.

Table 3.1 lists the three source and their respective proportion of the simulated effluent

TABLE 3.1

SOURCES OF SIMULATED FUTURE EFFLUENT

Source	Proportion
Evaporator condensate from heat recovery	10%
Fourth stage TMP cleaners rejects	80%
Chip wash water	10%

This mixture was used for most of the experimental portion of this work.

Table 3.2 shows the results of an analysis that was done on the three effluent sources and the resulting quality of the simulated effluent.

TABLE 3.2

ANALYSIS OF SIMULATED FUTURE EFFLUENT

Chemical analysis	Units	Evaporator condensate	Cleaner rejects	Chip wash water	Simulated effluent
pH		4.7	4.7	4.6	4.7
conductivity	µmho	500	720	800	710
SO4 2-	mg/L	140	185	195	180
CO3 2-	mg/L	5	8	15	8
Na +	mg/L	103	311	119	271
Ca 2+	mg/L	10	25	30	24
Mg 2+	mg/L	2.0	5.6	6.8	5.3
total dissolved solids	mg/L	1500	2500	2550	2400
total suspended solids	mg/L	360	31000	3500	25000
extractives	mg/L	225	170	110	170
total organic carbon	mg/L	600	690	1160	730

The resulting concentration of suspended solids in the mixture is very high (25000 mg/L), which makes the mixture difficult to handle. Because of the high concentration, the suspended solids did not settle well. The bulk of the suspended solids was removed by screening. In a full scale installation, this step could be performed by inclined screens. The resulting mixture had a suspended solids concentration of 500 mg/L, made of mostly fine fibres.

After the effluent flow reduction, the next step is to start recycling the treated water back to the mill. As the portion of the flow recycled increases, the inorganic contaminants that are not removed by the treatment will start to build up in the effluent. The characteristics of the water reaching the treatment process will change. To simulate this effect, in a second part of the experimental program, inorganic dissolved solids were added to the mixture, to study the effect on the treatment efficiency.

3.4 Data validation

Two tests have been done to verify the validity of the data obtained:

- mass balances
- repeats for critical points

Mass balances were performed, to verify if the total of the measured suspended and dissolved solids were equal to the calculated mass balance, obtained from the initial level plus the chemicals added. Figure 3.1 shows such a mass balance for one of the series of tests of the screening experiments.

To get a better measure of the error, in the experimental program, repeats have been done for the most critical point. Table 3.3 gives an example of the variability that was observed for each parameter measured. The data shown is for the centre point of the central composite design. This experimental point was performed four times.

FIGURE 3.1
MASS BALANCE

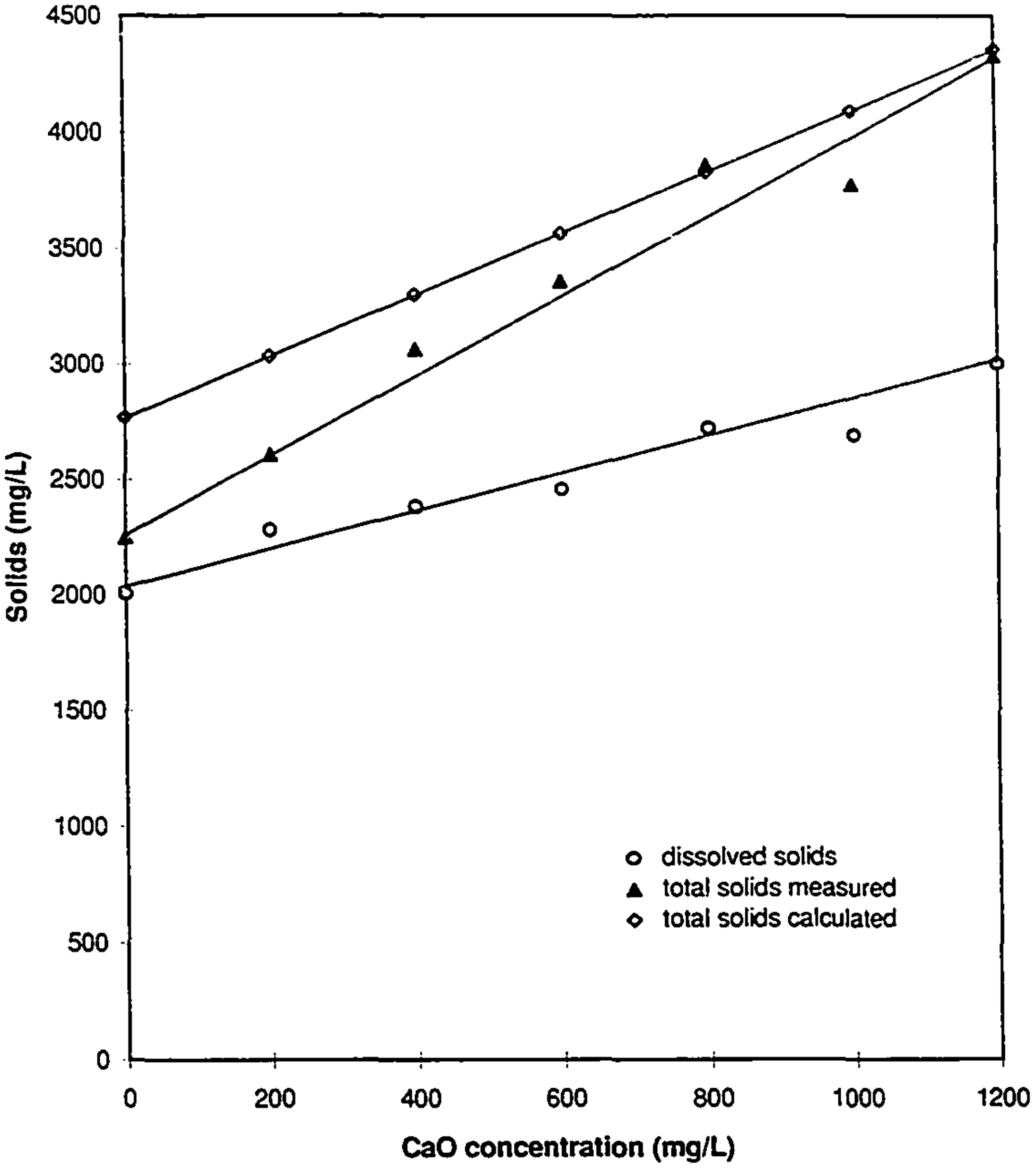

TABLE 3.3

VARIABILITY IN MEASURED PARAMETERS

Parameter	Units	Average	Minimum	Maximum
pH		11.2	10.9	11.9
Total dissolved solids	mg/L	3422	3384	3469
Total organic carbon	mg/L	931	830	1048
Extractives	mg/L	23	12	36
Colour	c.u.	508	486	535
Turbidity	NTU	57	42	63
Calcium	mg/L	265	246	322
Magnesium	mg/L	1.1	1.0	1.2
Phosphate	mg/L	0	0	0
Carbonate	mg/L	45	39	55

3.5 References

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4.0 SCREENING EXPERIMENTS

As seen in section 2, a large selection of chemicals were available for the physical-chemical treatment. Moreover, these chemicals have been used in many different combinations and over a very wide range of concentrations.

In order to save resources and time, screening experiments were performed. They were necessary to help in the development of the detailed experimental program. The specific objectives for the screening experiments were as foilow:

1. To identify which chemicals are most efficient at removing dissolved inorganic and organic matter.

2. To identify a range of concentrations that is appropriate for this particular application.

Lime (CaO) was selected as the main treatment chemical because of its low cost and its availability.

The potential effect of the treatment chemicals on the paper properties when the treaied water is recycled, was also considered in the treatment chemical selection. For example, alum was rejected because aluminum can cause reversion in paper at relatively low concentrations.

Table 4.1 lists the four series of trials that were experimented.

TABLE 4.1

TRIALS PERFORMED IN SCREENING EXPERIMENTS

Trial	Chemicals Tested	Range of Concentrations mg/L
1	Lime (CaO)	0 - 30 000
2	Magnesium oxide (MgO)	0 - 2000
3	Magnesium oxide (MgO) Lime (CaO)	100 0 - 1200
4	Lime (CaO) Activated carbon	1000 350

4.1 Results and discussion

The results obtained for trials number 1 to 3 are shown in Figures 4.1 to 4.5. Results obtained for the fourth trial are shown in Figures 4.6 and 4.7.

4.1.1 Lime and Magnesium Oxide

The results obtained from the first three series of trials are shown together on the graphs, to get a better comparison of the effect of each chemical.

In general, the addition of lime alone, and the addition of lime with magnesium oxide, gives overlapping curves, which indicates that MgO did not enhance the effectiveness of CaO. Addition of magnesium oxide alone gives results that are quite distinct.

FIGURE 4.1
Effect of chemicals dosage on pH

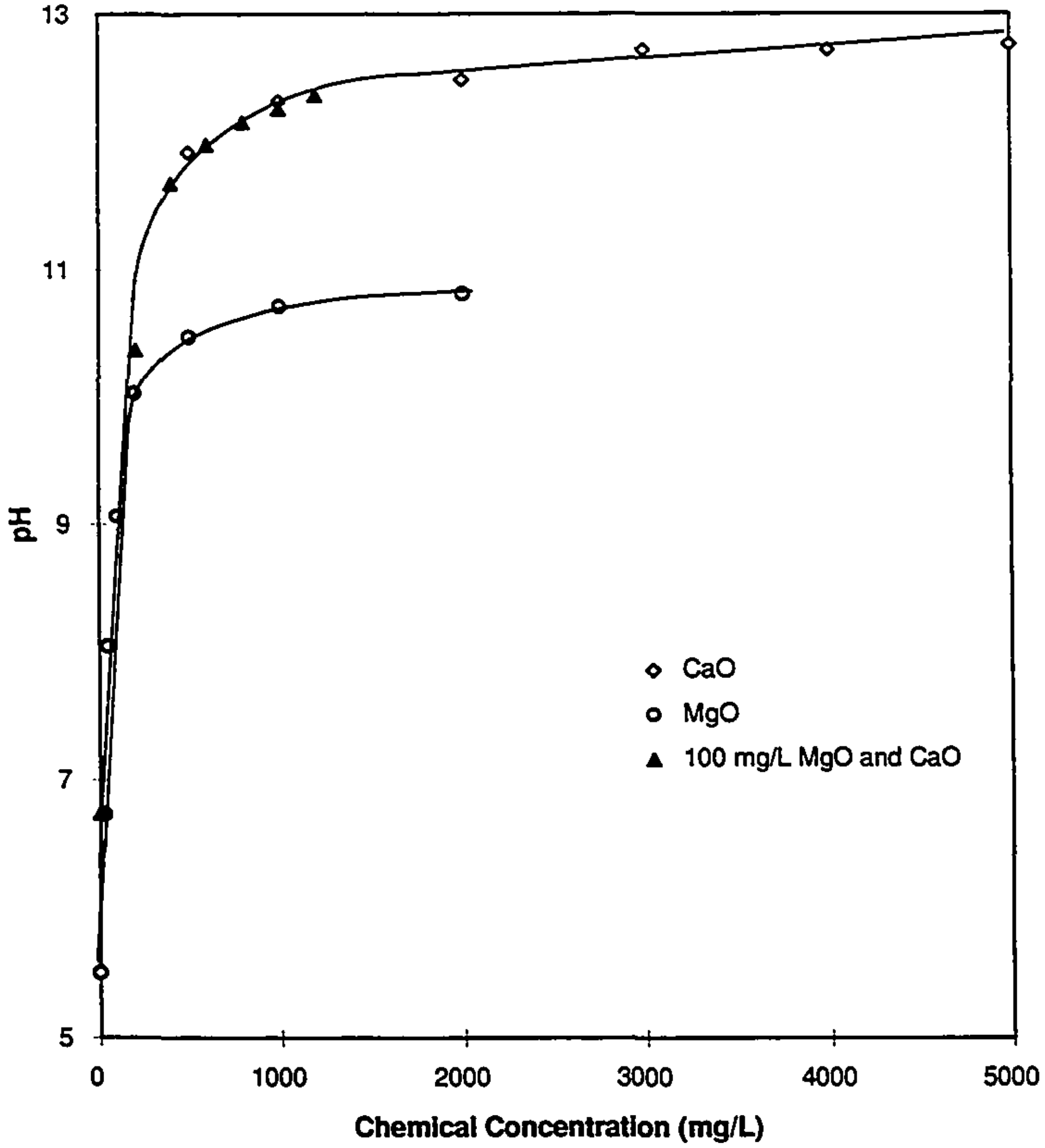


FIGURE 4.2
Effect of chemicals dosage on conductivity

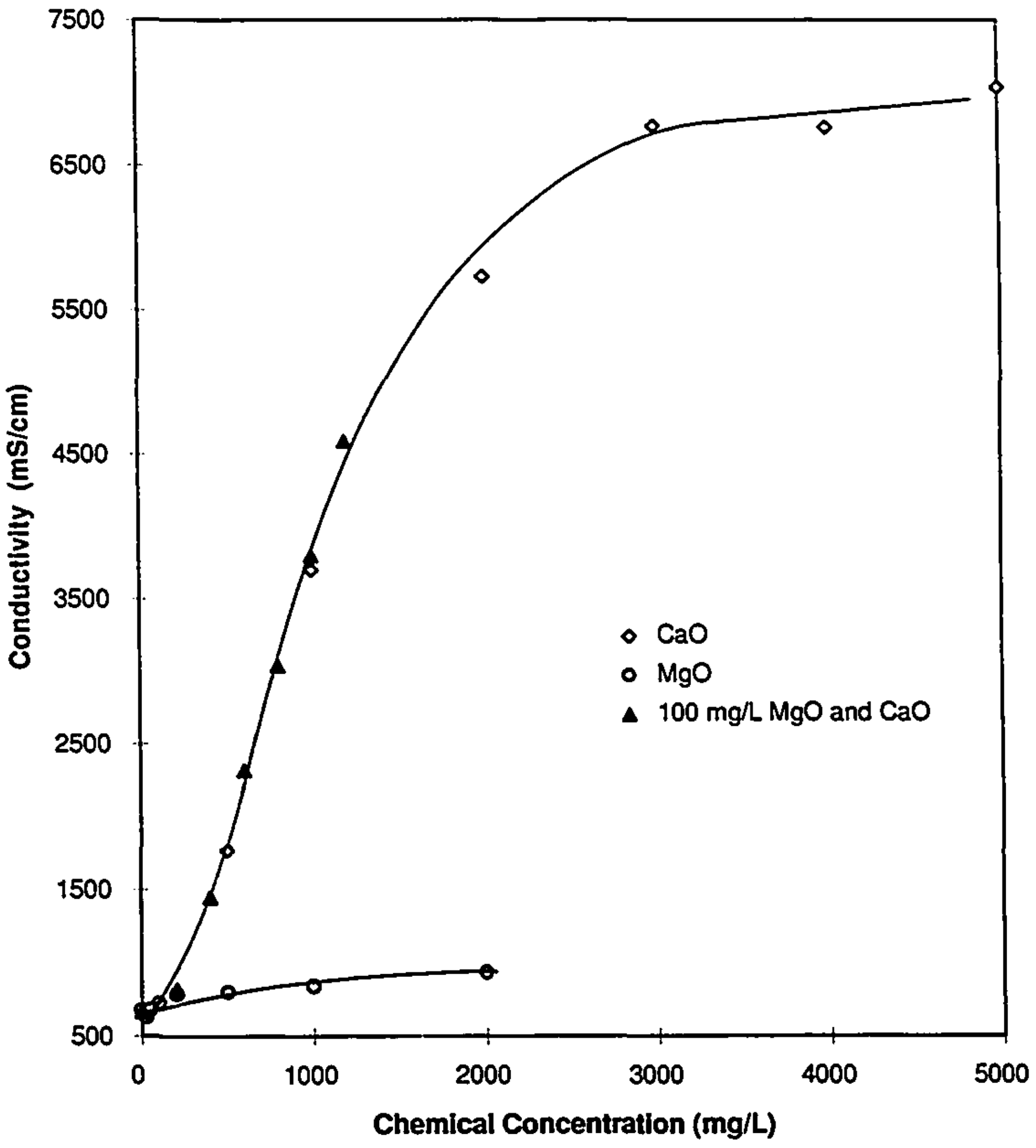


FIGURE 4.3
Effect of chemicals dosage on total dissolved solids

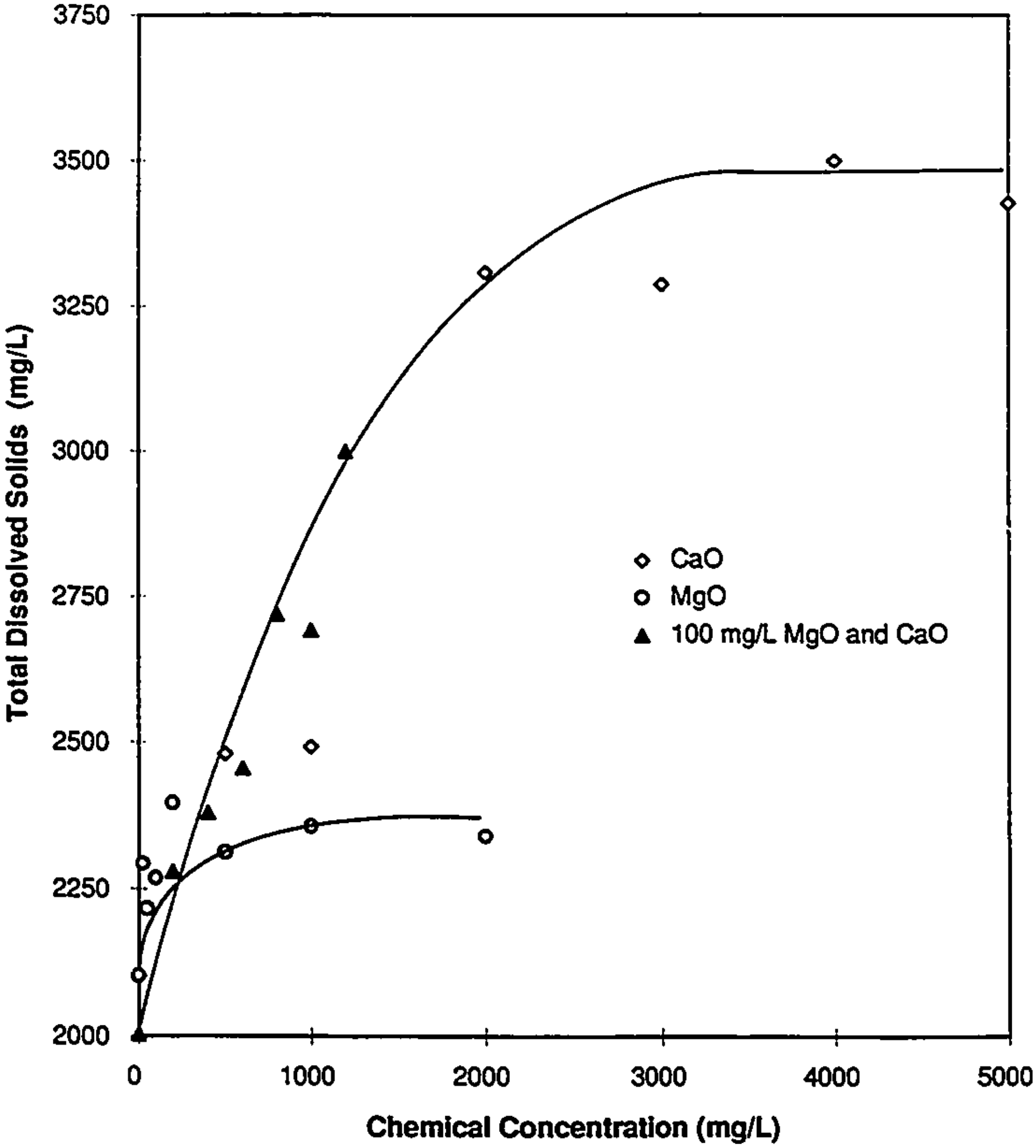


FIGURE 4.4
Effect of chemicals dosage on extractives

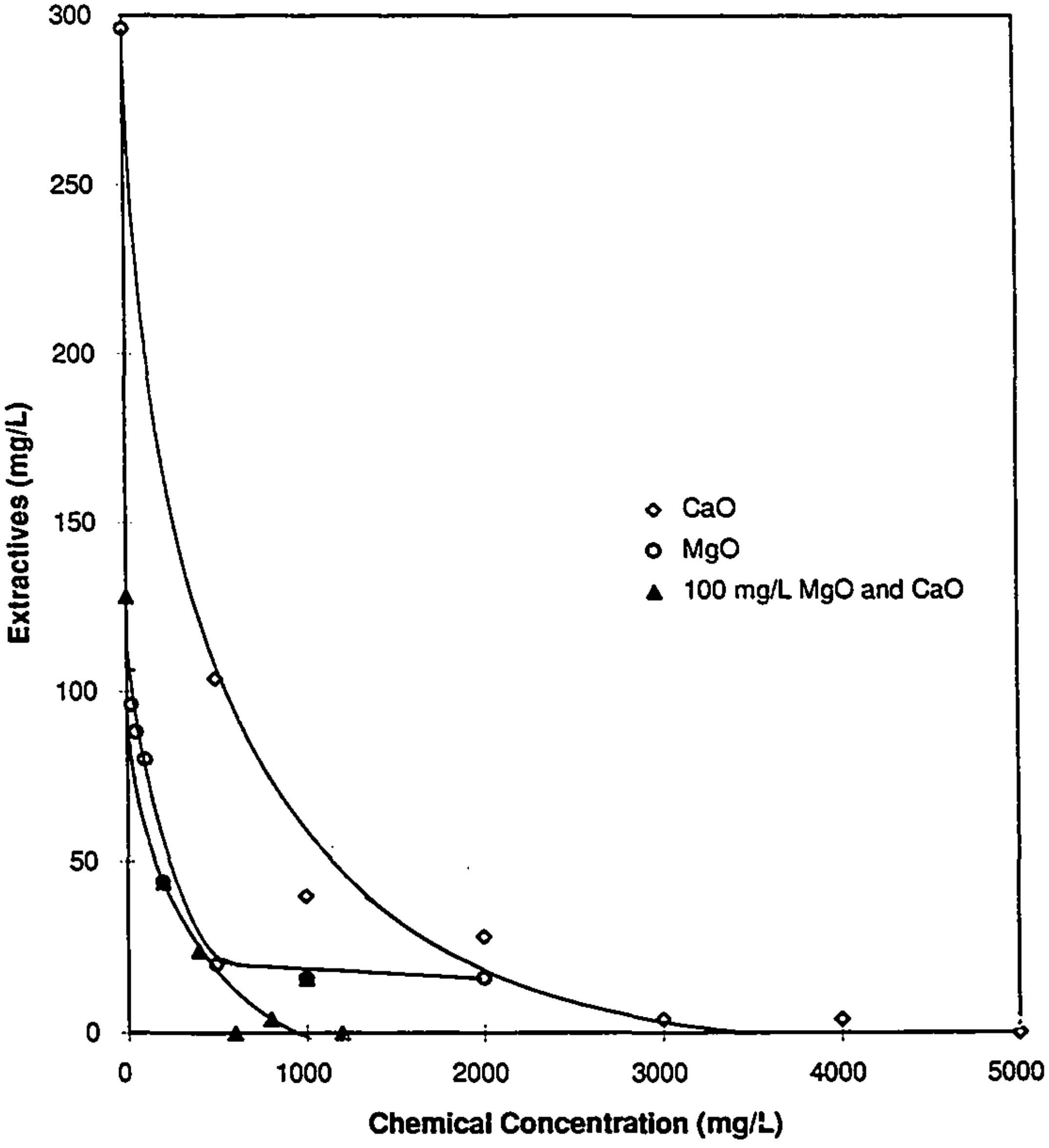


FIGURE 4.5

Effect of chemicals dosage on total organic carbon

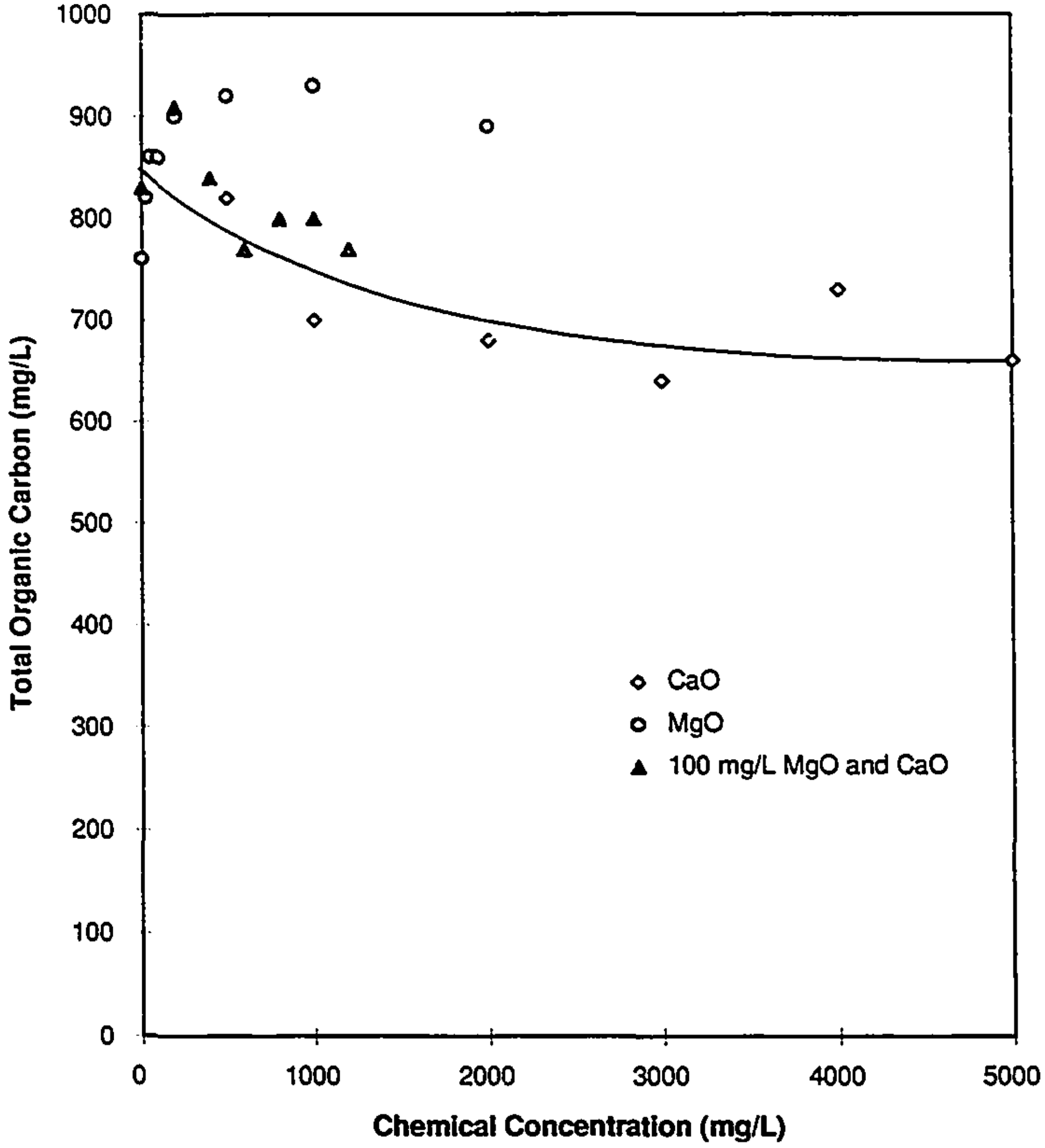


FIGURE 4.6

Effect of lime and activated carbon on total suspended solids

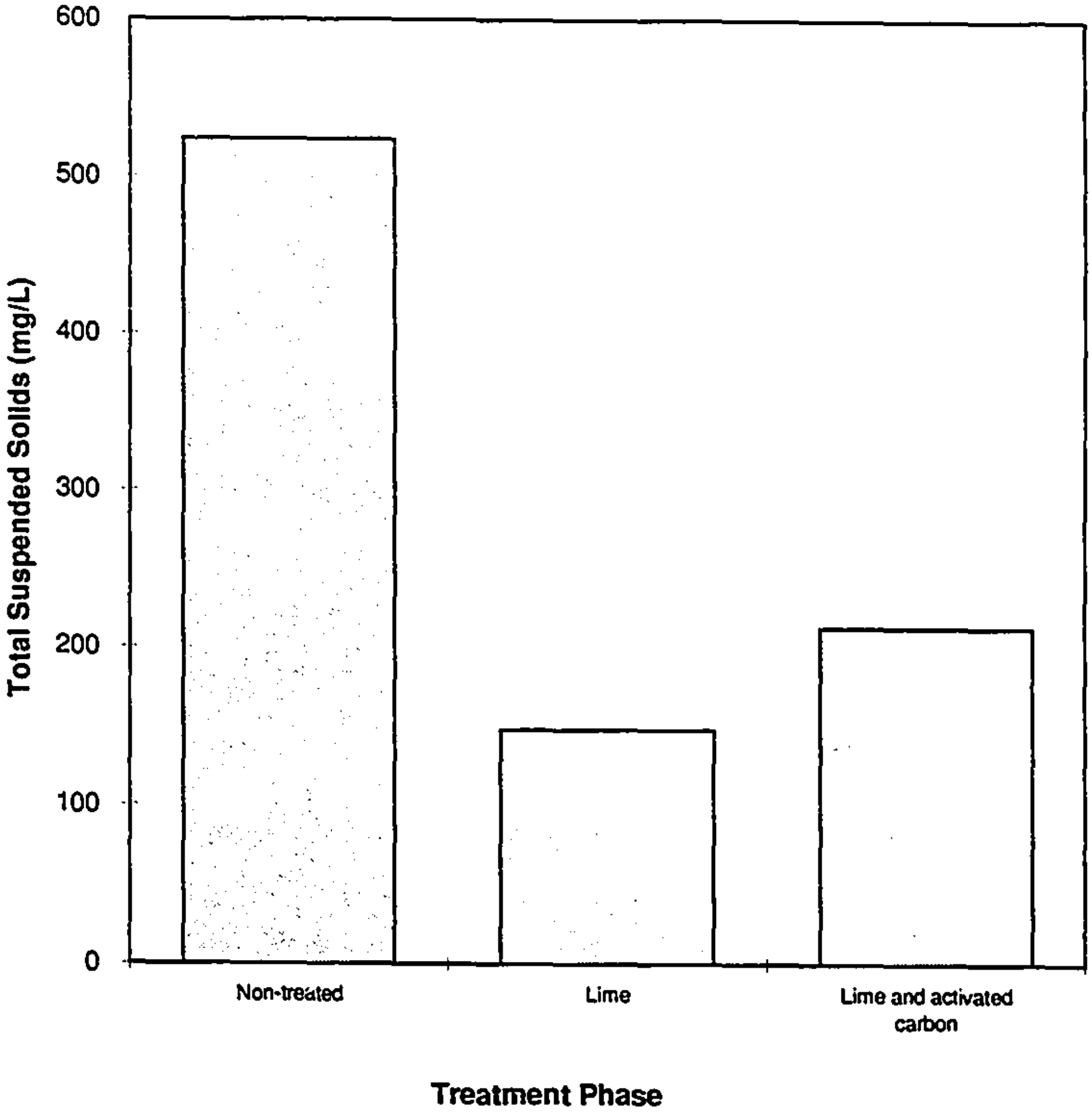
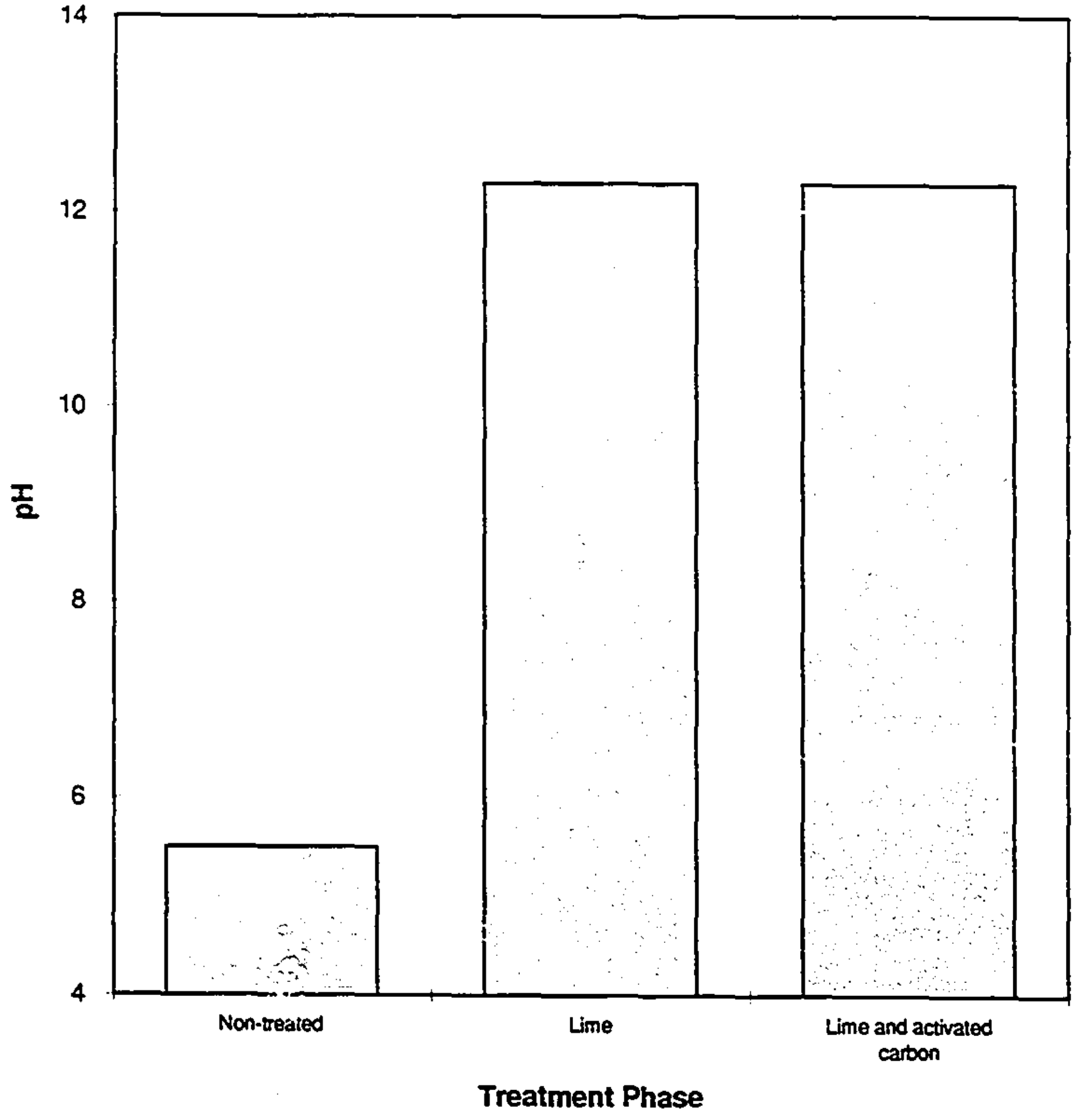


FIGURE 4.7
Effect of lime and activated carbon on pH



Figures 4.1 and 4.2 show pH and conductivity as a function chemical addition. Magnesium oxide has less effect than lime on both parameters. Conductivity stays low when MgO is added alone. Since conductivity is an indirect measure of inorganic dissolved solids, this suggests that dissolved solids stay about constant with MgO addition but increase with lime addition.

Figure 4.3 shows total dissolved solids results. It confirms what was expected from the conductivity measurement. Dissolved solids increase rapidly with lime addition and reach a plateau at a dosage of about 3000 mg/L of lime. With the addition of magnesium oxide, dissolved solids increase very little and rapidly reach a low plateau.

Figure 4.4 shows extractives concentration as a function of chemical addition. Magnesium oxide addition is more effective than lime to remove or break down extractives. The removal occurs at a lower dosage. The addition of 100 mg/L of MgO before lime addition, greatly improves the reaction efficiency. By using this combination, 100 % removal can be obtained with 1000 mg/L instead of the 4000 mg/L that are required if lime is used alone.

Total organic carbon seems to decrease a little with lime addition or with MgO and lime addition (Figure 4.5). However, the trend is not very marked and it is therefore impossible to draw a definite conclusion regarding organic carbon with this series of experiments.

4.1.2 Activated Carbon

The results obtained from the lime and activated carbon trials demonstrated that this treatment combination is very effective at removing extractives from the effluent.

The addition of activated carbon also improves the visual appearance (colour, suspended solids and turbidity) of the treated effluent. After activated carbon addition, the water appears free of colloidal material, and has very few suspended solids (refer to Figure 4.6). Activated carbon addition does not change the pH of the water, which remains high (above 12), due to the lime addition as shown in Figure 4.7.

However, there is an important concern with this combination of chemicals. The few suspended solids remaining in the treated water are very fine black flocs of activated carbon. They do not settle, and when poured on paper, they leave a dark trace.

These particles cannot be recycled to the process because they might cause pitch on the paper, and could accumulate in the process if the water is recirculated. This concern alone is sufficient to make this alternative not acceptable.

4.2 Conclusions

The preliminary experiments showed that magnesium oxide greatly improves the removal of extractives when used in combination with lime. This fact is illustrated in Table 4.2, which shows the concentration of treatment chemicals that is required, for the three different treatment schemes, to reach 95% extractives removal. By adding only 100 mg/L of MgO prior to the addition of lime, the required dosage of lime can be reduced to one fourth.

It was therefore decided to use this combination of treatment chemicals (magnesium oxide and lime) in the experimental design of the formal experiments.

TABLE 4.2

COMPARISON OF TREATMENT CHEMICALS COMBINATIONS

Treatment chemicals	Dosage for 100 % removal of extractives
MgO	> 2000 mg/L
CaO	~ 4000 mg/L
100 mg/L MgO + CaO	CaO: < 1000 mg/L

The level of dissolved solids increased with chemical addition. This suggests that the increase is due to dissolved calcium, which was added as lime, and remained in solution. This calcium causes hardness in the treated water and has to be removed.

A third chemical, potassium phosphate, was added to the list of variables to be tested in the formal experiments. This chemical would be used to reduce the permanent hardness of the water to a level that is acceptable for recycle to the mill. Experiments were required to verify that the chemical is suitable for the effluent being treated and to quantify its treatment efficiency.

5.0 FORMAL EXPERIMENTS

From the results obtained in the preliminary experiments, it was decided to study the following variables in more detail:

MgO:	The effect of adding magnesium oxide on the treatment efficiency.
CaO:	The effect of adding lime on the treatment efficiency.
KH_2PO_4:	The effect of adding potassium phosphate on the treatment efficiency.
Pre-treatment:	The effect of an additional pre-treatment using polymer to obtain a better removal of suspended solids was investigated, to see if it has an effect on treatment efficiency. The polymer used for this application was Alkox E-240 Q602 from Quadra Chemicals.
Inorganics:	The physical-chemical treatment was tested on the effluent mixture, as described in section 3.3. It was also tested on a modified mixture, to which inorganic chemicals (NaCl, Na_2SO_4 and Na_2CO_3) were added. This modified mixture is a simulation of the effluent after reduction of its flowrate to about 10 m^3/ton. The chemicals were added to simulate the effluent after closure of the water cycle, when the level of inorganic contaminants has increased. The effect of the higher level of inorganics on the treatment efficiency was studied.

The treatment efficiency is a global term that is used to summarize the removal efficiency of extractives, hardness, color, turbidity, etc.

The trials were performed in two separate series of experiments. The first one was to study the effect of dosage of the three selected treatment chemicals, MgO, CaO and KH_2PO_4 on treatment efficiency. The second one was done to study the effect of pretreatment and inorganic dissolved solids addition and their interaction with the treatment chemicals dosage.

5.1 Effect of MgO, CaO and KH_2PO_4 addition

The objective of the first set of experiments was to determine the effect of the three treatment chemicals.

These trials were done on the effluent mixture without polymer pre-treatment or inorganic chemicals addition. They were simulating treatment of the effluent from a very low water usage TMP-newsprint mill, that is still discharging its effluent to the environment.

5.1.1 Statistical design

The statistical design used for this experimentation is known as the central composite design (CCD), and was briefly explained in section 2.7.2. Table 5.1 presents the levels that were used for the dosing concentration of each chemical.

TABLE 5.1

LEVELS FOR THE CCD SET OF EXPERIMENTS

VARIABLES	LEVELS				
	-*	-1	0	+1	+*
MgO	0	122	300	478	600
CaO	0	405	1000	1595	2000
KH_2PO_4	0	203	500	797	1000

The levels were selected to have the most efficient dosage found in the preliminary experiments at the centre point. This method allows the study of a good range of variation, and helps to refine and verify the efficiency of the dosage previously found in the preliminary experiments.

5.1.2 Results and Discussion

Figures 5.1 to 5.10 show the effect of the chemicals on the treated water. In each graph, the parameter being analyzed is plotted as a function of chemical addition. The three data sets presented are for KH_2PO_4, MgO and CaO addition.

For each set of data, the following procedure was followed for the preparation of the graphs. While the dosage of one chemical is varied, the dosage of the other two treatment chemicals is kept constant at the centre point. For example, while lime addition is varied from 0 to 2000, MgO and KH_2PO_4 addition were kept constant at 300 mg/L and 500 mg/L respectively The abscissa then represents the concentration of lime that was added. The centre point dosage for the three chemicals was as follow:

FIGURE 5.1
Effect of treatment chemicals on pH

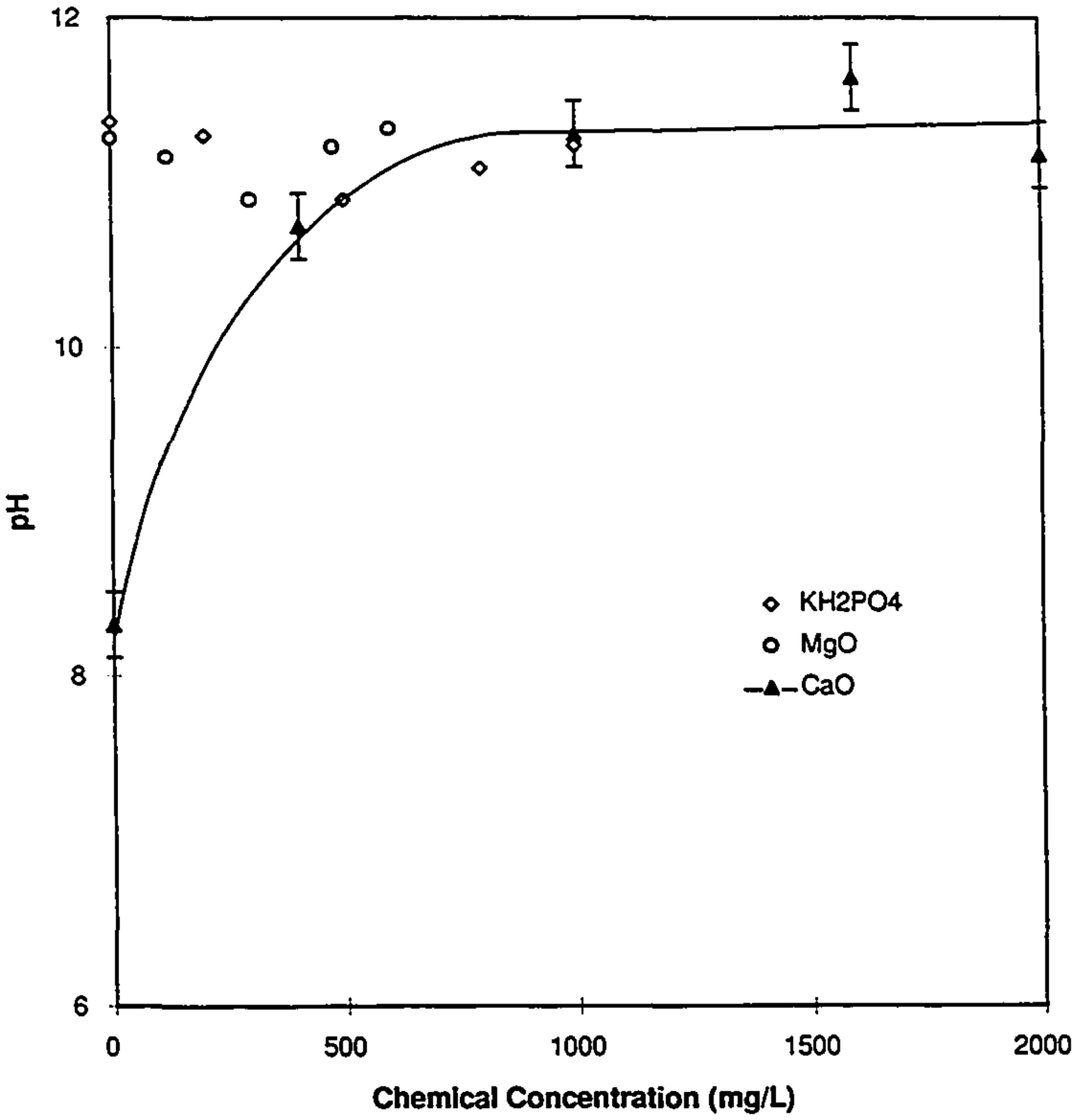


FIGURE 5.2
Effect of treatment chemicals on total dissolved solids

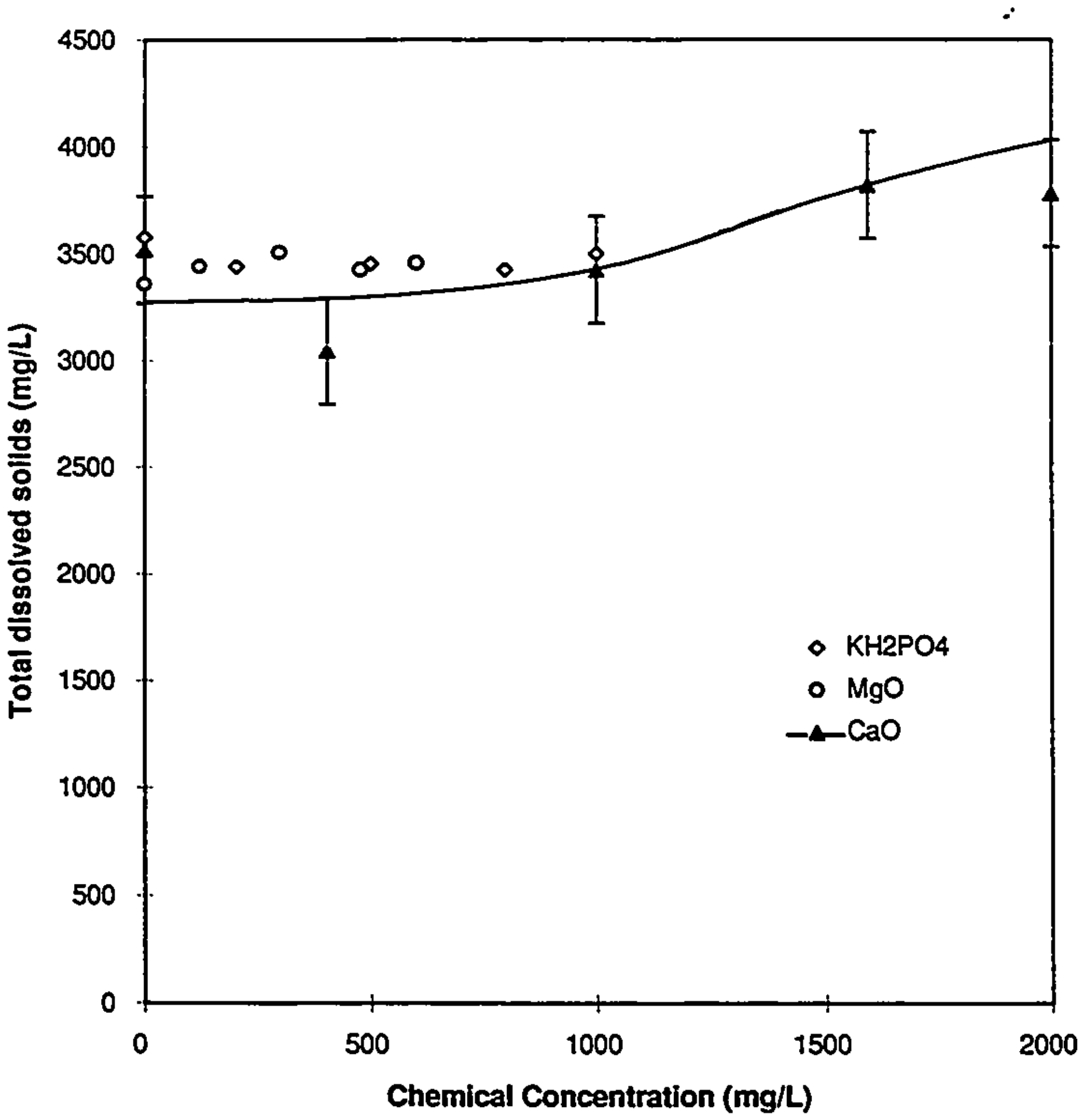


FIGURE 5.3
Effect of treatment chemicals on total organic carbon

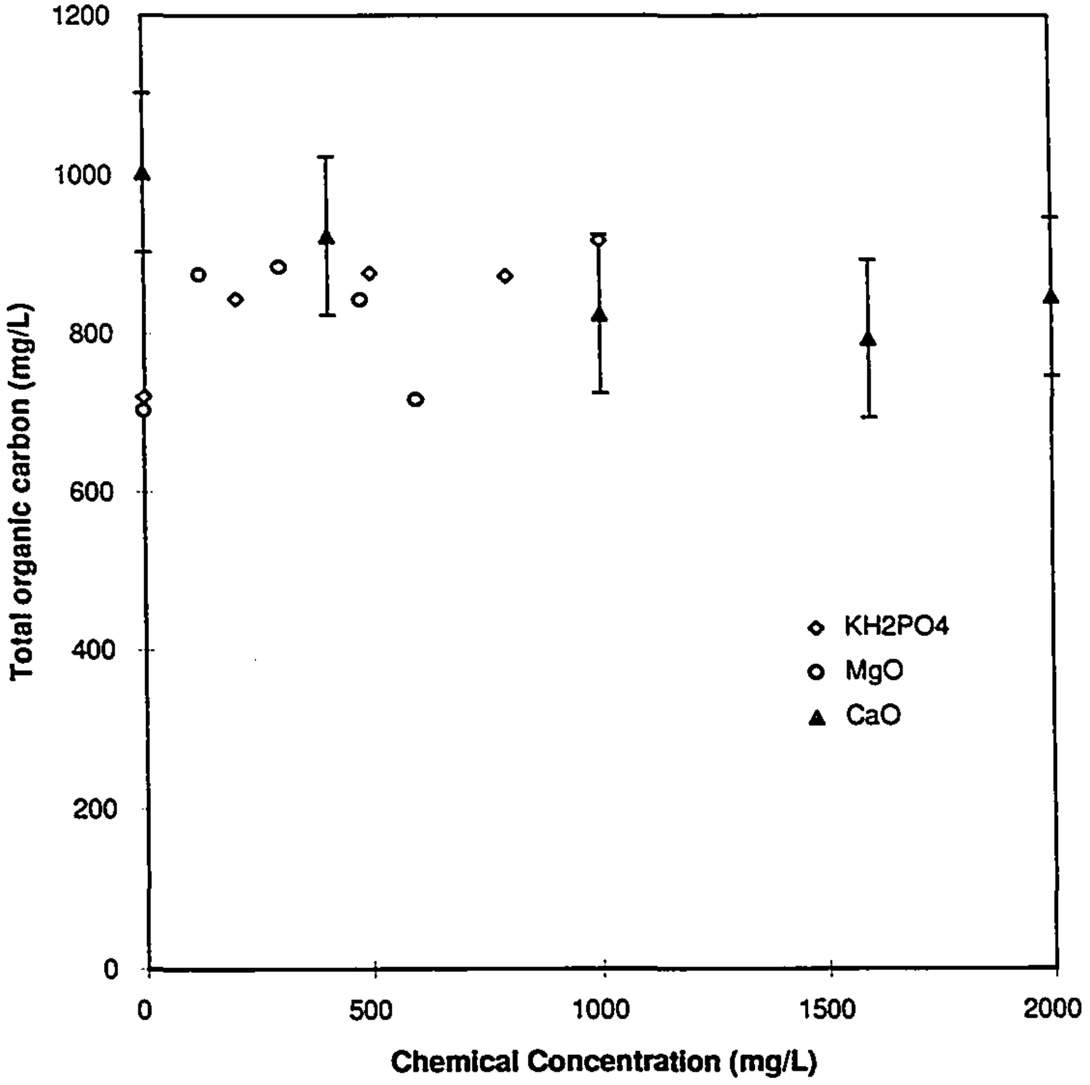


FIGURE 5.4
Effect of treatment chemicals on extractives

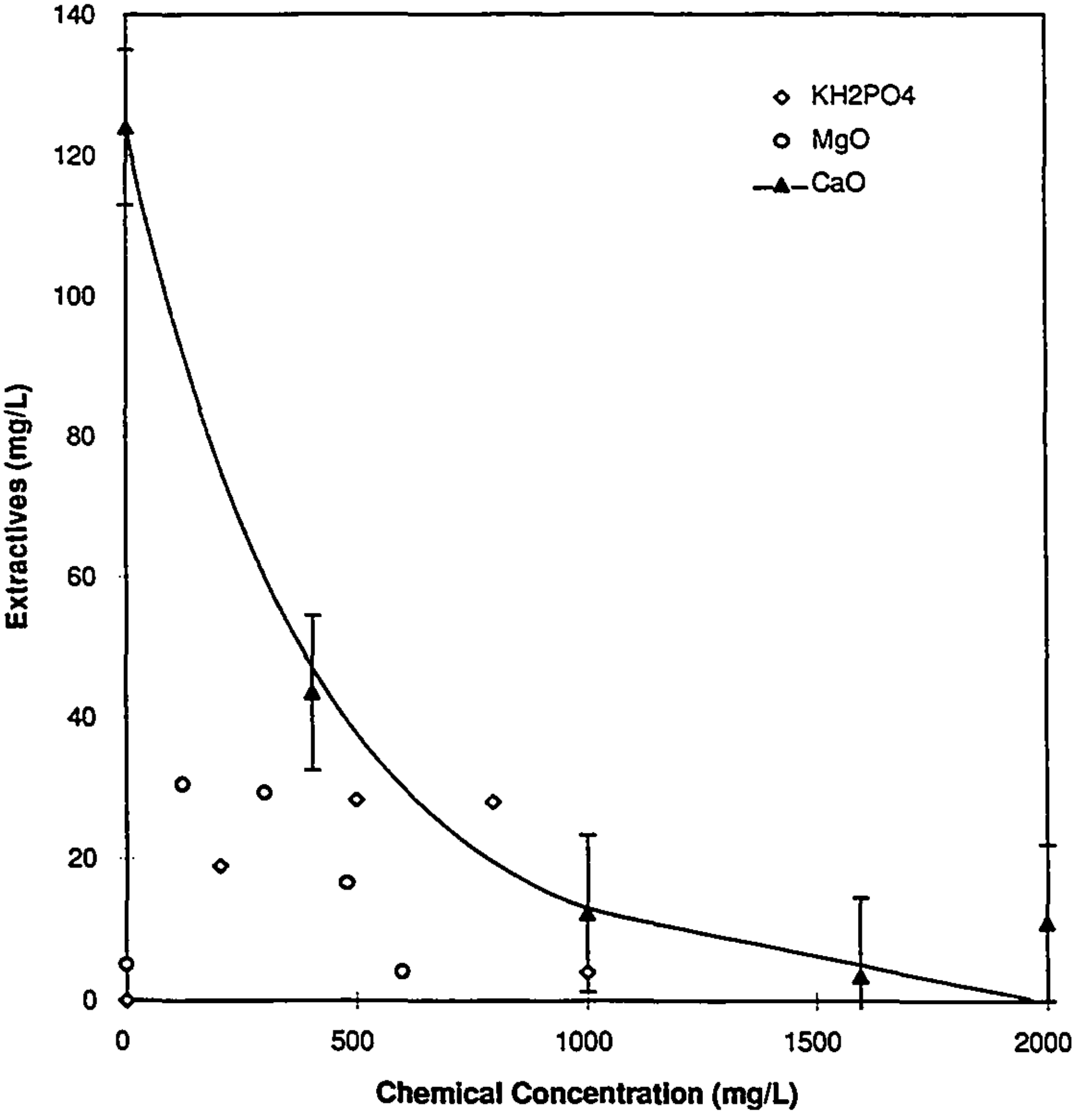


FIGURE 5.5
Effect of treatment chemicals
on color

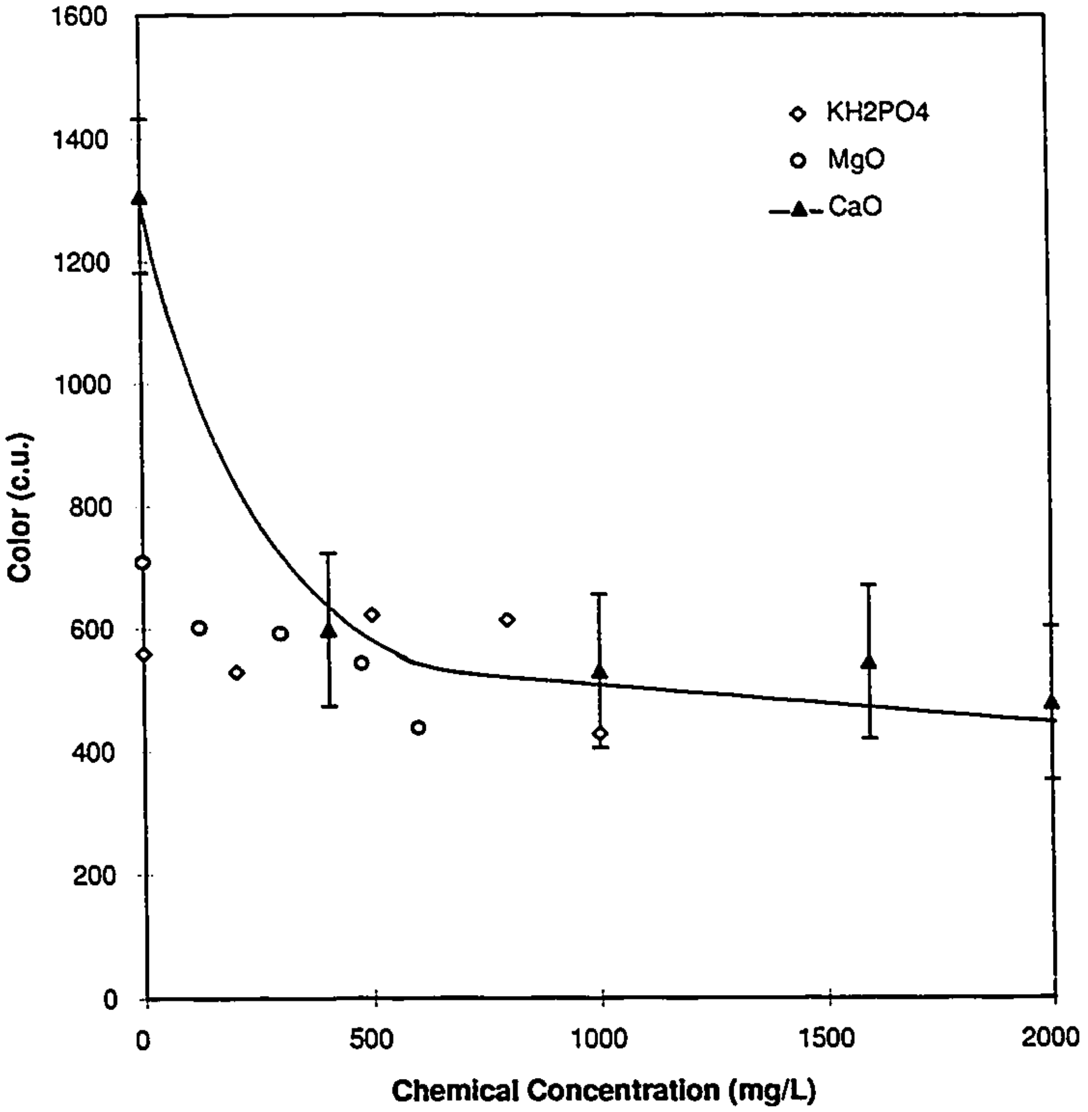


FIGURE 5.6
Effect of treatment chemicals on turbidity

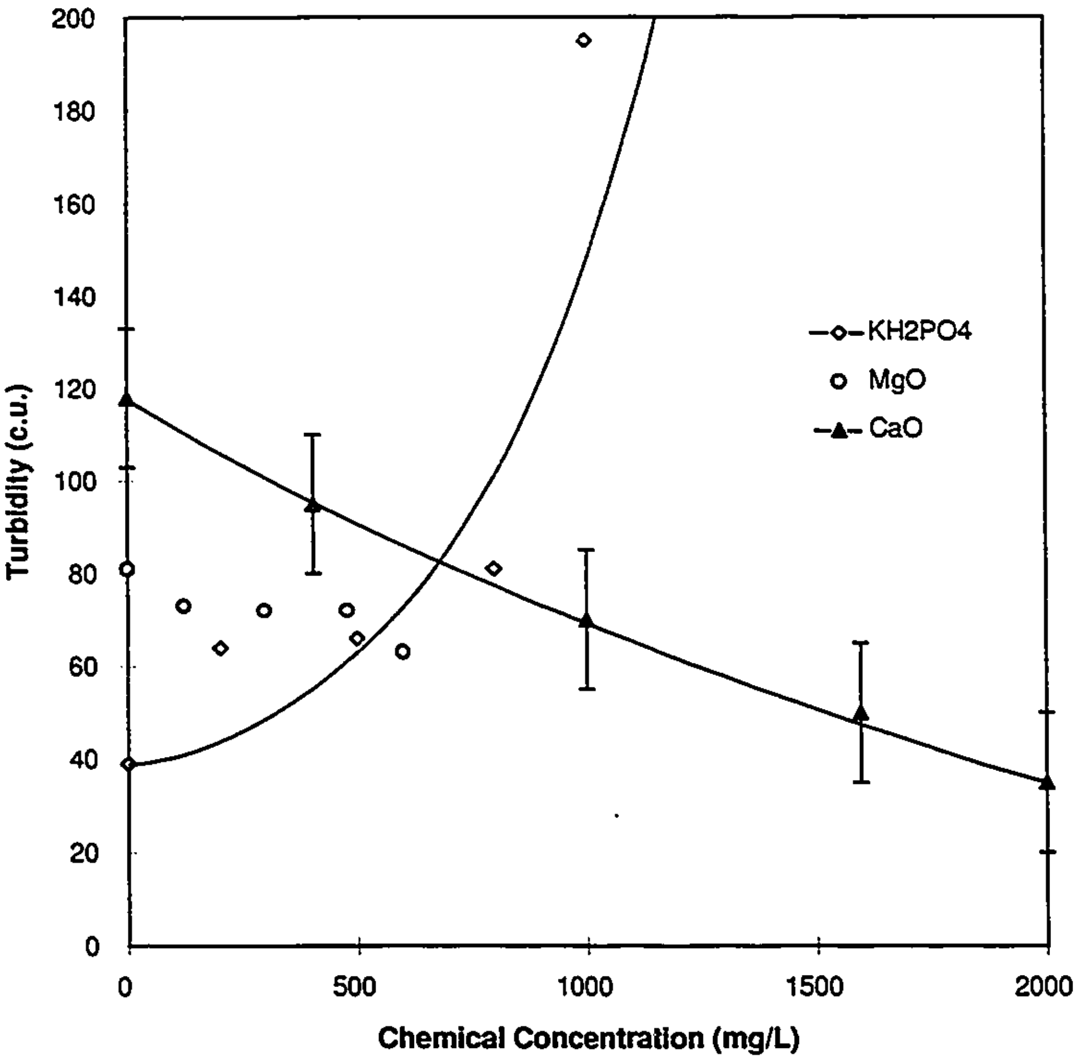


FIGURE 5.7
Effect of treatment chemicals on calcium

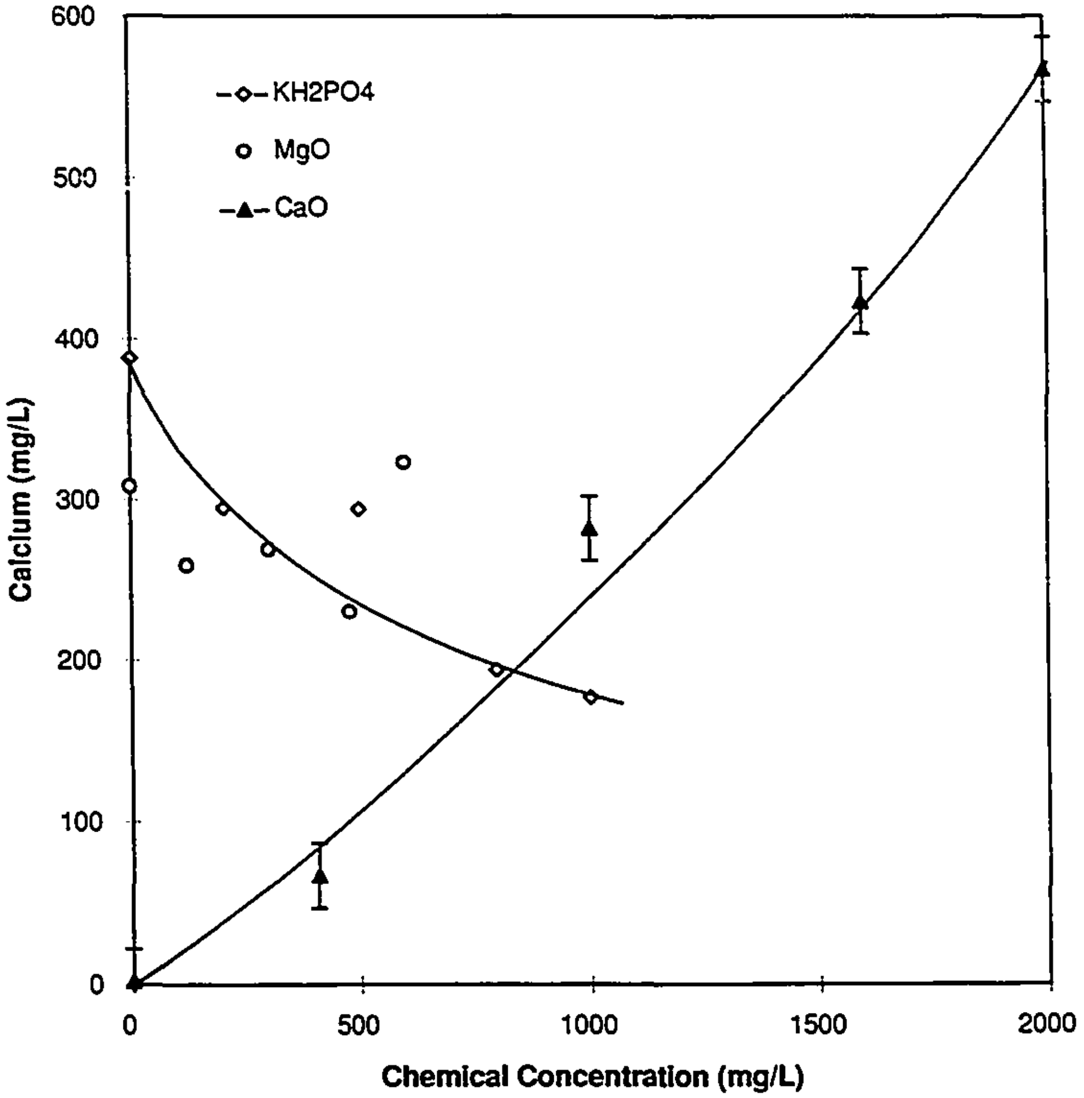


FIGURE 5.8

Effect of treatment chemicals on magnesium

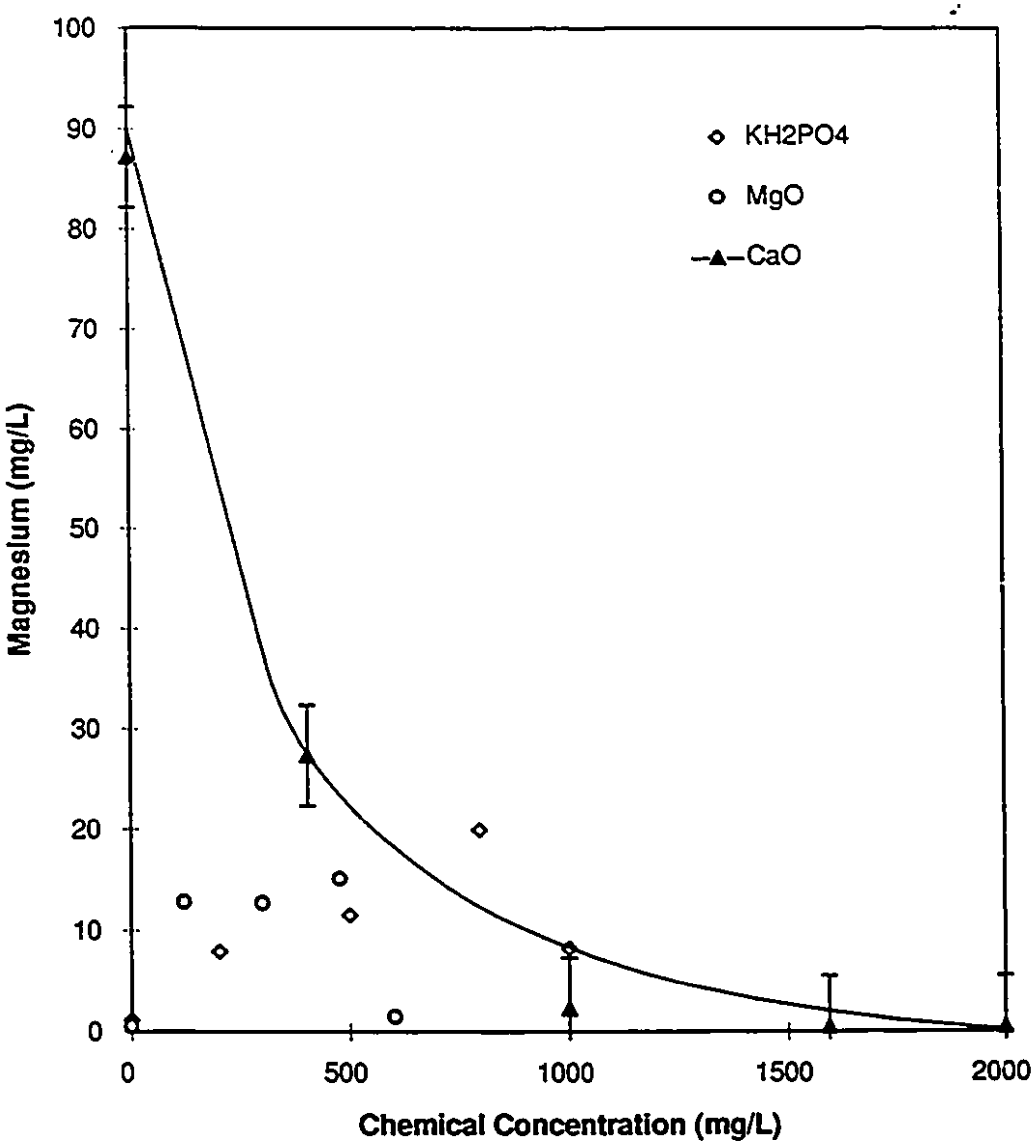


FIGURE 5.9
Effect of treatment chemicals
on carbonate

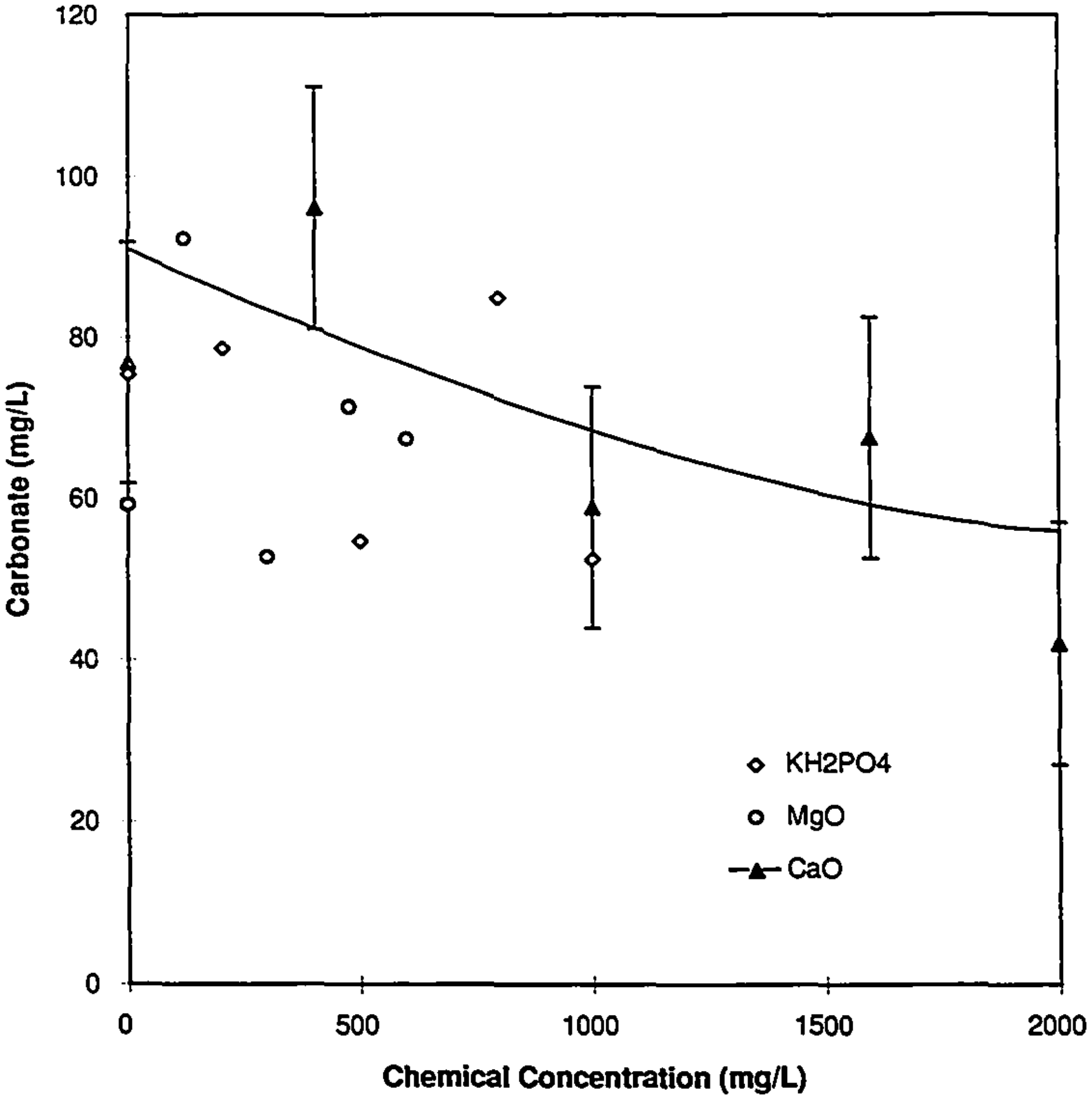
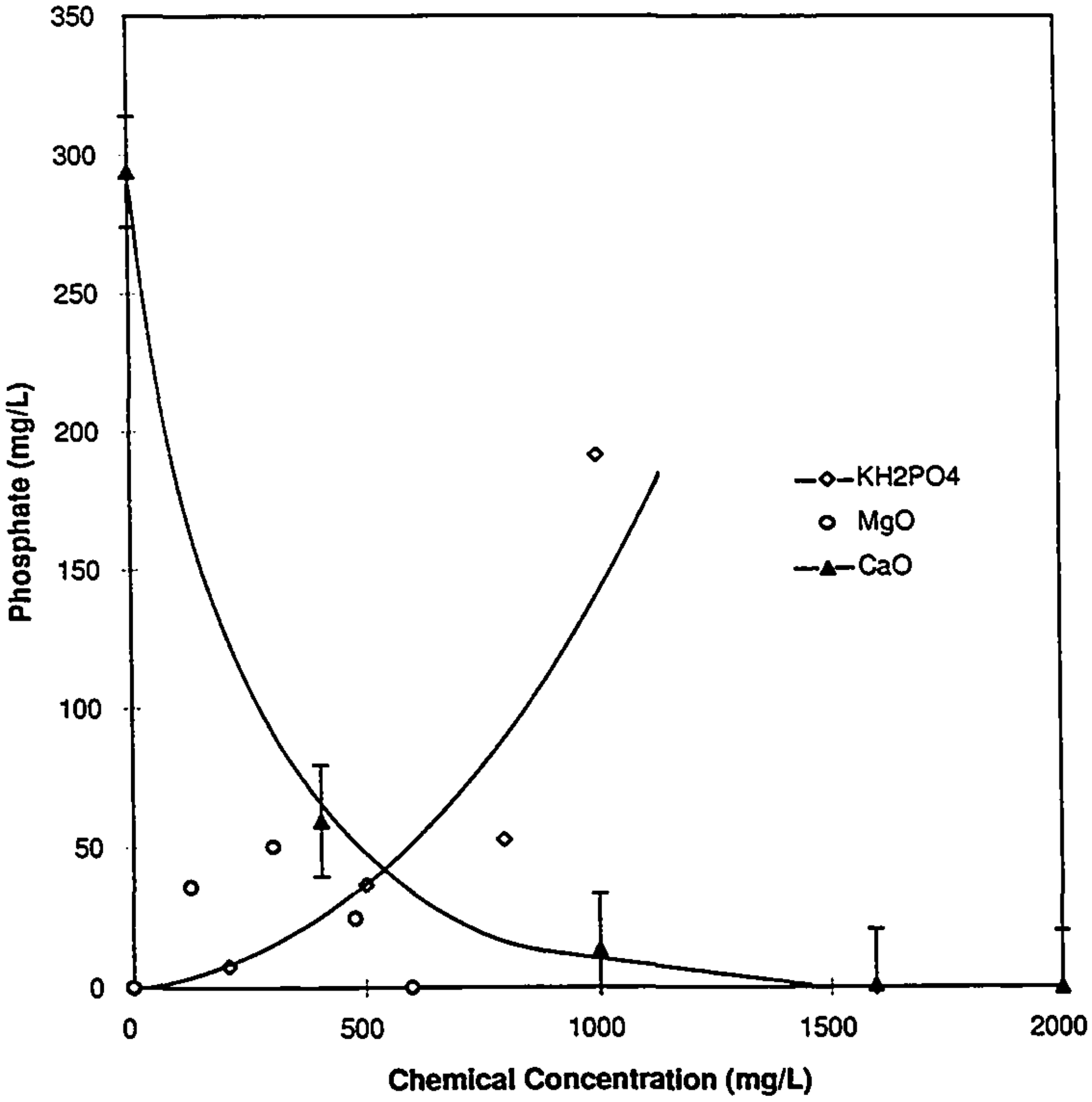


FIGURE 5.10
Effect of treatment chemicals on phosphate



- MgO: 300 mg/L
- CaO: 1000 mg/L
- KH_2PO_4: 500 mg/L

When the statistical analysis showed that the observed variation was significant, a curve was drawn. However this curve should only be viewed as a trendline. When the variation was found to be within the error of the test, no curve was drawn.

Error bars have been added to the lime addition points. They are added to put the results obtained into prospective. They represent the minimum total error due to variations in effluent mixture, experimental error, analytical error, etc.

When looking at the graphs, it must be kept in mind that this is an analysis around the optimum point. This means that the dosage of one chemical was varied around the optimum concentration while the dosage of the other chemicals was kept at the optimum. The measured variation will then be less than if the chemical dosage variation would have been done from zero.

In the following paragraph, each parameter is reviewed, to see how it is affected by chemical addition.

pH: pH is affected by lime addition only. Since pH is a logarithmic scale, the effect is very marked at low concentration but reaches a plateau at about 1000 mg/L, at a maximum pH of about 11.5. Because the extent of the reaction is linked to the pH at which it occurs, and because the optimum dosage is before the plateau, it is important to ensure that in the full scale process, only the minimum concentration required is added. Adding more lime than required does not have a beneficial effect (see Figure 5.1).

Dissolved solids: Only lime was found to have a significant effect on the level of dissolved solids: however this effect is small. No trends can be observed (see Figure 5.2).

Organic carbon: Lime addition does remove total organic carbon (TOC). However, this trend is not significant statistically. Because of the large variability in the TOC measurement, many replicates would be required to verify if this apparent trend is real or if it is only due to chance (see Figure 5.3).

Extractives: The removal of extractives is very sensitive to lime addition and reaches a plateau at a near zero concentration at about 1000 mg/L of lime dosage. The addition of MgO does not have a significant effect on extractives removal. At the lime dosages that are required to obtain an acceptable water quality, MgO addition does not have a measurable effect. Therefore it would not be required for the full scale application (see Figure 5.4).

Colour: The colour of the treated effluent does not vary significantly around the centre point. However a minimum dosage of lime is necessary to bring it down to its "final" colour. This minimum dosage is well below the dosage that would be used in the physical-chemical treatment process.

It is important to note that the initial colour of the effluent is light beige, and that the effluent is opaque. When a small quantity of either MgO or CaO is added, the colour turns into a dark brown-red. This is the initial high colour and the starting point for the discoloration. After some further addition of chemical, the colour then starts to get paler, until it reaches a pale yellow. It is therefore important that a minimum quantity of chemicals be added to go beyond this darker phase. When colour removals are mentioned later in this work, they are based on the initial pale colour of the effluent, before it starts to get darker. (see Figure 5.5)

Turbidity: The turbidity of the treated water is strongly affected by two treatment chemicals. Lime addition decreases the turbidity by about 60 %, by reacting with the colloidal materials. However slight variations in lime addition do not make a noticeable difference. Potassium phosphate addition increases the turbidity. This increase is exponential and starts increasing very rapidly after the optimum point. This can be explained by the following hypothesis. If potassium phosphate is added in greater amounts than required, it reacts with the lime that would otherwise have reacted to precipitate the colloidal material. Lime probably reacts preferentially with KH_2PO_4. Therefore, in the full scale process, it will be important to monitor potassium phosphate addition so that it stays near optimum at all times (see Figure 5.6).

Calcium: The residual calcium in the treated water is very dependent on lime and on potassium phosphate addition. Results show that because of the rapid increase in residual calcium with lime addition, KH_2PO_4 addition is required and works well to bring it down to acceptable levels (see Figure 5.7).

Magnesium: The level of residual magnesium is rapidly brought down to nearly zero with lime addition. Potassium phosphate addition increases the residual level slightly, but this effect would not affect the resulting quality of the water enough to impact the process.

Because of the very low residuals for magnesium around the optimum point, this parameter is not of great concern (see Figure 5.8).

Carbonate:	The addition of lime lowers the level of carbonates in the water, as expected from theory because carbonates play an important role in the chemical reactions involved (see Figure 5.9).
Phosphate:	Residual phosphates in the treated water are readily removed by lime addition. An increase in the dosage of potassium phosphate increases this residual, as expected (see Figure 5.10).

5.1.3 Conclusions

1. Extractives are efficiently removed by the lime-potassium phosphate process.
2. The lime-potassium phosphate treatment has little effect on dissolved solids.
3. MgO addition does not have a significant effect on the quality of the water obtained, and could therefore be omitted in the full scale process.
4. Total organic carbon seems to be removed, but there is no statistical evidence of this trend. A substantial number of additional experiments would be required to confirm this trend.
5. The colour of the treated effluent does not vary significantly if enough lime is added (more than 250 mg/L).
6. Lime addition decreases the turbidity significantly while potassium phosphate addition increases it.

7. Because of the rapid increase in residual calcium with lime addition, KH_2PO_4 addition is required and works well to bring it down to acceptable levels.

8. Magnesium residual is always near zero for the dosages considered.

9. The addition of lime lowers the level of carbonates in the water.

10. Residual phosphates are effectively removed by lime addition.

5.2 Effect of a high level of inorganic contaminants and a pre-treatment

The effect of an additional pre-treatment using polymer to obtain a better removal of suspended solids was also investigated, to see if it has an effect on treatment efficiency. The polymer used for this application was Alkox E-240 Q602. This pre-treatment lowered the suspended solids content of the mixture from 540 mg/L to 60 mg/L, a removal of about 90 %.

Once the treated effluent is completely recycled to the mill, the contaminants that are not removed by the closed cycle technology and that are added on a continuous basis to the process will increase in concentration. This is the case for the pulping and bleaching chemicals. For the mill considered in this work, the most critical ions that are likely to accumulate are Na^+, SO_4^{2-}, CO_3^{2-} and to a lesser extent, Cl^-.

For this series of trials, treatment chemicals were experimented on the normal effluent mixture and on a high inorganics effluent mixture. For the high inorganic contaminants effluent, 5000 mg/L of NaCl, 10000 mg/L of Na_2CO_3 and 10000 mg/L of Na_2SO_4 were added to the mixture described previously. The resulting level of inorganic dissolved solids, about 25000 mg/L, is similar to what has been suggested could be reached in effluent free mills (1).

5.2.1 Statistical design

The statistical design used for this series of experiments is known as a Taguchi L16 design, and was briefly explained in section 2.6.2. Trials were also performed at the centre points for both the low and high levels of inorganics, to get a better measure of the error. These are referred to as centre point 1 and 2. Table 4.4 presents the levels that were used for each variable.

TABLE 5.2

LEVELS FOR THE TAGUCHI SET OF EXPERIMENTS

VARIABLES	LEVELS			
	1	2	Centre Point 1	Centre Point 2
Pre-treatment	no	yes	no	no
Inorganic chemicals	no	yes	no	yes
MgO	25	300	163	163
CaO	100	1000	550	550
KH_2PO_4	25	500	263	263

This design allows the study of the effect of each variable, and the main interactions between them.

5.2.2 Results and Discussion

The effect of the pre-treatment was never found to have a significant impact on the treatment efficiency. This means that the physical-chemical treatment is quite robust to a wide range of variations in suspended solids loading. This is an important point because the effluent quality at a pulp and paper mill is highly variable.

The results on the effect of inorganics on the treatment efficiency demonstrated that the interactions between the level of inorganic dissolved solids and the dosage of treatment chemical were significant and important for most parameters.

Table 5.3 compares the quality of the water for both the low and the high levels of inorganics. Results are shown for the centre point:

- 163 mg/L of MgO
- 550 mg/L of lime
- 263 mg/L of KH_2PO_4

TABLE 5.3

QUALITY OF TREATED EFFLUENT FOR LOW AND HIGH LEVELS OF INORGANIC DISSOLVED SOLIDS

Parameter	Units	Low inorganics Non treated	Low inorganics Treated	High inorganics Non treated	High inorganics Treated
pH		6.6	10.1	6.6	10.4
Dissolved solids	mg/L	3045	3195	28 045	28 206
Extractives	mg/L	150	47	150	61
Colour	c.u.	1304	865	1304	1259
Turbidity	NTU	280	94	280	73
Calcium	mg/L	28	188	28	35
Magnesium	mg/L	5	22	5	20
Phosphate	mg/L	0	58	0	116
Sodium	mg/L	260	228	9805	9518
Sulphate	mg/L	396	321	7157	7069
Carbonate	mg/L	252	99	7481	5587

Note in the table the important difference in the level of inorganics, in the water to be treated. The significant differences in the treatment efficiency are for the following parameters:

Colour:	Even after lime addition, colour remains higher. A greater dosage of lime is required to bring it down.

Residual calcium:	The residual calcium is much lower with the high level of inorganics in the water, due to its lower solubility. This residual is decreased by almost 90 %.
Residual phosphate:	The residual phosphate is doubled when the high inorganics effluent is treated. This might be explained by the fact that phosphate reacts with the calcium in solution to form a precipitate. Because the level of calcium in solution is much lower, there is not enough left to react completely. Lower dosages of potassium phosphate would probably be required to obtain the same residual calcium under closed cycle conditions.

The treatment does not remove sodium and sulphate in either types of effluent being treated. This implies that if these contaminants build up and start to cause problems in the papermaking process, they will have to be removed in a polishing treatment.

5.2.3 Conclusions

1. The physical-chemical treatment is robust to variations in suspended solids loading. Suspended solids do not interfere with the treatment process at concentrations that are typical for a clarified effluent (up to 500 mg/L).

2. The level of inorganic dissolved solids in the effluent being treated has an important impact on the dosage of treatment chemicals required to obtain a certain quality of water. Under closed cycle conditions, it is expected that:

    - More lime will be required to obtain a similar visual appearance.
    - Removal efficiency of extractives will not change significantly.
    - Less or even no potassium phosphate will be required to obtain the same residual hardness in the treated water.

5.3 Summary of findings

Table 5.4 summarises the effect of the five variables investigated on the parameters measured. In the case of the three treatment chemicals, the effect shown is that of the chemical itself on the parameter. In the case of the pretreatment and inorganics, it is the effect of this variables on the treatment efficiency.

TABLE 5.4

SUMMARY OF EFFECT OF VARIABLES ON MEASURED PARAMETERS

Parameter	MgO	CaO	KH_2PO_4	Pretreatment	Inorganics
pH	negligible	strong	negligible	negligible	negligible
Dissolved solids	negligible	weak	negligible	negligible	negligible
Organic carbon	negligible	to be verified	negligible	negligible	negligible
Extractives	negligible	strong	negligible	negligible	negligible
Colour	negligible	moderate	negligible	negligible	strong
Turbidity	negligible	moderate	strong	negligible	negligible
Calcium	negligible	strong	strong	negligible	strong
Magnesium	negligible	strong	weak	negligible	negligible
Phosphate	negligible	strong	strong	negligible	moderate
Sodium	negligible	negligible	negligible	negligible	negligible
Sulphate	negligible	negligible	negligible	negligible	negligible
Carbonate	negligible	strong	negligible	negligible	strong

Table 5.5 compares the quality of the water obtained after treatment for both the low and high level of inorganic contaminants. The quality shown in the table is that obtained after addition of the following dosage of chemicals:

- MgO: 300 mg/L
- CaO: 1000 mg/L
- KH_2PO_4: 500 mg/L

TABLE 5.5

QUALITY OF THE TREATED WATER

Parameter	Initial level	Final Level	
		Low Inorganics	High Inorganics
Extractives	150	15	25
Colour	1304	570	890
Turbidity	280	75	125
Calcium	28	275	50
Magnesium	5	3	15
Phosphate	0	20	270

If at a high level of inorganics, potassium is not added, the phosphate level will be zero, without raising the calcium level, as demonstrated previously.

5.4 References

1. Bowers, D.F., "Corrosion in closed white water systems", *Tappi*, Vol. 61, No. 3, March 1978, p. 57.

6.0 ADDITIONAL EXPERIMENTS

6.1 Treatment of the three individual effluent streams

A series of additional experiments were performed, to study separately, the behaviour of the three components of the effluent mixture:

- Chip wash water
- Evaporator condensate
- Fourth stage cleaners rejects

This information can be used for two main purposes:

1. If one of the components behaves very differently from the other ones, it might be desirable to use a different treatment or dosage and treat this component separately.

2. It is possible that after implementing the modifications for effluent reduction, it is realised that the relative importance of each stream is quite different from what was expected. By knowing the behaviour of each component separately, it will be possible to predict the resulting effect on the physical-chemical treatment.

The following dosage of treatment chemicals was added:

- MgO:	300 mg/L
- CaO:	1000 mg/L
- KH_2PO_4:	500 mg/L

The results are shown in Figures 6.1 to 6.9. Each graph compares the water quality before and after treatment for each effluent stream.

Surprisingly, even though the characteristics of the components are quite different prior to treatment, the quality of the treated water is very similar in all three cases, for each parameters. All streams react well to the treatment, and the treatment minimizes the differences in the quality of the streams.

6.2 Effect of potassium phosphate at low and high levels of inorganics

A second set of additional experiments was performed, to verify the need of potassium phosphate at both low and high levels of inorganics. In section 5.2, it was found that potassium phosphate would not be required to reduce hardness of the water under closed cycle conditions. This set of experiments were performed to verify that under closed cycle conditions, potassium phosphate does not have any measurable benefit, and that its addition can be discontinued.

Table 6.1 shows the treatment conditions that were tested.

FIGURE 6.1
Effect of treatment on pH for the three effluent streams

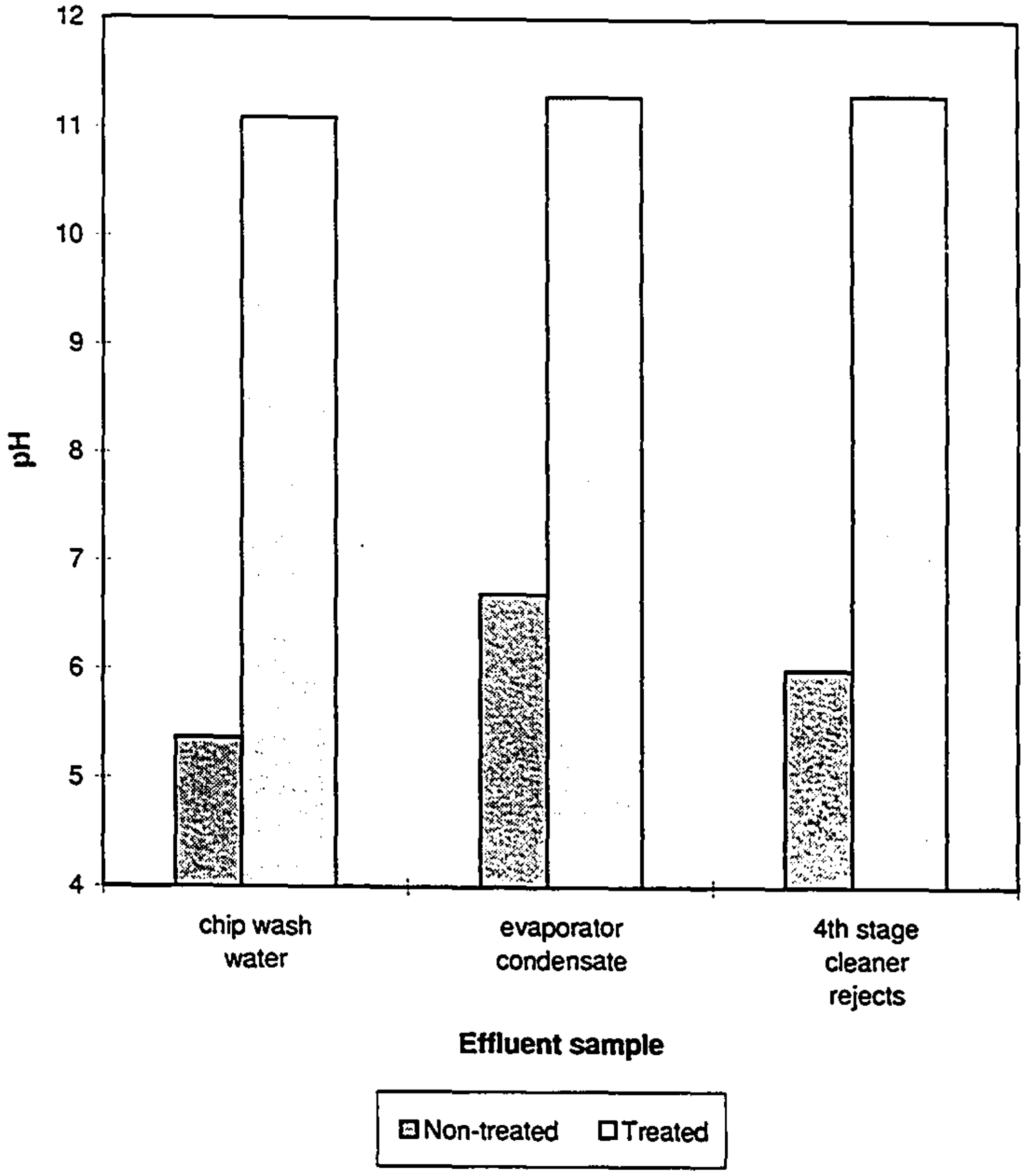


FIGURE 6.2
Effect of treatment on total dissolved solids for the three effluent streams

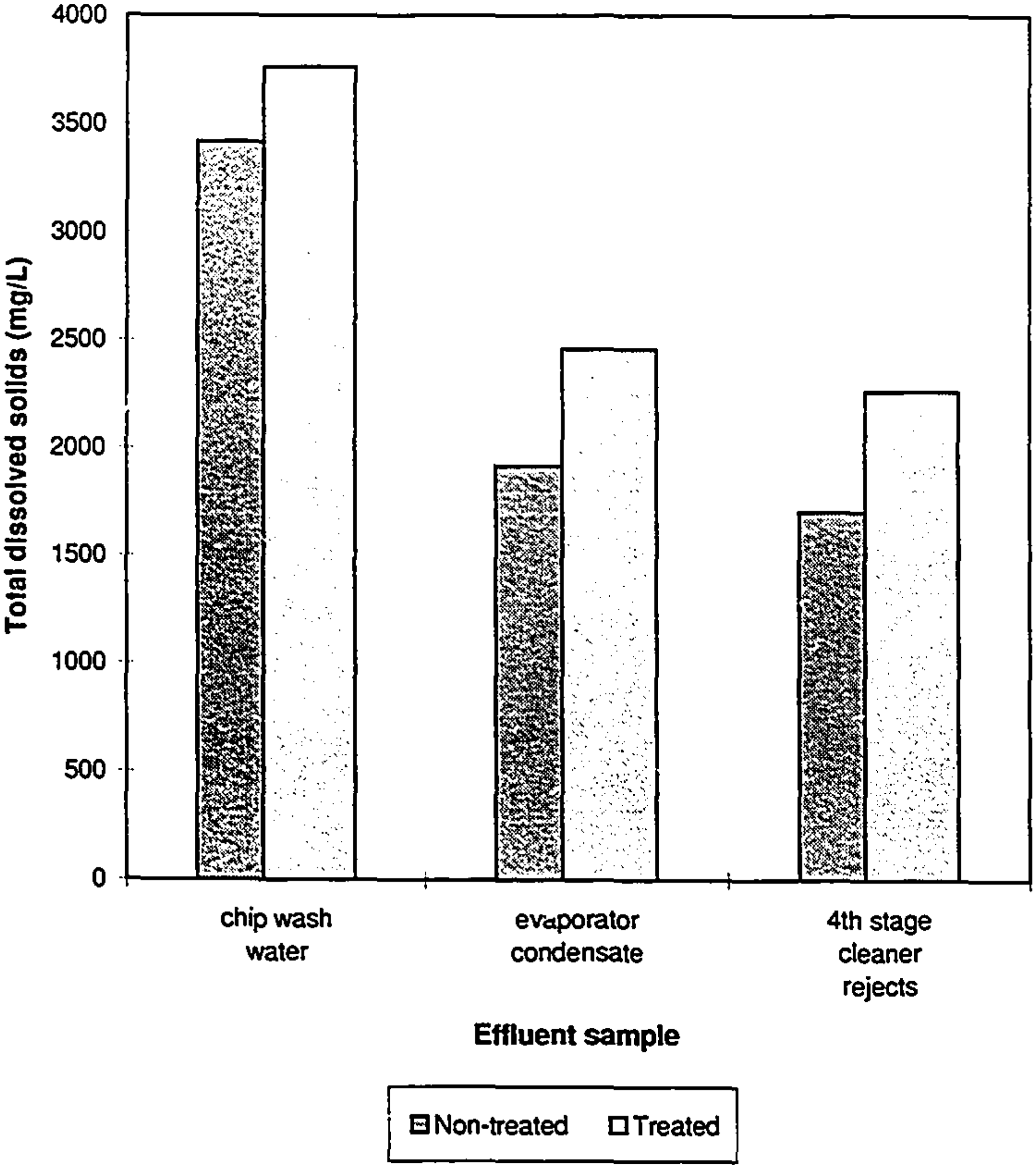


FIGURE 6.3
Effect of treatment on extractives for the three effluent streams

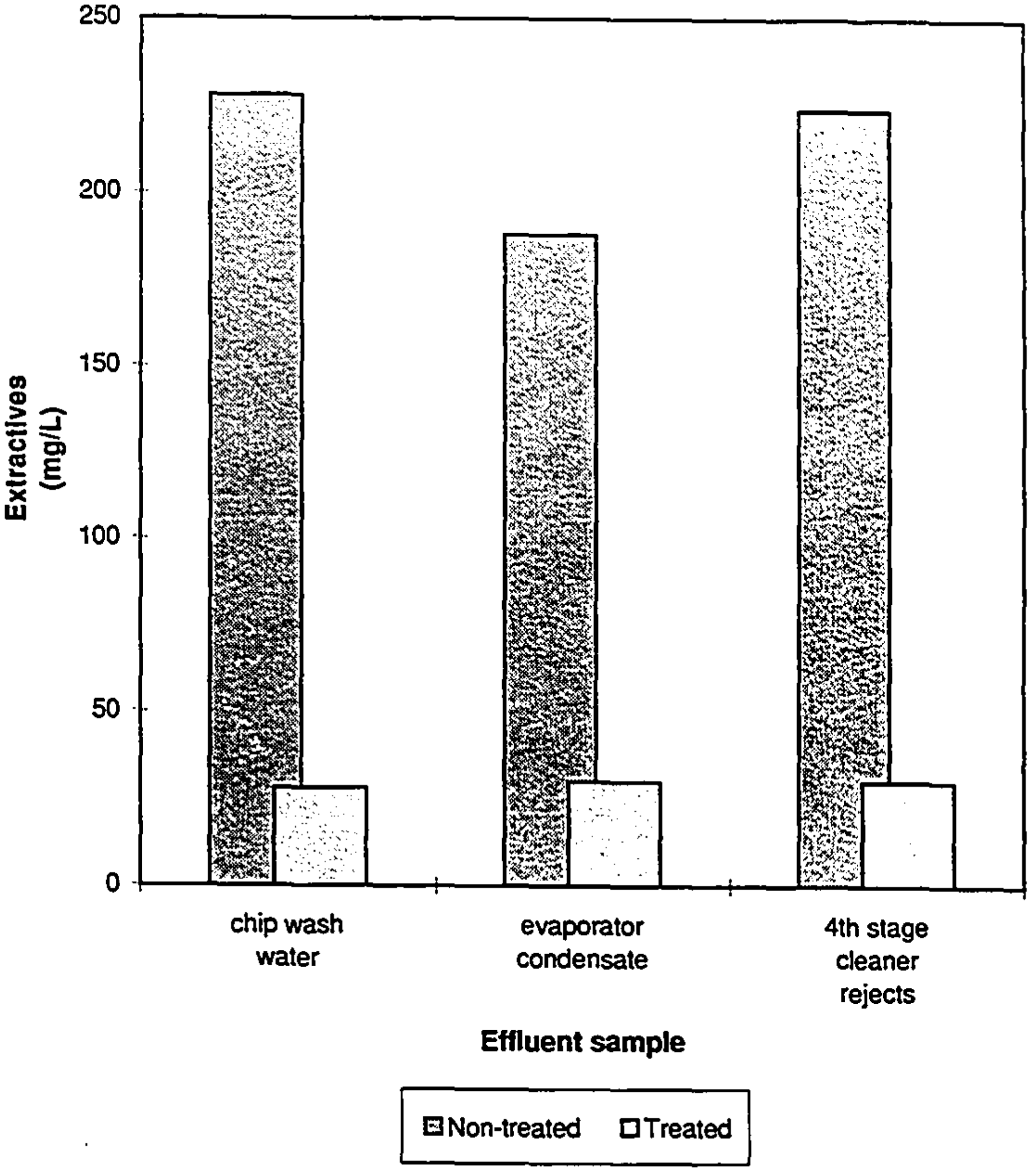


FIGURE 6.4
Effect of treatment on total organic carbon for the three effluent streams

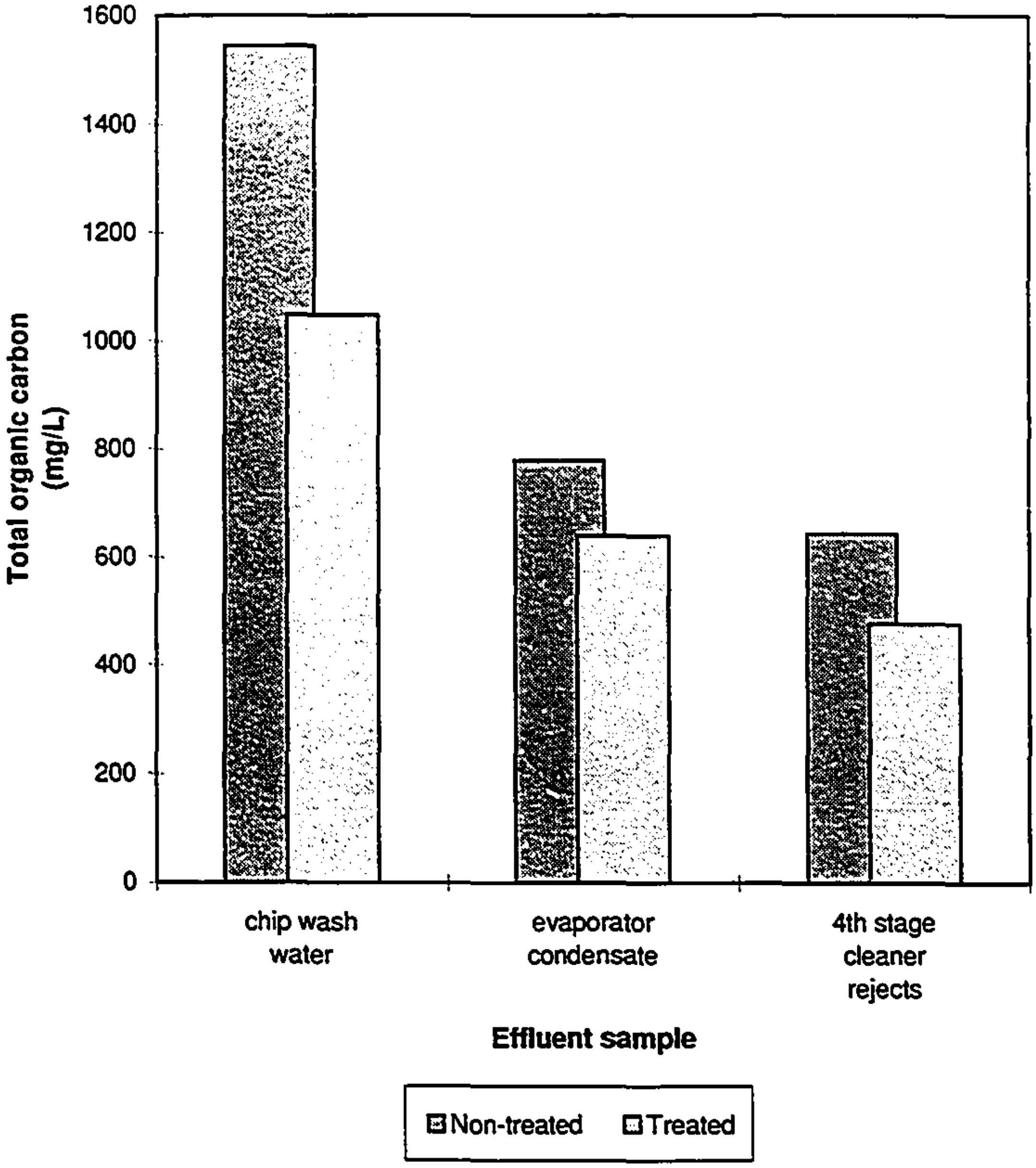


FIGURE 6.5
Effect of treatment on color for the three effluent streams

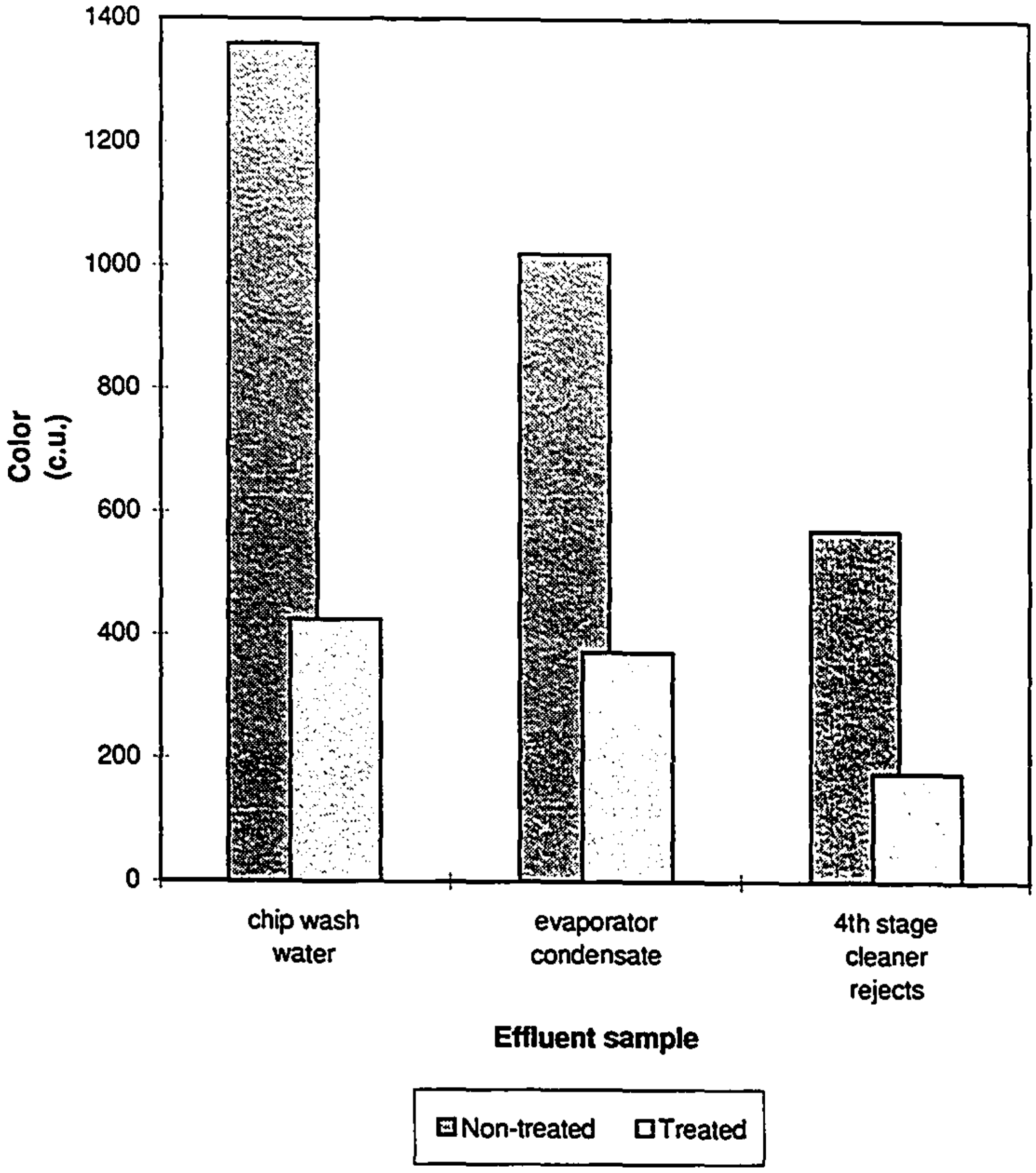


FIGURE 6.6
Effect of treatment on turbidity for the three effluent streams

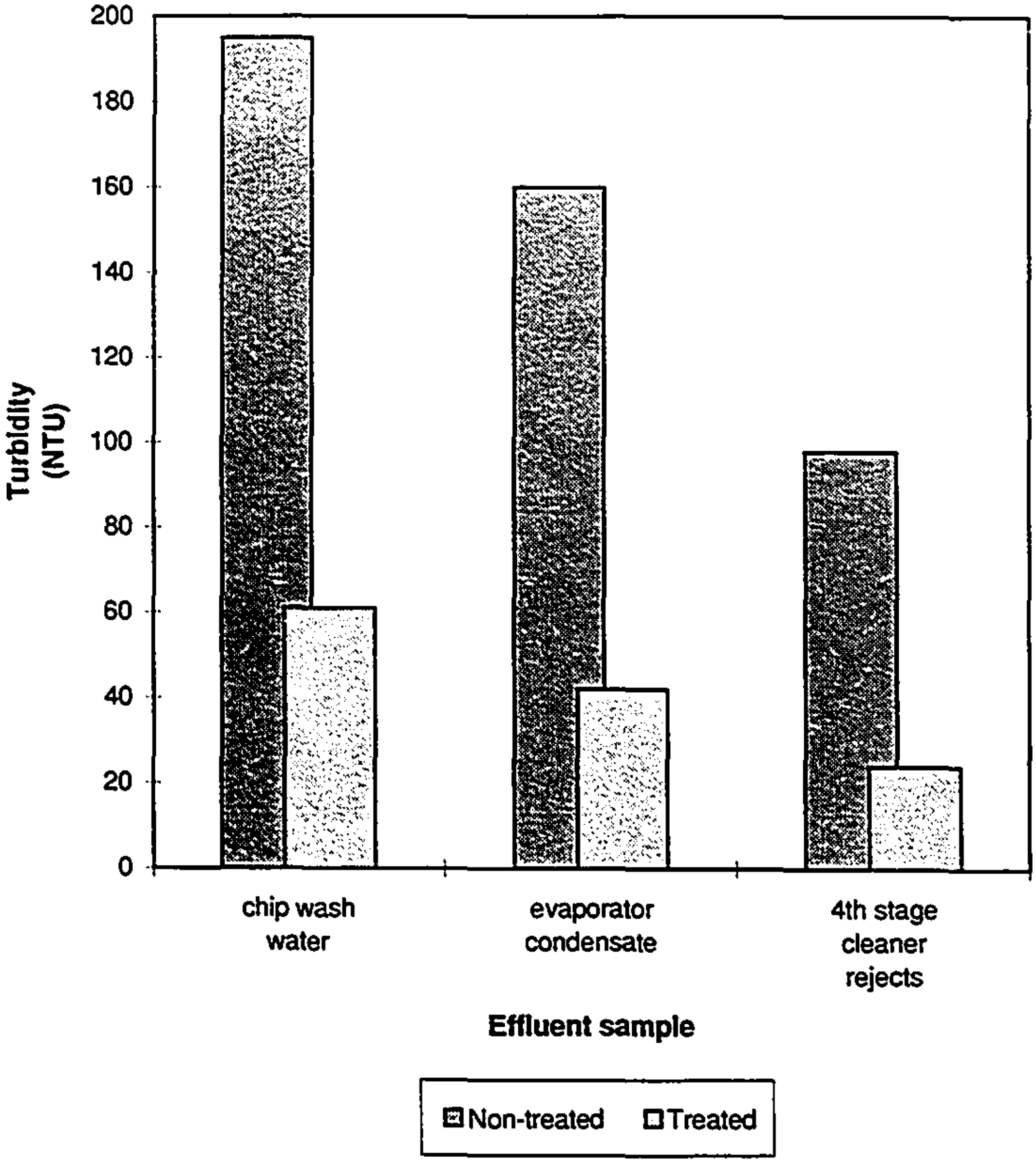


FIGURE 6.7
Effect of treatment on calcium for the three effluent streams

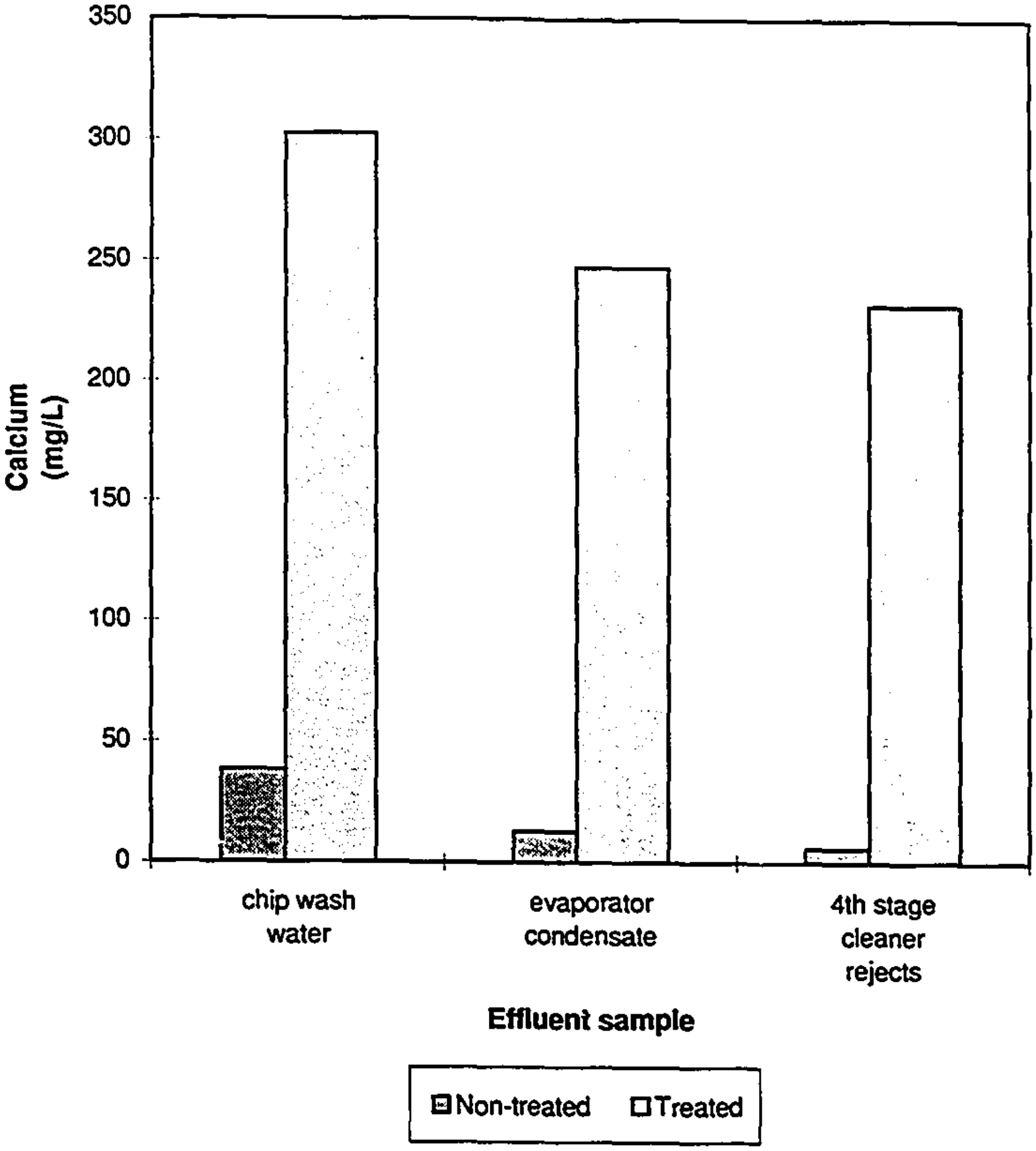


FIGURE 6.8
Effect of treatment on magnesium for the three effluent streams

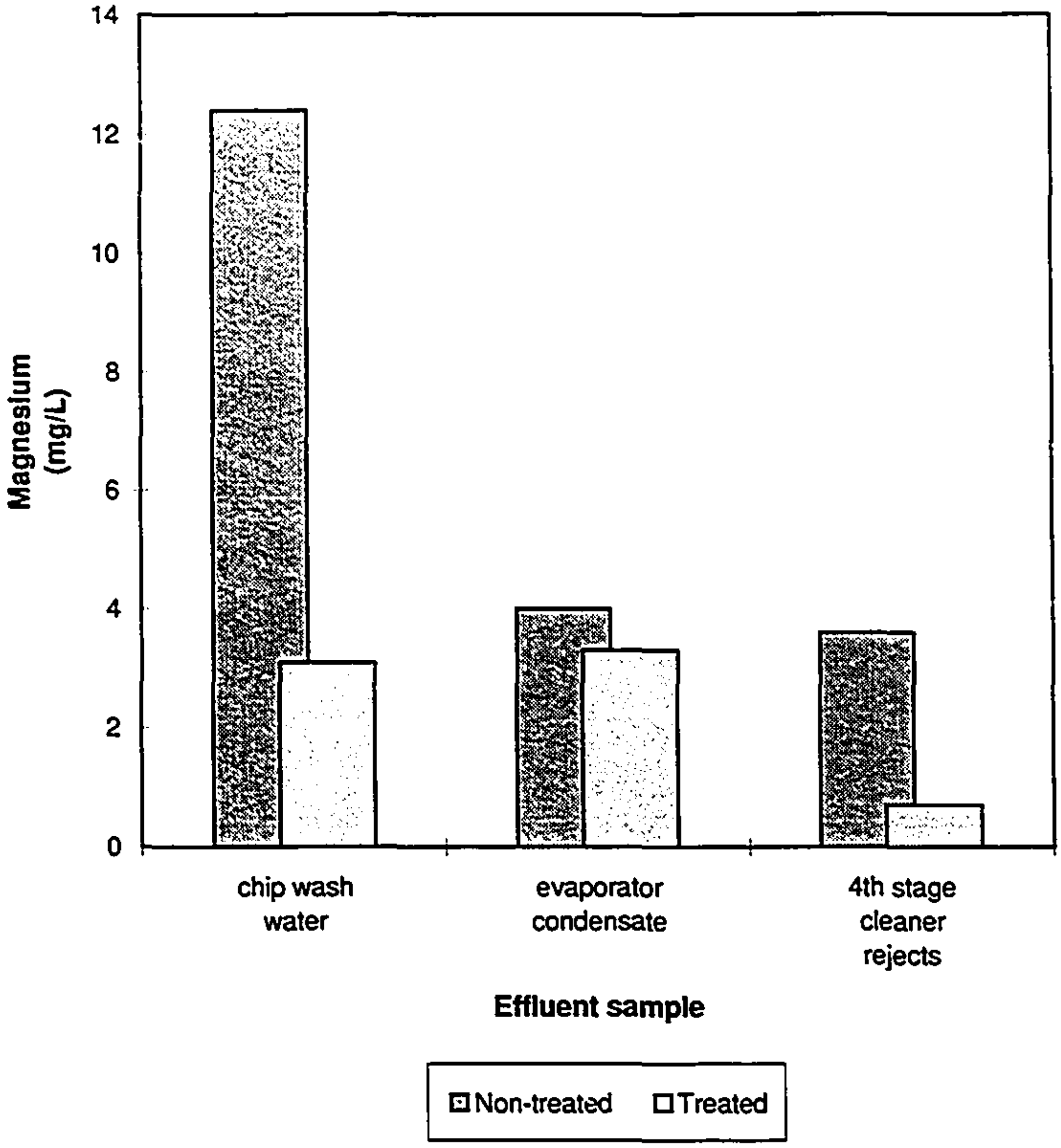


FIGURE 6.9
Effect of treatment on phosphate for the three effluent streams

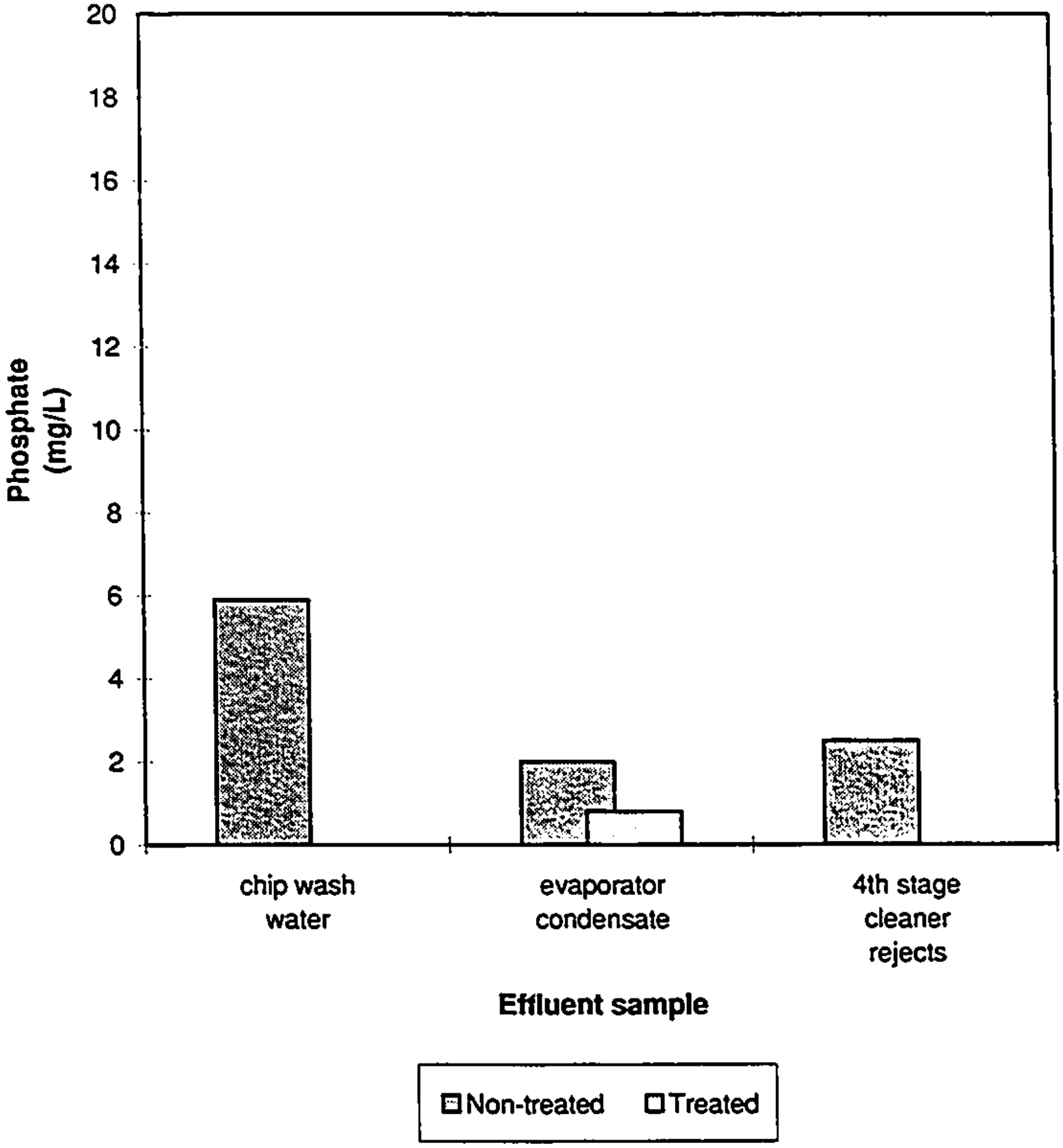


TABLE 6.1

LEVELS FOR THE TESTING OF KH_2PO_4 ADDITION UNDER CLOSED CYCLE CONDITIONS

Inorganics	MgO mg/L	CaO mg/L	KH_2PO_4 mg/L
low level	1000	5000	0
low level	1000	5000	200
low level	1000	5000	2000
high level	1000	5000	0
high level	1000	5000	200
high level	1000	5000	2000

Results are shown in Figures 6.10 to 6.12.

Even at the very high dosage of lime tested, the residual calcium is very low when the high inorganics effluent is tested. The residual goes from over 600 mg/L down to less than 50 mg/L. Potassium phosphate is not required with closed cycle. Also, at the high level of inorganics, residual phosphate level rises rapidly to very high level (over 900 mg/L). Finally, Figure 6.12 shows that potassium phosphate is no longer required to get a low turbidity.

All results obtained by treating effluent with a high level of inorganics, demonstrate that under closed cycle condition, potassium phosphate is not required to maintain low hardness, and has no other benefits from the point of view of water quality.

FIGURE 6.10
Effect of KH2PO4 on Calcium for low and high inorganics levels

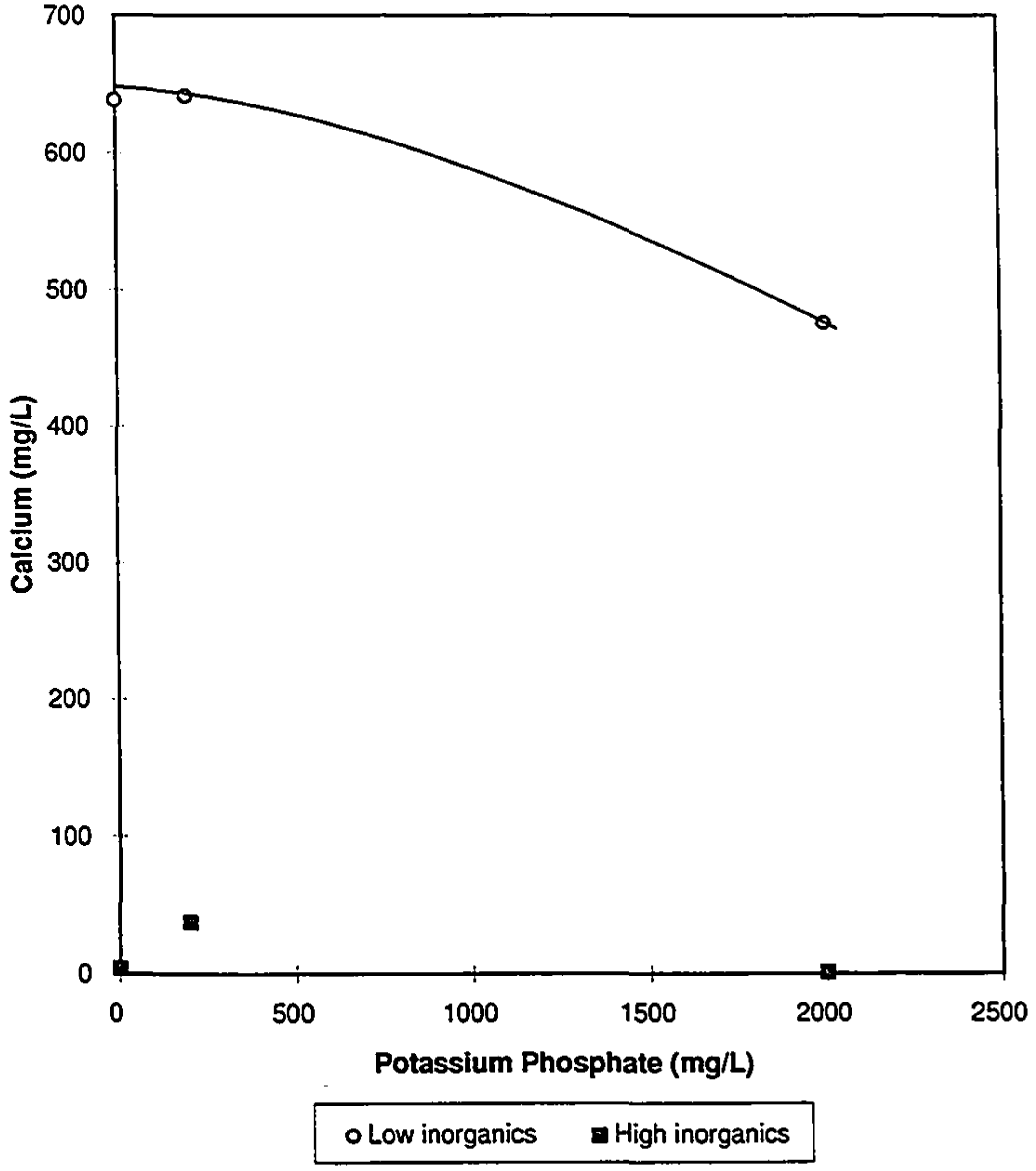


FIGURE 6.11
Effect of KH2PO4 on phosphate for low and high inorganics levels

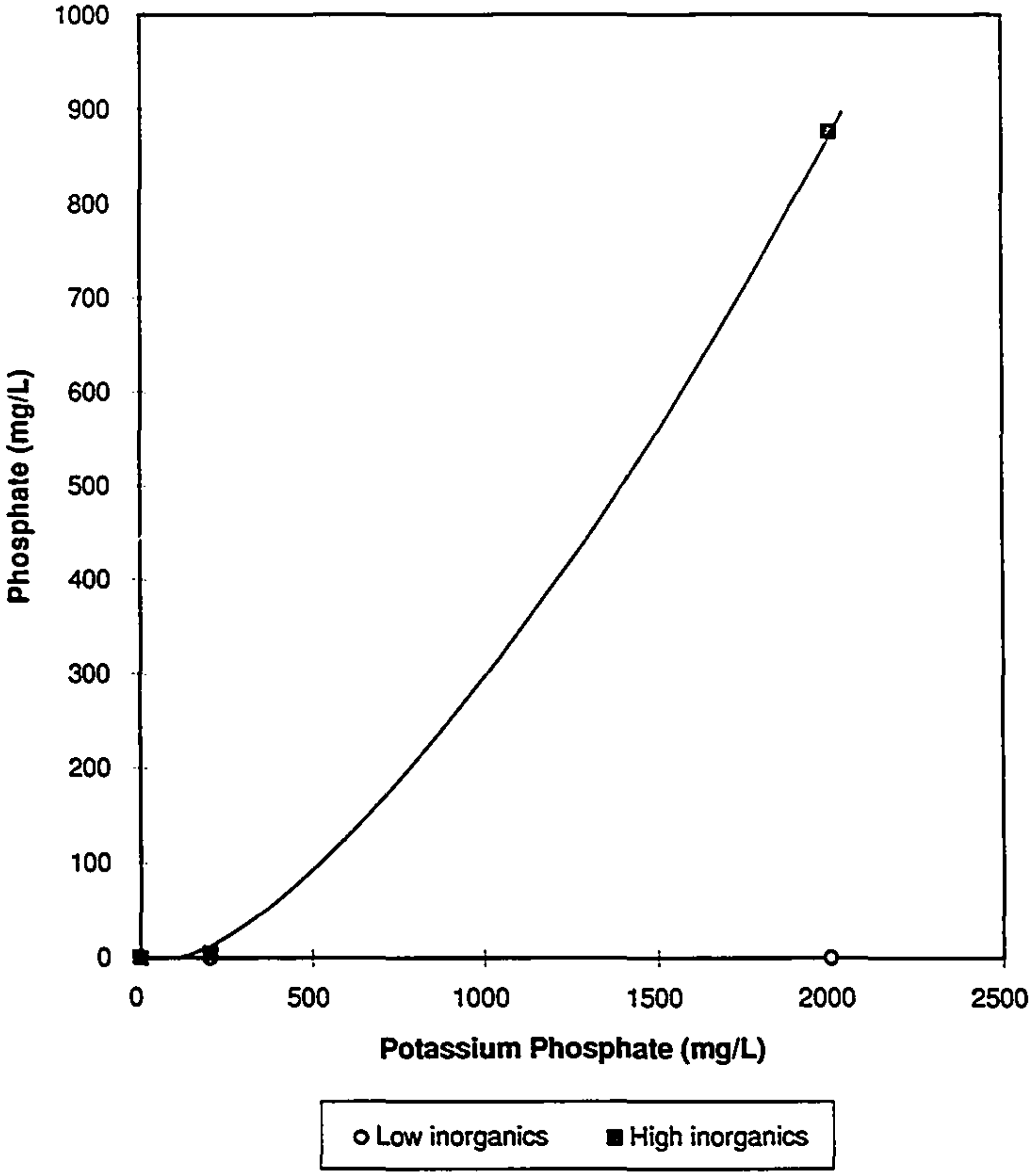
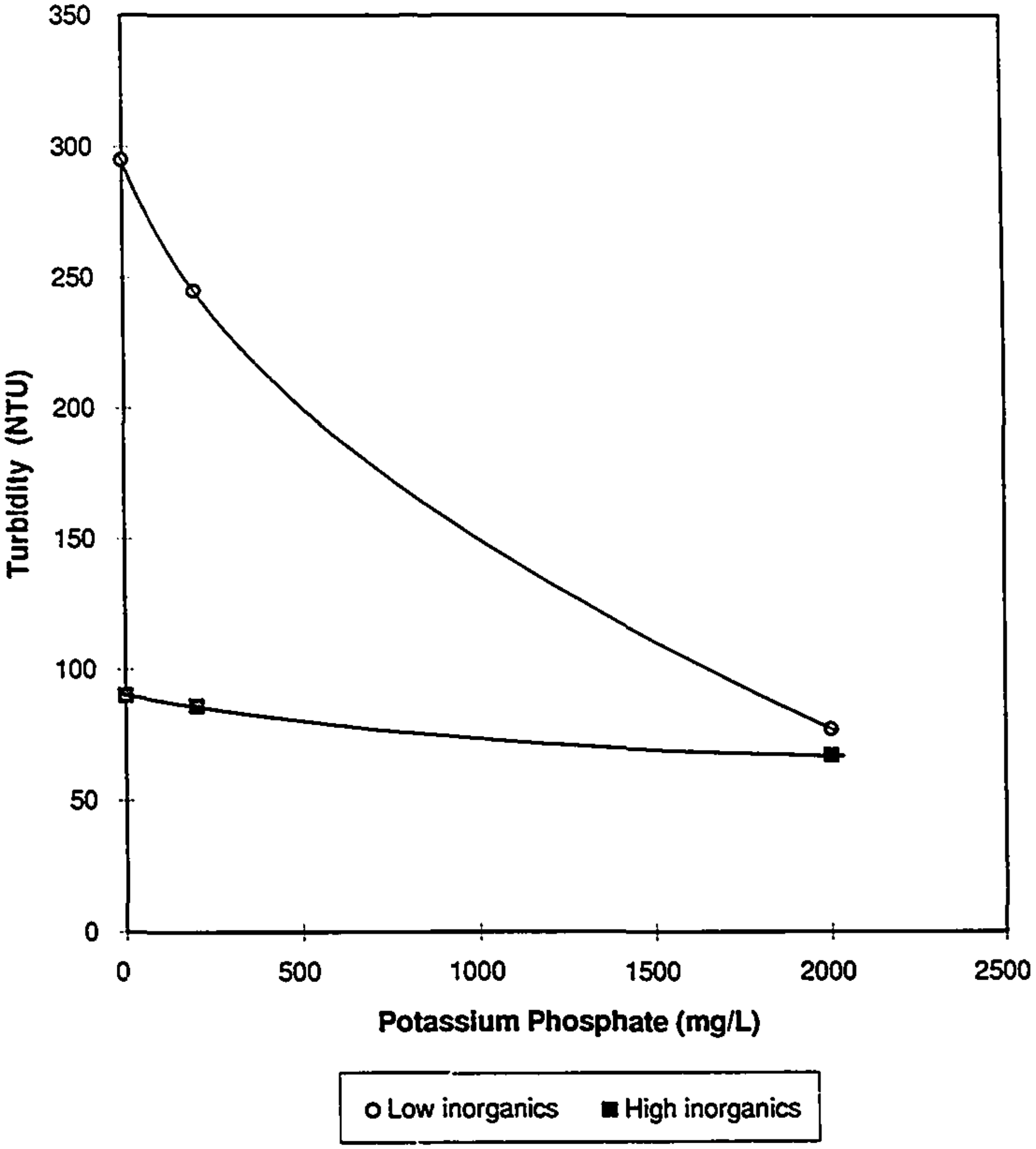


FIGURE 6.12
Effect of KH2PO4 on turbidity for low and high inorganics levels



7.0 PROPOSED CLOSED CYCLE SCHEME

Figure 7.1 shows a simplified flowsheet of the proposed closed cycle process. Each component is described in the following paragraphs. This process would be implemented for a reduced mill effluent flow rate of less than 10 m^3/ton, for treatment and complete recycle of the effluent.

The experimental part of this work involved only the physical-chemical portion of the treatment scheme. The expected performance of the complete scheme should therefore be verified with pilot trials at the mill when the effluent flow rate will have been reduced to the target level.

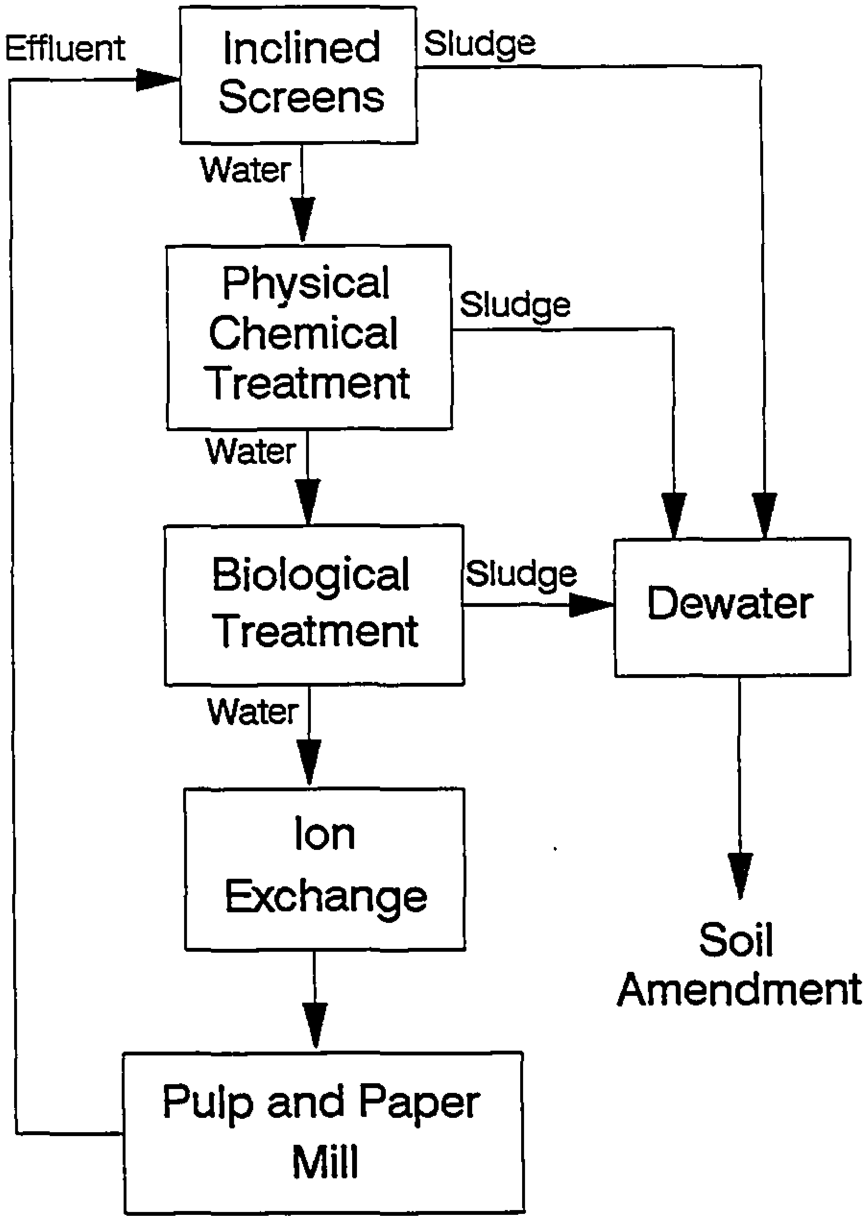
7.1 Inclined Screens

Inclined screens are an efficient and quite inexpensive way to remove suspended solids. They can easily take variations in feed suspended solids loading. They would provide a water similar in quality to the water that was used throughout this experimental program.

7.2 Physical-chemical Treatment

The physical-chemical treatment would consist of chemical addition and mixing, followed by a clarifier to settle and remove the sludge. During implementation, the portion of the treated water being recycled to the mill could be increased gradually, to allow monitoring of the effect of recycling on the paper, until all treated water is reused in the process.

FIGURE 7.1
PROPOSED SCHEME



Under low levels of effluent recycle, when the level of inorganic contaminants is still low, potassium phosphate will be required to reduce the hardness of the recycled water to acceptable levels. As the closure of the water cycle is implemented, the level of inorganics will rise and the dosage of potassium phosphate should be reduced, so that only the amount required is added. The required dosage of CaO will have to be gradually increased, so that the applied concentration gives a constant water quality.

The treatment efficiency of the physical-chemical process is increased if the effluent being treated is at an elevated temperature. This is a good justification for having this treatment immediately following suspended solids removal. At this moment, the effluent is at its highest temperature, and therefore, the reaction is most efficient.

7.3 Biological treatment

The biological treatment would include a trickling filter and a secondary clarifier. Biological treatment is required because the physical-chemical treatment alone does not remove the organic contaminants. However, biological treatment is a logical complement to the physical-chemical treatment because bacteria is most efficient at metabolizing shorter chain organics. If biological treatment alone is used, long chain organics such as extractives, resin and fatty acids and lignin will accumulate in the process.

A trickling filter would be a good choice of biological treatment. This type of equipment does not require a large land area, and is low maintenance. Because the effluent was pre-treated in the physical-chemical treatment, the organic material is more readily available to the biomass, and the retention time required is therefore reduced. In a trickling filter, retention times are short, because it is a high rate treatment.

The trickling filter also acts as a cooling tower, because the effluent is cooled by the air passing through the water. The filter then becomes a way to eliminate excess heat.

A clarifier is required following the trickling filter to remove the biological solids that were formed.

7.4 Ion exchange

An ion exchange unit would not be required at the beginning of the recirculation program. As the effluent will be recycled, the level of sodium in the process water will increase. However, it is not expected that problems will arise initially, because relatively high sodium levels can be tolerated. Only after a high degree of recycling has been achieved, that ion exchange might become necessary.

Because ion exchange units can be designed to have a very high efficiency, it is more than likely that only a part of the total effluent will need to be treated in this process. The ratio to be treated should be adjusted to give a sufficient purge of sodium while minimizing the size to the equipment required.

7.5 Sludge handling

Sludge from the three main treatment processes will be dewatered, and then used for soil amendment.

Sludge from the pulp and paper industry is usually appropriate for soil amendment but lime must be added to obtain a ratio of calcium to magnesium higher than 6. Since lime sludge would be mixed with the primary sludge, no further lime addition would be required in this particular case.

8.0 CONCLUSIONS

8.1 Summary of accomplishments and findings

An experimental program was set-up to develop a physical-chemical treatment of TMP-newsprint effluent. This treatment would be used in a closed cycle scheme, where the total mill effluent would be treated, and then recycled to the mill to be used in the process.

Screening experiments were first performed, to find the most efficient treatment chemicals. It was found that a combination of magnesium oxide, lime and potassium phosphate was most efficient at removing extractives from the effluent.

The main experimental program was divided into two parts. First, the combination of chemicals found in the screening experiments was used to treat effluent from a very low water usage mill that would still be discharging its effluent to the environment. It was found that:

1. At the levels of lime addition required to obtain a good treatment efficiency, magnesium oxide addition did not bring a measurable improvement, and therefore would not be necessary in a full scale process.

2. The physical-chemical treatment proved to be effective at completely removing extractives, bringing colour and turbidity to very low levels, and maintaining a low hardness.

In the second part of the main experimental program, treatment of a low water usage mill with complete recycle of its effluent was studied. Inorganic contaminants were added the

the effluent mixture to simulate the build-up that would occur in these conditions. The effect of a suspended solids removal pretreatment on treatment efficiency was also tested. It was found that:

1. The efficiency of the physical-chemical treatment is not affected by suspended solids concentrations up to 500 mg/L.

2. Under complete recycle of the effluent, the dosage of lime will need to be increased to obtain a comparable water quality.

3. Under complete recycle of the effluent, addition of potassium phosphate to control the residual level of calcium will no longer be required.

8.2 Recommendations for future work

This project was designed to be an exploratory program, to evaluate the possibility of using a physical-chemical treatment as part of a closed cycle treatment scheme. Before this process can be used in an actual mill, it has to be studied more carefully.

The following experimental tests would give valuable information and would be a critical step toward implementation:

1. Perform validation tests on the actual mill effluent after reduction of the flow.

2. Study the effect of the treated water on the paper properties, and evaluate more closely what level of contaminants can be tolerated by the process.

3. Test the sludge to verify if it is suitable for soil amendment.

4. Test the whole treatment scheme using pilot plant scale equipment at the mill site.