NIVA - REPORT

Norwegian Institute for Water Research NIVA

Royal Norwegian Council for Scientific and Industrial Research

Adress:
Postbox 333, Blindern
Oslo 3
Norway

Telephones
No 47 2 23 52 80
No 47 2 46 69 60

Report No.: 0-81084

Sub-No.:

Serial No.: 1402

Limited distribution:

Report title:
Treatment of Potable Water Containing Humus by Electrolytic Addition of Aluminum

Date: 12. 8. 1982

Project No: 0-81084 / F-80415

Author(s):
Eilen Arctander Vik

Topic group: SEKVAT

Geographical area: Oslo, Bærum and Nes municipality

Number of pages (incl. app.): 297

Contractor:
University of Washington (Valle scholarship)
NTNF

Contractors ref. (or NTNF - No):

Abstract:

The written document provides the rationale, theory, laboratory and field evaluation of the electrochemical addition of aluminum to drinking water to provide for coagulation of humus. The dissertation presents information on the removal of total organic carbon from water and on maximum obtainable removal of aquatic humus from six Norwegian lakes.

A comparison of water quality obtained by optimal coagulation, using the electrochemical process and conventional treatment was done. The two processes are similar in treatment efficiency. The advantage of the electrochemical process is in the ease of operation, and especially in its applicability to remote regions.

The dissertation provides an extensive review of the literature.

4 keywords, Norwegian
1. Naturlig humus
2. Koagulering med aluminium
3. Elektrokjemisk koagulering
4. Drikkevann

Humus
Aluminium
Engelsk

4 keywords, English
1. Natural Humus Water
2. Coagulation Using Alum
3. Electro Coagulation
4. Potable Water

Humus
Alum
English

Project leader
Eilen Arctander Vik
Eilen Arctander Vik

For the administration
John Erik Samdal

Division leader
Arild Schanke Eikum

Lars Overrein
Lars N. Overrein

ISBN 82-577-0520-9

NIVA – REPORT

Norwegian Institute for Water Research NIVA

Royal Norwegian Council for Scientific and Industrial Research

Adress:
Postbox 333, Blindern
Oslo 3
Norway

Telephones
No 47 2 23 52 80
No 47 2 46 69 60

Report No.:	0-81084
Sub-No.:	
Serial No.:	1402
Limited distribution:	

Report title:

Treatment of Potable Water Containing Humus by Electrolytic Addition of Aluminum

Author(s):

Eilen Arctander Vik

Date:	12. 8. 1982
Project No:	0-81084 / F-80415
Topic group:	SEKVAT
Geographical area:	Oslo, Bærum and Nes municipality
Number of pages (incl. app.)	297

Contractor:
University of Washington (Valle scholarship)
NTNF

Contractors ref. (or NTNF - No):

Abstract:

The written document provides the rationale, theory, laboratory and field evaluation of the electrochemical addition of aluminum to drinking water to provide for coagulation of humus. The dissertation presents information on the removal of total organic carbon from water and on maximum obtainable removal of aquatic humus from six Norwegian lakes.

A comparison of water quality obtained by optimal coagulation, using the electrochemical process and conventional treatment was done. The two processes are similar in treatment efficiency. The advantage of the electrochemical process is in the ease of operation, and especially in its applicability to remote regions.

The dissertation provides an extensive review of the literature.

4 keywords, Norwegian
1. Naturlig humus
2. Koagulering med aluminium
3. Elektrokjemisk koagulering
4. Drikkevann

Humus
Aluminium
Engelsk

4 keywords, English
1. Natural Humus Water
2. Coagulation Using Alum
3. Electro Coagulation
4. Potable Water

Humus
Alum
English

Project leader

Eilen Arctander Vik

Eilen Arctander Vik

For the administration

John Erik Samdal

Division leader

Arild Schanke Eikum

ISBN 82-577-0520-9

Lars Overrein

Lars N. Overrein

Treatment of Potable Water Containing Humus by Electrolytic Addition of Aluminum

by

Eilen Arctander Vik

A dissertation submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy

University of Washington
1982

Approved by ____
(Chairperson of Supervisory Committee)

Program Authorized to Offer Degree: Civil Engineering

Date ____

Doctoral Dissertation

Signature Eilen Arctander Vik

Date 6/27/82

University of Washington

Abstract

TREATMENT OF POTABLE WATER CONTAINING AQUATIC HUMUS BY ELECTROLYTIC ADDITION OF ALUMINUM

by Eilen Arctander Vik

Chairman of the Supervisory Committee: Professor Dale A. Carlson
Department of Civil Engineering

The overall objective of this study has been:

1) to clarify the basic principles of the coagulation process of aquatic humus, using aluminum as coagulant;
2) to develop information on the maximum obtainable total organic carbon removal from potable water; and
3) to elucidate the electrochemical process for aluminum addition in coagulation of humus in potable water.

Several water sources with different total organic carbon (TOC) concentrations have been studied. Conventional coagulation experiments (jar tests) showed that restabilization did not occur, and indicated that the dominating mechanism involved in coagulation of aquatic humus is sweep coagulation.

The maximum obtainable removal of aquatic humus varied from one potable water source to the other. The relative molecular weights of the aquatic humus from Hellerudmyra, Tjernsmotjern and Småputten were determined. The highest removal of aquatic humus, measured as 82 percent total organic carbon (TOC) removal was obtained for Hellerudmyra. Hellerudmyra also contained the greatest fraction of high-molecular size organics. Småputten contained the greatest fraction of low-molecular size organics and only 63 percent TOC

removal was obtained. This corresponded to residual TOC concentrations of 3.4 and 2.0 mg C/l, respectively.

A comparison of water quality obtained by optimum coagulation using the electrochemical process and conventional treatment using the jar test showed the only major differences to be:

1) higher pH of treated water using the electrochemical process;
2) higher specific conductivity on treated water using conventional treatment due to the sulfate addition;
3) the higher residual aluminum-concentrations of the electrochemical process due to the higher pH in treated water; and
4) higher chemical demand for the electrochemical process to obtain maximum TOC removal when treating raw waters with high pH (pH > 6.5).

Design criteria were determined for the electrochemical process. Pilot scale experiments with the electrochemical unit indicated the importance of optimizing the flotation process and sludge collection system, maintaining a minimum water velocity between the electrodes of 5 cm/sec and the minor need for maintenance of the process. Further work was proposed.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the guidance and assistance of her Supervisory Committee; Professor Dale A. Carlson, Chairman; Professor John F. Ferguson; Dr. Arild S. Eikum; Professor Eugene B. Welch; Professor Dimitris E. Spyridakis, and Professor Bjorn Hrutfiord, Graduate Faculty Representative. Particular appreciation is expressed to Dr. Arild S. Eikum and Dr. Egil T. Gjessing at the Norwegian Institute for Water Research for their tireless advice, which was a key to successful completion. The practical assistance from Åse Gudmundson Rogne, Arne Veidel and Arne Lundar is gratefully appreciated. Particular appreciation is expressed to Professor Dale A. Carlson who made it possible to communicate and discuss problems associated with this work, in spite of the distance between Oslo and Seattle. His comments and advice written on the state-of-the-art reports are gratefully appreciated. A special note of thanks is given to the Norwegian Institute for Water Research; the Royal Norwegian Council for Scientific and Industrial Research; and the Valle Scandinavian Exchange Program for financial assistance which made this work possible.

The assistance of Mrs. Oddny Falck in the typing and preparation of this document was critical to its completion and is gratefully acknowledged by the author.

Finally, special thanks are due to the author's husband, Tom Edvardsen, without whose practical assistance in looking after our three children, Askild, Marte, and Maren, this work could never have been completed.

TABLE OF CONTENTS

Page

Table of Contents, cont. Page

APPENDICES

LIST OF TABLES

List of tables, cont.

List of tables, cont.

LIST OF FIGURES

List of figures, cont.

List of figures, cont.

List of figures, cont.

Number Page

List of figures, cont.

List of figures, cont.

List of Figures, cont.

List of figures, cont.

Number Page

1. INTRODUCTION

1.1 Background

1.1.1 The Importance of Aquatic Humus

There are several factors which make aquatic humus an important constituent in natural water systems:

1) Aquatic humus is normally present in natural waters in total organic carbon (TOC) concentrations greater than 1 mg C/l whereas identifiable organic compounds may be present at concentrations which are orders of magnitude lower (Gjessing, 1976; Wetzel, 1975).

2) Humus shows ion exchange and complexing properties associated with most constituents found in water, including nutrients, trace metals, toxic elements and micropollutants (Gjessing, 1976; Wetzel, 1975; Schnitzer & Khan, 1972).

3) Humus in water acts as a transport vehicle, easily transporting toxic elements and organic micropollutants (Gjessing, 1976; Schnitzer & Khan, 1972; Gjessing, 1980; Gjessing & Berglind, 1981; NAS, 1977).

4) Chlorination of aquatic humus in potable water supply forms chlorinated organic compounds. Not only are chloroforms formed (Stevens et al., 1976; Rook, 1974; Bellar et al., 1979; Stevens, 1978), but also complex chlorinated compounds (OECD, 1980; Oliver, 1978; Stevens et al., 1980; Christman et al., 1980; Peters & Perry, 1980), many of which might have health effects (OECD, 1980; T & P Council Statement, 1974; Cantor & McCabe, 1978; Simmon & Tardiff, 1978; Cantor et al., 1978; Bull, 1979).

Total organic carbon (TOC) concentrations vary over a wide range (Symons et al., 1975; Cross, 1972) as illustrated in Figure 1 (after Kavanaugh, 1978)). The median level of TOC in 62 surface water supplies surveyed in the USA (Symons et al., 1978) was 3.5 mg C/l (NORS in Figure 1). According to Stumm & Morgan (1970) and Wetzel (1976), the particulate organic carbon, including planktonic organisms, generally accounts for about 10 percent of the total organic carbon. The dissolved organic carbon is predominantly humus.

Surface waters in Norway are highly colored due to naturally occurring organics (aquatic humus). The total organic carbon concentrations vary over a wide range, but no mean concentrations have been determined. More than 95 percent of the Norwegian population, i.e. 3.8 million people, use surface water for potable water supply (Gjessing, 1978).

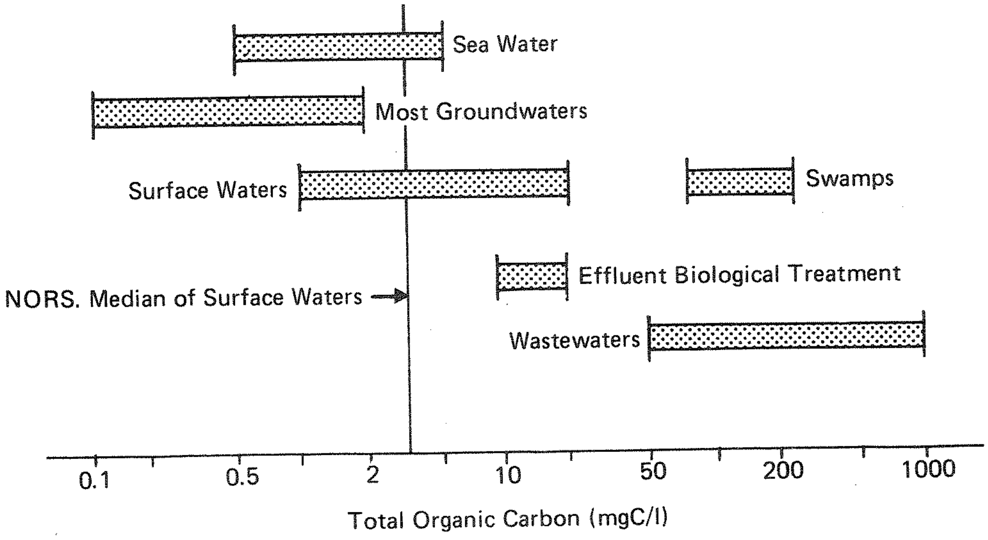


Figure 1. Ranges of total organic carbon (TOC) reported for a variety of natural waters (Kavanaugh, 1978).

Increasing research is underway (Gjessing, 1980) regarding the effects of micropollutants associated with humus. Gjessing & Berglind (1981) studied the complexation of polycyclic aromatic hydrocarbons (PAH) with aquatic humus. Their results suggested that some of the more important (carcinogenic) PAHs were so strongly bound to the aquatic humus that widely used analytical methods were insufficient to determine the total PAH-amount in water. Their findings suggested also that humus acts as a transport vehicle for heavy soluble PAH in water.

Gjessing (181) showed that the cadmium toxicity to salmon and algae is reduced considerably when humus is present. Gjessing considers one of the most important aspects of humus to be that it acts as a "vacuum cleaner". Its molecule can take up and increase the environmental distribution of inorganic and organic micropollutants. These can include metals and persistent organics such as PCBs, DDTs, and PAHs (Josephson, 1982).

Alberts et al. (1974) present results indicating that interaction between mercury and humus has to be considered as a possible mobilization pathway for mercury and its compounds in the environment.

Humus, whether in soil, sediment, or water column, often is found to be associated with toxic organic materials. Shin et al. (1970) determined that, in soils, humus materials were the components most successful in adsorbing various pesticides. Wershaw et al. (1969) have shown that the solubility of DDT in 0.5 percent aqueous sodium humate solution is at least twenty times greater than in water, i.e. humus has a solubilization effect on DDT. Ballard (1971) has also demonstrated the solubilizing effect of humic acid. Schnitzer & Khan (1972) point out the importance of the fact that humus substances act as DDT carriers, affecting the mobility of insecticides which are otherwise highly insoluble in water. Hassett & Anderson (1979) present data indicating that cholesterol is bound to dissolved organic matter and is thus stabilized in the aqueous phase: The natural organic matter is thus capable of binding the hydrophobic compounds (including PCB) and thus inhibiting adsorption of the compounds onto river and sewage particulates.

The occurrence of trihalomethanes in water supplies was first demonstrated by Rook (1974) who associated their formation with the process of chlorination. Chloroform was found to be present at the highest concentration (Symons, 1975). Naturally occurring organics (humus) have been shown to be precursors for trihalomethane formation. Growing international concern, associated to some extent with the suggested carcinogenicity of chloroform, has resulted in incorporation of this group of compounds into water quality standards. In 1979, the United States Environmental Protection Agency (1979) established a maximum contaminant level of 100 μg/l of total trihalomethanes (including chloroform, dibromochloromethane, bromodichloromethane and bromoform). So far only a few countries have set standards (Peter & Perry, 1980):

The USA:	100 μg/l
Canada:	350 μg/l
Germany:	The recommended guideline is 25 μg/l
The Netherlands:	The recommended guideline is 75 μg/l.

A number of European countries are envisaging the future adoption of guidelines. Among the halogenated compounds in drinking water, most of the attention of health authorities has been given so far to the trihalomethanes, as this group of compounds is both the easiest to identify and the main group individually (~20 percent quantitatively of total organohalogens) found in drinking water. Chloroform represents about 15 percent of total organohalogens (OECD, 1980). A number of these organohalogenated compounds, whether volatile (of which THM is the major part) or nonvolatile, are shown to be highly resistant to biodegradation (OECD, 1980). Leach et al. (1976) showed that chlorinated constituents originating in bleach plant caustic extraction effluents were more resistant to biodegradation than naturally occurring wood extractives. These organohalogenated compounds are not only highly resistant to biodegradation, but they can accumulate either in sediments or in the biomass. The more they are halogenated, the more they become lipophilic and can be regarded as suspect or potentially harmful, even at very low concentrations in the case of long-term exposure (OECD, 1980). The frequency of liver tumors in mice exposed to chloroform, has been shown to be high (Eidsness, 1974). Lovelock et al. (1973) have shown that cancer rates were higher in Louisiana parishes that used the Mississippi River as a water source. It is not clear, whether the apparently higher cancer rates where surface drinking water is consumed, is due to organochlorides or industrial contaminants (OECD, 1980). So far not much attention has been paid to the health effects of total organohalogens. Oliver (1978) has studied the chlorinated non-volatile organics as well as the volatile organics produced by reaction of chlorine with humic material. The same has been done by Stevens et al. (1980). Future research regarding chlorinated organics will probably be concentrated on the total product and not on the chloroforms which comprise only 15 percent of the total. Trihalomethane formation by chlorination of aquatic algae has been studied by Oliver & Shindler (1980). Kaiser & Lawrence (1977) studied the formation of chloroform by chlorinating some of the most widely used polyelectrolytic coagulants. Both algae and polyelectrolytes were shown to contribute to the trihalomethane formation.

The presence of trihalomethanes (THMs) in potable water supply in Norway was studied by Carlberg et al. (1980). Both raw water, treated water and water from the distribution lines from different locations in Norway were analyzed. In 42 out of 45 analyses on treated water, haloforms were detected. Chloroform, the main component, was higher than 100 μg/l in only two locations. The highest detected chloroform concentration was 260 μg/l.

The THM-concentrations in Finnish waterworks also have been studied (Hiisvirta, 1981). The aim of Hiisvirta's study was to find the maximum THM-level in Finnish drinking waters. Samples from ten water supplies were examined, all having high concentrations of organic material in the raw water (TOC: 10-40 mg C/l), and strongly eutrophicated raw water sources, using high chlorine doses in the pre-chlorination stage (chlorine dosages of 10-20 mg/l) and long contact time. Of 123 samples analyzed, 94 had higher THM-concentrations than 100 μg/l. In two water supplies, using chemical flocculation in the treatment, more than 1000 μg/l were measured. The maximum values found were

1300 and 1400 μg/l in July-August. In most cases, the measured THM-concentrations ranged between 100 and 400 μg/l. A study of the relationship between cancer incidence and drinking water quality is underway (Hiisvirta, 1981).

1.1.2 Methods for the Removal of Humus from Water

Available methods for humus removal are:

- oxidation
- adsorption
- coagulation and separation
- reverse osmosis
- ion exchange.

Oxidation. Some decades ago bleaching of colored water by ozone was introduced as a treatment method (Gjessing, 1980). Ozonation of humus-water, which has a combined disinfecting and bleaching effect, results in color-reduction which, according to Mallevialle (1979), is due to transformation of the organic materials into lower molecular-size fractions. This transformation results in an increased availability of the carbon for microbial growth in the distribution system (Gjessing, 1979). Additional disinfection ith chlorine to control this growth in practice leads to idealizing conditions for maximum formation of trihalomethanes. Miller et al. (1978) pointed out an interesting process combination for organics removal, namely activated carbon with pre-ozonation, popularly referred to as Biological Activated Carbon. In this process the organic macromolecules are thoroughly oxidized with ozone to lower molecular size fractions before they are removed by adsorption on activated carbon. The "capacity" of the activated carbon is increased compared with the same system without pre-ozonation.

Berglind & Gjessing (1979, 1981) studied mineralization of humus, using UV-radiation in the presence of active oxygen (hydrogen peroxide). Several factors have been studied in order to understand the reactions occurring. Lipowicz (1981) described the process as a free radical oxidation process. The free radicals - largely the potent hydroxyl radical (OH·) - are generated by cavitational shock, by catalytic splitting of hydrogen peroxide (HOOH), and by ultraviolet (UV) irradiation. The free radicals split organic molecules, yielding new free radicals that can split other molecules - a chain reaction. The free radicals in the presence of catalysts or sensitizers, are believed (Rogne et al., 1981) to be very reactive. Mixing, using UV-radiation without hydrogen peroxide addition, has been shown to increase the color reduction. Storage of treated water has a positive effect on organics removal. Increasing the temperature during storage results in increased removal. Research on the effects of storage is in progress.

Adsorption of aquatic humus using activated carbon has been studied by several. Symons et al. (1979, 1976) studied powdered activated carbon (PAC) and concluded that the high doses needed for effective adsorption of trihalomethanes (THM) and their precursors make this process uneconomical. Granular activated carbon (GAC) has, however, proved more effective and has been recommended by the EPA as the method most suitable for THM reduction (USEPA, 1979; Symons et al., 1976). When fresh, the activated carbon has been shown to adsorb most of the trihalomethane precursors (as, for example, humus) and produce a water with low overall concentration of organic matter (Symons et al., 1976, 1979). The major disadvantage is that the activated carbon must be regenerated frequently to prevent breakthrough and maintain the high removal efficiency for organic matter. The frequency of regeneration is determined by the concentration of the organics and also the type of precursors to be removed. Symons et al. (1976) showed that when GAC was used for the removal of THM in the finished waters, the effectiveness of GAC is only maintained during the first two to three weeks of operation. Berglind & Gjessing (1981) used granular activated carbon columns for adsorption of humus, showing high initial color removal (83 percent), but only 19 percent color removal after one week of operation. The rate of filtration used was 10 m/h and the influent color of the water was equal to 150 mg Pt/l.

In spite of the high costs involved in this process, activated carbon is an effective process for organics removal, and several types of pretreatment have been used to increase the time of operation. Not only pre-ozonation (Miller et al., 1978), but also coagulation (Peters & Perry, 1980) are actual pretreatment processes. Semmens & Field (1980) also pointed out the importance of appropriate pretreatment to extend the bed life when applying granular activated carbon treatment. Randtke & Jepsen (1980) studied coagulation and softening as pretreatment for activated carbon adsorption. The purpose of the research was to explore the interactions of these processes with the subsequent activated carbon adsorption. They showed that alum coagulation resulted in markedly increased adsorption isotherms except when little or no TOC was removed during coagulation. Softening, on the other hand, did not significantly alter the adsorption isotherm of peat fulvic acid even though 75 percent TOC removal occurred during softening.

Coagulation belongs to the most important processes used in treatment of surface waters (Southeimer, 1978). Relatively few investigations reported in the literature deal specifically with the coagulation of naturally occurring organics (Committee Report, 1979), but much has been done with regard to color (Committee Report, 1967) and turbidity removal. Relatively few investigations deal with coagulation of humic and fulvic acids. The humic acid fraction of humus has been shown to contribute more to color per unit weight, undoubtedly because of its larger size (Ghassemi & Christman, 1968). Babcock & Singer (1977) showed that chlorination of the fulvic acid fraction yields less than half as much chloroform as the humic acid fraction. They also showed that 86 percent TOC was removed by coagulation of humic acid while only 22 percent of the TOC was removed from the fulvic acid fraction, thus indicating that coagulation is an effective way of reducing THMs. Kavanaugh (1979) discussed the wide range of TOC removals by coagulation reported in the literature. Symons et al. (1975) reported an average total organic carbon (TOC) removal of 30 percent in 63 plants with conventional treatment. About 60 percent TOC removal has been reported from Ohio River water (Symons et al., 1976). Kavanaugh (1979) described studies from the Rhine and Alpine Lakes in Germany which indicated 25-40 percent removal of dissolved and colloidal organic carbon by alum at pH 7.0.

Hall & Packham (1965) and Babcock & Singer (1977) showed that up to 90 percent of the humic acid fraction can be removed by using

Al(III) and Fe(III), while the removal of fulvic acids is more difficult. Color removal from highly colored surface waters with ferric sulfate was shown to range between 87 and 98 percent (Black et al., 1963). Kavanaugh (1977) showed that the optimum pH values for turbidity and TOC removal are not necessarily the same. Also Semmens & Field (1980) pointed out the differences that exist between turbidity and organics removal even though good turbidity removal always coincided with good organics removal. Alum and ferric salts are not the only reactants used in coagulation. Thompson et al. (1972a, 1972b) showed that magnesium carbonate, hydrolyzed with lime, could give as good results as coagulation with alum.

A variety of organic polyelectrolytes has been used for organic removal (Kisla & McKelvey, 1978; Edzwald et al., 1977; Glazer & Edzwald, 1979) all showing good humus removal.

Randtke et al. (1981) studied removal of soluble organic contaminants by lime-soda softening. The major component of the precipitate is $CaCO_3$, but if magnesium (Mg) is present and pH is sufficiently high, $Mg(OH)_2$ will also be formed. The process was shown to effectively remove several humic substances, including a fulvic acid. The removal increased with increasing pH, increasing amount of precipitate and decreasing concentrations of TOC. Removal was significantly enhanced by the presence of magnesium or phosphate, especially when the amount of precipitate formed was small.

Neither microstraining nor conventional sand-filtration removes aquatic humus from water to any great extent. Oztürk (1971) and

Gjessing (1972) showed that filtration of lake water through slow sand-filters resulted in only 11 percent removal of organic substances. Ozonation of the water before filtration resulted in 30 percent removal. Addition of chemicals (coagulation) to the water before filtration (direct filtration) indicated high color and TOC removal (Edzwald, 1979; Scheuch & Edzwald, 1979; Edzwald, 1980). Scheuch & Edzwald (1979) did experiments with humic acid extracted from peat, using cationic polymers and direct filtration. They showed that color was reduced from 55 and 110 Pt/Co units to 5, while TOC was reduced from 2.8 to 1.0 mg C/1 (64 percent removal), and from 5.2 to 1.3 mg C/1 (75 percent removal). When using natural organics from the Raquette River, the color was reduced from 65 and 70 to 10 Pt/Co units, while TOC was reduced from 5.2 to 3.8 (27 percent removal) and from 6.2 to 4.0 (35 percent removal).

Edzwald (1980) discussed coagulation, sedimentation and filtration processes for removal of organic substances and pointed out that direct filtration is one option that should be considered. Additional research is needed, using natural waters and larger pilot scale and full plant scale filters.

A status report on direct filtration (Committee Report, 1980) discussed the result of a worldwide survey of direct filtration plants. Color exceeding 30-40 Hazen units or turbidity greater than 15 FTU on a continuing basis were pointed out as problem situations. On a short-term basis, polyelectrolytes were proposed as a substitute for all or part of the primary coagulant required, thus reducing the quantities of solids to be removed in, and eventually, from the filter. The mixing energies for coagulation and flocculation are pointed out as important process adjustments.

Reverse Osmosis almost completely removes large, complex organic substances (Nusbaum & Riedinger, 1978). Koottatep (1979) showed that the humic substances from natural waters could be removed easily by reverse osmosis. He used three different laboratory scale reverse osmosis units in his study, a spiral-wound module from Osmonics, a plate and frame module from DDS (De Danske Sukkerfabrikker) and a tubular module from PCI (Peterson Candy International Limited). Both pH (varied between 3.5 and 7.0) and pressure (varied between 7.5 and 10 bar) were shown to have no significant effect on the removal of humic substances. The membrane pore size was shown to have a significant effect. For the selected membranes, 80-100 percent color removal and 50-90 percent permanganate removal was attained. Membrane fouling was studied by increasing the bentonite concentration from one mg/l to 3000 mg/l measured as suspended solids. Suspended solids concentrations up to 100 mg/l did not affect the product water flow while 130 mg SS/l decreased the product water flux by 50 percent during three hours of running. Daily water cleaning of the membranes improved the initial product water flux while detergent cleaning also improved the average daily flux. Thorsen (1981) studied reverse osmosis in water treatment, and an economic evaluation was made comparing this process with activated carbon and chemical treatment, all for humus removal. His economic evaluation showed reverse osmosis had the lowest investment and operational costs when treating less than 10 m^3/h of water.

Ion Exchange for aquatic humus removal has been studied by several researchers (Anderson & Gaier, 1979; Evans & Maalman, 1979; Halle, 1979). Anderson & Gaier's (1979) study focused on the use of anion exchange resins. They studied 1) the efficiency obtained in organics removal, and 2) the possibility for regeneration of the resins. Batch tests were used to measure relative selectivity of commercially available anion exchange resins. Mississippi River water was used. The strongly basic anion exchange resins were shown to be more effective for organics removal than the weak basic resins. Organics measured as total organic carbon in this study were removed below the limits of detection. No long-term test of resin life was carried out.

Evans & Maalman (1979) reported results from a two-year test period on use of weak basic resins for removal of humic acids from Rhine River Water. The process was shown to remove 60 percent of the humic acid. The authors pointed to the low chemical requirements and hence the lower waste volumes as advantages of the process.

Strongly basic anion exchange resins have been used for humus removal by the Fuhrberg water treatment plant (Hannover), first at pilot scale, and from July 1978 at full scale (Kölle, 1979). Highly colored groundwater containing iron, manganese, and about 130 ppm of sulfate was treated by aeration, chlorination, lime, potassium permanganate, filtration, and breakpoint chlorination. The iron and manganese were removed, and dissolved organic carbon was reduced from 9 to 6 ppm. Additional flocculation did not reduce the humic acid content, but use of strongly basic anion exchange resins resulted, immediately after regeneration, in about 58 percent carbon removal and 67 percent reduction in permanganate consumption. An increase of organic carbon content in the regeneration solution was registered without seeing any effect on the efficiency of the resin.

Halle (1979) used two different ion exchange resins, one strongly basic and one medium basic anion exchange resin. Mean color removal for both resins was 44 percent, while based on UV absorption (254 nm) a mean removal of 62 percent was obtained. Several factors were shown to influence the effect of the ion exchange resin, a high turbidity resulted in low humus removal, and pH reduction reduced the humus removal. The resins proved to be more effective on low (color = 40 mg Pt/l) humus concentrations than on high (90 mg Pt/l).

1.2 Research Objective

In Norway, several small water treatment plants for removal of aquatic humus exist, and more will probably be constructed in the near future. Conventional water treatment, coagulation, sedimentation and filtration, is used in most cases. Activated carbon is used occasionally. Most of the treatment plants are small with little inspection occurring, and investigation has clearly shown that only a few plants operate according to their objective (Damhaug, 1980). The qualifications and interests of the operators are the most important factors influencing the treated water quality. The direct filtration process is looked upon as an interesting capital saving process if given sufficiently long filter runs when treating highly colored surface water. The direct filtration process treating colored waters was studied in detail in Trondheim (Eikebrokk, 1982). Several studies have stressed the importance of a proper pretreatment process to obtain effective treatment with direct filtration plants, as well as with activated carbon. The coagulation process is the most effective pre-treatment method used today. Few investigators have, however, studied the use of this process in the treatment of naturally occurring organics. The coagulation mechanisms involved in aquatic humus removal, the maximum obtainable TOC removal, and the optimum coagulation conditions including dose requirements and pH, are important factors that need to be investigated with respect to the naturally occurring organics. In this study, aluminum has been suggested as the coagulant since polymers are looked upon with scepticism by the Norwegian health authorities. The conventional way of adding aluminum is by use of aluminum sulfate. In this project, electrolytic addition of aluminum was used. The amount of electric current on the aluminum electrodes controls the rate of anodic dissolution of aluminum and thus the amount of coagulant added. The water is not simultaneously acidified as in conventional coagulation with aluminum sulfate. These aspects make the process very interesting at small water treatment plants where simple operation is of major importance.

The research objectives have been:

1) to clarify the basic principles of the coagulation process of aquatic humus, using aluminum as coagulant.

2) to develop information on the maximum obtainable total organic carbon (TOC) removal from potable water.

3) to elucidate the electrochemical process for aluminum addition in coagulation of humus in potable water.

It was found important to determine whether it is possible to make general conclusions regarding coagulation of aquatic humus with aluminum. The investigations were therefore performed with three different water sources containing different concentrations of organic carbon and different molecular size distributions. The research program was divided into three parts.

Part one contained work with the electro-chemical process. A laboratory scale unit was used to study the factors affecting the aluminum dosing, the necessary potentials, the coagulation efficiency of the various sources, and also a detailed study of the process.

Part two contained work with the conventional coagulation process. Standard jar-test equipment was used to study the coagulation mechanisms involved in the removal of aquatic humus.

Part three contained pilot plant studies of the electrochemical process. Based on the results from part one, a pilot scale electrochemical unit was constructed, the unit installed in a small trailer and transported to a small colored lake. The intention was to run experiments with the electrochemical unit followed by a dual media filter. The pilot scale experiments with the electrochemical unit stressed, however, the importance of proper flotation and sludge collection. It was found to be more important to optimize the flotation process than to run filtration experiments. The filtration process was previously investigated by several researchers. In the pilot plant studies of the electro-chemical process, the sludge production and the practical aspects relating to operation of the plant and design of the process were the major factors studied.

2. LITERATURE REVIEW

2.1 Characteristics of Aquatic Humus

The yellowish-brown color of natural water (aquatic humus) is the water-extractable fraction of the soil humus, and it is a product of decayed plant residues. There is general agreement that the differences in the physical and chemical properties between humus in soil and humus in water are relatively small. According to Packham (1964), Berzelius was one of the earliest investigators in the field of aquatic humus; in 1806 he identified humic materials as being responsible for the light-yellow color of a spring water.

2.1.1 Origin, Formation and Distribution

Kononova (1966) stated that in soil humus one can expect the presence of substances related to following groups of organic compounds:

1. Fats and similar substances
2. Carbohydrated and related substances
3. Proteins and their derivatives
4. Lignins and their derivatives
5. Tannic substances in simple and condensed forms
6. Resins and terpenes.

The synthesis of humus is based on plant residues, and Flaig (1963) suggested that 50-60 percent carbohydrates, 1-3 percent proteins and 10-30 percent lignins participate in the humification process. Gjessing (1976) (Figure 2) suggested how the humification process took place.

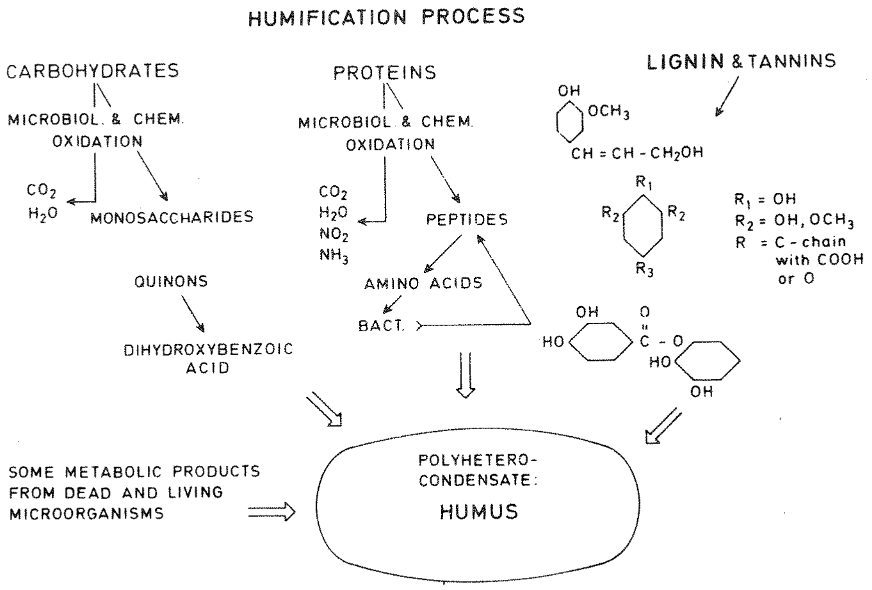


Figure 2. Natural synthesis of humus (Gjessing, 1976).

Among these groups of organics, lignin is considered to be the most important, since carbohydrates and proteins have a higher rate of chemical decomposition and are more available to soil organisms than lignin (Flaig, 1964).

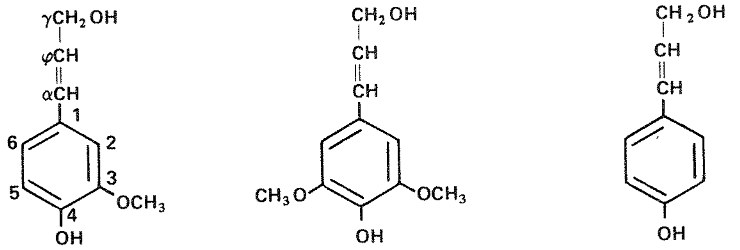
According to Thurman & Malcolm (1979), 30-50 percent of the dissolved organic carbon in surface waters is predominantly aquatic humus. This is because honhumus organic substances are easily degraded by microorganisms whereas humus is relatively resistant to microbial degradation. Mathur & Paul (1966) used carbon dating techniques on "mobile" humic acids from a Black Chernozemic soil, to show that the mean residence time of the carbon was about 800 years, indicating that the greatest proportion of this carbon has a very low turnover rate.

The formation of humus is dependent on factors such as vegetation, population and activity of the microorganisms (Gjessing, 1976), and on the hydrothermal conditions. The physical and chemical properties of the soil are of great importance, both in regard to the rate of the humification process and to the composition of the humus products.

Kostychev (1886) showed that the decomposition and mineralization of organic matter in soil have their maximum at temperatures of 35 °C, and at about 35 percent moisture. Excessive soil moisture apparently promotes the formation of small molecular-size humus because it prevents the removal of condensation by-products (water), and thereby hinders the growth of the molecules. Gjessing (1980) emphasized that bogs and marshes were areas where high soil humidity and acidity, low temperature, particular geology and topography, have resulted in accumulation of organic matter. Low temperature areas (winter temperatures below 0 °C and summer temperatures in the plus Celsius range) will consist of boggy area which in turn may result in a noticeable brownish-yellow color of the surface water.

Lignin is probably the most important group of organics in the aquatic humus. This unique biopolymer occupies a central position in the earth's carbon cycle. An international seminar on lignin biodegradation was organized and held May 1978 at the U.S. Forest Products Laboratory in Madison, Wisconsin (Kirk et al., 1980).

It has been shown that lignin (Sarkanen & Ludwig, 1971), which comprises 17 to 33 percent of wood, is a complex aromatic polymer and has a role in cementing the polysaccharide components in cell walls both chemically and physically, thus increasing the mechanical strength of wood as a composite material and its decay resistance toward microorganisms. Lignin is generally classified into three major groups based on their structural monomer units. Gymnosperm lignin is a dehydrogenation polymer of coniferyl alcohol. Angiosperm lignin is a mixed dehydrogenation polymer of coniferyl and sinapyl alcohols and grass lignin is composed of a mixed dehydrogenation polymer of coniferyl, sinapyl and p-coumaryl alcohols as shown in Figure 3.



(1) Coniferyl alcohol

(2) Sinapyl alcohol

(3) *p*-Coumaryl alcohol

Figure 3. Major monomer units in lignins.

Christman & Oglesby (1971) extensively treated the subject of microbial degradation and formation of humics from lignin. The primary organisms responsible for degrading lignin on the forest floor are the white rot fungi, belonging to the class Basidiomycetes. Figure 4 schematically illustrates the overall process thought to occur.

In summary (Christman & Oglesby, 1971), one begins with a large, poorly-defined molecule (lignin) and ends up with another large molecule (humus) even more amorphous than the starting material. To assume that lignin is the sole precursor of humus is an oversimplifi-

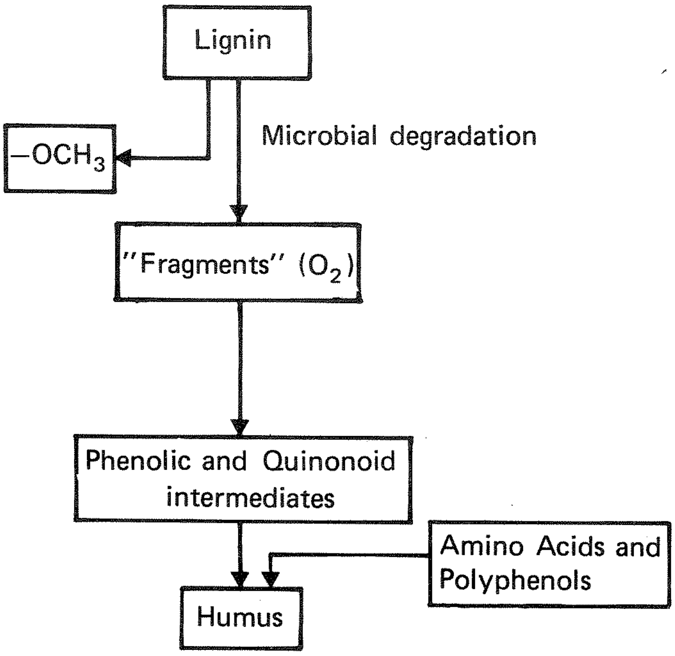


Figure 4. Schematic Illustration of Lignin Humification (Christman & Oglesby, 1971)

cation. Soil is not the only site for humification. Nissenbaum & Kaplan (1972) were able to provide evidence that marine humic matter has its origin in the sea rather than by transport from terrestrial sources. Also Jackson (1975) emphasized that humification is a general process of nature. The point is made that the accumulation of humic matter over geologic time is responsible for the coal and oil reserves available today. Jackson states that the holding of these tremendous amounts of carbon in a relatively inert state, may in part be the reason why large concentrations of oxygen were able to be built up in the atmosphere. Humification may be an essential process of nature.

2.1.2 Chemical Composition

Work by several investigators (Black & Christman, 1963; Gjessing, 1980) confirms that humus consists of a complex aromatic "core" (perhaps polymerized hydroquinones and polymerized lignin-like monomers). Gjessing (1980) has proposed a humus molecule, shown in Figure 5.

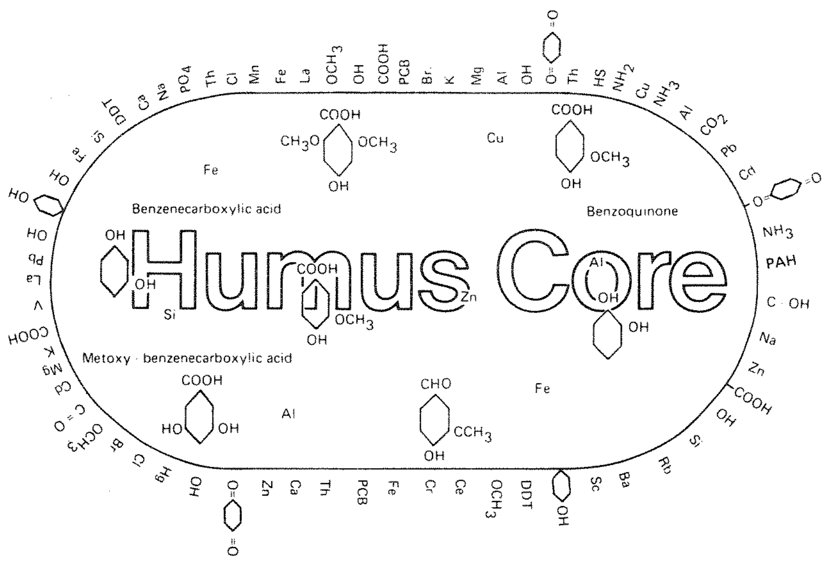


Figure 5. Humus molecule unit (Gjessing, 1980).

Because of the complex nature of humus substances, they have traditionally been classified by the operational procedures needed to separate them from a mixture of components. Oden's classification into humus coal, humic, fulvic and hymatomelanic acids (Oden, 1919) has been used since its introduction in 1919 (see Table 1). Other fractionating systems have been described by Schnitzer & Khan (1972) who summarized the results of elemental analyses performed on six soil humic acids, three soil fulvic acids, and two soil humins. The results, presented in Table 2, show that fulvic acids contain more oxygen, but less carbon and nitrogen than humic acid. Schnitzer & Khan (1972) have also summarized studies of the distribution of oxygen-containing functional groups in soil humic acids and fulvic acids by a series of researchers, showing that a marked difference exists between fulvic and humic acid, the latter containing less total and carboxyl acidity primarily.

Based on the assumption that lignin plays an essential part in the humification processes, Christman & Ghassemi (1966) proposed a molecular structure for the humus molecule (Figure 6). Considering that the number of units (n) may vary within a wide range, and that groups of organic and inorganic compounds may be attached to the unit and also substitute for others, the possibilities are, however, many.

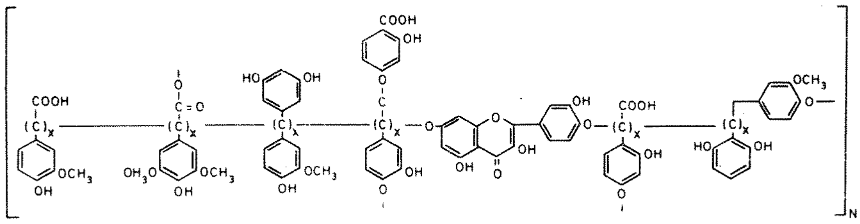


Figure 6. Proposed structure of the colored humus molecule (Christman & Ghassemi, 1966).

Black & Christman (1963a, 1963b) and Packham (1963) used aquatic humus and separated it into Oden's classical fractions. The results, summarized in Table 3, show that 80-90 percent of the aquatic humus belongs to the fulvic acid fraction, while 10-20 percent to the

Table 1. Oden's Classification of Humic Substances (Oden, 1919).

Group Name	Definition
Humus coal	Insoluble in water and NaOH
Fulvic acid	Soluble in mineral acid and NaOH
Hymatomelanic acid	Soluble in NaOH and alcohol; insoluble in mineral acid
Humic acid	Soluble in NaOH; insoluble in mineral acid and alcohol

Table 2. Summarization of Elemental Analyses of Soil Humic and Fulvic Acids (Schnitzer & Khan, 1972).

Element	Percentage Dry, Ash-Free Weight	
	Humic Acid	Fulvic Acid
Carbon	50 - 60	40 - 50
Hydrogen	4 - 6	4 - 6
Oxygen	30 - 35	44 - 50
Nitrogen	2 - 6	<1 - 3
Sulfur	0 - 2	0 - 2

Table 3. Aquatic Humus Separated into Classical Fractions (Black & Christman, 1963a, 1963b; Packham, 1964).

Sample No.	Fulvic Acid %	Hymatomelanic Acid %	Humic Acid %
1	83.0	13.1	3.9
2	85.4	10.2	4.4
3	86.0	10.2	3.8
4	65.5	18.3	16.2
5	76.5	18.6	5.0
6	80.9	13.9	5.2
7	57.8	32.2	10.0
8	87.0	11.2	1.8
9	87.5	11.6	0.9
10	87.7	10.3	2.0
11	89.6	9.6	0.8
12	88.8	11.1	0.1
13	87.9	11.3	0.8
14	85.0	14.3	0.7
15	89.5	8.4	2.1
16	86.4	12.9	0.7
17	82.8	16.6	0.6

hymatomelanic acid and only up to 5 percent is humic acid.

Aquatic humus is the predominant form of dissolved organic material in many aquatic systems, and several different methods, such as filtration, centrifugation, gel chromatography, adsorption or differential precipitation have been used to fractionate natural organic material. In addition, osmometry, cryoscopy, diffusion, viscosity, and light scattering have been used for determining the molecular size of humus. Gjessing (1976) reviewed molecular size measurements and the great differences found depending on method used. Chemical methods give values of about 1300-13,000 for humic acids, while osmometry, cryoscopy and the diffusion and viscosity methods give values of about 700-26,000 for humic acids and 200-300 for fulvic acids, and ultracentrifugation and light-scattering methods give 30,000-80,000. Gjessing & Lee (1967) found most organic color in the molecular size range of 10,000-50,000. The fulvic acid fraction has been shown to have a lower average molecular size than the humic acid fraction.

Thurman et al. (1981) studied molecular sizes of aquatic humus, and discussed the different methods available for size computation. In their study, small-angle X-ray scattering was used to measure the range of particle sizes present in aquatic humus, and their results are compared with those reported in the literature for various aquatic humus. Thurman et al. (1981) concluded that two fractions occur, a colloidal humic acid fraction and a dissolved fulvic-acid fraction with a molecular weight ranging from 500 to 2,000 daltons.

The limitations of Sephadex gel filtration were discussed by Thurman et al. (1981). Adsorption onto the gel with longer retention results in an underestimate of molecular weight. Another error is charge exclusion of the anionic humus by the slight anionic charge of the gel, resulting in molecular weights that are too high. Thurman et al. (1981) concluded that, within broad limits, molecular size determined by gel filtration is meaningful when estimating the range of molecular sizes.

Also molecular size estimation by ultrafiltration was discussed, and Thurman et al. (1981) concluded that membranes only give a range of molecular sizes and a good selection of membranes and their respective cutoffs are the PM-30 for greater than 30,000, PM-10 for less than 10,000, and UM-05 for less than 200 in molecular weight.

Thurman & Malcolm (1981) proposed a three-fold approach to study the structure of aquatic humus, namely 1) separation and purification of humic substances by liquid chromatography; 2) degradation by oxidative procedures and methylation of humic substances by carbon-13 reagents; and 3) identification of products and structural components by the latest analytical methods, such as capillary gas chromatography--mass spectroscopy and carbon-13 nuclear magnetic resonance (^{13}C-NMR). Thurman & Malcolm (1981) used their three-fold approach to fractionate and characterize fulvic acid from the Suwannee River in southeastern Georgia. Comparison between this method and standard methods of characterization, such as elemental analysis and functional-group titration, showed this method to be useful. Based on the preceding characterization, the fulvic acid in the Suwannee River was thought to consist of a mixture of plant degradation products, such as: lignin, terpenoids, flavonoids, and hydrolyzable tannins.

Dawson et al. (1981) reported molecular sizes in the range of 810 to 930 for the mobile fulvic acid fraction. Their results were based on gel filtration experiments of two forest soils and adjacent stream waters.

2.1.3 Colloidal Characteristics

In modern terms a colloidal dispersion is defined as a system in which particles of colloidal dimensions (∼1 nm-1 μm) are dispersed in a continuous phase of different composition (van Olphen, 1977). The two major classes of hydrous colloidal systems are the hydrophobic and hydrophilic colloids. They were formerly called suspensoids and emulsoids, respectively. A typical example of a hydrophobic colloid is a gold sol, which is a dispersion of submicroscopic gold particles in water. Typical hydrophilic colloids are colloidal solutions of gums. According to van Olphen (1977) the terminology "hydrophobic" colloid is somewhat misleading. With the growing knowledge of colloidal systems present day classification and nomenclature, according to van Olphen, are based on more fundamental characteristics of colloidal systems. It has been recognized that the hydrophilic sols which are prepared from organic macromolecular substances such as natural and synthetic gums, should be considered true solutions of macromolecules or macroions. Consequently, the hydrophilic colloids are now called macromolecular colloids or polyelectrolyte solutions. Their "colloidal" properties are a result of the large size of the dispersed molecules with respect to the size of the liquid medium. Van Olphen (1977) emphasized that hydrophobic and macromolecular sols can be distinguished by a great difference in sensitivity toward the addition of salt. The hydrophobic sols flocculate in the presence of rather small amounts of salts, while the macromolecular sols, which are true solutions, are rather insensitive toward salt. A large amount of salt may adversely affect the solubility of the macro-ions and may cause the precipitation of the macromolecular compound. According to van Olphen (1977), many macromolecular compounds remain dissolved in highly concentrated, even saturated, salt solutions.

Humus colloids are able to retain a dispersed or dissolved state (here termed: stability). The stability arises from the predominance of forces associated with the solid-liquid interface. The interfacial forces promoting the stability of a colloidal disperson arise from 1) the presence of surface charge at the interface between colloid and liquid, and 2) the hydration of surface layers of the colloid.

Bratby (1980) discussed organic color, whether color is colloidal or in true solution. Shapiro (1957) suggested that color compounds were straight-chain-substituted fatty acids in true solution and that colloidal properties exhibited by these compounds were due to complex formation with iron if present in solution. Packham (1965) has suggested that, for the humus present in natural waters, the humic acid fraction is colloidal whereas the fulvic acid fraction is in true solution. He also suggested that organic color is in true solution, but that a proportion of the molecules is large enough to exhibit colloidal properties. Furthermore, in the presence of iron, coordination reactions may occur, giving rise to colloidal characteristics.

The humus molecule has been shown to contain carboxyl-, phenolic-, alcoholic-, ketonic-, quinonoid-, and methoxyl groups in varying quantities, which affect the stability of the organic colloids in water. The dissociation constants attributed to the carboxyl and phenolic functional groups associated with humus have been summarized (Committee Report, 1979) and are presented in Table 4.

Table 4. Comparison of Humus Dissociation Constants (Committee Report, 1979).

Material	Dissociation constants of carboxyl functional groups pK	Dissociation constants of phenolic functional groups pK	Investigator
fulvic acid	4.9	8.0	Narkis & Rebhun (1977)
humic acid	4.6	8.2	Narkis & Rebhun (1977)
humic acid	4.51		Glaser & Edzwald (1979)
aquatic humus	4.23	8.71	Wilson & Kinney (1971)

For the pH of most natural waters, humus materials are negatively charged macromolecules (anionic polymers). Considering the apparent complexity of humus and the inability to find simple repeating monomeric units, it seems probable that structurally there may be many different carboxylic and phenolic groups present in an average humus molecule.

Humus consists of colloidal particles in the submicroscopic particle range. Not much work has been done regarding the particle size of the humus molecules. Black & Christman (1963b) studied the characteristics of color in water and concluded that there is a range of particle sizes and that most of the color particles are in the 3.5-10 μm diameter range.

Ishibashi (1980) used the electron-microscope to study floc growth when coagulating organic color with alum. Brewed tea diluted with tap water was used as the organic color. According to Ishibashi, an organic color from brewed tea is considered a colloid of humic acid and its colloidal stability differs with the level of the pH value of a solution. The raw water used for the experiments, had a pH of 7.5, 15 color units and 24 mg/l of alkalinity. At pH 7.5, many dispersed, discrete particles and some agglomerates of the smaller particles were seen, but careful observations suggested that the organic color particles are of almost the same size, ellipsoid, 0.05-0.07 μm of diameter, and may be discrete particles or the elements of agglomerates. The particles are shown schematically in Figure 7.

Hydrochloric acid was added to the raw water to obtain a pH of 4.5, and the electron microscopy showed many agglomerates and few discrete particles. The raw water was also mixed with clay colloid, resulting in 40 turbidity units. The organic color particles appeared to be adsorbed on the surface of the clay particles by mixing. Ishibashi (1980) suggested this to be due to some chemical reaction between the functional group on the surfaces of both particles, causing the adsorption to override the repulsion. Several authors have concluded that

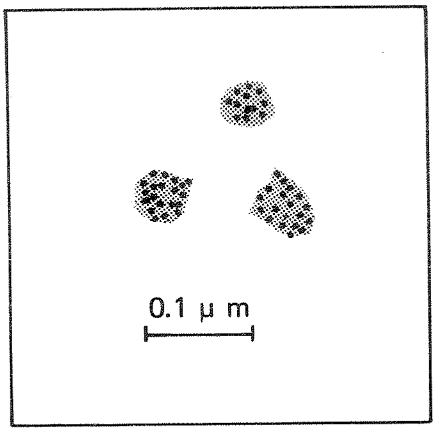


Figure 7. Organic color (schematic), made from brewed tea (Ishibashi, 1980).

humus has a net negative charge under normal conditions. Kodoma & Schnitzer (1968) stated that fulvic acid behaves like an uncharged molecule when the pH is below 4.

Gjessing & Gjerdahl (1972) studied the electromobility of the humus from Hellerudsmyra, using the isoelectric focusing technique. The method used was based on voltage applied to electrodes on both ends of an isoelectric focusing column. The column was filled with an acid anode solution with varying concentrations of sucrose to create a vertical density gradient. When voltage was applied to both ends of the column, a vertical pH gradient was developed and the aqueous humus migrated until it reached the pH zone where it was uncharged, i.e. the isoelectric point. The experiments showed that about 80 percent of the humus concentrated in the pH range of 1.25 to 1.75. The concentration of humus was measured as UV-absorption (cm^{-1}) at 254 nm. The UV-absorption is, in Figure 8 (Gjessing & Gjerdahl, 1972), presented as E_{254nm} (Extinction). The percent distribution of humus in different pH ranges is presented in Table 5. These results indicate that natural aquatic humus has a net negative charge even at pH = 1.5.

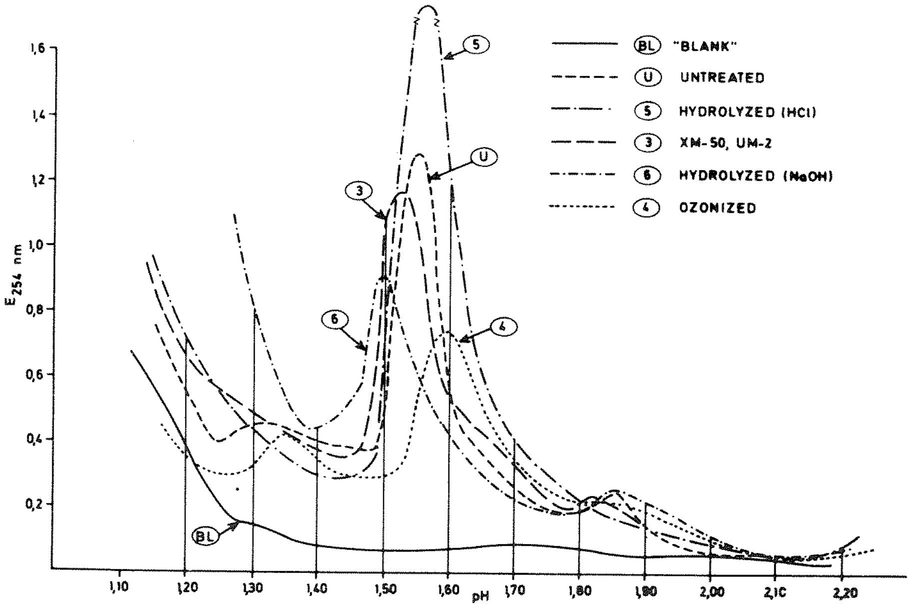


Figure 8. Effects of various pre-treatments of aquatic humus on its iso-electric focusing distribution pattern (Gjessing & Gjerdahl, 1972).

Table 5. Percent distribution of aquatic humus using isoelectric focusing technique (Gjessing & Gjerdahl, 1972).

Sample	pH-range			
	1.25 – 1.50	1.50 – 1.75	1.75 – 2.00	2.00 – 12
1	18	52	12	18
2	20	50	13	17
1, boiled	32	46	9	13
1, frozen	19	60	9	12
1 + ozon	25	45	16	14
1 + u.v.	10	22	22	46

Narkis & Rebhun (1977) studied humic and fulvic acids as anionic polyelectrolytes where the degree of ionization depends on pH. They used potentiometric titration of humic and fulvic acid. See Figure 9. Two inflection points were observed at the titration curves. The first, at pH 8.0 for humic acids and pH 8.2 for fulvic acids, was suggested to correspond to the phenolic - (OH) groups, and the second at pH 4.9 for humic acids and 4.6 for fulvic acid, to the carboxylic - (COOH) groups. The amount of the anionic functional groups expressed in me/100g of humic or fulvic acid was determined by the method recommended by Kononova (1966) and is presented in Table 6.

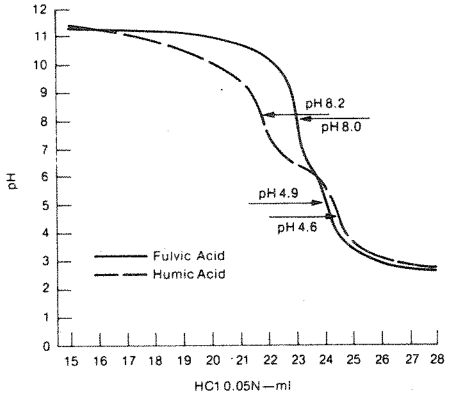


Figure 9. Potentiometric Titration curve of fulvic and humic acids (Narkis & Rebhun, 1977).

Table 6. Phenolic-OH and carboxylic-COOH groups in humic and fulvic acids (Narkis & Rebhun, 1977).

Acids	Anionic Groups		
	-OH me/100g	-COOH me Ca^{2+}/100g	Σ-COOH + OH me Ba^{2+}/100g
Fulvic	308	164	472
Humic	425	445	870

This table shows the exchange adsorption capacity of phenolate and carboxylate ionic groups in humic and fulvic acids. According to Narkis & Rebhun (1977), these anionic groups are responsible for the reaction of fulvic and humic acids with the chemicals used as flocculents in water treatment. At a pH below 8.0, the dissociation of the humic and fulvic acid is only partial. Narkis & Rebhun (1977) used this method to calculate the amount of effective positive charge in the flocculant molecule.

2.1.4 Humus - Metal Interactions

Ong & Bisque (1968) stated that humus can be considered true solutions of macro-ions or negative hydrophilic colloids and should have properties attributed to this type of colloid, such as coagulation of the humus colloids by different electrolytes. Ong & Bisque (1968) also report that coagulation of iron-humus complexes follows the Schulze-Hardy rule. The mean critical concentrations of ions of different valences are inversely proportional to the sixth power of their valence, i.e.:

$$(1/1)^6 : (1/2)^6 : (1/3)^6 = 1 : 0.016 : 0.0014.$$

Cations of the same valence with the largest ionic radius are the most effective coagulants. For the trivalent ions this rule does not apply, because they do not occur as simple cation species in solution, due to a high charge density. These results suggest that coagulation occurs by simple double layer compression. The double layer theory is, however, only valid for hydrophobic colloids. Ong & Bisque (1968) explained the effect of adding salt to the humus polyelectrolyte in the following way: "When the polyelectrolytes are dissolved in water, their functional groups, carboxyl and hydroxyl, become more or less dissociated. As a consequence of this, mutual repulsion of the negative functional groups occurs and the polyeletrolyte will assume a stretched configuration. Upon addition of salts, this behavior is radically modified. The cations will be attracted to the negative carboxyl and hydroxyl groups. This causes a reduction in the intramolecular coulombic repulsion in the polymer chain and thus favors coiling of the chain". This explanation follows the one proposed by Fuoss & Strauss (1948). Thus the humus macromolecule changes from a hydrophilic to a hydrophobic type of colloid which follows the Schulze-Hardy rule. Dempsey, O'Melia & Christman (1979) discussed the importance of cation-humus interaction which appears to be fairly strong. Moore (1977) found that more aluminum was needed to coagulate kaolinite in the presence of fulvic acid than without. He concluded that in the aluminum-fulvic acid-kaolinite system, fulvic acid must be titrated by aluminum before aluminum can react with the kaolinite or with hydroxide. Narkis & Rebhun (1975, 1977) found similar results when they used a cationic polyelectrolyte as a coagulant. When the polyelectrolyte was added to a clay or an organo-clay complex solution dispersed in humic or fulvic acids, the organic acids were found to react first. Only after complete reaction with the organic acids did the flocculation of the clay suspension begin.

Rashid (1971) extracted humic acid from marine sediments and fractionated these on Sephadex gels into different molecular weight fractions. He then determined the ability of a number of di- and trivalent metal ions to coagulate each of these humic acid fractions at pH 7.0. He found that the lowest molecular weight fractions complexed 2 to 6 times more metals than did the higher molecular weight fractions, and that the quantity of divalent metal complexed was 3-4 times higher than of trivalent metals. He also reported that the carboxyl groups participated in complexing of metals, but he could not find any evidence for the participation of phenolic hydroxyl groups.

Many authors have dealt with the humus-metal interactions, and Van Dijk (1971) pointed out that the capacity of humic acids to bind metal ions was, at most, equal to the number of titrable H^+-ions (carboxylic groups) divided by the valence of the concerning metal ions. Van Dijk (1971) used potentiometric titration in aqueous solution (humic acid prepared from soil) for studying the cation binding. He showed no large difference in bond strength for the divalent ions Ba, Ca, Mg, Mn, Co, Ni, Fe(II) and Zn at pH 5, but Pb(II), and Fe(III) were more strongly bound. At this same pH, Al-ions seemed to be quantitatively subject to the forming of hydroxide.

Wilson (1977) obtained data for metal-organic material interactions, and he combined the metal-organic data and the electrostatic information gathered in potentiometric titration measurements to model the competitive reactions (proton-organics vs. metal-organics) over a wide pH range. Dempsey et al. (1979) applied this same method for modelling the Ca(II) and humus interactions.

Clay minerals dispersed in natural waters adsorb humus. The extent of adsorption has been shown to depend upon the type of clay, the cationic form of the clay, and the pH (Schnitzer & Khan, 1972; Kodama & Schnitzer, 19-6). Greenland (1971) reviewed the adsorption of humus by clay and concluded that specific interactions between humus and polyvalent metals at the clay surface were responsible for the adsorption phenomenon. Greenland (1971) also emphasized the importance of iron and aluminum at the clay surface. The polyhydroxy complexes of these metals may provide positive sites on the clay surface and facilitate exchange adsorption. Like exchange reactions, this mode of adsorption is reversible and strongly influenced by the electrolyte concentration and pH.

Experiments have shown that a variety of metal ions may bind to humus (Gjessing, 1976). The nature of association is the subject of some debate. Mortensen (1963) has, according to Schnitzer & Khan (1972), described interactions between humus and metal ions as ion-exchange, surface adsorption, chelation, coagulation, and peptization processes. According to Snoeyink & Jenkins (1980) only two modes of binding appear to be significant. These are 1) the formation of complexes or chelates between the functional groups of the humus substance and the metal, and 2) an association between the humus substances and a colloidal particle of metal hydroxide (possibly through sorption on the surface of the particle) whereby the colloidal particles are peptized (stabilized) in suspension and prevented from coagulation or settling. Gjessing (1976) has reported results from metals bound to humus (Drozdova, 1968; Theile et al., 1960; Schnitzer & Hansen, 1970), see Table 7.

Table 7. Sorption of Cations onto Humus Substances (Gjessing, 1976).

Source	Type of Humus	pH	Series of Successive Sorptions
Drozdova (1968)	Humic acid from peat	--	Ra>Ba>Sr>Ca; Cs>Rb>K>Na>Li; $Zn^{2+}>Th^{4+}>La^{3+}>V^{3+}>Fe^{3+}>(UO_2)^{2+}$ $>Cu^{2+}>Fe^{2+}$
Tiele et al. (1960)	Peat suspension	--	Cu>Pb>Cd>Sr>Ca
Schnitzer & Hansen (1970)	Fulvic acid	1.7	$Fe^{3+}>$
		2.4	$Al^{3+}>$
		3.0	$Cu^{2+}>Ni^{2+}>Co^{2+}>Pb^{2+}$ $=Ca^{2+}>Mn^{2+}>Mg^{2+}$

Schnitzer & Khan (1972) have reported the findings of Szalay (1969) which indicate that the ability of humus materials to bind metals may lead to geo-chemical enrichments of 10^3 - 10^4:1 for metals including U, Co, Ni, Fe, Zn, Cu, and La. Gjessing (1976) suggested that it be differentiated between "outer" and "inner" humus-ion complexes. He suggested that a limited number of elements also form "inner" complexes with humus (Fe, Si, Al). Stevenson (1970, 1976) suggested that humus acts as an ultimate sink for trace metals in soils and sediments by removing metals from the water or by modifying the activity of the metals. Stevenson (1970) also pointed out the importance of understanding how humus becomes insoluble to describe how the "ultimate sink" functions. Nissenbaum & Swaine (1976) found that humus contained a sizeable portion of the Cu, Mo, and Sn found in sediments.

2.2 Aluminum

2.2.1 Aluminum Concentrations in Natural Water

The aluminum concentrations in natural waters vary a great deal. The concentration of aluminum in acidified lakes has been shown to be high. When soil is exposed to acid deposition, it acts as a buffer, and the most important cations for this buffering are calcium and magnesium. Aluminum, however, is present in much larger amounts in podsols, and when pH in the soil decreases, this metal will be solubilized.

Increasing leaching of aluminum has been noticed in lake waters. Dickson (1978) presented in Figure 10 the conditions in lakes of different pH on the Swedish west coast during the summer and autumn of 1976. The Al-concentrations increased from 10 to above 600 μg/l with decreasing pH from 7.5 to 4.0.

Wright et al. (1980) have presented data from 397 lakes in Europe and North America, showing total dissolved Al vs. pH. See Figure 11. The data presented in Figure 11 (Wright et al., 1980) show greater variance in total Al-concentration for a particular pH than Dickson's (1978) data show. The two "outliners" in Figure 10 represent two very

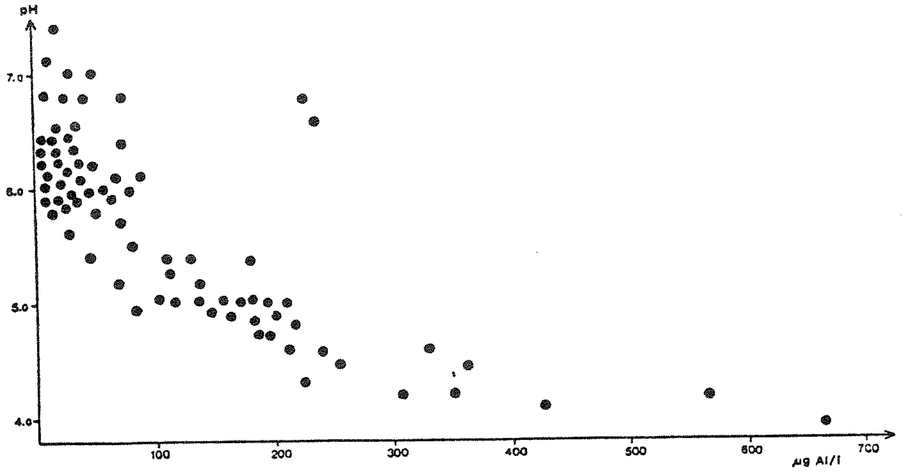


Figure 10. pH and concentration of aluminum in Swedish lakes, summer and autumn 1976 (Dickson, 1978).

brownish waters. It is known that organic matter, humus, may form complexes with aluminum, and the solutions of near neutral pH may contain 10-100 times the concentration of aluminum predicted from solubility data if formation of organic complexes is ignored (Lind & Hem, 1975).

Perdue et al. (1976) showed that a moderately good correlation existed between dissolved organic matter (DOM) and the concentrations of iron and aluminum in the Satilla River system in south-eastern USA. An excellent correlation between DOM and the sum of Al and Fe concentrations was, however, observed, indicating that the total solubility of the two metals is determined by the complexing capacity of the DOM. In Figure 12 the calculated least square line does not pass through the origin, possibly indicating that a small fraction of the available complexing sites is occupied by metals other than Al and Fe. Based

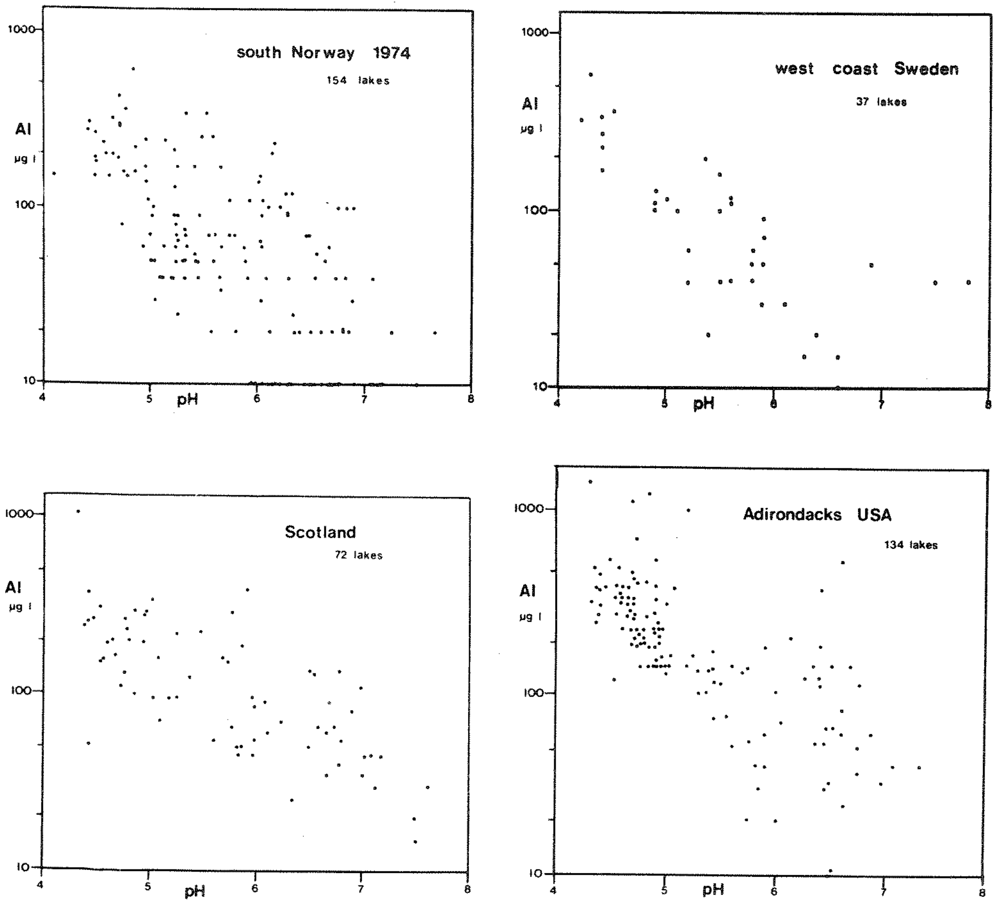


Figure 11. Total dissolved Al (note log scale) vs. pH in lakes in acidified areas in Europe and North America (Wright et al., 1980).

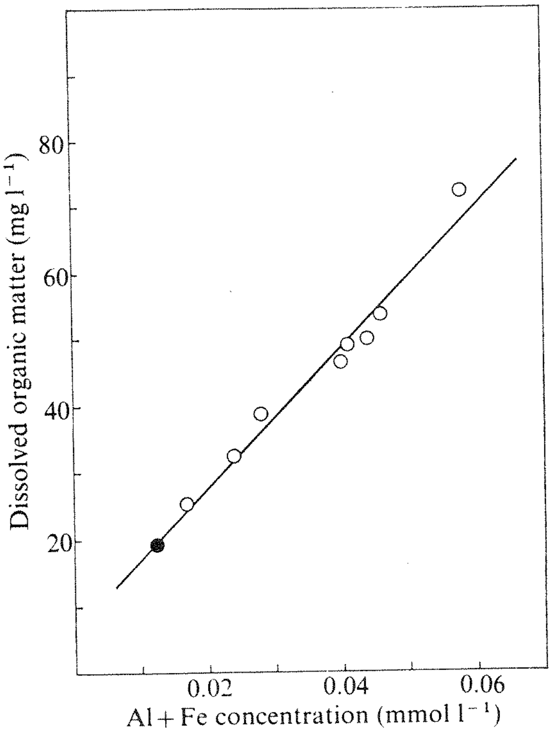


Figure 12. Correlation between dissolved organic matter (DOM) (mg 1^{-1}) and the sum of the concentrations of Al and Fe (mmol 1^{-1}) for the Satilla River system (○) and for the world average river (●).

The slope 1.058 + 78 (mg mmol^{-1}), intercepts at 6.6 and the correlation coefficient equals 0.984 (Perdue et al., 1976).

on stability constants of metal-fulvic acid complexes, Schnitzer & Hansen (1970) suggested Ca to be the only major cation which might be complexed to a significant extent.

The complexing capacity of humus has also been studied by Johansen (1978). During observations of lakes and rivers in regard to the acid rain project, a tremendous increase in aluminum concentrations was observed in storm periods. Johansen (1978) used natural humus water (Hellerudmyra) having a total Al-concentration of 400 μg Al/l, and added 250 and 1000 μg Al/l while pH was adjusted to 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, and 6.0. The samples were stored for one month, and then filtered through an ultramembrane filter where the main part of the humus was removed. The results showed that the highest amount of dissolved Al was found between a pH of 3 and 3.5. Increasing the pH resulted in increased amount of Al bound to humus. At a pH higher than 5.5 no Al went through the ultramembrane filter.

2.2.2 Aluminum Chemistry

The aqueous chemistry of aluminum is complex and diverse because of the numerous hydrolysis intermediates formed prior to the precipitation of aluminum hydroxide, $Al(OH)_{3(S)}$. The aluminum ion, Al^{3+}, behaves very much like Fe^{3+} in solution except that it has a greater tendency to form polynuclear species. According to Stumm & Morgan (1962) and Matijevic et al. (1966, 1964), there is a step-wise conversion of the positive aluminum hydrated ion to the negative aluminum ion. When aluminum salts are dissolved in water, the metal ion Al^{3+} hydrates coordinating six water molecules and forming an aquometal ion,

$Al(H_2O)_6^{3+}$. The aquometal ion can react forming several hydrolysis species, the simplest being monomeric and dimeric hydroxocomplexes where coordination occurs with OH ligands replacing the six coordinated H_2O molecules. For simplicity, the H_2O ligands attached to the Al ions are omitted and $Al(H_2O)_5OH^{2+}$ is written as $AlOH^{2+}$ etc. It is possible to suggest several hydrolysis species:

$$Al^{3+} \text{--->} AlOH^{2+} \text{--->} Al(OH)_2^{+} \text{--->} Al(OH)_{3(aq)} \text{--->} Al(OH)_4^{-} \text{--->}$$
$$Al(OH)_5^{2-} \text{--->} Al(OH)_6^{3-}$$

From the above species it is possible to build polymers with several of the hydrolysis products. The following products have been suggested:

$$Al_{13}(OH)_{34}^{5+};\ Al_7(OH)_{17}^{4+};\ Al_8(OH)_{20}^{4+};\ Al_6(OH)_{15}^{3+};\ Al_2(OH)_2^{4+}.$$

Different authors suggest different equilibrium constants for the aluminum products. There also exists a difference between freshly precipitated aluminum hydroxide, for example when adding aluminum to a water treatment process, and the thermodynamically stable $Al(OH)_{3(s)}$-phase, gibbsite. This material has the same composition. but a different, more well defined crystal structure (Snoeyink & Jenkins, 1980). The initial products of aluminum precipitation are amorphous with no definite ordered structure, but with aging they evolve into identifiable crystalline phases. At normal temperature, gibbsite forms very slowly in the acid pH range (Hayden & Rubin, 1974). Mixtures of pseudoboehmite, bayerite, and possibly norstrandite form in the alkaline range. Hayden & Rubin (1974) summarized solubility constants of the various phases. A few additional references are added in Table 8.

Table 8. Solubility constants for aluminum hydroxide.

The solubility constants refer to the following reactions:

$$Al(OH)_{3(s)} \overset{<---}{--->} Al^{3+} + 3\ OH^-$$

Phase	log K_{50}	Reference
Pseudoboehmite	-32.90 (20 °C)	Szabo et al. (1955)
	-31.72 (30 °C)	"
	-31.63	Hayden & Rubin (1974)
Bayerite	-32.95 (25°C)	Gayer et al. (1958)
Gibbsite	-32.65 (25 °C)	Hem et al. (1967)
	-33.51 (25 °C)	Frink (1960)
	-36.0	Snoeyink & Jenkins (1980)
Microcrystalline gibbsite	-32.0	Bersillon et al. (1978)
Synthetic gibbsite	-33.89	May et al. (1979)

Some of the various equilibrium constants involved in aluminum hydrolysis reactions are listed in Table 9. Researchers differ in their suggested equilibrium values.

Table 9. Equilibrium constants involved in the aluminum hydrolysis reaction.

	$\log {}^{*}K_{1.1}$	Reference
$Al^{3+} + H_2O \rightleftharpoons AlOH^{2} + H^{+}$	-5.55	Hayden & Rubin (1974)
	-5	Smith & Hem (1972)
	-5.01	May et al. (1979)
	-5.03	Kubota (1956)
Summarized by Hayden & Rubin (1974)	-4.89 (15 °C)	Bronsted & Volquartz (1928)
	-4.96 (25 °C)	Hartford (1942)
	-4.98 (25 °C)	Schofield & Taylor (1954)
	-5.10 (25 °C)	Ito & Yui (1954)
	-5.02 (25 °C)	Frink & Peech (1963)
	-5.00 (25 °C)	Raupach (1963)
	-4.75 (25 °C)	Hem & Robertson (1967)
	$\log {}^{*}K_{s4}$	
$Al(OH)_{3(s)} \rightleftharpoons Al(OH)_4^{-} + H^{+}$	-12.34	Hayden & Rubin (1974)
	-14.05	May et al. (1979)
Summarized by Hayden & Rubin (1974)		
Pseudoboehmite	-12.74	Szabo et al. (1955)
	-12.87	"
	-12.5	Brosset et al. (1954)
	-12.70	Hem & Robertson (1967)
Bayerite	-14.53	Gayer et al. (1958)
	-13.95	Hem & Robertson (1967)
	-13.84	Raupach (1963)

For more than twenty years, researchers have argued about the predominance and existence of the aluminum polymers. Hayden & Rubin (1974) designated $Al_8(OH)_{20}^{4+}$ as one of the principal species in equilibrium with $Al(OH)_{3(s)}$.

$$8Al^{3+} + 20\ H_2O \rightleftharpoons Al_8(OH)_{20}^{4+} + 20\ H^+,\ \log^* K_{8.20} = -68.7.$$

Stumm & Morgan (1962) suggested that $Al_2(OH)_2^{4+}$ and $Al_6(OH)_{15}^{3+}$ were present:

$$2Al^{3+} + 2H_2O \rightleftharpoons Al_2(OH)_2^{4+} + 2H^+,\ \log^* K_{2.2} = -6.27$$

(Kubota, 1956)

$$6Al^{3+} + 15H_2O \rightleftharpoons Al_6(OH)_{15}^{3+} + 15H^+,\ \log^* K_{6.15} = +163$$

(Brosset et al., 1954)

Snoeyink & Jenkins (1980) suggested that $Al_7(OH)_{17}^{4+}$ and $Al_{13}(OH)_{34}^{5+}$ were present:

$$7Al^{3+} + 17H_2O \rightleftharpoons Al_7(OH)_{17}^{4+} + 17H^+,\ \log^* K_{7.17} = -48.8$$

$$13Al^{3+} + 34H_2O \rightleftharpoons Al_{13}(OH)_{34}^{5+} + 34H^+,\ \log^* K_{13.34} = -97.4.$$

Amirtharajah & Mills (1980) emphasized that it is sufficient to accept the fact that these species exist, and that two important deductions follow from the existence of hydrolysis Al(III) species:

(1) Hydroxo metal complexes readily adsorb on surfaces and the charges that they carry, may cause charge reversals of the surfaces on which they adsorb (Matijevic & Stryker, 1966; O'Melia, 1972). It is evident that the hydrolysis products of aluminum in aqueous solution are adsorbed more readily than the free Al^{3+} ion. Matijevic et al. (1961) showed that the hydrolyzed aluminum species reversed the charge of the originally negative hydrolyzed halide ion whereas the simple hydrated Al^{3+} did not. According to Matijevic (1973), the greater the degree of hydrolysis, the more extensive the adsorption.

(2) The sequential hydrolysis reactions, release - H^+-ions, lowering the pH of the solution in which they are formed, and additionally, the concentration of the various hydrolysis species will be controlled by the final concentration of H^+-ions, i.e. pH (Amirtharajah & Mills, 1980).

In addition to the hydroxy-compounds formed by Al, other complexes are formed, such as the fluorides and sulfate complexes. Hem (1968) and Seip (1980) discussed their importance in natural waters. The stability constants for the fluoride complexes seem well established (Hem, 1968). Although fluoride is a minor constituent of most natural waters, the complexing action is strong enough to have a considerable influence on the form of dissolved aluminum even when very little fluoride is present. Seip (1980) did equilibrium calculations using the program MINEQL (Westall et al., 1976). Figure 13 presents one of his calculations based on the conditions described below the figure.

Aluminum sulfate is generally recognized as a more effective coagulant than aluminum nitrate. According to Black et al. (1933), sulfate has the effect of broadening the pH range of coagulation to the acid side.

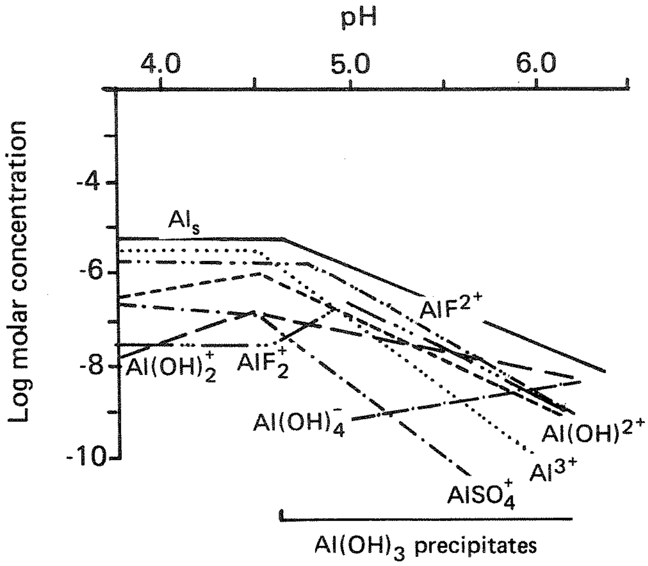


Figure 13. Concentration of main aluminum species under specific conditions.

Aluminum and Iron Concentrations:
$(Al)_T$ (incl. precipitate) $= 5 \cdot 10^{-6}$ mol/l = 135 μg/l
$(F)_T$ $(SO_4)_T$ $= 1.5 \cdot 10^{-6}$ mol/l = 28.5 μg/l
Al_S is the sum of aluminum species in solution
(Seip, 1980).

Figure 14 is taken from their work, illustrating the importance of increasing sulfate concentration. With increasing sulfate concentration progressively greater opportunity is afforded for the formation of mixed ligand complexes.

Matijevic (1973) reported the probable predominance of tetrapositively charged mixed ligand complexes of the form $Al_8(OH)_{10}(SO_4)_5^{4+}$ at pH values in the region 4.5 to 7.0 for aluminum sulfate applied to destabilize silver halide sols. Hanna & Rubin (1970) investigated the coagulation of the Gram negative bacterium Escherichia coli using aluminum nitrate and aluminum sulfate. Changes in turbidity during

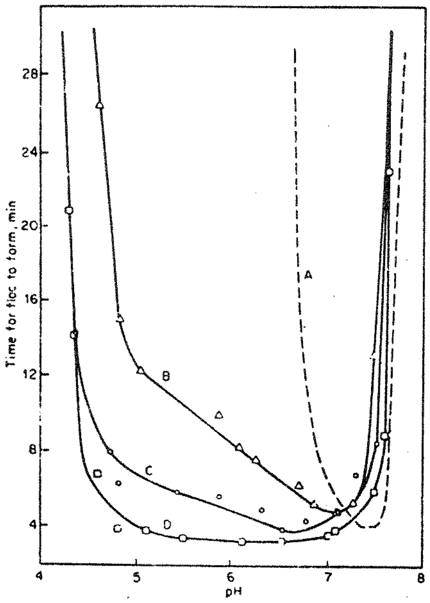


Figure 14. Effect of sulfate ion on time of formation of alum floc. Broadening of the pH zone of coagulation by sulfate ion.

Curve A, alum (35 mg 1^{-1}) and sodium hydroxide;

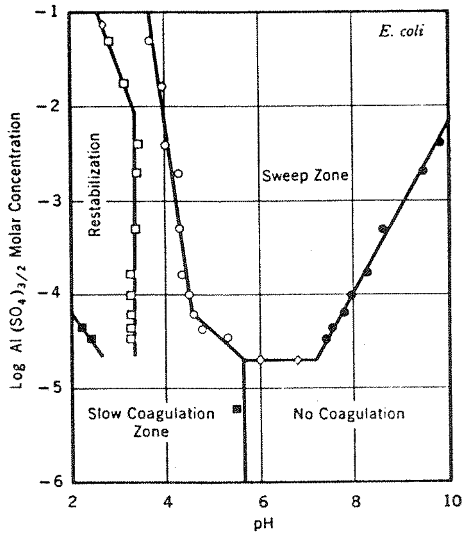
Curve B, addition of 25 mg $1^{-1}SO_4$;

Curve C, addition of 50 mg $1^{-1}SO_4$;

Curve D, addition of 125 mg $1^{-1}SO_4$.

(Black et al., 1933.)

settling were used as an indication of aggregation, and the entire aluminum nitrate- and aluminum sulfate concentration - pH "domain of stability" for the coagulation of the organisms was established. Nitrate is considered a weak coordinator with aluminum and the results were assumed to be due only to hydrogen ions and Al^{3+} and its hydrolysis products. Their results are presented in Figures 15 and 16, where Figure 15 contains only the aluminum sulfate domains and Figure 16 has filled in the data from aluminum nitrate.



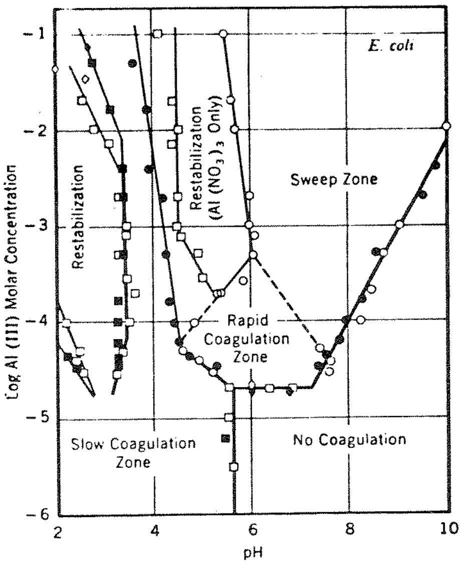


Figure 15. Aluminum sulfate domain stability (Hanna & Rubin, 1970).

Figure 16. Comparison of aluminum nitrate and aluminum sulfate domains (Hanna & Rubin, 1970).

Hanna & Rubin (1970) showed also that addition of a slight amount of sodium sulfate to the same concentration of aluminum nitrate produced and immediately widened the sweep zone toward lower pH while having no effect on the higher pH boundary. Hanna & Rubin (1970) reported the differences between the two domain diagrams to be related to the basicity of the anions and consequently to the coagulating or aggregating species formed. Bratby (1980) summarized the effect of the presence of sulfate anions on destabilization with metal coagulants as follows:

> At pH values greater than approximately 7.0, added sulfate has very little effect since minimal displacement of OH^- occurs. As the pH is lowered, SO_4^{2-} progressively displaces OH^- forming complexes with an $[Al] : [OH]$ ratio of 1 : 1.25 compared to complexes with an $[Al] : [OH^-]$ ratio of 1 : 2.5.

2.2.3 Reaction Rates for Aluminum Compounds

Not only is the equilibria of Al(III) hydrolysis important, it is also important to analyze the kinetics of the coagulation reactions. The coagulation reactions are interactions between the hydrolysis products of Al(III) and the colloidal suspension. A few attempts have been made to establish the rate of these reactions. O'Melia (1972) summarized the data presented by Hahn (1968) concerning the reaction rates of hydrolysis and polymer formation for Fe(III) and Al(III). The time necessary for the formation of monohydroxo-complexes ($AlOH^{2+}$), which are readily adsorbed at interfaces, is very short, probably in the order of 10^{-10} seconds. The formation of polymers is slower, in the order of 10^{-2} to 1 sec. After being either formed within the system or added to it, these polymers are next adsorbed on the particles to be aggregated. The transport of polymeric species to these interfaces is accomplished by diffusion. Hahn (1968) estimated the time required for the adsorption of Al(III) hydroxometal polymers to be in the order of 10^{-4} sec., for larger materials with molecular weights of a few million, one or a few seconds may be required for significant adsorption to occur. Wiese & Healy (1975) did heterocoagulation studies with mixed colloidal dispersions of titania and alumina. They found the heterocoagulation to depend markedly on the conditions of mixing and equilibration of the dispersions. The effects were shown to be due to the dissolution of Al(III) species and their subsequent readsorption at the titania-water interface. The adsorption step was shown to be faster than the rate of coagulation with the result that the rate of heterocoagulation was determined by the rate of dissolution of alumina. Bratby (1980) summarized data on reaction rates and the time needed for adjusting the structure of the double layer to be of the order 10^{-8} sec. and for a Brownian collision (diffusion) of the order 10^{-7} to 10^{-3} sec. According to Amirtharajah & Mills (1980), sweep coagulation which involves formation of $Al(OH)_{3(s)}$ and entrapment of the colloid amidst the precipitate is a slower process and occurs in the range of 1-7 sec.

2.2.4 Effects of Residual Aluminum Concentrations

A water of pH 4-5 is toxic to many fish species. According to Dickson (1978), a naturally occurring concentration of 0.2-0.6 mg Al/l and a low pH will increase the toxicity considerably. Jones (1964) set the lethal concentration limit for aluminum to 0.07 mg/l (stickleback) in acidic water. Everhart & Freeman (1973) stated that in less acidic water tolerable concentrations of Al should not exceed 0.1 mg/l for sensitive fish species. Driscoll et al. (1980) subdivided the total Al-concentration in three fractions; organic monomeric aluminum including the organically chelated aluminum, inorganic monomeric aluminum including free aluminum, and aqueous inorganic complexes (fluorides, hydroxides and sulfates). The third fraction, acid soluble aluminum, was determined as total aluminum minus total monomeric colloidal, extremely stable organic and hydroxy organic complexes. According to Driscoll et al. (1980), the inorganic aluminum forms seem to be the major species of concern in regard to aluminum toxicity in fish. In acidified Adirondack waters the organically complexed aluminum was the dominant form, and according to this work, the complexation of aluminum with organic ligands seems to eliminate toxicity.

Burrows (1977) discussed the toxicity of aluminum and emphasized that,since aluminum is such a ubiquitous element, the toxicity is very difficult to resolve. Although the toxicity of soluble aluminum has been demonstrated for a wide spectrum of plants and animals, the overwhelming percentage of aluminum in the world is without measured toxic effect.

A few countries throughout the world have drinking water standards for aluminum:

<u>Denmark</u> (Miljøministeriet, 1980):

Maximum level:	0.2 mg Al/l
Recommended level:	0.05 mg Al/l

Norway (SIFF, 1976):	
Maximum level for Al-treated water:	0.1 mg Al/l
West Germany:	
Maximum level:	0.2 mg Al/l
Belgium:	
Maximum level:	0.1 mg Al/l
France:	
Maximum level:	Acceptable
Sweden:	
Maximum level:	0.15 mg Al/l.

The Norwegian drinking water standards give only a maximum level for Al when the water is treated with aluminum. According to SIFF (1976), too high a residual Al-concentration after water treatment might result in precipitation of aluminum hydroxide in the pipes. Such precipitation usually occurs if the Al-concentration is higher than 0.1 mg/l.

Costello (1980) discussed the problem of postprecipitation in distribution lines in systems feeding high dosages of alum to eliminate color. Costello (1980) referred to the water facility in Manatee County, Florida. The color is reduced from 300 to 5 mg Pt/l by aluminum sulfate treatment. The treated water has a turbidity of 0.5 JTU when leaving the plant, but when entering the tap, the turbidity has increased to 2.0 JTU. The aluminum concentrations in treated water were found to be high, and this aluminum caused flocculation to occur thus increasing the turbidity.

2.3 Coagulation

2.3.1 Definitions and Possible Mechanisms

Bratby (1980) gave a few definitions which will be used here. Conversion of the stable state of a given dispersion or solution to an unstable state is termed destabilization. Such processes could either 1) alter the surface properties of particulate material and thereby increase the adsorptivity of the particles to a given filter medium or generate a tendency of aggregation of small particles into larger units, or 2) precipitate dissolved material and thereby create particulate material for which separation by sedimentation and/or filtration is feasible.

Coagulation is the process whereby destabilization of a given suspension or solution is affected. That is, the function of coagulation is to overcome those factors promoting the stability of a given system.

Flocculation is the process whereby destabilized particles, or particles formed as a result of destabilization, are induced to come together, make contact and thereby form larger agglomerates.

Coagulation and flocculation involve aggregation of particles into larger, more readily settleable aggregates. Aggregation of colloidal particles can according to O'Melia (1972), be considered to involve two separate distinct steps:

(I) Particle transport to affect interparticle contact. (fluid and particle mechanisms.)

(II) Particle destabilization to permit attachment when contact occurs. (colloid and surface chemistry.)

There exist four distinct methods for destabilization of colloids:

(1) Compression of the diffuse layer

(2) Adsorption to produce charge neutralization

(3) Enmeshment in the precipitate

(4) Adsorption to permit interparticle bridging.

O'Melia (1972) discussed the four methods:

(1) Compression of the diffuse layer involves purely electrostatic interactions. The phenomenon is described by the theoretical Verwey-Overbeek model and the empirical Schulze-Hardy rule. The coagulants are called indifferent electrolytes and they are of limited interest in water and wastewater treatment processes. The concentrations of Na^+, Ca^{2+} and Al^{3+} required to destabilize a negatively charged colloid are observed to vary approximately in the ratio of 1 to 10^{-2} to 10^{-3}. The ionic strength is of major importance, but the salt concentration required for effective destabilization is too high for water treatment applications. Overdosing of chemicals is not possible.

(2) Adsorption and charge neutralization produce destabilization at low dosages and restabilization occurs. Restabilization is accompanied by charge reversal. If coulombic interaction were the only driving force for destabilization, such an adsorption of excess counter ions

to produce reversal of charge and restabilization would not be possible. Aluminum salts used in coagulation have been shown to follow this mechanism at low Al-dosages.

(3) Enmeshment in a precipitate (also called sweep coagulation) can occur at high dosages of metal salts. The concentration of $Al_2(SO_4)_3$ must be sufficiently high to cause rapid precipitation of $Al(OH)_{3(s)}$ so that the colloid particle can be enmeshed in these precipitates. To the first approximation, the rate of precipitation of a metal hydroxide is dependent upon the extent to which the solution is oversaturated. The extent of oversaturation is described by $\{Al^{3+}\} \cdot \{OH^-\}^3/K_s$. For very rapid precipitation, the ratio must be 100 or even larger. In neutral and acid pH the rate of precipitation is also increased by the presence of anions in solution. Sulfate ions are particularly effective. The colloidal particles serve as nuclei for the formation of the precipitate so that the rate of precipitation increases with increasing concentration of the colloidal particles to be removed. The greater the amount of colloidal material in water, the lower the amount of metal coagulant required.

(4) Adsorption and interparticle bridging usually occurs when polymers are used as destabilizing agents in the treatment of water and wastewater. The mechanism will therefore not be discussed here.

Bratby (1980) illustrated the three first mechanisms, in Figures 17a and 17b.

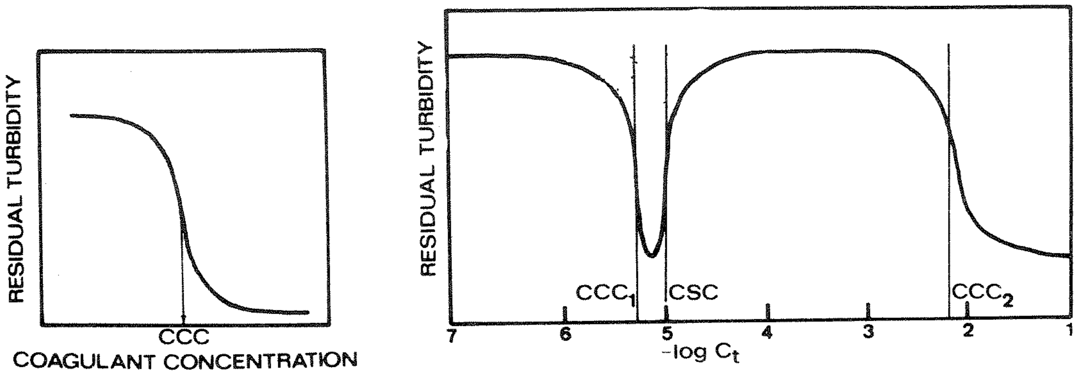


Fig. 17a: Destabilization characteristics where an electrical double layer repression mechanism is predominant. Increasing the coagulant concentration beyond the critical coagulation concentration (CCC) has no effect.

Fig. 17b: Destabilization characteristics where adsorption of coagulant species to colloidal particles is operative. CCC_1 and CSC signify the concentrations, C_t, of coagulant necessary to destabilize and restabilize, respectively, the dispersion. A further critical coagulation concentration; CCC_2, indicates the occurrence of a double layer repression or enmeshment mechanisms of higher coagulant dosages (Stumm & O'Melia, 1968).

Figure 17. Determination of critical coagulation concentration (CCC) (Fig. 17a) and critical stabilization concentration (CSC) (Bratby, 1980).

Amirtharajah & Mills (1980) did an extensive literature review, summarizing important coagulation studies. In Figure 18 they summarized in schematic form the proposed predominant mechanism in coagulation with alum as coagulant, and in Figure 19 a design and operational diagram for alum coagulation. Skeletal forms from Rubin & Kovac (1974) and McCooke & West (1978) have been used. Figure 19 shows the very specific areas where coagulation would occur and also the major mechanisms causing coagulation. According to Amirtharajah & Mills (1980), minor changes should be expected on the restabilization zone depending on the type of colloid. The area for optimum sweep coagulation, that is

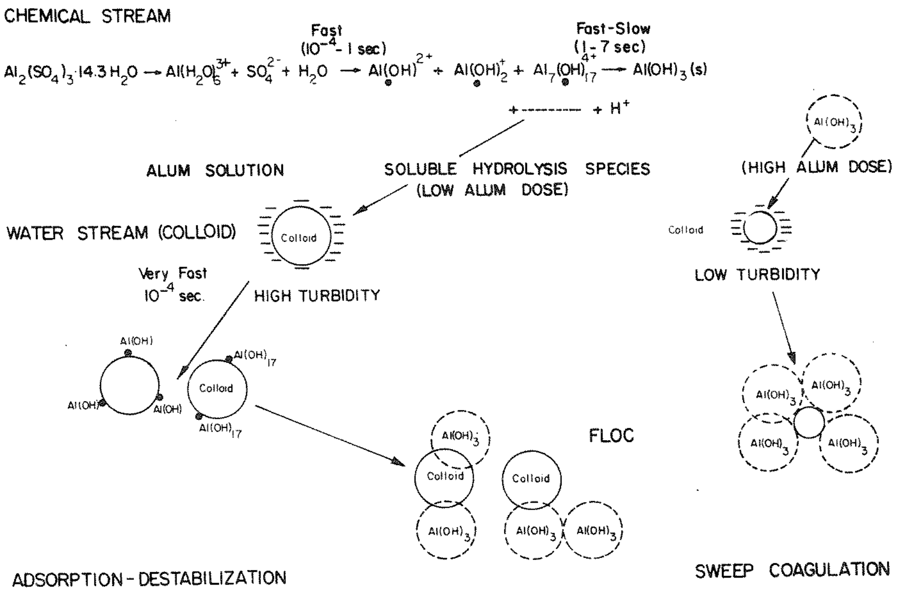


Figure 18. Reaction schematics of coagulation (Amirtharajah & Mills, 1980).

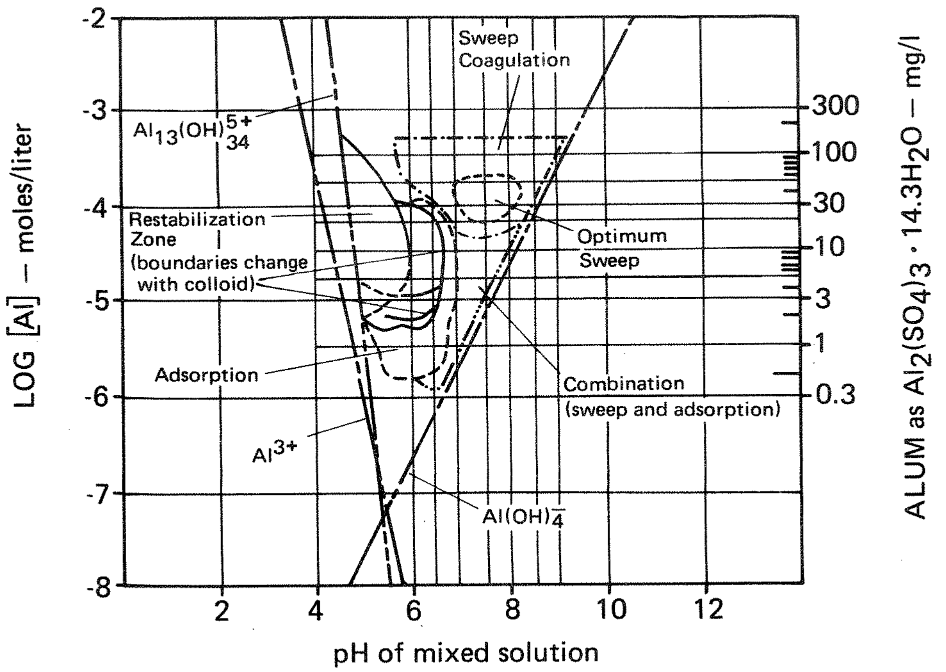


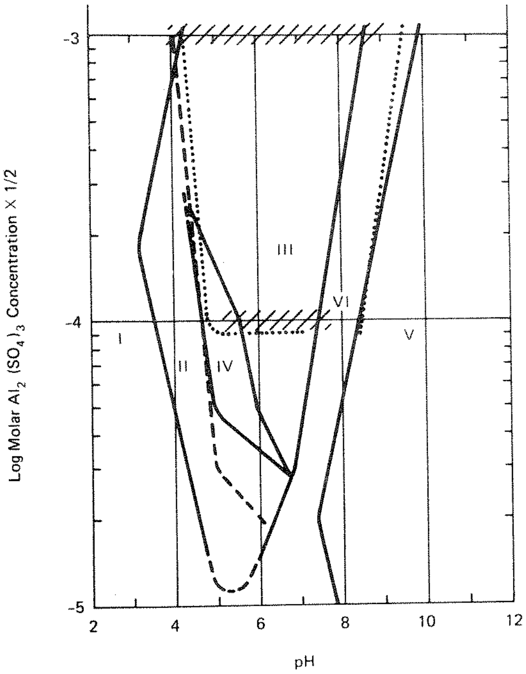
Figure 19. Design and operation diagram for alum coagulation (Amirtharajah & Mills, 1980).

the area for best settling floc with the lowest coagulant dosages, is specifically defined by the major parameters of alum dose of 20-50 mg/l with a final pH of 6.8-8.2.

2.3.2 Destabilization of Aquatic Humus

Very few investigations reported in the literature deal specifically with the coagulation of naturally occurring organics (aquatic humus), while a few deal with humic and/or fulvic acid and color. Hall & Packham (1965) found a stoichiometric relationship between the optimum coagulant dose for 50 percent organics removal and the raw water concentration of humic and fulvic acids, with a higher coagulant dosage required for fulvic than for humic acid. Narkis & Rebhun (1977) also found a stoichiometric relationship between humic and fulvic acid content in solution and the cationic polyelectrolyte or alum dose required for effective flocculation. The stoichiometry between raw water color and optimum coagulant dosage has also been reported by Black et al. (1963). Ferric salts, in general, have been found to yield slightly lower color residuals after destabilization. However, the optimum dosage for lowest residual color in each case appears, according to Bratby (1980), to be the same if concentrations are expressed in terms of the metal ion. The mechanism of destabilization for the different coagulants is therefore suggested to be the same. In Mangravite et al.'s (1975) coagulation study, humic acid was used. The system clearly demonstrated the complex phenomena involved when humic acid interacts with aluminum salts. Clarification of humic acid suspension after coagulation with $Al(NO_3)_3$ and $Al_2(SO_4)_3$ was studied (Mangravite et al., 1975). Turbidity as a function of pH was used to define the critical pH values separating pH regions of differing sol stability. The aluminum sulfate - pH stability domain determined for the humic acid sol is presented in Figure 20.

The humic acid remained stable in region I. In region II the sols were coagulated or precipitated by soluble, hydrolyzed, polynuclear aluminum cations. The boundary between region I and II below $2x10^{-4}$ M Al coincided with the hydrolysis of the aluminum ions. Within region III the humic acid was unstable. Based on equilibrium constants for



Regions: I, stable sols; II, sols coagulated by soluble aluminum species; III, sols destabilized, aluminum hydroxide present; IV, sols coagulated but stable; V and VI, stable sols. Dotted lines outline the region within which aluminum hydroxide precipitates in the absence of humic acid. Dashed line gives the pH of humic acid–$Al_2(SO_4)_3$ systems before pH adjustment. Systems with pH values greater than the dashed line had their pH adjusted with NaOH. Systems at pH values lower than the dashed line had H_2SO_4 added. Hatching gives pH range where 50 per cent or greater humic acid removal occurred after 5 min of microflotation at 10^{-3} and 10^{-4} M aluminum [$Al_2(SO_4)_3$].

Figure 20. Aluminum sulfate-pH stability domain for the humic acid sol (5.0 mg/l) 24 hr after mixing the reacting components (Mangravite et al., 1975).

the formation of $Al(OH)_3$ and $Al(OH)_4^-$, and on the experimental conditions for $Al(OH)_3$ precipitation in the absence of sols (dotted lines), the presence of aluminum hydroxide is expected throughout this region. Humic acid was removed both in regions II and III, showing that aluminum hydroxide precipitation is not the only condition necessary for color removal. In region IV the sols are aggregated but stable. Electrokinetic data suggest that the stability in region IV is accompanied by charge reversal. The region's lower boundary is the result of an insufficient number of aluminum ions to stabilize the particles whereas its upper boundary or point is believed to result from coagulation of the positively charged sols by divalent sulfate ions. In region VI the sols are stable, but exhibit turbidities higher than uncoagulated humic acid. Formation of aluminate anion is expected in regions V and VI but especially in region V. The destabilization was shown to be fastest in the region where aluminum hydroxide was formed (region III, Figure 20). Between about pH 4 and 6, adsorption of highly charged aluminum species produced charge reversal and sol stability.

Edzwald (1978) illustrated also the stoichiometry in coagulation of humic acid with alum as presented in Figure 21.

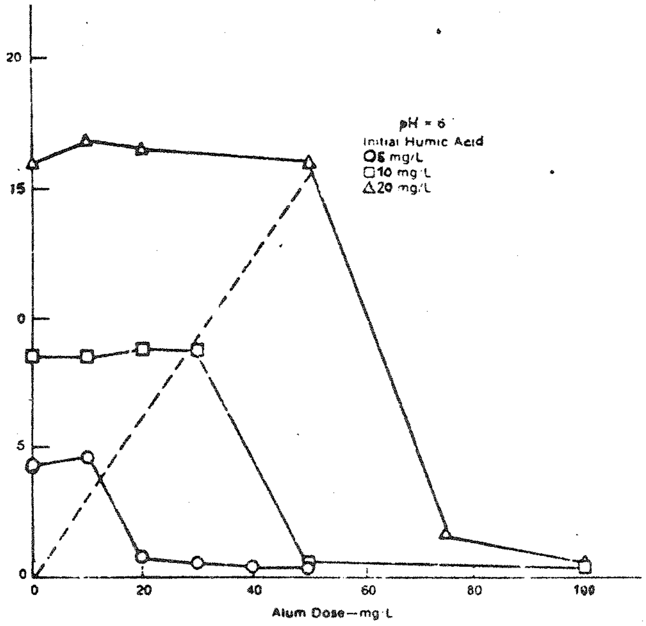


Figure 21. Stoichiometry of coagulation of humic acid with alum at pH 6 (Edzwald, 1978).

The coagulation of humus with aluminum can, according to a Committee Report (1979) be accomplished through two mechanisms of destabilization; charge neutralization or precipitation. The destabilization accomplished by charge neutralization results from a specific chemical interaction between positively charged aluminum species and the negatively charged groups of the humus colloids. This could be accomplished over a narrow pH range (pH 4-6) and a stoichiometric relationship between the raw water humus concentration and the optimum coagulant dosage would be observed. Humus can form water-soluble and water-insoluble complexes with metal ions. As the alum dosage is increased, precipitation may occur; however, destabilization by this mechanism may incorporate the humus material within the aluminum hydroxide floc (sweep coagulation) or co-precipitate it as aluminum humate. The optimum operation region for water treatment plants was pointed out to be the hatched area in Figure 20 (region III).

Also Semmens & Field (1980) studied the organics removal using alum. They used water from the Mississippi River taken close to the point of extraction for the Minneapolis water treatment plant. The total organic carbon content varied between 10 and 16 mg C/l, and the turbidity ranged between 2 and 25 NTU. The water was freeze concentrated. The coagulation process with alum as the sole coagulant resulted in significant organics removal from the Mississippi River water. The removal was found to be strongly pH and dose dependent, see Figure 22. Semmens & Field (1980) reported a difference in pH measured before flocculation and after filtration. See Figure 23. The final pH of the water was generally higher, according to the authors, because of CO_2 loss in the

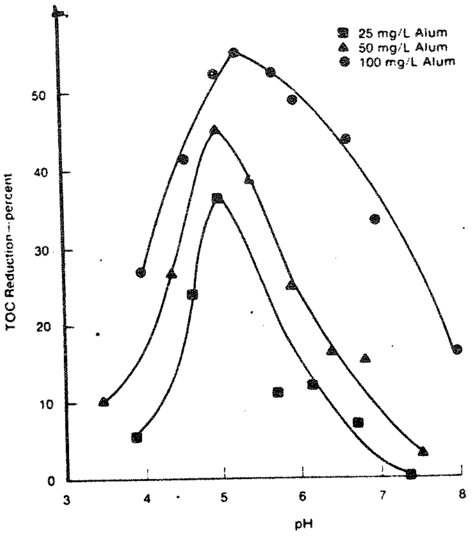


Figure 22. TOC removal as a function of pH and alum dose (Semmens & Field, 1980).

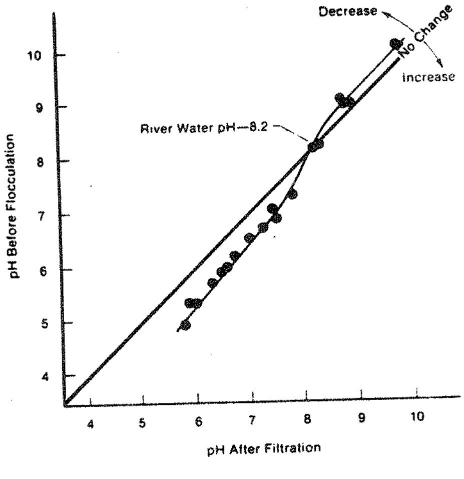


Figure 23. Relationship between pH before flocculation and pH after filtration (Semmens & Field, 1980).

flocculator. The optimum pH was found to be pH 5.0 in the rapid mix, corresponding to a final pH of 5.6 to 5.8.

Also the influence of varying flocculation times on turbidity and organics removal was examined. The flocculation time was varied between 10 and 30 min. The authors showed that the organics removal was unaffected by the mixing time.

The order of addition of chemicals was also studied. The experimental procedure used was addition of alum followed by pH adjustment, all prior to the flocculation process. The same water sample was studied over the entire pH range changing the order of addition and showed no significant impact on organics removal.

Semmens & Field (1980) proposed that several mechanisms were involved in organics removal including adsorption of the organics to insoluble aluminum species. TOC removal data obtained at fixed pH (5.0; 6.0; and 7.0) were used to construct a plot of organic loading per mg Al versus the final organic concentration (TOC_f). See Figure 24. The organic loading of the alum increased linearly with the remaining TOC. The results clearly document the poorer organics removal capacity of alum at higher pH values. Semmens & Field (1980) pointed out that the intercept on the abscissa should reflect the portion of the initial organic content that was impossible to remove effectively by alum. The intercepts obtained at pH values of 5.0 and 7.0 were almost identical and indicate that 6.9 to 7.2 mg C/1 or 35-40 percent of the TOC in the sample tested could not be removed by coagulation. The authors suggested that the increase in TOC loading of the alum with increasing solution TOC values (equilibrated solution) was similar to adsorption

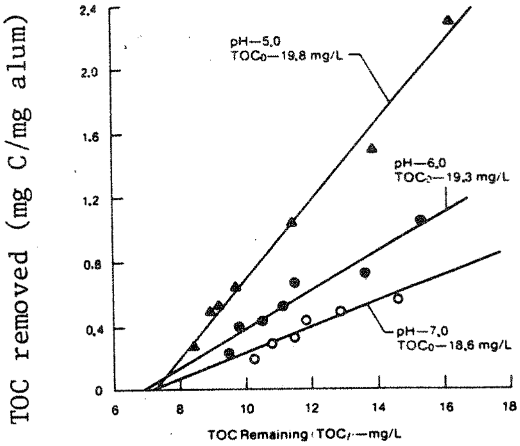


Figure 24. Organics loading as a function of TOC remaining and pH (Semmens & Field, 1980).

isotherms obtained for TOC removal with powdered activated carbon, indicating adsorption of organics to the $Al(OH)_3$ precipitate to be important.

Kavanaugh (1978) presented data from a case study at the Bollman Water Treatment Plant where enhancement of coagulation was studied as a method for reducing the trihalomethane precursors. Standard jar test techniques were used to determine optimum coagulation conditions for reduction of TOC. The initial TOC concentration was approximately 5.6 mg C/l. The results were presented as a log alum dose versus pH. The dashed lines are isoconcentration levels (isopleths) of TOC remaining after coagulation and settling. The optimum pH was between 5 and 6. The minimum TOC level attainable was 1.5 mg C/l with doses of 1.1 mM/l. See Figure 25.

Narkis & Rebhun (1975) studied the mechanism of flocculation processes in the presence of humic substances and showed that the presence of organic matter inhibited the flocculation process for

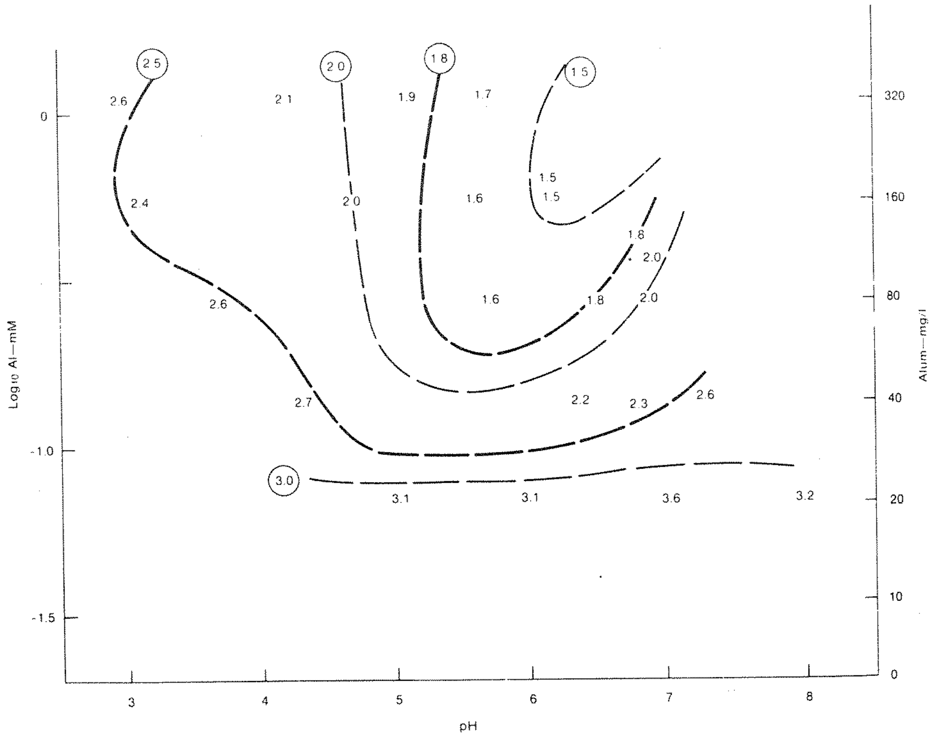


Figure 25. Coagulation of Contra Costa Canal water with Al(III).

Circled numbers indicat TOC isoconcentration lines developed from jar test studies. Initial TOC value = 4.5 mg C/l, temperature = 18°C (Kavanaugh, 1978).

clay removal thus requiring large alum dosages.

In the pulp and paper industry the increasingly stringent regulations of the quality of wastewater have resulted in studies on the coagulation process for color removal. Clarke & Davis (1969) studied color removal from kraft mill chlorination-stage bleachery waste. Both $Al_2(SO_3)_3$, pH adjusted with NaOH, and $AlCl_3$, pH adjusted with $Ca(OH)_2$, were used. The raw water had a color of 320 mg Pt/l, TOC of 90 mg C/l, and pH of 2.2. The results are presented in Figure 26(A) and (B) and show that a maximum of 40-50 percent of the carbon can be

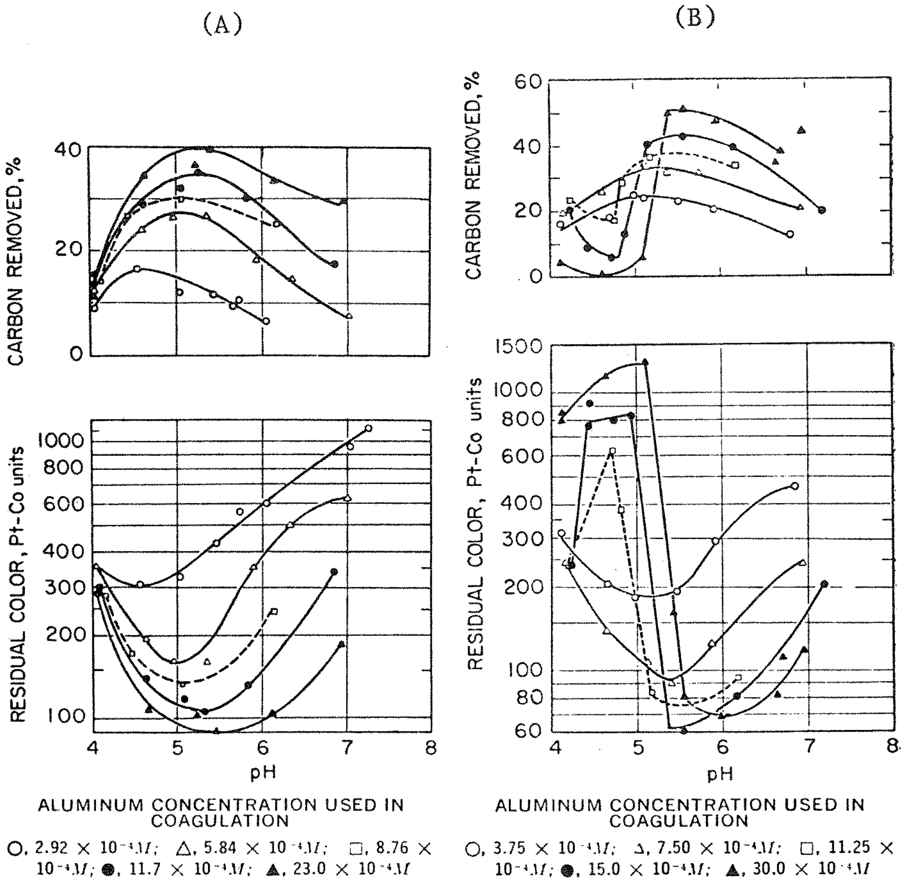


Figure 26. Effect of pH and aluminum concentration on residual color and carbon from kraft mill chlorination bleachery waste

(A) the $Al_2(SO_4)_3$ - NaOH system

(B) the $AlCl_3$ - $Ca(OH)_2$ system (Clarke & Davis, 1969).

removed while more than 80 percent color can be removed. Optimum pH was around 5.5.

Tejera & Davis (1970) did a similar study on caustic extraction waste which accounts for about 90 percent of the total color found in the bleaching process. Al^{3+} concentrations, from 10^{-3} to $14x10^{-3}$ M were used, and pH was varied between 2 and 10 with NaOH and HCl for pH adjustment. The raw water used had the following composition; pH =

10.5; color = 10,000 mg Pt/l; TOC = 600 mg C/l. Optimum removal of color and TOC by $AlCl_3$ was obtained between pH 4.0 and 5.0.

Approximately 96 percent color removal and 85 percent TOC removal were obtained when using either $AlCl_3$ or $FeCl_3$ as coagulant. Both coagulants were about 12 times more effective for bleachery caustic extraction waste than for bleachery chlorination waste. The optimum color and TOC removal using either $AlCl_3$ or $Al_2(SO_4)_3$ was obtained in the pH range of 4-5. About 95 percent of the color and 76 percent of the TOC was removed at pH = 4.8 at an $Al(SO_4)_3$ dosage of 0.00167 mole/l (= 0.00335 mole Al/l). The results are presented in Figure 27(A) and (B).

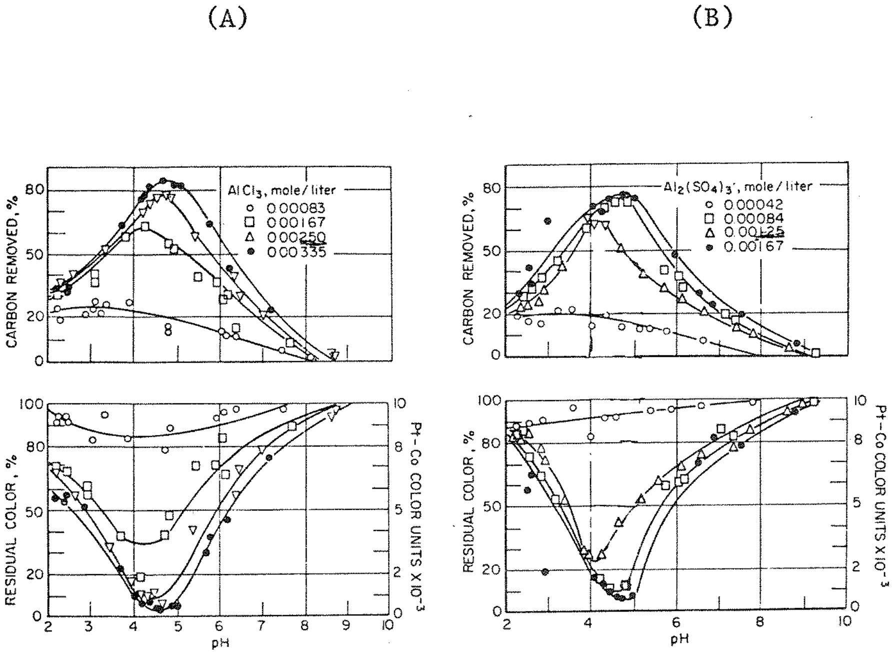


Figure 27. Effect of pH and aluminum concentration on color and TOC removal from caustic extraction waste
(A) $AlCl_3$ - NaOH(HCl) system
(B) $Al(SO_4)_3$ - NaOH(HCl) system (Tejera & Davis (1970).

Randtke & Jepsen (1980) studied coagulation of organic substances from five different sources in order to increase the adsorptive capacity of activated carbon. The five sources of organics were (1) a local ground-water supply, (2) a humic acid, (3), (4) and (5) different preparations of fulvic acid. There were differences in the coagulant used, the initial concentration of TOC, and the percentage of removable TOC for the different sources of organics. Randtke & Jepsen accounted for this by the use of the "Stoichiometric Coagulant Dosage Index" (SCDI) defined by;

$$\text{SCDI} = \frac{1000\ (\text{CD}_{50})}{\text{TOC}_R}$$

where TOC_R = concentration of removable TOC in mg/l

CD_{50} = coagulant dosage, mM required to remove 50 percent of TOC_R.

In using the SCDI, it was assumed that only removable organics exerted a coagulant demand. The SCDI for experimental data is presented in Table 10.

Table 10. Stoichiometric Coagulant Dosage Index (SCDI) for organic substances coagulated with alum and ferric sulfate at pH 6.0.

Substance	Humic acid	Podzol-soil fulvic acid	Peat fulvic acid	Urbana ground water
Alum	4.2	8.4	10.8	16.9
Ferric sulfate	17.0	-	22.7	24.5

The humic acid exerted a lower coagulant demand than fulvic acid. Alum was superior to ferric sulfate for the removal of these particular organics. The removable organics in the ground-water appeared to be similar to fulvic acid, although a large fraction of the organics in the ground-water was not removable. Randtke & Jepsen (1980) also illustrated the importance of inorganic water quality. Addition of $CaCl_2$ or synthetic tap water rather than distilled deionized water markedly decreased the alum dosage required to remove peat fulvic acid. The effect of cations, such as calcium or magnesium in reducing the required dosage of coagulant, suggested that complex formation plays an important role in the removal of organics by coagulation.

The removal characteristics are discussed by the authors, defining a type I pattern of TOC removal, being characterized by a sharp increase in removal at a certain coagulant dosage below which removal was minimal and above which removal was essentially complete. The second pattern of removal, type II, was characterized by a gradual increase in removal with increasing concentration of coagulant, approaching maximum, but incomplete removal, at high coagulant dosage. Type I removal was observed in all the three types of fulvic acids and for the humic acid while type II removal was observed for the natural ground-water sample. Interesting to notice is that Babcock & Singer (1979) observed type I removal for the humic acid studied and with respect to the color removal of the fulvic acid, but type II for the TOC removal of the fulvic acid. Randtke & Jepsen (1980) indicate the possibility that type I removal could be expected for relatively homogeneous colloidal suspension while type II removal could be expected for soluble organics.

2.3.3 Factors Affecting the Coagulation Process

There are several factors affecting the coagulation process. Hahn & Stumm (1968) summarized the rate of agglomeration to be a function of (1) the collision frequency which can be determined by physical parameters such as colloid size and concentration and velocity gradients in the medium, and (2) the collision efficiency factor reflecting the stability of the colloid, where the relative stability can be determined as a function of chemical solution parameters such as pH, the ratio of coagulant concentration and surface concentration of the dispersed phase. In addition to these factors, aluminum sulfate is, according to Hanna & Rubin (1970), generally recognized as a more effective coagulant than aluminum nitrate. The authors referred to a study by Miller, who already in 1925 investigated the influence of sulfate, chloride, phosphate and oxylate on the coagulation of aluminum salts. He reported that the pH of coagulation was dependent on the anion present. Miller postulated that the effects were due to the formation of a solid solution of aluminum salts in aluminum hydroxide. Similar studies reported by other investigators, evolved a pattern. Chloride ion at high concentrations was found to shift the pH of optimum coagulation slightly to the acid side. Sulfate, in concentrations of 25 to 250 ppm, was found to widen the range of rapid coagulation toward the acid side, the widening effect becoming greater with increasing concentration of sulfate ion. A somewhat different effect was found with phosphate; even at very low concentrations a marked shift in the pH of optimum coagulation to lower pH values resulted in little or no broadening of the pH range. Hanna & Rubin (1970) established the entire log concentration - pH domain of stability for coagulation by aluminum sulfate and compared this with the similar stability domain previously established for coagulation by aluminum nitrate. The domains showed differences related to the basicity of the anions and consequently to the coagulating species formed.

De Hek et al. (1978) compared the role of the sulfate ion with other anions (NO_3^-, Cl^-) and suggested it to be like that of a catalyst which removed the free energy barrier to the orientation and ordering of plate like, highly charged, polynuclear complexes into growing solid particles, so that precipitation occurred at a much earlier stage (OH/Al ratio$\gtrsim$0.4).

Hahn & Stumm (1968) noted that the rate of formation of coagulating species by hydrolysis and condensation reactions of Al(III) was strongly dependent upon the reaction temperature, the reaction proceeding slowly at low temperature. Few researchers have studied the effect of low temperature although several have registered reduced treatment efficiency.

Mohtadi & Rao (1973) studied the effect of temperature on coagulation of aluminum sulfate with bentonite and kaolinite clays dispersed in distilled water. The optimum pH for a given degree of flocculation was shown to vary with temperature. Hedberg (1975) studied soft, highly colored surface water using aluminum sulfate as coagulant. Decreasing the temperature from 20 ^oC to 0 ^oC increased the viscosity 50 percent. Increased viscosity made it difficult to obtain even distribution of coagulant in the raw water. The mixing was reduced for the same energy input. Hedberg discussed the increase in shear forces with increasing viscosity noting that the flocs formed were reduced and the sedimentation rate reduced. Results from the laboratory research are presented in Figure 28, showing that decreased temperature reduces the sedimentation rate.

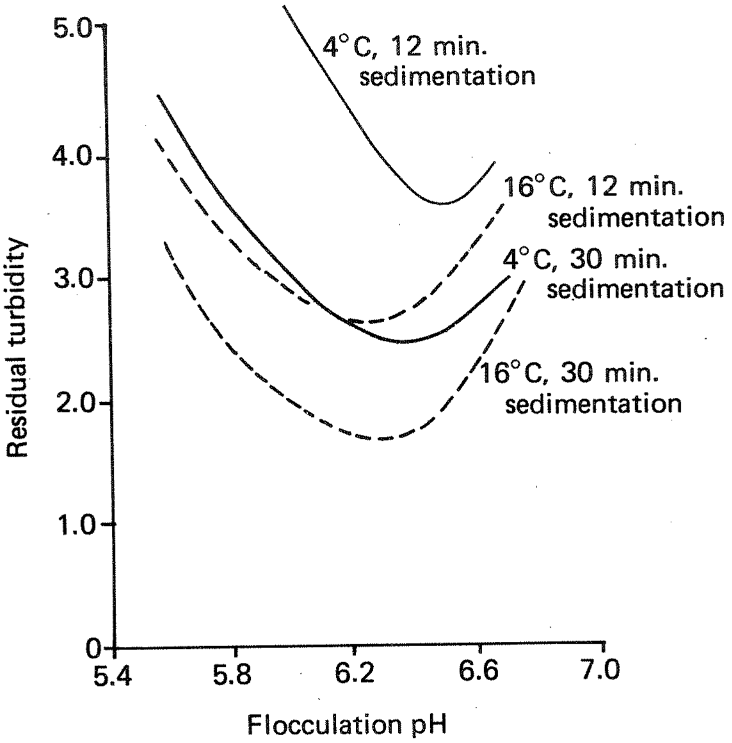


Figure 28. Turbidity as a function of pH for water temperatures 4°C and 16°C after 12 and 30 minutes of sedimentation (Hedberg, 1975).

Jeffcoat & Singley (1975) studied the effect of alum dilution on coagulation and showed that better turbidity removal occurred when more dilute alum solutions were added. Kawamura (1973) performed coagulation tests on four different waters and varied the alum solution from 0.05 to 20 percent. He found poor turbidity removal occurring in a concentration range of 0.25 to 5.0 percent alum. The floc formation time was always greater in the range of 0.25-2.5 percent alum. Kawamura placed the alum dose into the sample jar before addition of the water sample. This might account for the fact that his results differ so much from others (Griffith & Williams, 1972).

Jeffcoat & Singley (1975) discussed different aspects regarding the chemical addition sequence. The chemical addition sequence was studied by Nickel (1945) who stated that in organic-color coagulation the addition of lime or some other type of alkali should be made after the addition of alum. He further stated that, for turbidity removal, any pH adjustment should be well ahead of the coagulant addition in order to obtain the most economical results. Mofett (1968) stated that all pH-affecting chemicals, such as lime, soda ash, acid and chlorine, should be added upstream of the rapid mixer to ensure complete dissolution and mixing. According to Jeffcoat & Singley (1975), Walker (1971) reported that all pH adjustments should be made before the addition of alum. He stated that "lime added simultaneously with the alum (or iron) may cause mechanical growth problems on the rotating mixers".

Kawamura (1973) studied the effects of the sequence of chemical addition on both turbidity and color removal. Table 11 is a summary of the results obtained by Kawamura. He stated that the colloidal particles would be stabilized if lime were added before or with alum. This stabilization would be the result of the adsorption of calcium, hydroxide and carbonate ions on the micelle structure of the colloidal particles. He concluded that lime should be added 10-20 s. after the addition of alum.

Table 11. The effects of sequence of lime and alum addition on turbidity and color removal (Kawamura, 1973).

Sequence of lime addition	Lime dosage mg/l	Alum dosage mg/l	Residual turbidity FTU	Residual color Hazen u
Before alum	5	40	1.7	3.0
With "	5	40	2.5	3.5
After "	5	40	1.0	2.8
Before alum	10	45	2.5	3.5
With "	10	45	2.5	3.5
After "	10	45	1.8	3.0
Before alum	40	120	3.5	3.5
With "	40	120	3.8	3.5
After "	40	120	3.0	3.3

Jeffcoat & Singley (1975) concluded from their study of turbidity removal that the best results at an alum dosage of 40 mg/l were obtained when lime was added before alum. At dosages of 50 and 60 mg/l the best results were obtained when lime was added before alum down to a concentration of 0.25-0.5 percent alum. The simultaneous addition of alum and lime produced the best results when alum solutions containing $\leq$ 0.25-0.5 percent alum were used.

The importance of rapid-mix parameters has been discussed by several researchers. The major consideration in rapid mixing has been uniform dispersion of the coagulant with the raw water in order to avoid over and under treatment of the water. Amirtharajah & Mills (1980) discussed the two modes of destabilization in relation to influence of rapid mix, based on the reaction rates previously discussed in Figure 18. For adsorption-destabilization, they emphasized that the coagulants had to be dispersed in the raw water stream as rapidly as possible (less than 0.1 sec.) so that the hydrolysis products, which develop in 0.01 to 1 sec., cause destabilization of the colloid. For sweep coagulation the reactions occur in the range of 1-7 sec. The extremely short disperson times and high intensities of mixing are thus not so crucial as when adsorption-destabilization is the predominant mechanism. Vråle & Jorden (1971) discussed the importance of rapid mix and recommended instantaneous blender type mixing (< 1 sec.) based on chemical theories of adsorption-destabilization. They also discussed the different destabilization theories in regard to mixing conditions. Letterman et al. (1973), however, recommended detention times of several minutes for rapid mixing for promoting best floc characteristics for subsequent flocculation and settling without discussing the coagulation mechanisms involved.

Amirtharajah (1978) recommended that the rapid mix device be a high intensity blender type or a back mix reactor depending on the major mode of coagulation. Amirtharajah & Mills (1980) established boundaries under which conditions for each mechanism predominate. See Figure 19. They did experiments to determine whether the kinetics of coagulation of the various mechanisms were influenced by the coagulant transport step needed for hydrolysis and precipitation of alum to occur. A suspension of colloid with an initial turbidity of 17-27 T.U. and alkalinity of 80 mg $CaCO_3$/l was used. The alum dosages varied between 1 and 40 mg/l and pH between 4 and 9 to cover the specific zones in the alum stability diagram. Three different modes of rapid mixing were utilized; (1) the flat bladed mixer in the standard jar-test apparatus providing a velocity gradient, G of 300 $sec.^{-1}$ for 60 sec., giving a Gt value of 18,000; (2) a propeller type mixer giving a G value of 1,000 $sec.^{-1}$ for 20 sec., giving a Gt value of 20,000, and (3) a blender giving a G value of approximately 16,000 $sec.^{-1}$ for approximately 1 sec., giving a Gt value of 16,000. The rapid mixing of a sample of 500 ml was followed by slow mixing at a G value of 25 $sec.^{-1}$ for 20 minutes and the settled supernatant was measured at intervals of 15 minutes for a period of two hours. The results were presented in Figure 29.

Amirtharajah & Mills (1980) summarized the results:

(1) Under optimum sweep conditions (Figures 29 (D) and (F)) there is no difference in results when varying the G value.

(2) Under adsorption-destabilization conditions (Figures 29 (C), (E) and (G)) the high intensity blender type rapid mixing is superior to the backmix reactors.

(3) In the restabilization region (Figure 29 (B)) there is no difference in the results.

(4) In the region defined as combination coagulation the rapid mixing mode produces no significant difference in the rate of coagulation-flocculation-sedimentation. (Figure 29 (A).)

It is generally recognized that the velocity gradient or G-value concept is a gross, simplistic and totally inadequate parameter for design of rapid mixers. However, until a more detailed understanding of rapid mixing is possible, this parameter will continue to be used as the only available means for designing the hardware of a rapid mix unit. The particle transport occurs either by (1) Brownian motion (perikinetic); or (2) velocity gradients in the suspended medium

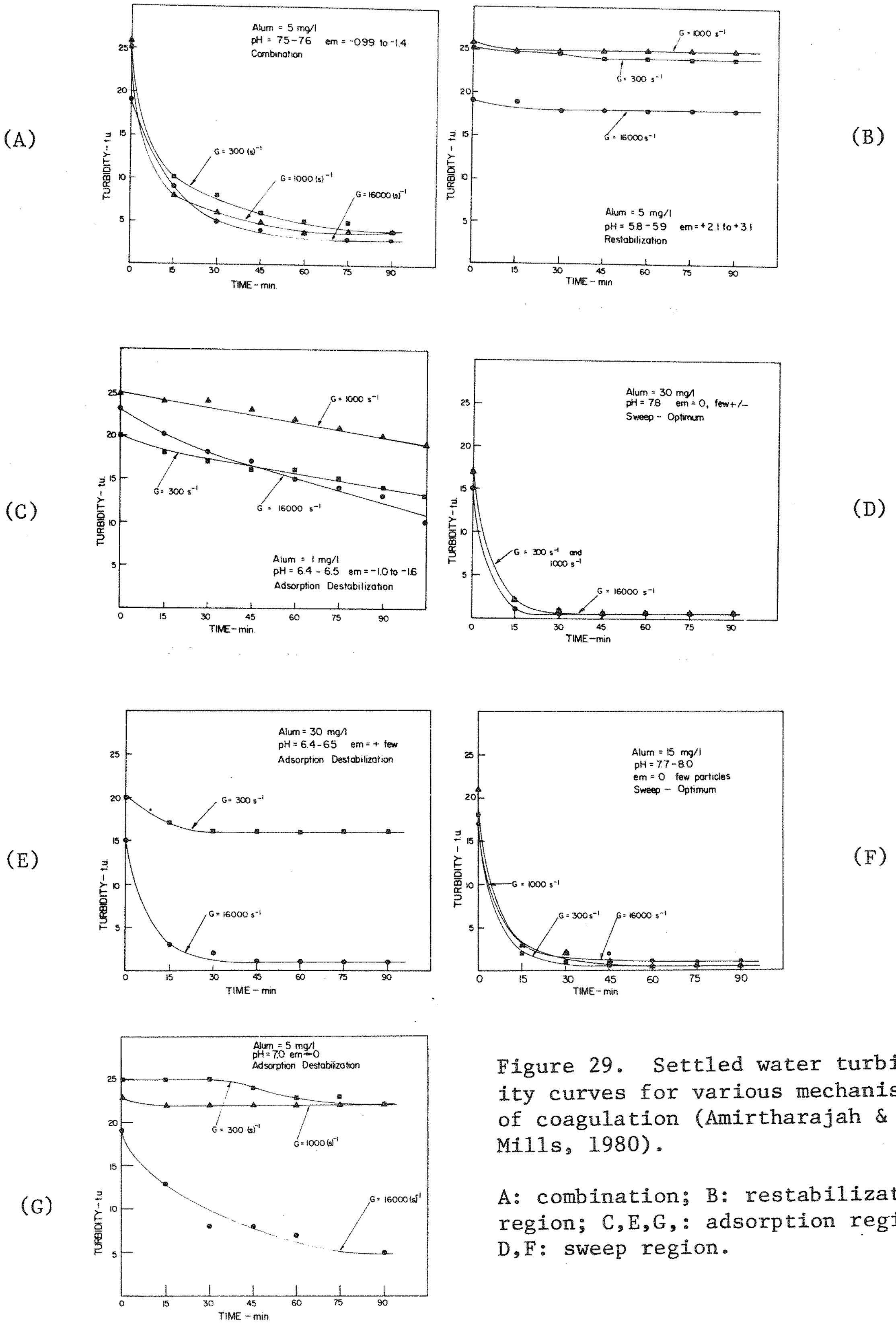


Figure 29. Settled water turbidity curves for various mechanisms of coagulation (Amirtharajah & Mills, 1980).

A: combination; B: restabilization region; C,E,G,: adsorption region; D,F: sweep region.

(orthokinetic), which depends on temperature, velocity gradients, number, concentration, and size of colloidal particles. O'Melia (1972) discussed the particle transport as;

(1) Perikinetic flocculation for a suspension of particles of uniform size. The role of change in the total number of particles is

$$\frac{dN}{dt} = -\frac{4}{3}\frac{kTN^2}{\mu} \qquad (1)$$

where N is the total number of particles at time t,

k is Boltzmann's constant,

T is the absolute temperature, and

μ is the fluid viscosity.

(2) Orthokinetic flocculation , a homogeneous suspension subjected to agitation causing velocity gradients. The rate of change in the total number of particles is

$$\frac{dN}{dt} = -\frac{2}{3}G\,d^3N^2 \qquad (2)$$

where G is a mean velocity gradient and

d is the diameter of the particles.

Both these equations assume 100 percent efficiency of coagulation. The relative importance of these two mechanisms is

$$\frac{\text{Orthokinetic rate}}{\text{Perikinetic rate}} = \frac{\mu\frac{1}{2}Gd^3}{kT} \qquad (3)$$

This ratio is unity at 25 °C, 1 μm particle diameter and a velocity gradient of 10 sec.^{-1}.

Camp and Stein (1943) presented an equation for estimating the mean velocity gradient, G ($sec.^{-1}$), in terms of the power input, P (watts), to the system as

$$G = \left(\frac{P}{\mu V}\right)^{\frac{1}{2}} \qquad (4)$$

where μ = dynamic viscosity of the liquid (NS/m^2)

and V = volume of the system (m^3).

Fair et al. (1968) discussed two different systems;

Baffled flocculation chambers;

$$\text{The power input, } P = Q \cdot \rho_1 \cdot g \cdot h_f \qquad (5)$$

where Q = the flow rate (m^3/s)

ρ_1 = fluid density (kg/m^3)

g = gravity acceleration constant (m/s^2)

h_f = head loss in the tank (m)

The mean velocity gradient;

$$G = \left(\frac{Q \cdot \rho_1 \cdot g \cdot h_f}{V \cdot \mu}\right)^{\frac{1}{2}} = \left(\frac{g \cdot h_f}{\nu \cdot \bar{t}}\right)^{\frac{1}{2}} \qquad (6)$$

where ν = kinematic viscosity

$\bar{t}$ = mean detention time of the fluid in the tank.

Using Fair et al. (1968)'s concept for calculation of the head loss in a baffled channel (Figure 30) with (n-1) equally spaced baffles and velocity v_1 and v_2 gives:

$$h_f = n \cdot v_1^2/2g + (n-1) \cdot v_2^2/2g \qquad (7)$$

The normal channel friction is not included in this equation.

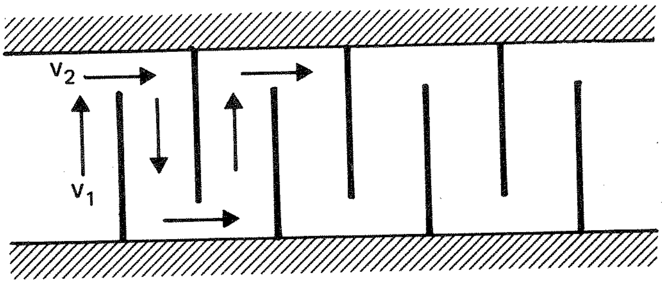


Figure 30. Flow through a (n-1) equally spaced over- and under- or around-the-end baffles. (Okun et al., 1968).

Amirtharajah (1978a) reviewed typical alternatives in design, mechanical mixing, in-line blenders, hydraulic mixing, diffusers and injection devices. For the most commonly used unit, the mechanical mixer with a propeller impeller, the requirements have been suggested by ASCE, AWWA and CSSE (1969) (Table 12).

Table 12. Contact time and velocity gradient for rapid mixing (ASCE, AWWA & CSSE, 1969).

Contact time, sec.	20	30	40	>40
Velocity gradient, sec^{-1}	1000	900	790	700

Typical practice in design is, according to the same reference, to provide 10 to 30 sec. contact time.

Camp (1968) presented velocity gradient calibration curves for water, using the 2 l pyrex beaker often used in jar-tests (Figure 31). The curves show that 100 rpm, which is often used in jar-tests, gives a velocity gradient around 100 sec^{-1} which, according to Table 12, is low for rapid mixing.

In-line blenders are favored by several authors. Kawamura (1976) gives three reasons: (1) they provide good instantaneous mixing with little short-circuiting, (2) there is no need for head loss computations, and (3) cost can be reduced by omitting a conventional rapid mix facility. According to Amirtharajah (1978a), Hudson (1976) suggested using in-line blenders with residence times of 0.5 sec. and water power of 0.37 kW per 43.8 l/sec of flow. Head losses in the manufactured units range from 0.3 to 0.9 m.

Hydraulic jumps used for mixing need no replacement parts and are easy in operation. Typical head losses are 0.3 m or greater with detention times of 2 sec. and G-values of 800 sec^{-1}. Diffusers and injection devices have proved to be effective. Vråle & Jorden (1971) showed that a tubular orifice reactor proved superior in performance to the backmix reactor. The reactor functioned with low head loss at an approximate G-value of 1000 sec^{-1}.

Kawamura (1976) described design of an injection nozzle-type flash mixing unit. The design criteria suggested were:

- G = 750 to 1000 sec^{-1}
- dilution ratio at maximum alum dosage = 100:1
- velocity at injection nozzles = 6 - 7.6 m/sec
- mixing time = 1 sec.

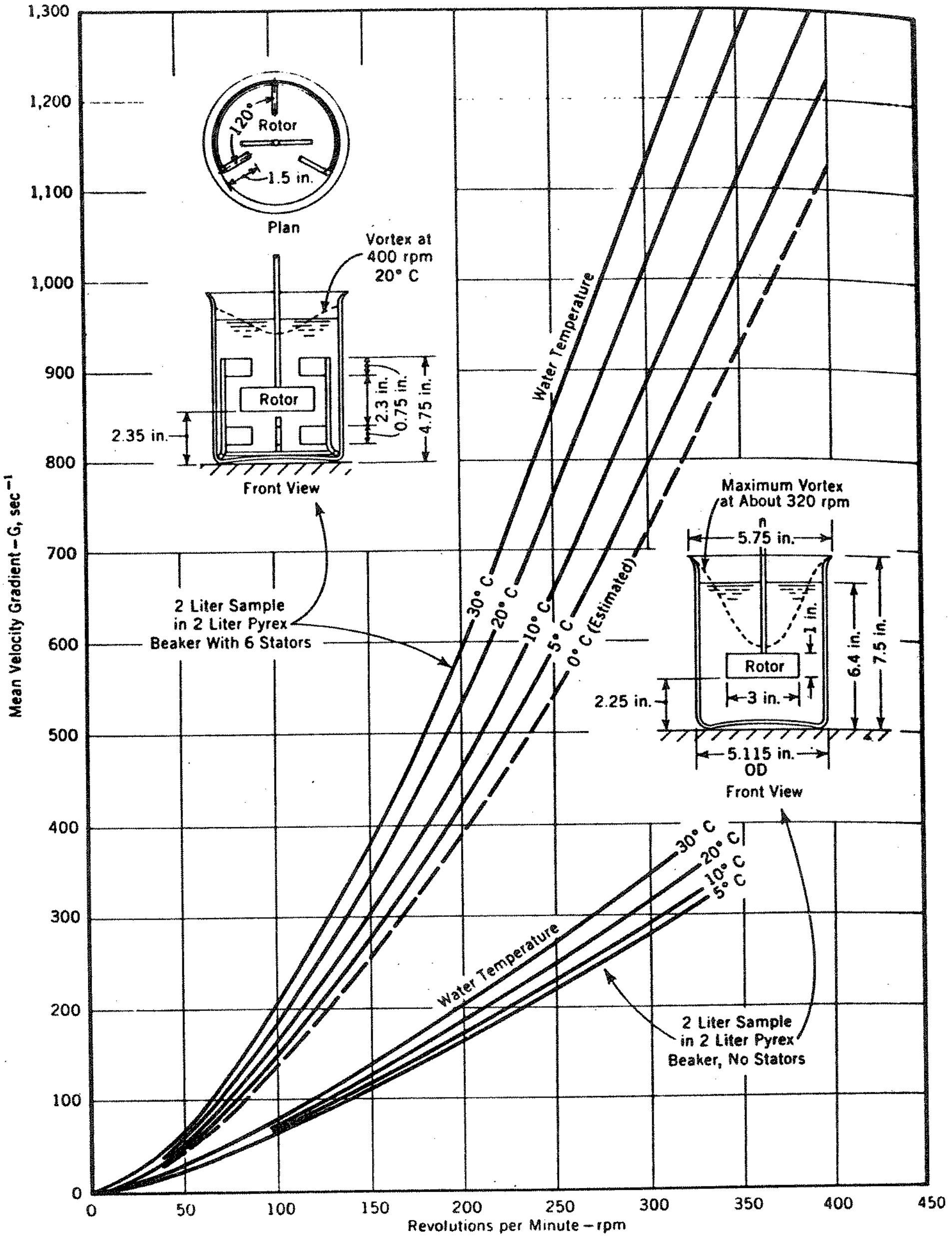


Figure 31. Velocity gradient calibration curves for water (Camp, 1968).

Amirtharajah (1978a) summarized available experience and concluded that for the adsorption-destabilization mechanism the coagulants must be dispersed in the raw water as rapidly as possible (less than 0.1 sec), and instantaneous mixing or an in-line blender would be an appropriate design. However, when the major mechanism appears to be sweep coagulation, a backmix reactor would be efficient.

2.3.4 Electrochemical Processes in Water and Wastewater Treatment

Early development of electrolytic sewage treatment had a primary interest in generating chlorine for deodorizing and disinfecting wastewater. Eugene Hermite (Marson, 1965) took out two British and French patents in 1887 describing a method of treating sewage by mixing it with a proportion of seawater and electrolyzing. He believed that magnesium salts in seawater had a useful effect. An electrolyzer was used involving carbon anodes surrounding a revolving platinum-covered cylinder which was continuously wiped to remove the deposit of magnesium carbonate building on it. The most impressive effect of the process was the de-odorization. The town of Worthing was almost ruined by a typhoid epidemic in 1892, and the following year an experimental Hermite plant was installed (The Engineering, 1894). Ipswich had an odor nuisance from the main sewer under the market place, and after witnessing the Worthing tests, the Council installed a plant which was completely successful running for ten years. The price of platinum increased dramatically, but the second process was continuously used, seawater being electrolyzed and added to the sewer. Further plants were installed in East London, Le Havre and other towns during the 1980s.

Miller & Knipe (1963) made a survey of published work on electrolytic treatment of sewage and wastewater. They referred to the earliest record found on electrolytic sewage treatment, a patent issued to William Webster in 1889 (U.S. Patent, 1889). The sewage was electrolyzed with iron electrodes at a potential of about 10 volts. If insufficient chlorides were present to generate chlorine, seawater or salt was added. Iron electrodes were specified to take advantage of the formation of hydrated iron oxides which aided in sludge flocculation. A plant was built in Salford, England, for purifying canal water. In 1909, J.T. Harries received a patent (U.S. Patent, 1909) on a method for purification of wastewater by electrolysis. This system was unique in that both iron and aluminum were used together as anodes and were allowed to corrode during electrolysis. It was claimed that if either metal was used alone, it could not be completely precipitated; however, almost complete removal of metal ions could be achieved with the combination and better clarification of the solution. Copper was employed to aid in disinfection. A small electrode, either anode or cathode, was claimed to be sufficient and not to add "harmful" amounts of copper to the solution. Electrolytic sewage treatment plants were in operation as early as 1911 in Santa Monica, California, and Oklahoma City, Oklahoma (Collier, 1912). Much of the technical literature and about half of the patents concerning electrolytic sewage treatment in the U.S. are related to the system patented and promoted by C.P. Landreth (Miller & Knipe, 1963). The process consisted of a rectangular wooden box containing many vertical steel plates about 12.5 mm apart and so arranged that the sewage flowed in thin sheets between them. The plates were alternately connected to the positive and negative terminals of a D.C. power supply.

The exact number of electrodes varied, but one demonstration unit built at Elmhurst, New York City, contained 1100 electrodes 25 by 40 by 0.5 cm. The space between the plates contained paddles mounted on shafts passing through and insulated from the electrodes, rotating to assure thorough mixing of the solution, to prevent polarization of the electrodes, and to remove any scum formed on the electrodes. Lime was added to the sewage just prior to entering the electrolyzer. This served to increase the conductivity of the sewage and to raise pH which passivated the steel (slower corrosion). The residence time was about one minute. Several demonstration plants were built, and they all were, according to Miller & Knipe (1963), praised for their supposedly high quality effluent and lack of odor. Some reservations were made on operating cost since sludge from the settling tanks had to be hauled away. Compared with the present day treatment plants, the result of the controversy might have been another than abandoning all plants as was done in 1930. The cost of operation was estimated to be as much as double that of more conventional methods. Miller & Knipe (1963) concluded that the high costs of the electrochemical treatment of wastewater did not make it suitable as a process for the Advanced Waste Treatment Research Program, where low conductivity water was to be treated.

Hemphill & Rogers (1973) determined the nature and rate of organic degradation from domestic wastewater produced by electrolysis. A 50 A/hour, 12 V automobile battery (lead-lead dioxide) was used (without the H_2SO_4 electrolyte). A variable voltage, 0-100 V D.C. capable of providing 20 A current was used as an electrolysis power source. Initial experiments indicated that the COD decay pattern followed first order kinetics and that 80 percent COD removal could be achieved with less than 25 watt-hours of electrical energy. The relationship was expressed as;

$$C/C_o = e^{-kE} \qquad (8)$$

C_o = initial COD concentration

C = COD concentration at some value of E

E = electrical energy, watt-hours^{-1}

k = reaction rate constant, watt-hours^{-1}

Hemphill & Rogers (1973) suggested that the efficient oxidation yield produced by lead-lead dioxide electrolysis was prompted by two complementary factors, free radical production where the OH· radical was the primary oxidant involved and lead dioxide anodic oxidation. The oxidation rates, as k values, was shown to vary with the voltage settings using constant energy (6 watt-hours). See Figure 32.

Føyn (1950) described the electrolytic treatment of wastewater, using magnesium salt and alkalization to precipitate phosphates. Figure 33 depicts Føyn's process with seawater as the magnesium source. The purpose was precipitation of magnesium hydroxide to remove phosphates. The specific conductivity was thus increased, resulting in low electrical resistance in the solution. When current passed through the cell the chloride ions in the seawater were oxidized to chlorine gas at the anode. The hydrogen ions were simultaneously reduced to hydrogen gas at the cathode. This reduction resulted in an excess of hydroxyl ions and an increase in the pH. Magnesium ions in the seawater precipitated as $Mg(OH)_2$ in the alkaline

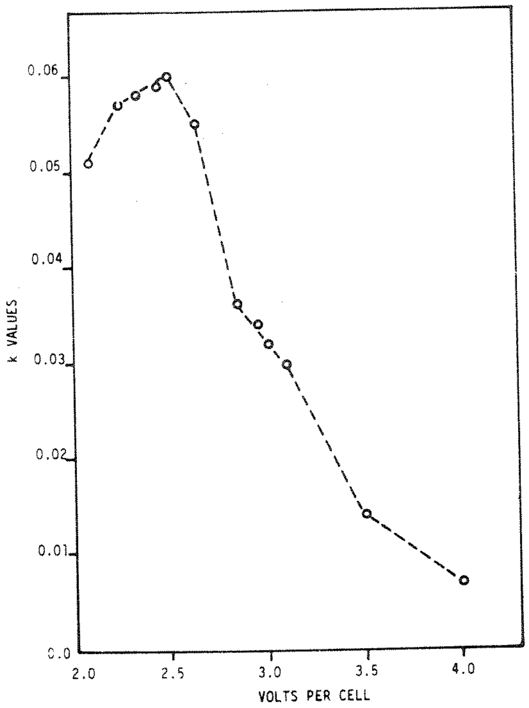


Figure 32. Variations in oxidation rate k values with various voltage settings using constant energy (6 watt-hours) (Hemphill & Rogers, 1973).

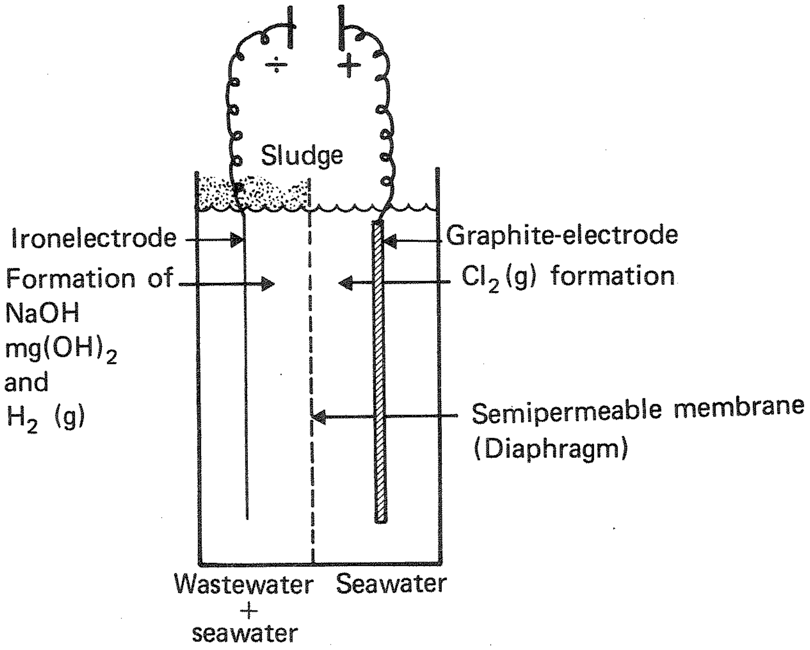


Figure 33. Principle of Føyn's process (Føyn, 1950).

environment and the flocculated particles were carried to the surface of the cell by the rising hydrogen bubbles. Based on laboratory experiments a biological treatment plant with chlorination was compared with an electrolytic wastewater treatment plant as shown in Table 13 (Føyn, 1950).

Table 13. Comparison of electrolytic wastewater treatment with biological wastewater treatment + chlorination (Føyn, 1950).

	Biological wastewater treatment plant + chlorination	Electrolytic wastewater treatment plant
Detention time	5-10 h	20-30 min
volume of plant (m^3)	100	10
% suspended solids removal	90	>90
% bacteria removal	>100	>100
% dry solids in sludge	3	9
sludge volume (m^3/d)	10.0	3.3
investment cost per 500,000 persons (1950 NOK)	75-100 million	14-22 million
operation cost per person and year (1950 NOK)	20.-	19.- - 20.-

A pilot scale wastewater treatment plant was built at Huk outside Oslo (Føyn, 1963). The outdoor plant was built with two parallel cells, one with a diaphragm and the other without, with a maximum capacity of 10 and 7 l/sec. A D.C. power supply with maximum 9 V and 6000 mA was used. After some time of operation a thin layer of $CaCO_3$ started building up on the cathodes resulting in decreased hydrogen gas development and, thus, ineffective flotation. Changing the polarity of the cells was effective with regard to the carbonate precipitation, but resulted in dissolution of the cathodes. Also, brushing of the electrode removed the calcium carbonate. Dybwad (1968) made a technical and economical evaluation of Føyn's process based on the pilot plant at Huk which treated 280 m^3/day (1000 persons). Approximately 12 percent seawater was added. He concluded that small electrochemical treatment plants could possibly be built and operated economically depending upon the need for such an advanced wastewater treatment. Romslo (1968) evaluated Føyn's process based on a plant treating water for 100,000 to 200,000 persons. He concluded that the process was effective, but that the important question was whether the public was willing to pay the costs of this advanced treatment. The energy requirement for the electrolyzing process was found to be 1.85 kWh/m^3 wastewater. In both these economic evaluations Føyn's process was compared with biological treatment although the process also contained phosphorus and nitrogen removal. Poon (1973) and Poon & Brueckner (1975) used Føyn's process in order to a) delineate the mechamisms of phosphate and nitrogen removal, b) identify the control variables and methods of operation in order to obtain a better quality effluent than from secondary treatment, and last c) conduct a continuous-flow study in order to compare it with the results from the batch study. Poon & Brueckner showed clearly that because of the very high pH in the batch process, the mechanism of phosphate removal was the adsorption onto the $Mg(OH)_2$ flocs. Analysis of the floating scum also supported this conclusion. The dominant reactions for nitrogen removal were found to be the formation of NH_2Cl and its subsequent destruction (equation (9)).

$$2\ NH_2Cl + HOCl \longrightarrow N_{2(g)} + 3\ HCl + H_2O \qquad (9)$$

Reducing the pH resulted in further nitrogen removal probably due to formation of dichloramine. The changes of pH, ammonia nitrogen, combined chlorine, and free residual chlorine concentration with respect to increasing detention time in the batch cell is presented in Figure 34.

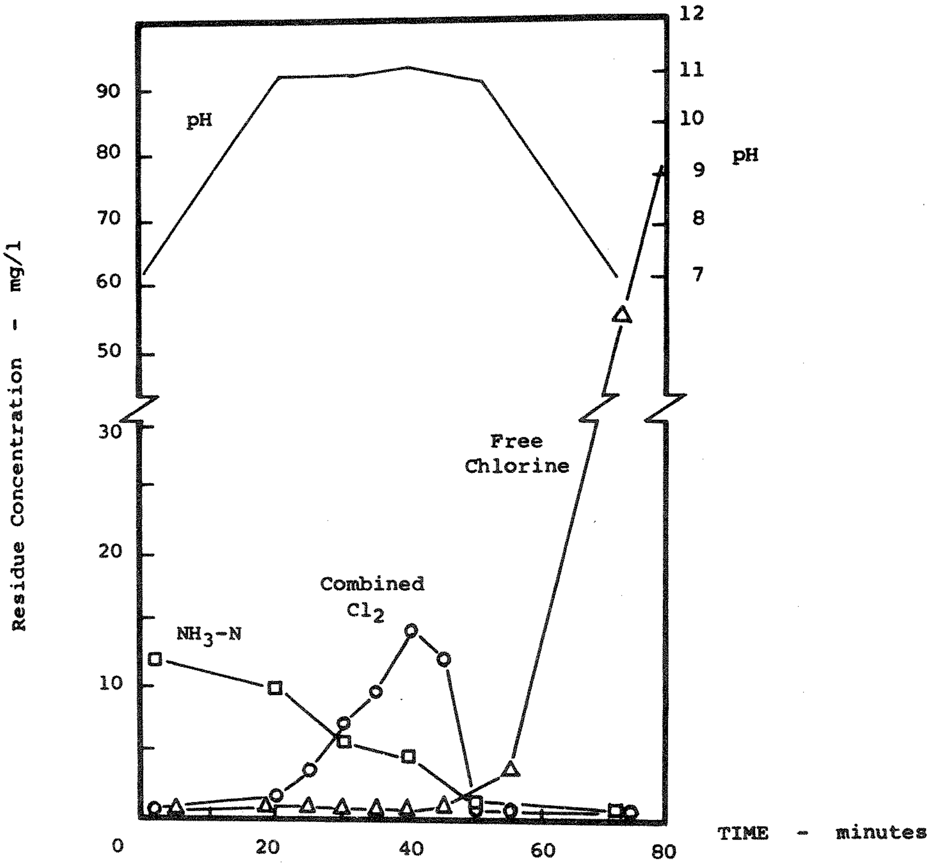


Figure 34. Changes of pH, ammonia nitrogen, combined chlorine, and free residue chlorine concentrations with respect to time (Poon & Brueckner, 1975).

The BOD removal was also studied. At 60 min. the average removal was found to be 85 percent. The temperature was found to have very little, if any, effect on the BOD removal efficiency. The disinfection of the wastewater was complete after 40 min., and the residual chlorine concentration was found to be prohibitively high for discharge if the treatment period extended beyond 50 min. (see Figure 34). Shortening the treatment period, however, reduced the BOD, nitrogen and suspended solids removal. The most critical factor of control in the batch electrolytic process was shown to be maintaining a good stratification of wastewater above the seawater electrolyte. The average energy consumption with good stratification was found to be 1.2 kWh/m^3 of wastewater treated. The continuous flow study emphasized the problem of maintaining stratification, and the difficulty of maintaining a very high pH for maximum phosphate removal. Loss of stratification and lowering of pH resulted in higher power consumption and lower phosphate removal. Poon & Brueckner (1975) noted, however, that critics of this process had completely overlooked the fact that the manufacture of chemicals for phosphorus removal and chlorine or hypochlorite for disinfection also needed power as well as shipping of the chemicals to the treatment plant. The authors suggested use of lead dioxide-lead combination of the electrodes to improve the system.

Føyn (1980) discussed his electrochemical process again, but this time compared it with chemical treatment using lime and seawater, with an additional remark about nitorgen removal ($\sim$80 percent). He emphasized that it was possible to solve the problem of cleaning the electrodes.

Beck et al. (1973) studied electrocoagulation of food wastewater. The tank acted as a cathode and a plurality of anodes were placed in the wastewater. In the system studied a special alloy was used to ensure an appreciable dissolution rate. In these experiments electrocoagulation was compared with chemical treatment + dissolved air flotation. The chemical treatment consisted of 200 ppm ferric sulfate, 50 ppm calcium hydroxide, and 2 ppm anionic polymer. Floc formation for both processes was very rapid (2 min.). However, the time required to raise or settle a floc by buoyancy was rather lengthy. Comparing (to a solids content of 10 percent) the floc by buoyance or gravitation often required 10-20 min. The electrocoagulation process, on the other, surfaced a floc in 2-3 min. and compacted it in 3-10 min. A residual floc remained in the chemically treated wastewater whereas all the flocs surfaced in the electrolytically treated wastewater.

Glembotskiry et al. (1973) studied the size of gas bubbles formed under electroflotation conditions. The principal factors influencing bubble size were pH, the electrode material, and the temperature. They emphasized the importance of small gas bubble production to improve the flotation process. The bubbles were smallest in neutral (for all cathode materials) and alkaline regions (for copper and tin media) i.e. in pH regions corresponding to maximum hydrogen overvoltage. The influence of the cathode material on bubble size was particularly marked in an acid medium where the mean bubble diameter scattered in the range of 20 to 70 μm. The temperature of the water varied between 5 and 75°C with bubbles at 5°C having the smallest diameter

(30 μm), while those with the greatest (50 μm) were formed at 75°C. Existing methods of dispersing air give bubble sizes of 0.8-0.9 mm using impeller flotation machines, 0.1-0.2 mm using vacuum flotation, and, in some cases, 0.06-0.08 mm using compressor installations.

2.3.5 Electrochemical Water Treatment Using Soluble Anodes

Strokach (1975) reviewed research on electrochemical purification of water using soluble anodes. Most of the work referenced is not translated. In the Soviet Union, however, electrochemical water purification with a soluble iron anode was first used at the Shatura Power Station around 1925. The energy requirement varied between 1 and 20 kWh per m^3 treated water.

Stuart (1946) presented results from research using a small electronic water coagulator with a series of aluminum sheets. He pointed out that the electronic purification process did the same coagulation job as when alum was added to the water, except that this process is faster and needs less technical control. Some water quality results from the experiments done on colored waters were presented (Table 14). Stuart showed that good floc formation could be achieved during a contact time of 15 to 45 seconds in his coagulator with aluminum sheets spaced 3 mm apart and having a surface area of 180,000 cm^2. The author presented no data on the amount of aluminum dissolved. Floc formation and pH data are given in Table 15 for coagulated Detroit raw water.

Table 14. Data from electronic water purification of colored waters (Stuart, 1946).

Water / Parameters	Moores bridges soft surface w.		Dismal swamp water		Miami hardwell supply		City of Miami tap water	
	[1] Raw	Treated	[2] Raw	Treated	Raw	Treated	Raw	Treated
Color ▲	90	10	400	10	70	11	27	7
pH	6.8	8.6	5.0	7.5	7.3	7.2	9.5	6.8

1) Norfolk, VA, 2) Elizabeth City, NC.

▲Hazen units.

Table 15. Electronic water purification of Detroit raw water (5 A, 6V) (Stuart, 1946).

Water	pH	Floc Formation
Detroit raw water	7.0	
Treated:		
5 seconds	8.2	pin point floc
10 seconds	8.2	floc formed with clarity
20 seconds	8.2	fast floc formation - settled well
40 seconds	8.2	big floc - settled well
80 seconds	8.0	large floc - floated
160 seconds	8.0	gel-type floc

Bonilla (1946) discussed the electronic coagulator proposed by Stuart and gave a good description of the cell which was composed of parallel aluminum sheets connected alternately to the opposite poles of a low-direct current voltage. Raw water passed between the plates; aluminum dissolved, forming aluminum hydroxide reacting with color colloids and thus behaving the same way as conventional coagulation except that:

- the water was not simultaneously acidified; as a matter of fact, pH mostly increased.
- the rate of addition of aluminum hydroxide was simpler to control by using electric current.

Bonilla (1947) discussed the costs of electricity and alum in this process compared to conventional alum coagulation. His cost data from 1947 were based on treatment of water from the Potomac River, the cost for sheet aluminum was then 20 times higher than for aluminum sulfate, and he assumed equivalent amount of aluminum needed from the sheet which gave an estimated price of the electrolytic aluminum process 1.7 times higher than aluminum sulfate. When soda ash was included to adjust pH for conventional treatment and energy was considered for the electrolytic treatment, his estimate was $12 per million gallons for the conventional coagulation process and $18 for the electrolytic system based on a low-current density cell (large cell). With the same assumptions, a small cell was estimated to cost $30 per million gallons of water treated. Bonilla suggested the most economical cell size was in the range of one cubic foot for each three to five gallons per minute of water treated ($\sim$1.5-2.5 min. residence time). He believed that if the electrolytic coagulator were operated under suitable conditions, it could compete favorably with alum coagulation especially in small installations where raw water pH needed to be increased.

Strokach (1975) described two types of equipment for electrochemical purification and decontamination of water aboard river ships and for agricultural applications in the Soviet Union. The equipment included an electrolyzer with aluminum anode and stainless steel cathodes, a two layer pressure filter and an electrolyzer with silver electrodes. With voltage up to 12 V and current 10-20 A the equipment purified 250-500 l/h of polluted river water to drinking water standards. Strokach et al. (1973) investigated the influence of physical-chemical, electrical and hydrodynamic factors on electro-coagulation purification of water for removal of different contaminants in order to minimize the consumption of aluminum and electricity. He used water from the River Dnepr and alkaline extract humus-carbonate and podzol earths were used to color the water. The feed water temperature was varied between 2 and 80 °C and good contaminant (color, turbidity, silicon, iron, phytoplankton) removal was achieved over the whole temperature range although temperatures higher than 20 °C resulted in highest removal; for example, color was reduced from 150 to 8 mg Pt/l at 2 °C and reduced to 6 mg Pt/l at 20 °C. pH was changed and highest removal of color, phytoplankton, and turbidity occurred at pH in the range 4.0 to 7.0.

Strokach et al. pointed out that increasing the current density resulted in a great increase in the electric energy consumption, and the effectiveness of removal of silicon and iron from the water decreased.

They recommended current densities of 1-2 mA/cm^2 with a voltage on the electrodes of 2.5 to 4 V.

Gjessing (1968) studied electrolytic treatment of surface waters. Color was reduced from 19 to 0 mg Pt/l for tapwater and for swamp water from 83 to 17 mg Pt/l. The amount of aluminum dissolved was found to be approximately 0.5 mg/l mA h. which showed that 2.5 mg Al/l was needed to reduce color from 83 to 17 mg Pt/l. The pH was 6.6 before treatment and 7.4 after treatment.

Holden (1956) studied electrolytic dosing of coagulants. The experiments started out using aluminum anodes and copper cathodes. Iron was, however, found to be economically favorable, and a small laboratory experiment was carried out in order to evaluate the metal of the electrodes. A pair of electrodes, area 23 cm x 10 cm, separated by 1.3 cm of water with specific conductivity of 910 μS/cm was used (Table 16). It was considered to be an advantage to use the same metal in both electrodes both in regard to design and operation.

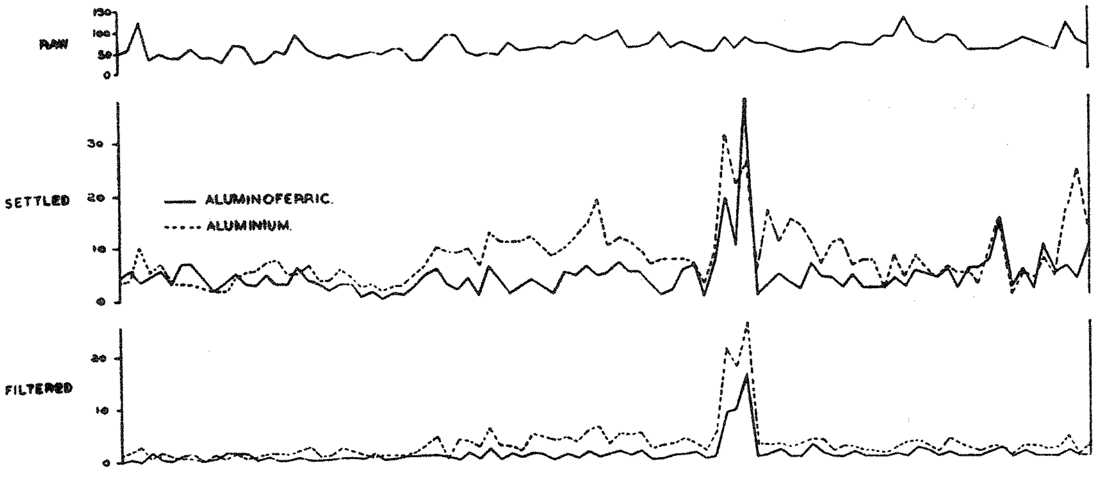
Table 16. Voltage necessary to pass 1 A for electrode pairs of different metals (Holden, 1956).

Anode	Cathode	Voltage necessary to pass 1 ampère
Aluminum	Aluminum	7.3
Aluminum	Copper	6.55
Iron	Copper	6.0
Iron	Iron	5.6

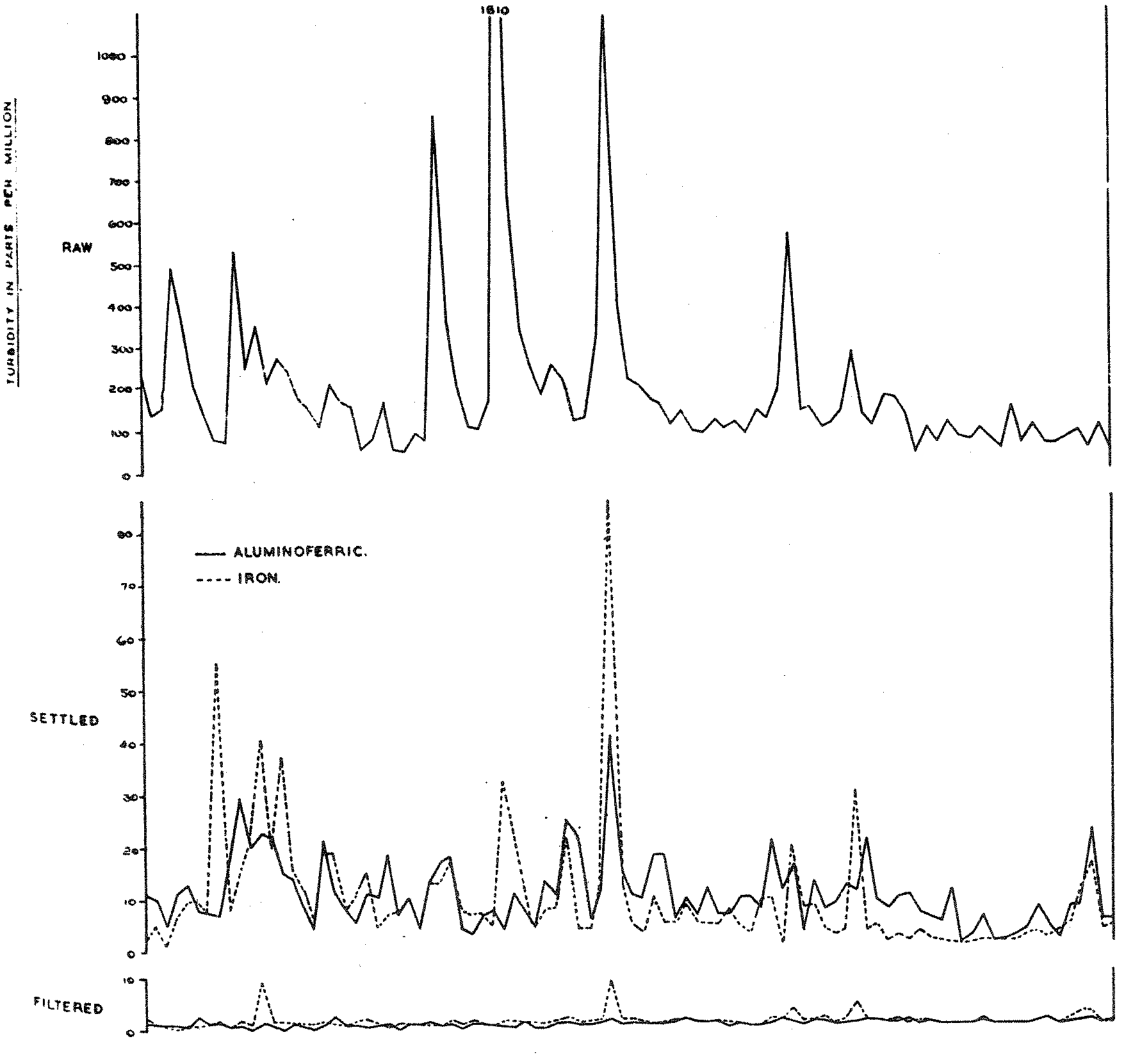
The cost of the electrodes would equalize the costs of chemicals, and occasional reversal of the current would help to keep the plates clean and produce more uniform conditions.

In one study series aluminum - copper electrodes were used, and in a second one iron - copper. The treatment plant studied was supplied with water pumped from the River Severn into a primary sedimentation tank, then to the electrolyzer and the sedimentation tank, and at last to a rapid gravity filter. In two periods, each of three months, this treatment plant was run in parallel with a second plant, identical, except for the chemical dosage arrangement. In the second treatment plant alumino-ferric was dosed to the mixing tanks. The results from the two periods are presented in Figure 35. Each treatment plant had a hydraulic capacity of 17 m^3/h. Holden (1956) showed no great difference in the running costs of the two different processes. He found it, however, rather difficult to make estimates on capital costs of the processes. The electrolytic process was favored as regards cleanliness and accuracy of dosing.

Sadek (1970) did a laboratory study on electrolysis using both aluminum and iron electrodes for removal of phosphates from waste water. The aluminum consumption averaged about 0.7 mass units per single mass unit of PO_4 removed for essentially complete phosphate removal. This mass ratio was about 2 for iron electrodes. The treatment costs (excluding labor and filtration) was estimated to be 2.5 cents per 1000 gallons and 8.0 cents per 1000 gallons when using iron and aluminum electrodes, respectively. Sadek (1970) also suggested use of flotation by means of the hydrogen generated during



1 MAY TO 31 JULY 1950.



8 FEBRUARY TO 10 MAY 1951.

Figure 35. Raw water from the River Severn treated with conventional water treatment using aluminoferric compared with electrolytic treatment with either aluminum anodes (first period) or iron anodes (second period)(Holden, 1956).

electrolysis to remove the suspended solids.

Herer & Woodard (1976) used electrolytic coagulation of lignin from kraft mill bleach plant wastewaters to remove color and other carbonaceous materials. The removal mechanisms were found to consist of coagulation by hydrated aluminum ions brought into solution by electrolytic dissolution of an aluminum anode. A maximum color removal of 99 percent was observed for the caustic extraction effluent and 92 percent for the chlorination effluent. The carbon removals were lower, 69 percent for the chlorination effluent and 89 percent for the caustic extraction effluent.

Jonsson et al. (1969) studied contact coagulation which was defined as a filter bed where the coagulation, flocculation, and filtration processes occurred. In their system raw water was added aluminum produced by electrolysis. The coagulated water was filtered in a multimedia filter. The quality of the treated water was found to be satisfactory as long as the raw water pH was below 7.0 Jonsson et al. studied the pH changes as a function of the Al-dosage (see Figure 36).

Wejman-Hane (1971) used the same electrolyzer as Jonsson et al., aluminum anodes and steel cathodes placed with 5 mm distance, with an area of 10 by 15 cm. Theoretical calculations of the aluminum dosage, after Faraday's law, were compared with practical measurements of the dosage showing a variation of $\pm 5\ ^{o}C$ of the two values. Colored surface water was treated and one series of experiments was done without pH regulation while, in the second series, carbon dioxide was added to keep the pH between 6.3 and 6.5. In the first series the residual aluminum concentration increased with increasing Al-dosage, up to 0.08

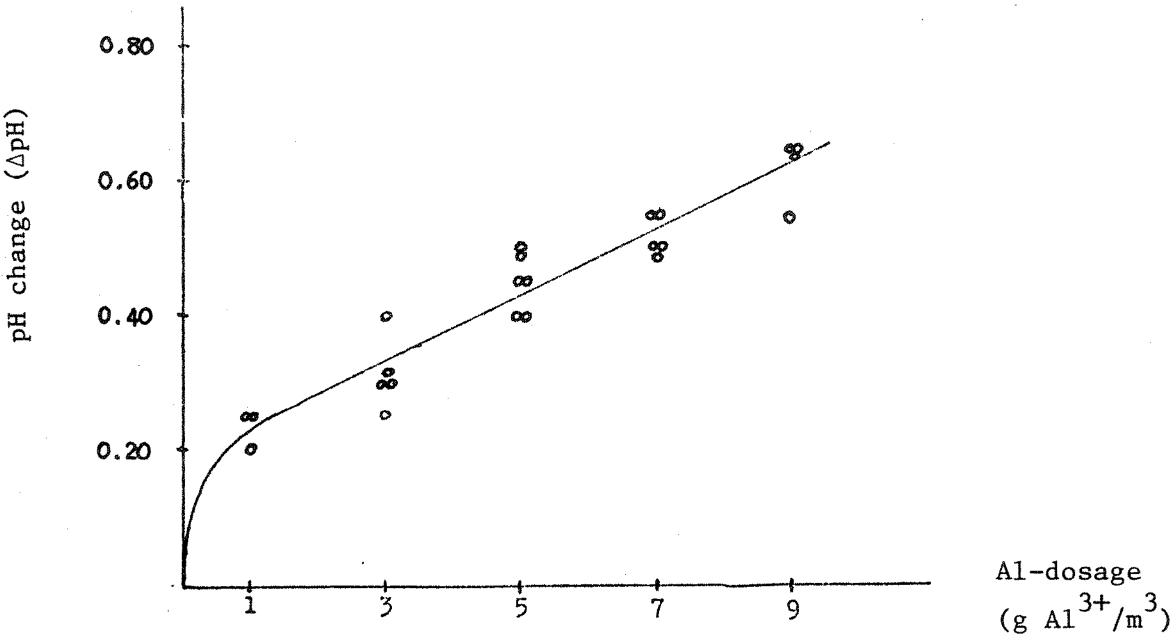


Figure 36. pH change as a function of aluminum dosage when raw water pH ≈ 6.8-7.2 (Jonsson et al., 1969)

Al/l for a dosage of 9 mg Al/l and a filtration rate of 8 m/h. In the series with pH regulation no increased Al-concentration of treated water was registered. The other results were the same for the two systems. The contact-coagulation system was studied in full scale at Finnsjön. Hedberg (1973) summarized the results from this full scale treatment plant. Figure 37 shows Hedberg's data on the effect of pH of electro-chemically treated water on the residual Al-concentration.

Rova & Källander (1972) studied the electro-chemical process for aluminum dosing. The electro-chemical reactor consisted of two concentric aluminum pipes where the outer Al-pipe was the cathode and the

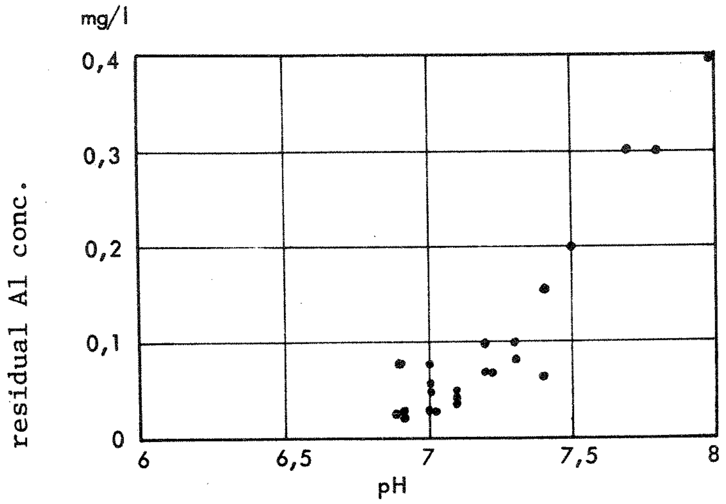


Figure 37. Residual aluminum concentration as a function of pH (Hedberg, 1973).

inner one the anode. A thin coating was formed which increased the resistance over the cell. Higher current densities resulted in faster formation of coating on the electrodes (Figure 38). Increased electrode distance decreased the rate of formation of the coating.

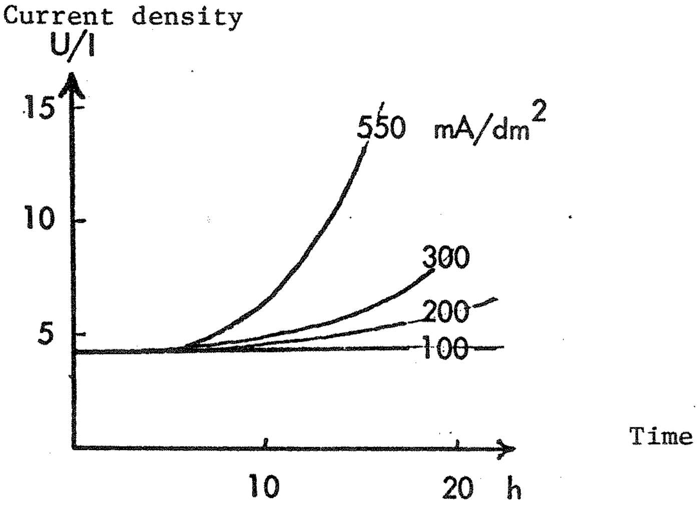


Figure 38. Increase in resistance in the electrolyzer with time as a function of current densities (Rova & Källander, 1972).

The use of stainless steel cathodes instead of aluminum resulted in slower rate of coating formation. Shaking the cell gave the same result.

Hanæus (1979) summarized all the studies at Chalmers University of Technology (CTH), Gothenburg. The treated water pH was shown to be higher than for untreated water up to the point where the raw water pH was around 8.5 (Figure 39).

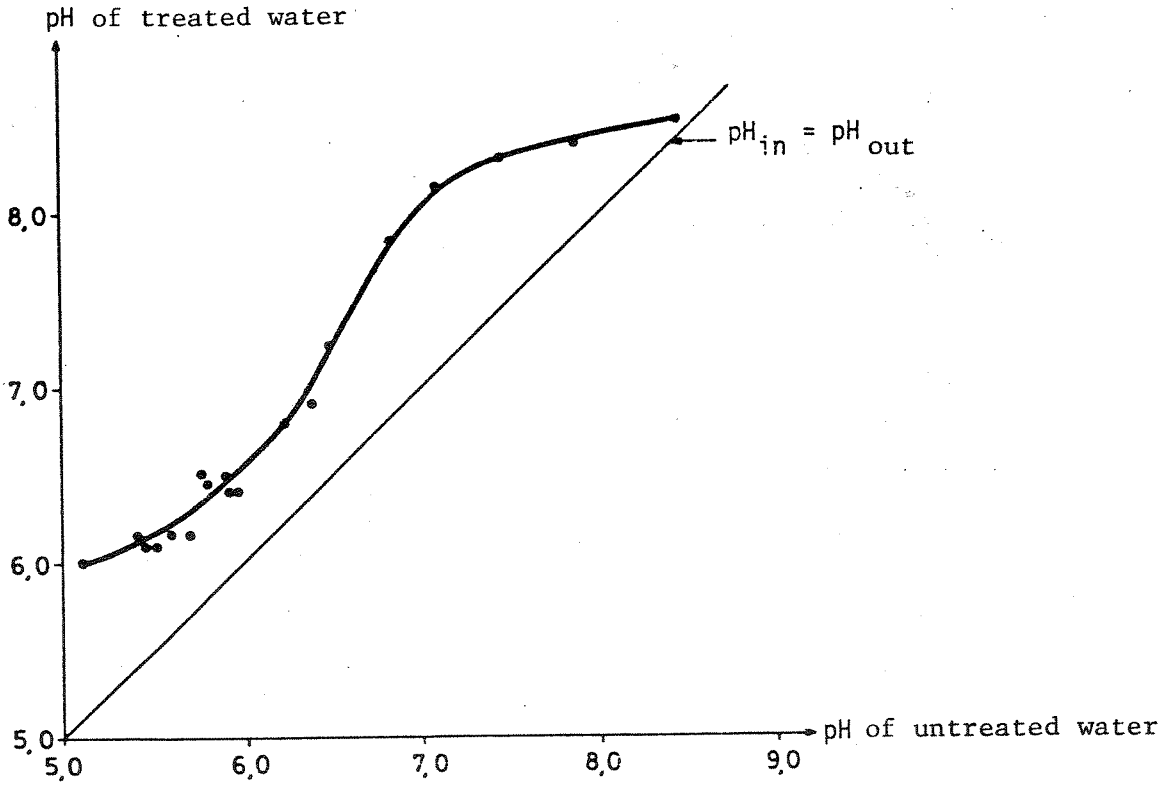


Figure 39. Changes in pH due to electrolytic treatment (Hanæus, 1979).

The main operational problem was found to be coating formation on the electrodes. Hanæus showed that a higher initial potential was needed to push the same current through the system when each experiment started up after down time than what was needed during the latter part of the experiments. Figure 40 shows how the initial potential increases with down time of the system.

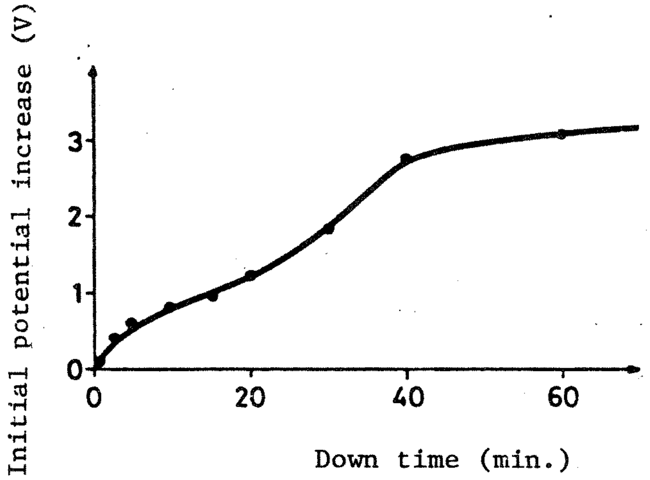


Figure 40. Initial potential increase as a function of down time of the electrolytic process (Hanæus, 1979).

2.3.6 Important Aspects in Regard to the Electrochemical Reactor Design

A typical electrochemical reactor is shown schematically in Figure 41. The anode is the electrode where positive current passes into the electrolyte. In a system where the anode is made of aluminum some of the actual electrode reactions could be as shown in Table 17.

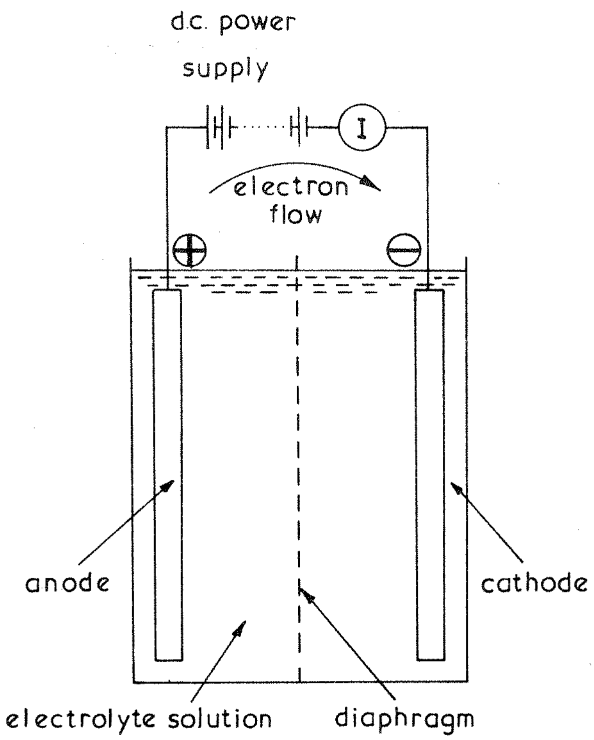


Figure 41. A simple electrochemical reactor.

Table 17. Possible electrode reactions when the anode is made of aluminum.

pH	Electrode reaction	Standard potential e ^{o}V
-	$Al \rightleftharpoons Al^{3+} + 3\ e^-$	- 1.66
7	$Al + 3\ H_2O \rightleftharpoons Al(OH)_{3(s)} + 3\ H^+ + 3\ e^-$	- 1.96
7	$2\ Al + 3\ H_2O \rightleftharpoons Al_2O_{3(s)} + 6\ H^+ + 6\ e^-$	- 1.90
0	$H_2 + 2\ H_2O \rightleftharpoons 2\ H_3O^+ + 2\ e^-$	0.00
7	$H_2 + 2\ H_2O \rightleftharpoons 2\ H_3O^+ + 2\ e^-$	- 0.414
14	$H_2 + 2\ OH^- \rightleftharpoons 2\ H_2O + 2\ e^-$	- 0.828
7	$2\ H_2O \rightleftharpoons O_2 + 4\ H^+ + 4\ e^-$	- 0.815

Faraday's Law gives the relationship between the current density (i.e. current per unit area of electrode) and the weight of material per unit area reacted at an electrode,

$$w = \frac{itM}{zF} \tag{9}$$

where w = the weight of material reacted per unit electrode area (g/cm^2)

i = the current density (A/cm^2),

t = time, duration of electrolysis (s)

M = the molecular weight

z represents the number of electrons involved in the oxidation/reduction reaction, and

F = the Faraday constant.

Dividing equation 9 by the molecular weight and differentiating with respect to time gives equation 10.

$$r = \frac{dn}{dt} = \frac{i}{zF} \tag{10}$$

where r = rate of reaction per unit area and

n = the number of moles reacted.

Equation 10 states that the rate of an electrochemical reaction is proportional to the current density. When the current flows through an electrode its potential $\varepsilon(i)$ assumes a value different from that in the absence of current, $\varepsilon(0)$. If the equilibrium is not disturbed the zero current potential will be the equilibrium potential, ε_o. The deviation of the electrode potential, ε, from the equilibrium value ε_o is called overvoltage η.

$$\eta = \varepsilon - \varepsilon_o = \text{overvoltage} \tag{11}$$

An anodic (positive) and cathodic (negative) current alwavs generates a positive and negative overvoltage, η, respectively. The overall electrode reaction is generally composed of a series of partial reactions. There exist several ways of defining the partial reactions occurring. Vetter (1967) distinguished four kinds of overvoltage. If only the charge-transfer reaction is hindered and none of the other preceding or following partial reactions, there exists only a charge-transfer overvoltage, η_t. If a chemical reaction is hindered, the rate constant, by definition, is independent of potential; there exists with the current flow a reaction overvoltage, η_r. Pure diffusion overvoltage, η_d, is encountered if mass transport by diffusion to and from the surface is the slowest process among the partial reactions involved. Hindrance of the process by which atoms are incorporated into or removed from the crystal lattice leads to crystallization overvoltage η_c. The sum of the diffusion and reaction overvoltages will be called the concentration overvoltage, η_C.

Others have used activation overvoltage, which according to Vetter (1967) is defined as equal to the charge-transfer overvoltage. Also the concept of resistance overvoltage has been introduced, η_Ω, as the ohmic potential drop within the electrolyte.

In our system, the measured overvoltage, η_{AP}, will be defined to consist of three terms; η_K, the kinetic overvoltage (concentration), η_{MT}, the mass transfer overvoltage (diffusion), and η_{IR}, the solution resistance overvoltage (IR-drop):

$$\eta_{AP} = \eta_K + \eta_{MT} + \eta_{IR} \tag{12}$$

The most desirable situation is when $\eta_{AP} = \eta_K$, i.e. the solution resistance, η_{IR}, is minimized and the concentrations of the participating species close to the electrode are quickly transferred to the bulk of the solution thereby minimizing η_{MT}.

The Butler equation discussed in Weber (1972) is the fundamental equation of electrochemical kinetics;

$$i = i_o \{\exp(\frac{-\alpha zF\eta}{RT}) - \exp(\frac{(1-\alpha)\ zF\eta}{RT})\} \tag{13}$$

where i_o is the exchange current density (A/cm^2), α is the charge-transfer coefficient (dimensionless), and η is the overvoltage (V). The reaction is based on relatively low overvoltages where the concentrations of the oxidized and reduced species are the same at the surface of the electrode as in the bulk solution. The exchange current density, i_o, is the rate of oxidation and reduction reactions at the reversible potential. It is a measure of "intrinsic reactivity" of a substrate for a given reaction. Equation 13 is, however, only valid for a simple process when the reaction involves only an electron transfer reaction, such as transfer from $Al \rightarrow Al^{3+}$, and no preceding or following chemical reactions. The complex redox reactions, like the dissolution of aluminum, can be described by a "modified" Butler equation:

$$i = i_o \{\exp(\frac{\eta}{\beta_a}) - \exp(-\frac{\eta}{\beta_c})\} \tag{14}$$

where β_a and β_c are determined experimentally and are dependent on the mechanism of the complex reaction.

The Tafel slope, b_o, is determined from the experimental data from the defining reaction

$$b_o = \left| \frac{\delta \eta}{\delta \log i} \right| \qquad (15)$$

Weber (1972) gives approximate data for an aluminum electrode:

$$i_o = 10^{-10} \ (\mathrm{A/cm^2}) \text{ and } b_o = 100 \text{ mV}$$

Figure 42 gives a schematic representation of the potential - log current density plot which can be found experimentally.

There exists a limiting current density, i.e., where the electrochemical reaction rate exceeds the rate at which material may be transported to the metal surface. The maximum rate of the electrode reaction is given by

$$i_\ell = zFk_f \, C \qquad (16)$$

where k_f is the mass transport rate constant (cm/sec) and C is the bulk concentration of the reacting species (moles/cm^3). The difference between Butler's equation and the maximum rate of the electrode reaction is that the latter one depends upon the properties of fluid in contact with the electrode and not upon the electrode properties.

The major parameters of importance in the anodic dissolution of aluminum are thus, 1) in regard to the electrodes; the chemical composition, the size and the distance between the electrodes, and 2) in regard to the solution; the flow conditions, the types of ions, and the amount of ions in solution (i.e., the conductivity).

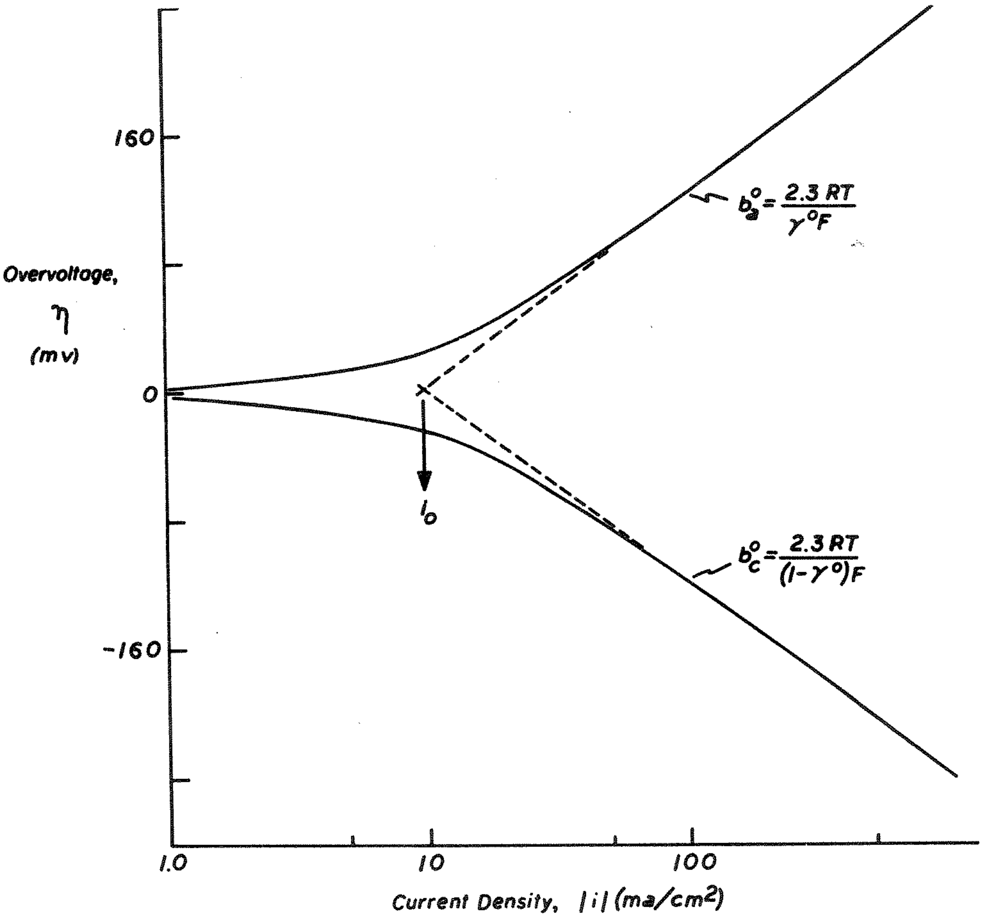


Figure 42. Schematic representation of anodic and cathodic polarization curves.

The solid line represents the "experimental data", the dashed line represents the extrapolations of the respective Tafel lines. b_a^o, b_c^o = the Tafel slope for anodic and cathodic reactions, respectively, γ^o = charge-transfer coefficient (Weber, 1972).

The solution resistance polarization, η_{IR}, will often be the current-controlling potential.

$$\eta_{IR} = I \cdot \rho \cdot \frac{d}{A} = I \cdot (\frac{d}{A\,\kappa}) \qquad (17)$$

where I = current (A)

ρ = specific resistivity (Ωm)

κ = specific conductivity (S/m)

d = distance between Al-sheets (m)

A = active anode area (m^2).

The chemical composition of the aluminum electrodes is of major importance. Pure aluminum is, of course, quite soft and weak and is alloyed to obtain increased strength. In general, the higher the degree of purity of Al, the greater its corrosion resistance. Malachesky (1976) mentioned that the corrosion resistance of Al declines appreciably as the purity drops from 99.998 percent to 99.98 percent. This comment is, of course, restricted to the usual impurities found in commercial Al. Aluminum belongs to the group of metals which have very negative electrode potentials and evolve hydrogen in contact with most aqueous solutions. For aluminum there is the added complication of the tendency to formation of a non-conducting oxide or amorphous hydroxide layer. According to Malachesky (1976), accurate and reproducible electrode potential data for aluminum in aqueous solution are thus not obtainable in the literature. Våland & Nilsson (1976) at the Norwegian Defense Research Institute started with as pure metal as possible (Al > 99.998 percent) and gradually introduced impurities in order to evaluate how the presence of impurities in the metal influenced the reactions taking place on the metal surface. These reactions are of importance for the stability of oxide film, and thus for the corrosion resistance of aluminum.

The high negative potential of aluminum, coupled with its low molecular weight (Malachesky, 1976), makes it quite attractive for use in electrochemical power sources. Commercial batteries utilizing Al anodes do not exist due to practical problems in regard to high corrosion rates and appreciable polarization in typical battery electrolytes. Våland & Nilsson (1976) studied the use of aluminum/air batteries where, according to Malachesky (1976), following reaction occurs:

$$2\ Al + 3/2\ O_2 + H_2O + 2\ OH^- = 2\ H_2AlO_3^-,\quad E^o = 2.75.$$

The work being done at the Norwegian Defense Research Institute uses the approach of alloying the aluminum to develop usable Al anodes. Iron-aluminum alloys, according to Våland (1981), give unfavorable properties, and the presence of silicon (Si) in addition to iron results in even worse properties. The presence of tin (Sn) in small amounts ($\sim$0.1 percent) has shown favorable properties, and the literature (Malachesky, 1976) indicates that zinc (Zn) also has a positive effect.

In electrolysis using aluminum electrodes, the cathode space becomes alkaline because of hydrogen evolution, whereas the anolyte becomes acidic because of the electrolytic dissolution of aluminum and thus formation of aluminum hydroxides. The amphoteric character of aluminum makes it dissolve in both acids and bases. Dobolyi (1978) did experiments using electrochemical methods for removal of phosphates. Aluminum anodes and cathodes were used. In electrolysis with combined electrode space it was found impossible to decide whether the dissolved aluminum ions resulted from electrochemical or from chemical dissolution by the base, or acid produced in the course of electrolysis. One experiment was performed to study the changes of pH in the electrolytic compartments. Figure 43 shows the equipment used.

A 0.1N KCl solution was used in this experiment, with 15 mm electrode spacing. The potential applied was 10 V and the current density 22.72 mA cm^{-2} at the anode and cathode alike. The electrolysis was continued 30 minutes during which the electrolyte was stirred and pH measured continuously. In the catholyte the pH increased from the initial 5.2 to 12.1, while in the anolyte it decreased from 5.2 to 4.4.

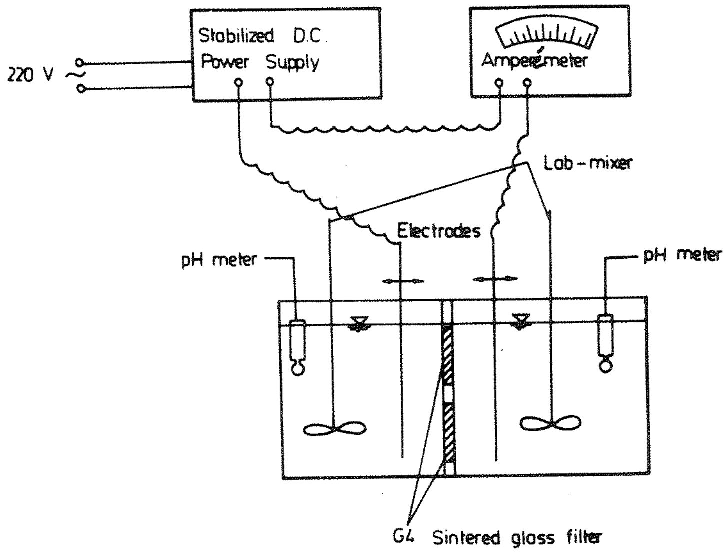


Figure 43. Circuit of electrolytic cell used in Dobolyi's (1978) experiments.

The pH increased suddenly in the catholyte, while it decreased slightly and at a uniform rate in the anolyte. Several experiments were then run to find the amount of aluminum dissolved due to the electrochemical process and due to chemical dissolution. Pure electrolyte was used for each experiment. The loss in weight of the anode was measured and checked against the electrochemical dissolution as determined analytically. The two sets of data agreed to within ±5 percent. The process in the catholyte was examined in one experiment by adjusting pH to 12.0 and in another by adjusting pH to around 5.0. At pH = 5.0 no loss in weight was observed. At pH = 12.0 the loss in weight of the electrode was found to be 1 mg min^{-1}. Dobolyi (1978) concluded that the loss in weight of the cathode was due to the dissolving effect of the base formed in both combined and separate electrode compartment electrolysis and was thus a purely chemical process.

2.4 Filtration/Direct Filtration

Filtration for water treatment is an old process. The first filter was constructed in London in 1829, as a slow sand filter. Due to space limitations, rapid sand filters were introduced at the end of the 19th century. For many surface waters, filtration did not give sufficient water quality since many of the particles were in the colloidal size range and were not easily removed in the filter. Coagulation followed by sedimentation became the conventional water treatment process. Several treatment plants then included the filtration process to improve the separation of particles. The high construction costs and the large area needed for this system compared to the efficiency in removal of contaminants, have increased the interest for the direct filtration process. Conventional water treatment includes the coagulation, flocculation, sedimentation, and filtration processes, while the direct filtration excludes the sedimentation process and in some instances, the flocculation process.

2.4.1 Theoretical Aspects of the Filtration Process

Filtration is probably one of the most widely used and extensively investigated processes in the field of sanitary engineering. Yet there is not at this time a clear understanding or an exact formulation of the mechanisms by which particle removal from water is accomplished by filtration. The modern approach to in-depth filtration was set forth by O'Melia & Stumm (1967), who described it as a removal process consisting of two steps; a transport step, which is a physical-hydraulic process, and an attachment step, which is a physical-chemical process. No attempt is made to review the different theories proposed as this has been done earlier (Vik, 1980). Also Adin et al. (1979) have reviewed the filtration theory based on the important aspects applying to pilot-plant design. They also proposed that the most important conclusion that can be drawn today concerning the transport step is its relative insignificance in filter design. Adin et al. (1979) suggested that control efforts might be made more fruitful and probably easier by viewing "attachment" as the major factor in filtration. This was also stressed by Edzwald (1979) who said that the most important aspect is to choose the best dosage for destabilization of the colloidal particles since the particle transport will not be a limitation in direct filtration.

Attachment depends on physico-chemical mechanisms which can be classified by models proposed by Hahn & Stumm (1968).

1. Reduction of potential energy of interaction between particles.
    a. Compression of double layer by counterions (Schultze Hardy).
    b. Decrease in surface potential owing to specifically adsorbed counterions or owing to surface reactions.
2. Bridge formation.

    Specially adsorbed polymeric species form bridges between colloids.

Several authors have discussed the importance of the bridge formation in water treatment and the dosage of coagulant has been shown to be dependent on the amount of colloid present ("stoichiometric"). The coagulation has also been demonstrated to rely on charge neutralization of the colloids present. These aspects were approached previously in the coagulation process discussion.

Saatçi & Oulman (1980) discussed three filter criteria for terminating the filter run:

(1) water quality breakthrough based on maximum acceptable concentration.

(2) maximum usable head loss.

(3) neither too short nor too long a filter run.

The first two criteria are illustrated in Figures 44 and 45. A balanced design in which all three criteria for terminating the filter run occur at about the same time is a worthy goal in the initial phases of a filter design.

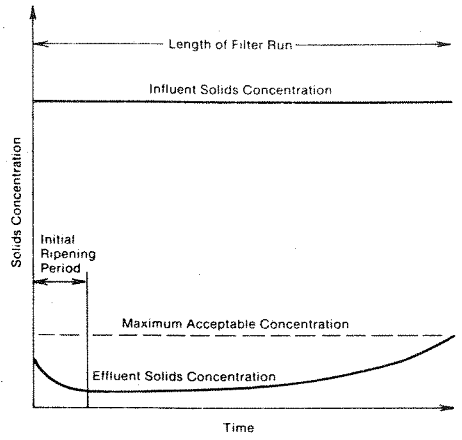


Figure 44. Effluent quality as a function of time: breakthrough concentration criterion (Saatçi & Oulman, 1980).

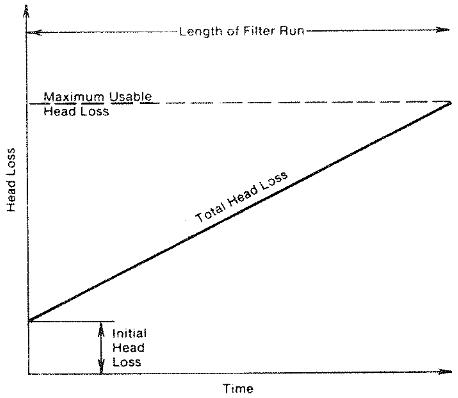


Figure 45. Head loss as a function of time: head loss criterion (Saatçi & Oulman, 1980).

Saatçi and Oulman (1980) described a design method, including the analytical solution for that part meeting the water quality criteria (Figure 44), called the bed depth service time method (BDST). The variables that determined the length of the filter run based on a given maximum effluent solids concentration included the concentrations of solids in the effluent, the characteristics of the suspended solids (including particle size, shape and surface properties), depth of filter media, the character of the media (size, shape and surface properties), flow rate, temperature, and chemical treatment employed. Treweek (1979) presented results from the second phase of a two-part pilot plant investigation prior to design of a 160 million m^3/d water purification plant (Utah Valley). He discussed the differences between the parameters related to removal efficiencies in sedimentation and filtration to be:

Filtration: the diameter and density of the aggregated particulate matter in the influent water supply.

Sedimentation: the size distribution of the influent aggregates; i.e., uniformly sized aggregates yield a predictable better removal efficiency.

Unlike sedimentation, aggregate removal by direct filtration is not dependent on the production of a large, bulky floc such as that produced by tapered flocculation. Indeed, better filtered water quality has been attained by high-intensity flocculation to produce a relatively small dense floc. Treweek (1979) used particle size distribution and variation of flocculation times to determine the minimum flocculation time necessary to achieve the desired particulate removal in a simple sand filter. He summarized three reasons for not specifying one flocculation time for all influent raw water supplies.

1. The aggregates produced may be too large for in-depth filter penetration.
2. Energy may be wasted in continually agitating a suspension that has reached or exceeded the optimum size distribution for removal.
3. The aggregates already formed may be sheared by extended agitation.

Treweek (1979) explained the available storage space in the filter for aggregated particulate matter to be limited to the porosity of the filter bed. Therefore, increasing the aggregate density enabled the filter bed to hold more particulate matter and thus provided for longer filter runs.

Treweek did experiments using a Phipps & Bird multiple stirrer with a speed of 120 rpm and various times of mixing resulting in Gt values between 12,000 and 270,000 ($2 < t < 45$ min), and using an alum dosage of 3 mg/l and 0.25 mg/l cationic polymer. The coagulated water was filtered through 30 cm sand (0.5 mm media). The experiments indicated that a flocculation time shorter than 7 min was not sufficient to produce the aggregation of the singlets required for their removal in the filter media. Increasing the flocculation time to 7 min or longer resulted in sufficient growth of aggregates to cause their removal in the subsequent filtration step. The production of a floc large enough to be visible was eliminated as a criterion in the design of the full scale treatment plant. Treweek (1979) showed in his experiments that Gt values of 100,000 to 200,000 were required for visible floc while a Gt value of 42,000 was adequate to produce direct filtration effluent turbidities and particle size distributions compatible with those achieved by a conventional treatment process and in compliance with current EPA drinking water standards.

The length of a filter run for coarse media filters was shown (Hutchison & Foley, 1979; Shea, Gates & Argaman, 1971; Hutchison, 1974) to be inversely proportional to the floc density. It is equally important that the uniformly sized floccules can penetrate throughout the depth of the filter bed.

Various mathematical models have been presented to predict filtrate quality (turbidity) and head loss development with time as functions of influent solids concentration, filtration rate, media grain size, and media depth. Hudson & Wolfner (1967) showed, however, that the destabilization and aggregation of suspended particulate matter during rapid mix and flocculation have greater overall effects on filtered water quality and filter head loss than the listed variables. They stressed that, unlike sedimentation dependent on the production of large, bulky flocs, the aggregate removal by direct filtration produced a better filtered water quality by high-intensity flocculation producing a relatively small, dense floc.

2.4.2 Experiences from Direct Filtration Used in Pilot Scale and Full Scale

Letterman & Logsdon (1976) did a survey of direct filtration practice in the United States; seventeen usable questionnaires were returned from plants with granular media filters. The design capacity of the plants ranged from serving 5,000 persons to 2 million. Rapid mix (baffles in pipes, static mixer, hydraulic jump, backmix or propeller in tank, and in-line propeller) was used by 15 of the plants, while 8 of the plants had flocculation with detention times ranging from 10 to 60 min. The operating filtration rate ranged from 2.4 to 14.7 m/h. Dual media (coal and sand) was used at 11 of the plants. The effective size of the coal was typically 0.9-1.1 mm and sand sizes were mainly in the range of 0.4-0.5 mm. Graded gravel was used as bottom support for 11 of the plants. Only four of the plants used air in the backwash procedure while 10 used surface wash. The backwash rates varied from 20 to 54 m/h. Average water volume required per backwash was 8.5 m^3/m^2. Five plants used alum, 6 alum and a polymer, and 3 cationic polymers. Seven plants used some type of polymer as a filter aid, i.e., added polymer immediately before the filter. Letterman & Logsdon (1976) indicated a relationship between polymer usage and the increasing need for water in the backwash procedures. Twelve of fifteen respondents achieved filter runs of 24 hours or more, while 9 had minimum runs of 6 hours and less due to high turbidity and phytoplankton in the raw water. An average turbidity of 3 Turbidity Units was exceeded at 50 percent of the plants, while the influent turbidity averaged 10 Turbidity Units or less.

Logsdon (1978) discussed the use of direct filtration. The Safe Drinking Water Act, 1974, giving a maximum contaminant level of 1 NTU would have potential impact upon large utilities presently relying on the watershed protection principle. Direct filtration was suggested as a possible solution. Logsdon (1978) pointed out some of the advantages and disadvantages of direct filtration compared to conventional water treatment;

Advantage:

> Cost Savings. Lower plant construction costs and possible savings on land cost. Elimination of settling basins yield capital savings of 20-30 percent (Culp, 1977). Additional savings stem from being able to treat water with 10-30 percent reduced chemical doses and having less equipment to operate and maintain. Logsdon et al. (1978) estimated the costs for direct filtration plants and related the costs to costs of existing plants.

Disadvantages:

> (1) The capital savings can be slightly offset by reduced length of filter runs.

(2) All solids are removed by the filter and practical upper limits exist in the turbidity, color, and algae that can be present in raw water without causing too many problems. Culp (1977) suggests:

turbidity: 100-200 NTU
color: 100 units
turbidity plus color: 25 units each
phytoplankton : 500-1000 asu/ml

(3) Due to the short residence time of water in a direct filtration plant, quality changes in raw water must immediately be considered, i.e., regulation of operation and monitoring of water quality is of major importance.

According to Logsdon et al. (1978), effluent turbidities of 0.1 NTU can be produced from direct filtration plant. They also pointed to the fact that the Duluth filtration plant was proven to be very effective in removing amphibole asbestos fibers when operating in the rapid mix filtration mode.

The importance of pretreatment is stressed by several investigators, and Monscvitz et al. (1978) presented interesting results obtained from the Southern Nevada Water System which supplied water to the Las Vegas area. The treatment plant was designed for 2 million people and the direct filtration processes used "flash mixers", i.e., the coagulation took place within the filter bed without floc formation before the water entered the filters. The raw water had an average low turbidity, less than one NTU, but periodically high amounts of plankton. Several problems have occurred since the plant started in 1971, primarily because of insufficient floc formation. Analyses showed that approximately 50 percent of the aluminum added to the flash mixers was carried over into the finished water. Jar-test studies indicated that 15 to 20 minutes flocculation to develop an adequate floc that could be retained in the filter media.

Because of the rapid growth of the Las Vegas area, an expansion of the plant was needed, and extensive pilot plant studies started to evaluate floc formation, zeta potential, filtering and settling characteristics for varying coagulant dosages. With the short detention time and mixing time of the full scale plant, a liquid alum dosage of 22 mg/l was required to raise the raw water zeta potential from a level of -20 to 0. Increasing the flocculation time decreased the required dose to a base level of approximately 8 mg/l liquid alum to produce zeta potential of 0. These results are presented in Figure 46. The importance of flocculation prior to the filter are demonstrated in Figures 47 and 48. Sedimentation prior to the filters was also evaluated in this pilot study, and at very low surface loading (0.6 m/h) a greater efficiency of plankton removal was found. This did not, however, according to Monscvitz et al. (1978), warrant the

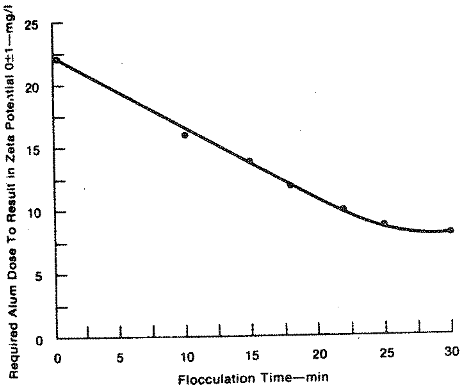


Figure 46. Effect of flocculation time on required alum dosage. (Monscvitz et al., 1978)

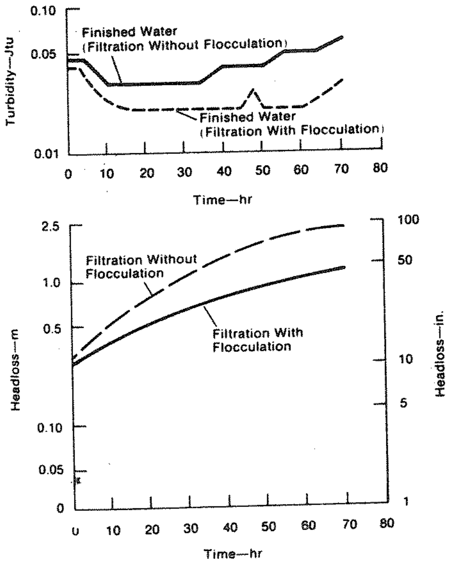


Figure 47. Typical filter permance with and without flocculation pretreatment. (Monscvitz et al., 1978)

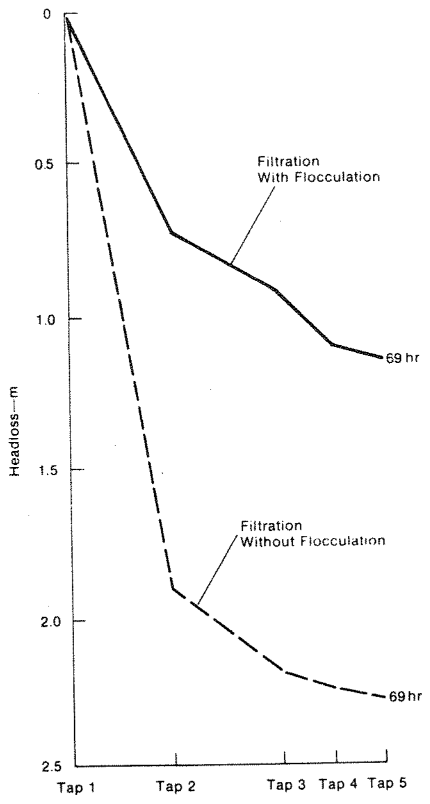


Figure 48. Headloss through filter media with and without flocculation pretreatment. (Monscvitz et al., 1978)

cost of providing clarifiers which would add more than 50 percent to the capital cost of the project.

Adin et al. (1979) stressed the importance of pretreatment.

Treweek (1979) pointed out the importance of aggregation of suspended particulate matter during rapid mix and flocculation on both filtered water quality and head loss.

Hutchison & Foley (1974) presented results from Canadian plants using direct filtration and stressed the importance of pretreatment.

They summarized factors directly increasing the probability for breakthrough in direct filtration when using alum as coagulant;

a. Increasing the filtration rate (> 6 gpm/sqf)

b. Increasing the effective size of the coal and sand

c. Increasing the alum dosage

d. Increasing the flocculation gradient 20-50 s^{-1}

e. Increasing the flocculation time to more than 10 min.

f. Decreasing the depth of media.

Adin & Rebhun (1974) studied contact flocculation, defined as direct filtration process without flocculation basin, using higher rates of filtration. When using alum as the only coagulant, efficient filtration was achieved only at filtration velocities of 5-10 m/h and with media of up to 0.6 mm grain size.

Mueller & Conley (1981) suggested that direct filtration gives relatively long filter runs and excellent water quality (0.2 units or less) when treating raw waters containing up to 15 turbidity or color units. Waters containing up to 50 turbidity or color units could also be treated successfully by direct filtration, but short filter runs would be typical (4-8 hours at 12 m/h). The effluent quality would be the same.

Fulton (1977) discussed conventional and direct filtration for treatment of surface water supplies in the New York City metropolitan area. He concluded that pilot plant research results would tend to favor direct filtration. Economic studies indicated that direct filtration should be equal to or less costly than conventional treatment as long as alum feed rates were 20 mg/l or less. The studies indicated also that improvement of the sedimentation process in the conventional treatment facilities could make this process less costly than the direct filtration alternative. Fulton (1980) presented the results from a pilot plant study comparing direct filtration, conventional (optimized) filtration and a conventional plant, showing that the construction costs of the direct filtration plant were around 11 percent lower than for the conventional (optimized) filtration plant. Gadkari et al. (1980) investigated the use of direct filtration for the raw waters of Bhatsai river near Bombay. The turbidity of the raw water ranged from 5 to 150 JTU, total solids from 100 to 200 mg/l, pH from 7 to 8. The results were as follows;

i) For raw water turbidities ranging from 100 to 130 JTU the filter runs ranged from 2 to 5 hours at a filtration rate of 7.4 m/h when the waters were fed the alum doses determined by jar-test, 20 to 25 mg/l. When the same waters were dosed with 10 to 13 mg/l alum, the filter run lasted only 30 minutes before the turbidity exceeded 5 JTU even at 6.1 m/h filtration rate.

ii) When raw water turbidity ranged from 80 to 100 JTU and alum dosage from 20 to 25 mg/l, the filter runs varied between 6 and 14 hours at a filtration rate of 7.4 m/h.

iii) At a filtration rate of 7.8 m/h and raw water turbidity ranging from 40 to 80 JTU, the filter runs varied between 5 and 10 hours.

iv) For raw water turbidities between 130 and 150 JTU at a filtration rate 6.1 m/h, the filters could only run for 1½ to 2 hours.

Direct filtration using alum for this raw water was not found to be practical due to the short filter runs.

Edzwald (1979) studied the removal of naturally occurring organics from a gravel pit added extracted humic acid and from Stonelick Lake using the direct filtration process. The study parameters were color, tirbidity removal and head loss development. Also the trihalomethane precursors were evaluated by measuring the trihalomethane formation potentials of the raw and filtered waters. Cationic polyelectrolytes were used and indicated that direct filtration was a feasible process for color and turbidity removal even at high color (340 Pt-Co units) and high turbidity (25 NTU).

In the Ontario district, Hutchison (1976) studied several variables influencing the direct filtration process, such as raw water turbidity, diatom concentrations, and mixing. Changing the filter media from sand to anthracite and sand increased the filter runs. Higher turbidity levels resulting in higher coagulant demand produced a larger and consequently weaker floc than that required by direct filtration. Increasing the flocculation time resulted in a corresponding decrease in filtration time, with breakthrough occurring earliest at the higher flocculation times. Ontario's water plants began having problems with slow-forming floc when the water temperature dropped below 3.3°C. The results from direct filtration experiments in pilot scale include (1) a nearly inversely proportional relationship between alum dosage and filter run, and (2) a small effect of turbidity on filter run all other variables being constant. Floc was found to be almost invisible at 10 ppm alum dosage, but the filter performed adequately. The minimum flocculation time studied was 16 min., resulting in no after-flocculation problems. Declining rate of filtration vs. constant rate of filtration was studied without seeing any effect. Also the residual aluminum content in treated water was measured and indicated the aluminum residuals were a function of the pH of the flocculated water only. When treated water pH of 7.4 or more was achieved the residual aluminum content exceeded 0.1 ppm.

Hutchison (1976) concluded that direct filtration can be a viable alternative to conventional sedimentation - filtration systems when the coagulant dosage is < 15 mg/l and the diatom concentration is below 1000 asu/ml. Residual aluminum concentrations in the treated water from some conventional water treatment plants in Ontario were found to cause "after-floc" in the distribution system when the level exceeded 0.4 mg/l. At alum dosages higher than 20 mg/l, the use of polymers was necessary to prevent turbidity breakthrough. The polymer dosage coupled with high coagulant dosage led to short filter runs (< 10 hrs) at 12 m/h filtration rate. Also ferric chloride was used indicating stronger floc and low iron residual (< 0.05 mg/l) in the pH range of 8.0-8.3. This provided good results, but the corrosive nature of ferric chloride created problems. In all experiments the probability of filter breakthrough prior to terminal head loss increased with higher coagulant dosage, with increasing filtration rate, with increasing flocculation gradient above 20 s^{-1}, with increasing flocculation time to more than 10 min., and with decreasing depth of media.

3. MATERIALS AND PROCEDURES

3.1 Analytical Procedures

3.1.1 Color

Color was determined using an EEL absorptiometer at a wavelength of 601 nm. A set of color standards (Platina) was run on the meter, and the curve is presented in Figure 49. The samples analyzed were not pH adjusted. Knowing that the color changes with pH, a series of color versus pH was run for the raw waters studied (Figure 50). In this research research the interest has been in color at the actual pH of the samples. No pH adjustment was done. Color was determined both on filtered (Glassfiber filter, type C) and unfiltered samples.

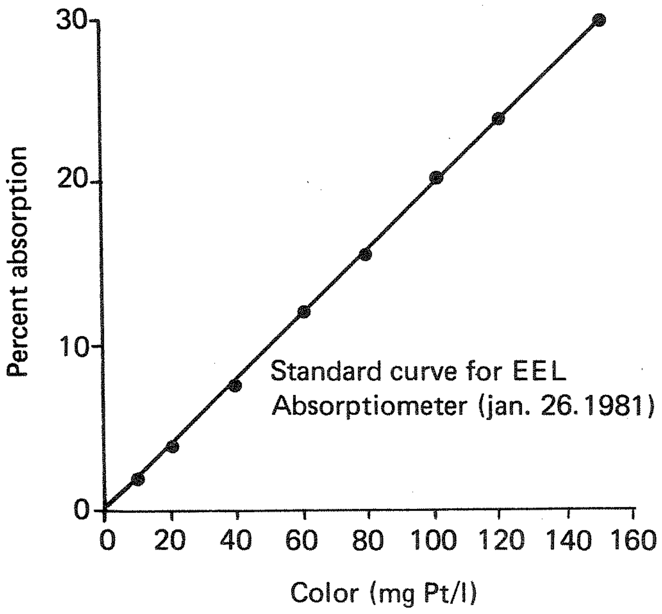


Figure 49. Standard color curve for photometer used in color determination.

3.1.2 UV Absorption

Percent transmission was determined at 253.7 nm wavelength on a Perkin Elmer photometer using a one cm cuvette. The UV absorption as cm^{-1} was calculated as the negative logarithm of 1/100 of the percent transmission. Only filtered (GF/C) samples were analyzed. UV absorption at different wavelengths was checked for one sample of the different waters studied. See Figure 50.

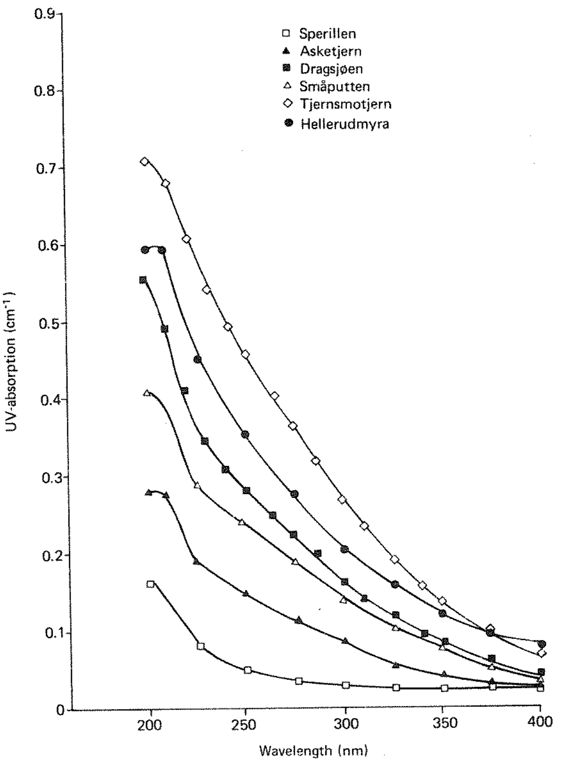


Figure 50. UV absorption at different wavelengths for the raw waters used in this study.

3.1.3 Total Organic Carbon (TOC)

TOC was determined on filtered samples (GF/C) on a Carlo Erba TCM 500/P TOC analyzer. The method includes oxidation of the organic compounds by catalytic combustion to carbon dioxide (CO_2). The CO_2 is reduced to methane (CH_4) which is determined by a flame-ionization detector (FID).

3.1.4 Hydrogen Ion Concentration (pH)

A Radiometer, Type PHM 29 with a combined electrode type GK 2311C, GK 2303C, was used to determine pH. The pH-meter was calibrated against Radiometer buffer solutions pH 6.50, pH 4.00 and pH 9.50.

3.1.5 Specific Conductivity

The specific conductivity was initially determined on unfiltered and filtered (GF/C) samples on an electrolytic conductivity measuring set (Electronic Switchgears, London). No difference in specific conductivity between the filtered and unfiltered samples was registered. Therfore specific conductivity was analyzed only on filtered samples.

3.1.6 Colloidal Charge

The colloidal charge of the samples was determined by a colloidal titration technique. Kawamura & Tanaka (1966) have shown this technique to be reliable for determination of the charge characteristics of colloids and the determination of the isoelectric point of systems.

Generally a negative colloid can be made to react with a positive colloid in a stoichiometric manner with a precipitate being formed near the isoelectric point. The reaction between polyvinyl sulfate-potassium salt (PVSK) with glycol chitosan (GC) is an example of this type of reaction. Polyvinyl sulfate-potassium salt, has an $-SO_4H$ functional group and is thus ionized to $-SO_4^-$ with the production of a negative colloid. Glycol chitosan (GC), on the other hand, has an amino ($-NH_2$) group which will add a portion to form $-NH_3^+$, resulting in a positive colloid. The two colloids will react in a nearly stoichiometric manner, neutralizing one another to form an insoluble precipitate. Toluidine blue (TB) was used as a color indicator in the determination of the endpoint of the reaction. When TB solution is mixed with a positive colloid, the color of the resulting solution is light blue. Adding TB to a suspension of a negative colloid results in a purple mixture.

For this research 2.5 ml of approximately 0.001 N glycol chitosan, Type (GC) (which is a standard positive colloid), and a few drops of 0.1 percent toluidine blue, Type (TB), indicator were added to a 100 ml filtered water sample and mixed with a magnetic stirrer. The solution was then supposed to have an excess amount of positive colloid and a light blue color. In the case of raw water of high pH, 5 ml GC was needed to obtain an excess amount of positive colloid. The excess of positive colloid was then titrated with a standard solution of 0.001 N polyvinyl sulfate-potassium salt (PVSK) until the color changed from light blue to purple, which indicated the equivalence point where there is a stoichiometric amount of negative and positive colloids. Exactly the same procedure was followed using 100 ml distilled water. The colloid charge of the sample was calculated as follows:

$$\frac{\left\{\begin{array}{l}\text{ml PVSK needed}\\ \text{for the sample}\end{array}\right\} - \left\{\begin{array}{l}\text{ml PVSK needed for}\\ \text{the distilled water}\end{array}\right\}}{\text{0.1 litre sample}} \times 0.001\ \text{meq/ml}$$

= colloidal charge (meq/l). (The method is discussed in Appendix 6.)

3.1.7 Alkalinity

Alkalinity was determined by titration of a 100 ml filtered (GF/C) sample with 0.01 N H_2SO_4 to pH 4.5 and was calculated as meq/l.

3.1.8 Potentiometric Titration

Potentiometric titration curves (Narkis & Rebhun, 1975) were made by adding NaOH to pH 10.00 and then titrating with HCl. The inflection points for phenolic-(OH) groups at pH around 8.0 and for carboxylic-(COOH) groups at pH around 4.7 were determined. Narkis & Rebhun (1975) calculated the inflection points as me/100 g humic or fulvic acid. Working with natural water, the inflection points were calculated as μeq/l and μeq/mg C.

3.1.9 Relative Molecular Weight Determination by Gel Filtration

The "relative" molecular weight of the three major water sources was determined using gel filtration (G-25 fine, molecular weight range 1,000-5,000) for concentrated water from Hellerudmyra, Tjernsmotjern, and Småputten. The method is described by Gjessing

(1973), but 0.02 N KNO_3 was used to elutriate the samples of the concentrated humus through the G-25 column. Blue dextran and 1 M KNO_3 were used to calibrate the gel columns. Williams (1974) stressed the expected difference in solute-gel interaction between high-molecular weight carbohydrates (dextrans) and yellow organic acids (aquatic humus) containing phenolic and carboxylic acid groups. In this study the different water sources were assumed to contain organic acids with similar groups, and the gel-filtration study was used to determine relative differences only.

3.1.10 Turbidity

The turbidity was determined on unfiltered samples using a Hach turbidimeter (Model 2100 A).

3.1.11 Aluminum and Iron[1]

Aluminum and iron concentrations were determined colorimetrically on a Technicon Auto Analyzer. Aluminum was complexed with pyrocatecol violet at pH 6.1-6.2 and was determined colorimetrically at 590 nm (Henriksen & Bergmann-Paulsen, 1975). Driscoll (1981) described a method for fractionation of the complexed aluminum into 1) organic monomeric aluminum including organically chelated aluminum, 2) inorganic monomeric aluminum including free aluminum and the aqueous inorganic complexes such as fluorides, hydroxides and sulfates, and 3) the extremely stable organic and hydroxo organic complexes. This method

---

[1] The analysis was performed following the procedure used at NIVA (Henriksen & Bergmann-Paulsen, 1975).

was used to provide some concept of the aluminum complexes present in one raw water sample and the treated water sample from Tjernsmotjern (Naas, 1982). A modification of the Henriksen & Bergmann-Paulsen (1975) method was used to determine the same fractions (Müller, 1982).

3.1.12 Calcium, Magnesium, Sodium, Potassium, Manganese, Copper and Lead[1]

The metals were determined by atomic absorption spectroscopy (Perkin Elmer Model).

3.1.13 Chloride, Nitrate, Sulfate and Phosphate[1]

Chloride, nitrate, sulfate and phosphate were determined colorimetrically by a Technicon Auto Analyzer. Modified *Standard Method* procedures were used for chloride (Henriksen, 1966), nitrate (Henriksen & Selmer-Olsen, 1970) and sulfate analyses (Henriksen & Bergmann-Paulsen, 1975). Phosphate was determined colorimetrically at 880 nm using a modified *Standard Methods* procedure (Koroleff, 1970).

3.1.14 Total Suspended Solids

Total suspended solids were determined gravimetrically. A 70 ml volume was centrifuged in a Sorvall Superspeed Centrifuge, Type SS-1, KSB-1 for approximately 10 minutes. The clear centrate was withdrawn from the centrifuge tube and the solids put in an aluminum foil dish and dried at 105° overnight. In the morning, they were placed in a

---

[1] The analyses were performed following the procedures used at NIVA (nitrate: Henriksen & Selmer Olsen, 1970; sulfate: Henriksen & Bergmann-Paulsen, 1975; phosphate: Koroleff, 1970).

dessicator and weighed.

3.1.15 Volatile Suspended Solids

Samples from the total suspended solids test were placed in a muffle furnace at 550°C for one hour. They were then placed in a dessicator and weighed.

3.2 Characteristics of Water Sources

There are at least 200,000 lakes in Norway. Most of the lakes are products of glacial activity, but compared to other similar areas, most Norwegian lakes are deep.

A large part of the precipitation during the year occurs as snow which means that the surface runoff is very low during the winter time. The melting in the spring and the period of heavy rain in the autumn result in the two periods with high surface runoff during the year. Most of the lakes have the following temperature pattern:

<u>Winter</u>, frozen lake, inverse temperature stratification.

<u>Spring</u>, heating of the surface water, resulting in complete mixing.

<u>Summer</u>, stratification.

<u>Autumn</u>, cooling, resulting in turnover (complete mixing).

Large areas in Norway contain almost insoluble rock types which means that lake water has about the same composition as rainwater. This in turn means that most of the surface water in Norway is soft and acid. The water of the lakes at low elevation in the eastern part of Norway is highly colored from humus extracted from soil and boggy areas. Many lakes in Norway are influenced by acid rain resulting in very low alkalinity and low pH. Lakes in the eastern part of Norway at elevations lower than approximately 210 m are located in the late-glacial upper marine limit. The sediments are thus composed of deposits of unconsolidated marine sediments containing such constituents as carbonates and sulfates. Therefore ground and surface waters are relatively well buffered and the pH is not influenced by acid rain.

Waters from several lakes in the eastern part of Norway have been used in this study. A few experiments were done using water from Sperillen, located in Ringerike municipality in Buskerud county (see Figure 51). The lake basin in this region consists mainly of

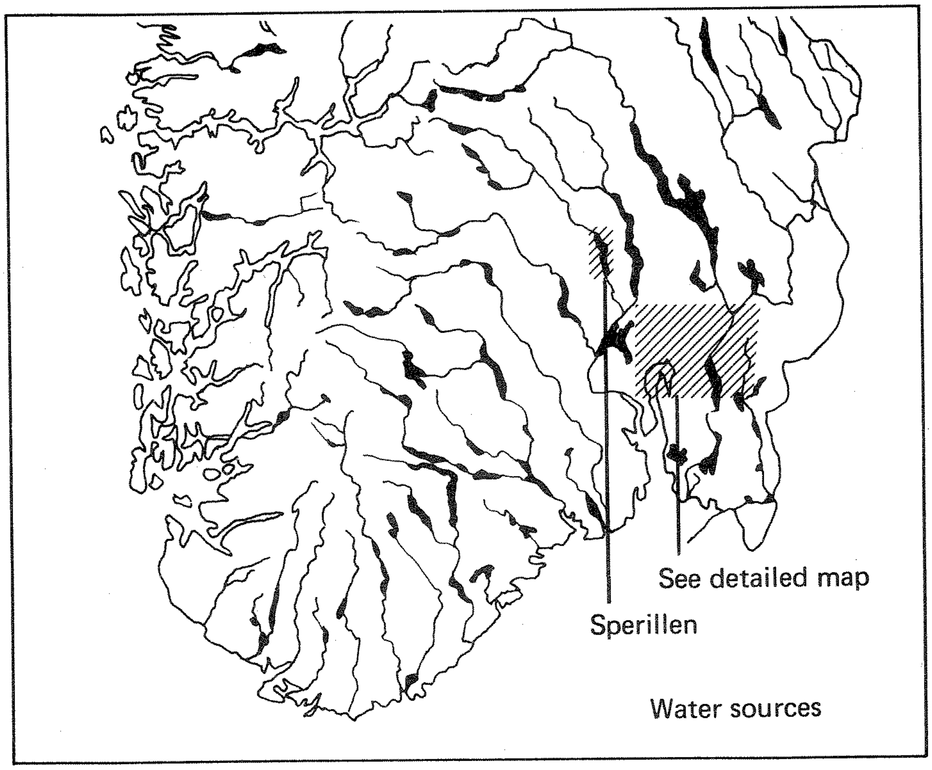


Figure 51. Locations of water sources studied in south-eastern Norway.

transformed cambrian species of rocks and sparagmites (metamorphous sandstone); further south the bedrock dominates. Here glacial scouring has produced a thin layer of loosened rock material.

The watershed (4,290 km^2) consists of approximately 28.8 percent forest, 3.7 percent boggy area, and 3.2 percent agricultural area. Settlement (4.5 person/km^2) and agriculture are of major importance in this area and account for the remainder of the land use.

The main data regarding the lake basin for Sperillen are as follows:

An elevation of	150 m
lake surface	37.6 km^2
maximum depth	123 m
mean depth	38.5 m
mean runoff	90 m^3/sec
theoretical detention time	210 days.

The water quality of Sperillen is very different from the other sources studied, and a comparative laboratory study was interesting.

The detailed map in Figure 52 illustrates the lakes mainly studied in this work. Water from Hellerudmyra and Tjernsmotjern was used during all the laboratory work while water from Småputten was used in full scale operation of the electrolytic process and in a few laboratory tests. Water from Dragsjøen and Asketjern was used in a few laboratory tests.

Dragsjøen, Tjernsmotjern and Asketjern are located in Nes municipality in Akershus county. The lake basins in this region are underlain by gneiss and gneissgranitic rocks and belong to the bedrock

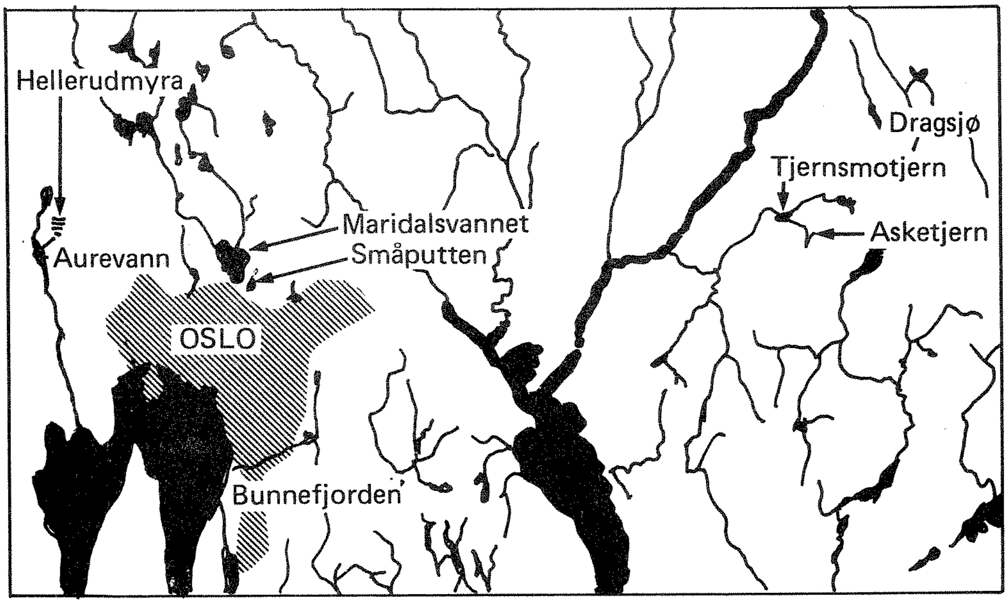


Figure 52. Detailed map of the water sources studied.

Primary sources: Tjernsmotjern, Hellerudmyra and Småputten.
Secondary supplies: Dragsjøen and Asketjern.

series in the eastern part of Norway. Glacial scouring has produced a thin layer of loosened rock material. The region contains large areas with boggy ground. In addition, the watershed is covered mainly with softwood. There are no settlements in the water shed. The main data regarding the lake basin of Dragsjøen are as follows:

An elevation of	176 m
surface of lake	0.5 km^2
maximum depth	41 m
mean depth	12 m
volume	6.4 mill. m^3
watershed surface	6.7 km^2

mean runoff	8,100 m^3/d
theoretical detention time	2 years.

Similar detailed information does not exist for Tjernsmotjern and Dragsjøen. These three water sources have been used as potable water supplies. Dragsjøen and Asketjern are still in use, while Tjernsmotjern is used only occasionally for potable water supply. The sources are highly colored, and do not fulfill the health authorities' requirements because of the high color.

Water from Hellerudmyra was taken from a creek flowing into Aurevatn, which is the drinking water source of Bærum municipality near Oslo. The creek comes from a bog (Hellerudmyra) about 800 meters from the lake (Aurevatn). The water was taken from the source of the creek, and will through all the further discussion be called Hellerudmyra. This water can be considered as containing freshly extracted humus. Gjessing (1970a, 1970b, 1971) has previously characterized the water, and the water taken was analyzed for different chemical parameters. Some of the most important characteristics will be summarized here. Gjessing (1971) showed color as a function of pH. See Figure 53. Gel filtration and membrane dialysis were used (Gjessing, 1971) to study the change in composition of humus with the change of pH. Presupposing that the general adsorption on Sephadex is small, Gjessing (1971) concluded that the molecular size of humus increased with increasing pH. His membrane experiments confirmed this result. Using Sephadex gel filtration of water from Hellerudmyra, Gjessing (1970a) showed that approximately 60 percent

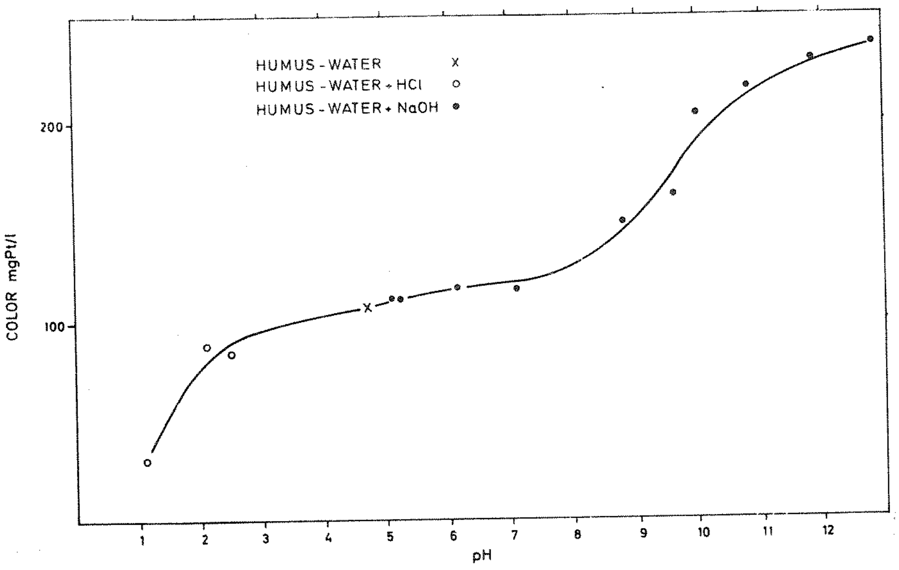


Figure 53. Change of color with change of pH (Gjessing, 1970a).

of the humus had a molecular weight between 5,000 and 50,000, while 40 percent was between 100 and 5,000.

Gjessing (1972) studied also the electromobility of the humus from Hellerudmyra, using the isoelectric focusing technique. As previously mentioned, his experiments showed that about 80 percent of the aquatic humus from Hellerudmyra had their isoelectric point in the pH range of 1.25 to 1.75 (Figure 54 and Table 18).

Småputten is a small lake draining a boggy area in the Oslo municipality. The lake belongs to the drainage area for Maridalsvannet (the drinking water source for Oslo). The lake is located in Lillomarka, the recreation area northeast of Oslo. Only a few houses are located near the lake. The lake does not receive wastewater. The

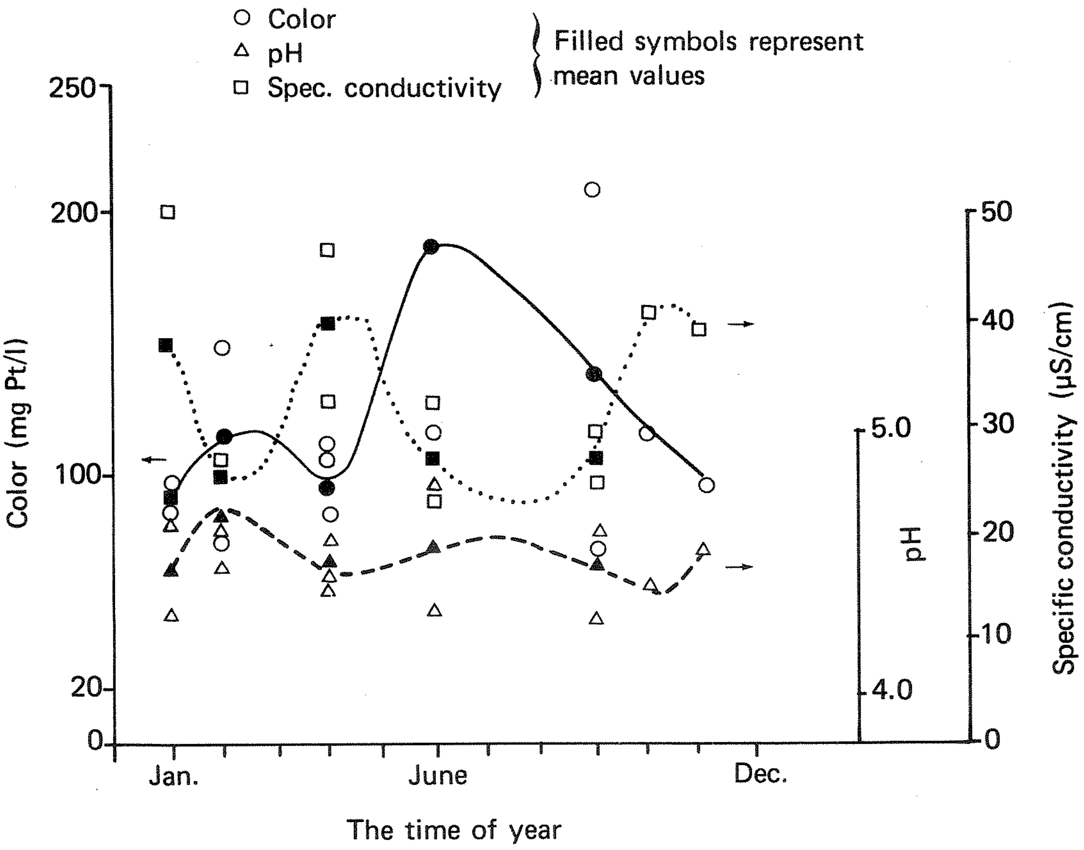


Figure 54. Color, specific conductivity and pH of Hellerudmyra water as a function of time of the year.

Filled symbols represent mean values.

Table 18. Important characteristics of water from Sperillen, Dragsjøen, Tjernsmotjern, Asketjern, Småputten and Hellerudmyra.

(Turbidity was analyzed on unfiltered samples, and the rest of the parameters were on filtered samples (GF/C filter)).

Lakes / Parameters	Sperillen	Dragsjøen	Tjernsmotjern	Asketjern	Småputten	Hellerudmyra
Turbidity (NTU)	0.75	3.5	0.9	0.35	0.95	0.9
Color (mg Pt/l)	10	75 - 78	110 - 140	42 - 39	44 - 78	105 - 110
UV-absorption (cm^{-1}) at 253.7 nm	0.089	0.43 - 0.44	0.53 - 0.65	0.25	0.26 - 0.35	0.50 - 0.52
TOC (mg C/l)	2.3	9.5 - 9.7	12.2 - 15.6	6.5 - 6.6	5.9 - 9.6	10.8 - 12.2
Spec. conductivity (μS/cm)	29	43 - 44	29 - 55	38 - 40	83 - 115	29 - 35
pH	6.9	6.2 - 5.9	6.0 - 6.5	5.8 - 6.3	6.2 - 7.3	4.3 - 4.9
Alkalinity (meq/l)	0.13	0.12 - 0.14	0.08 - 0.14	0.06 - 0.11	0.40	∼ 0

main data regarding the lake basin are as follows:

An elevation of	300 m
lake surface	0.02 km^2
maximum depth	4.5 m
mean depth	≈2.5 m.

The three major water sources studied show a few significant differences. Hellerudmyra has the lowest pH and almost no alkalinity, while Småputten has a high pH and alkalinity compared with other Norwegian lakes. The specific conductivity of Småputten is high compared with other lakes. Småputten has the lowest organic carbon content of the three water sources mainly studied. The organic carbon content of this lake varied during the study period. In the first part of the period this lake was not ice covered, and, in the last part, the lake was ice covered and anoxic.

The color and colloidal charge of the three sources, Tjernsmotjern, Hellerudmyra and Småputten, were determined as a function of pH (Figure 55). The zero point of charge of the three sources was for:

Hellerudmyra at pH 4.2
Tjernsmotjern at pH 4.9
Småputten at pH 4.2.

All the three sources showed higher color at higher pH.

For Hellerudmyra, at pH 3.0, the color equaled 80 mg Pt/l, and, at pH 10.0, around 130 mg Pt/l. For Tjernsmotjern, at pH 3.0, the color was equal to 85 mg Pt/l and, at pH 10.0, 125 mg Pt/l. For Småputten, at pH 3.0, the color was 58 mg Pt/l, and, at pH 10.0, 95 mg Pt/l.

Potentiometric titration curves were made for the three sources (Figure 56). The phenolic (-OH) and the carboxylic (-COOH) groups were determined by finding the two inflection points. Based on the Narkis & Rebhun (1977) study the necessary amounts of effective positive charge in the flocculant molecules were determined. The negative charge of the organics in each of the three water sources were determined by calculating the meq of HCl needed to change the pH from the initial pH at 17 ml of 0.01 N HCl to the pH at each inflection point. The charge was calculated as μeq/l and μeq/mgC for each of the three water types. The results are summarized in Table 19, showing the highest chemical demand for Småputten and the lowest for Hellerudmyra if both the carboxylic and the phenolic groups are ionized.

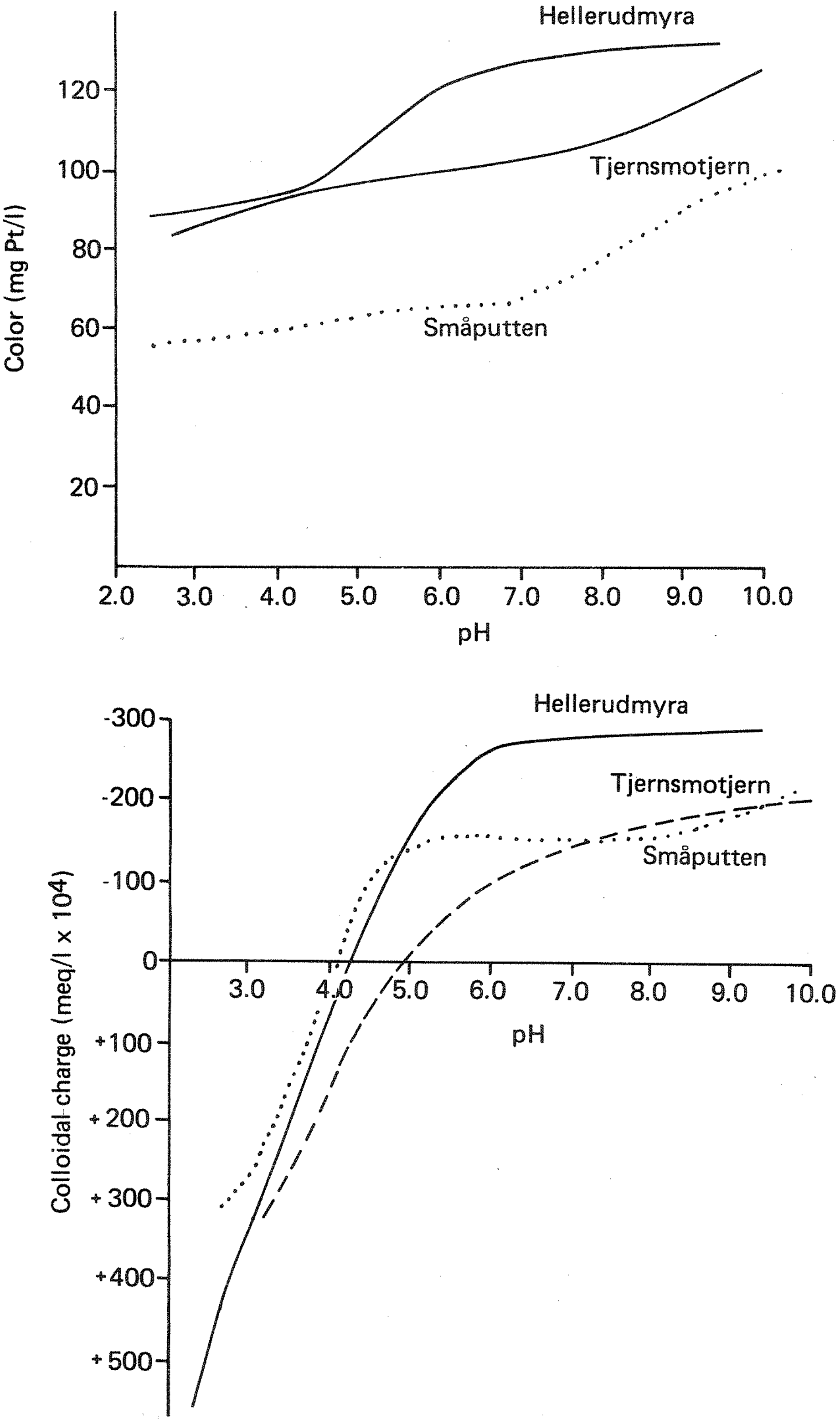


Figure 55. Color and colloidal charge for various pH-values for humus water from Tjernsmotjern, Hellerudmyra and Småputten.

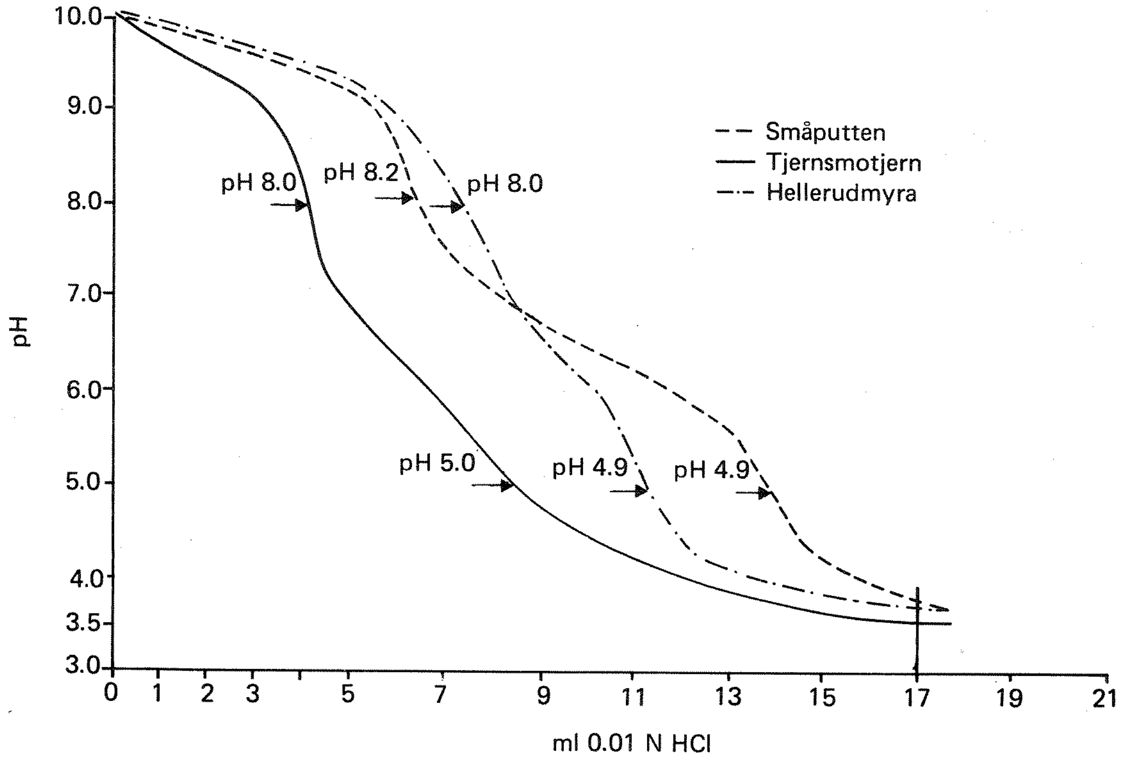


Figure 56. Potentiometric titration curves for Tjernsmotjern, Småputten and Hellerudmyra.

Table 19. Phenolic (-OH) and carboxylic (-COOH) groups in three different water sources.

Water sources	TOC (mg C/l)	-O-			-COO-			Σ-O- + -COO-
		pH	(μeq/l)	(μeq/mg C)	pH	(μeq/l)	(μeq/mg C)	(μeq/l)
Hellerudmyra	11.0	8.0	95	8.6	4.9	58	3.4	12.0
Tjernsmotjern	14.0	8.0	128	9.1	5.0	88	6.3	15.4
Småputten	6.4	8.2	107	16.7	4.9	32	5.0	21.7

Also gel-filtration curves, showing absorption as a function of elution volume (Figure 57), were made for the three major sources. The total area under the curves was determined, and percent excluded

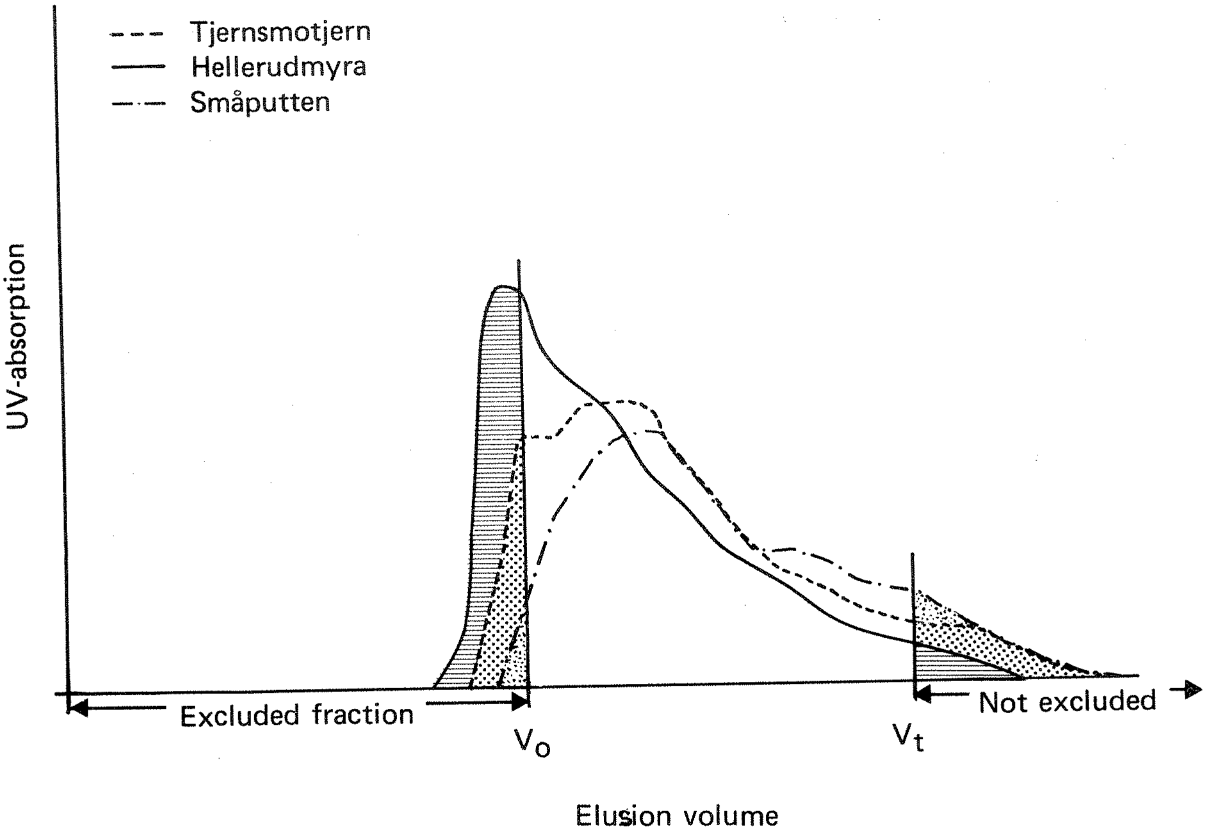


Figure 57. Results from gel filtration (G-25) of humus water from Hellerudmyra, Småputten and Tjernsmotjern.

KNO_3 was used to elutriate the samples.

fraction, percent fraction in the actual molecular weight limits for G-25 gel, and percent not excluded fraction were determined. See Table 20. Table 20 illustrates clearly that Hellerudmyra contains a higher fraction of high-molecular weight organics than Tjernsmotjern and Småputten. Småputten, however, contains the highest fraction of lower-molecular weight organics.

Table 20. Relative molecular weights for Hellerudmyra, Tjernsmotjern and Småputten.

Water sources	Percent excluded fraction	Percent fraction in the actual (1) molecular weight area	Percent not excluded fraction
Hellerudmyra	27	69	4
Tjernsmotjern	11	86	3
Småputten	4	86	10

(1) Based on the assumption that the same solute-gel interactions are occurring when filtering the aquatic humus of these three water sources as when filtering the dextrans, this actual molecular weight area would be between 1,000 and 5,000.

4. EXPERIMENTS

4.1 Laboratory Scale Experiments with the Electrochemical Reactor

Electrocoagulation was carried out in a small continuous flow electrochemical reactor containing 4 parallel aluminum sheets, each with a size of 14 by 21 cm and 2 mm thick, with a distance of 2.5 mm between each sheet. During the first part of the experiments the aluminum electrodes were removed from the reactor and weighed before and after each experiment. The basic principles involved in the electrochemical process are described in Figure 58 as is the water flow pattern. Raw water from Tjernsmotjern was used in those experiments studying factors of importance to the electrochemical process. Waters from Tjernsmotjern, Hellerudmyra, and Småputten were studied primarily in the conventional coagulation experiments. A few

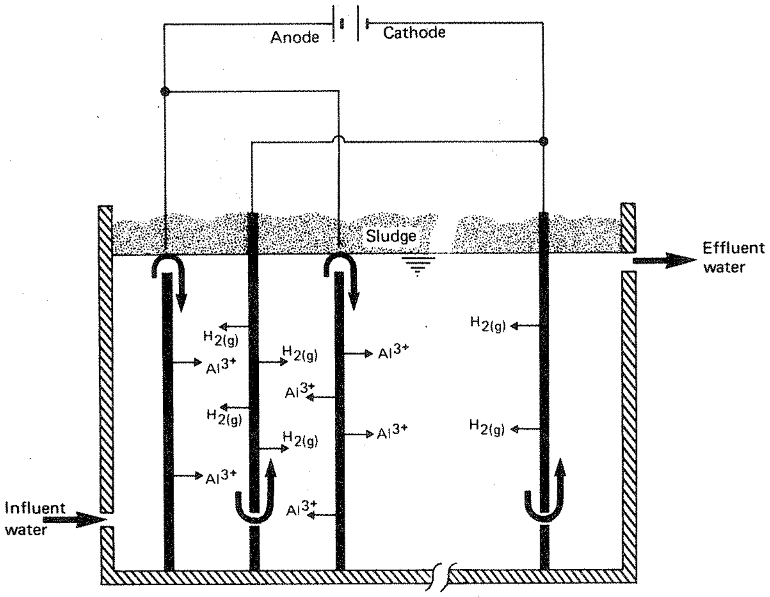


Figure 58. The basic principles involved in the electrochemical process.

coagulation experiments were performed with water from Sperillen, Asketjern, and Dragsjøen.

A stabilized DC power supply (6-12 V) was used, and a resistance box made it possible to regulate the current density on the sheets of aluminum. A multimeter was used to read the current values. The same multimeter was used to measure the applied voltage to the system. Figure 59 describes the system, and Figure 60 illustrates the setup.

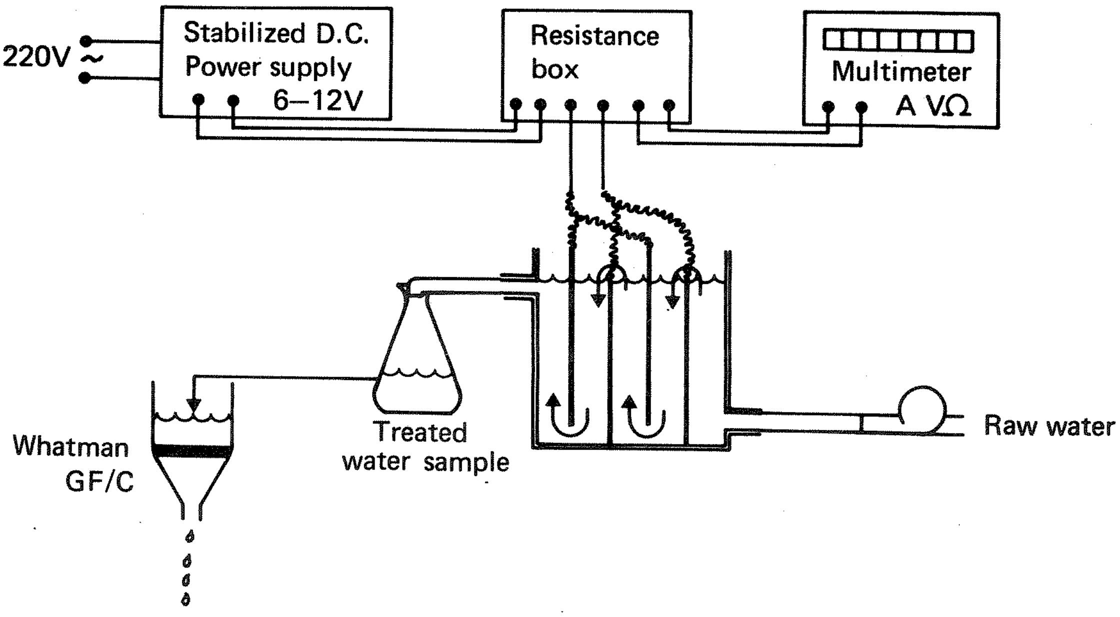


Figure 59. The equipment used in the electrochemical reactor study (laboratory scale).

In part of the experiments, a refrigeration unit (an Alfa-Laval unit) was used to maintain a cold storage bath for raw water to evaluate the importance of temperature on the electrochemical process.

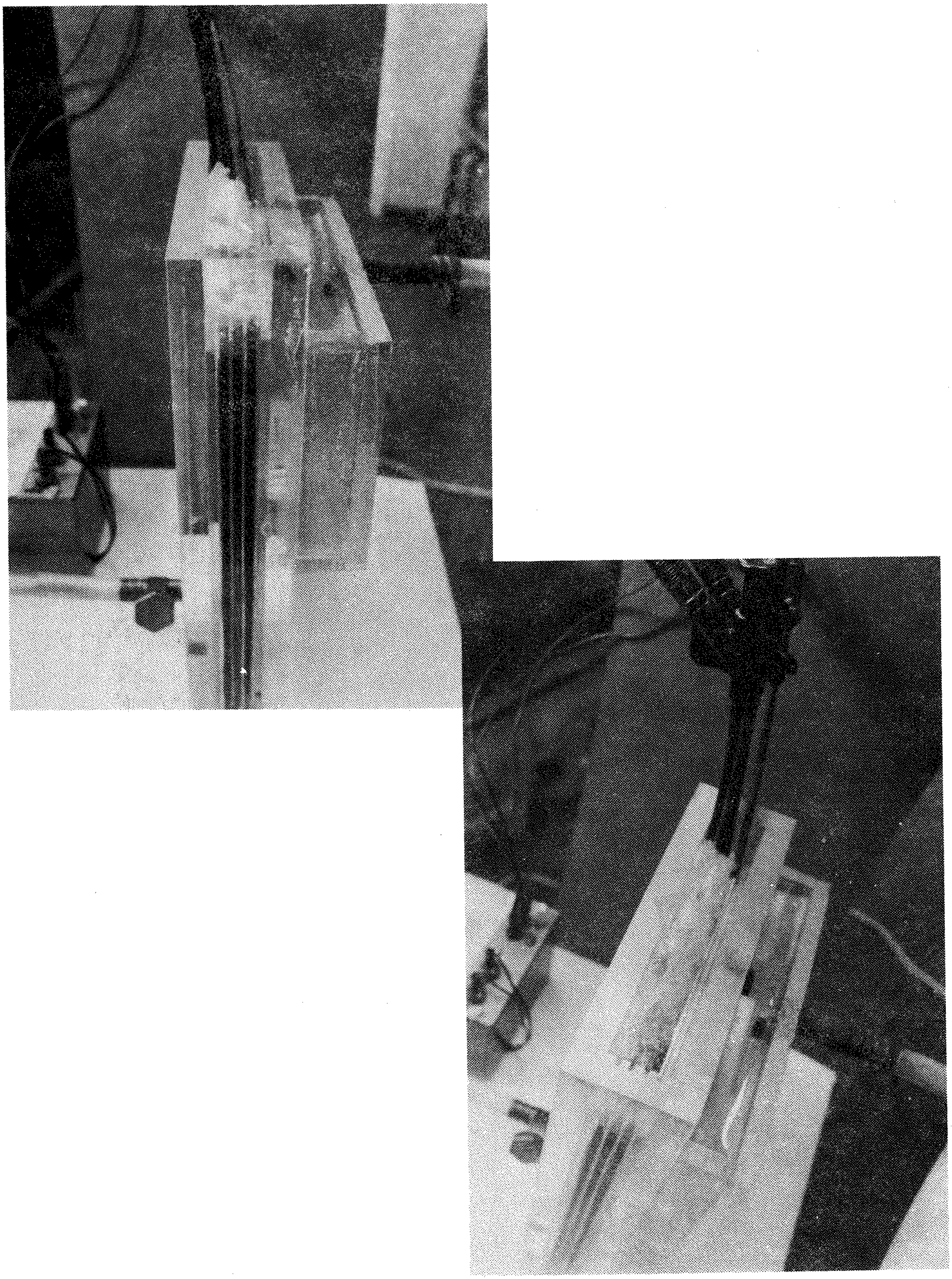


Figure 60. Photos from the laboratory scale experiments with the electrochemical reactor.

The water volume of the reactor was found to be 406 ml, and the theoretical detention time was compared with the experimental. In one experiment Rhodamine dye was added and the percent absorption was determined. The theoretical detention time was 30 seconds. In another experiment, table salt was used, and the specific conductivity at various time intervals was determined. In this experiment, the theoretical detention time was 72 seconds. The results are presented in Figure 61, showing good agreement between the two.

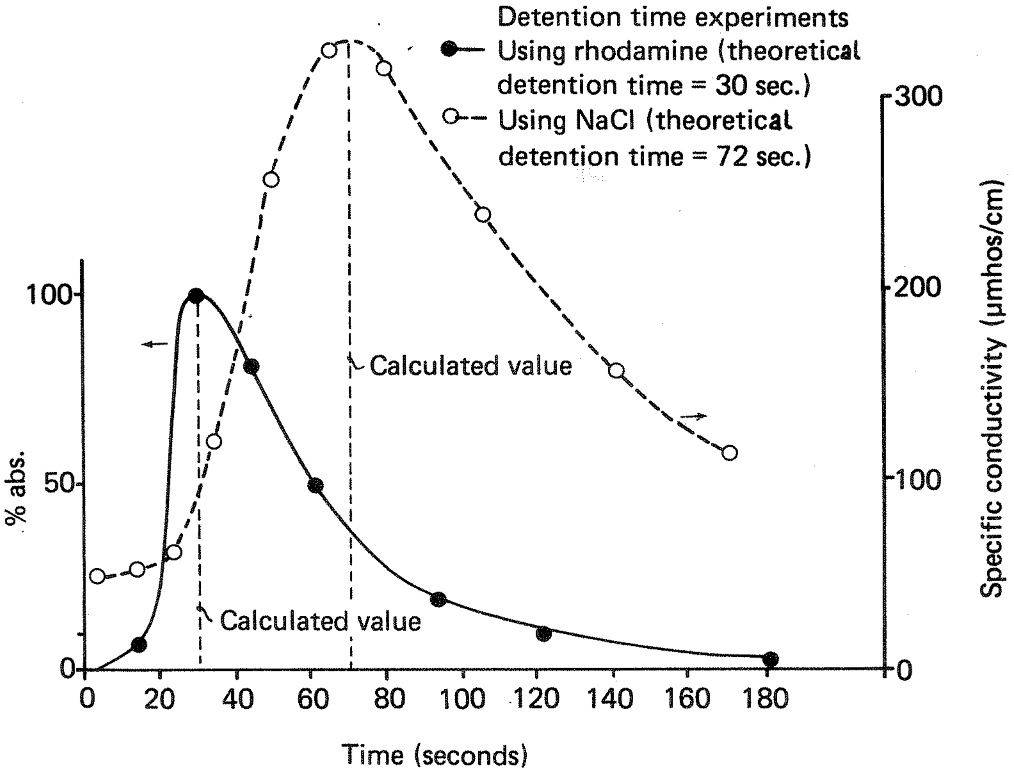


Figure 61. Results from detention time experiments using Rhodamine and table salt.

water flow in Rhodamine experiment = 0.81 l/min
water flow in table salt experiment = 0.34 l/min.

Also experiments have been conducted to estimate the necessary time interval for each experiment before steady state conditions were obtained. Samples were taken frequently during the 90 minute test period and analyzed for color and UV-absorption (254 nm). The results are presented in Figure 62. The figure indicates that steady state is obtained within the first 15 minutes. In the regular experiments, samples have been take after 45 minutes. The water flow in this experiment was 0.171 l/min., and this flow was used throughout the rest of the experiments.

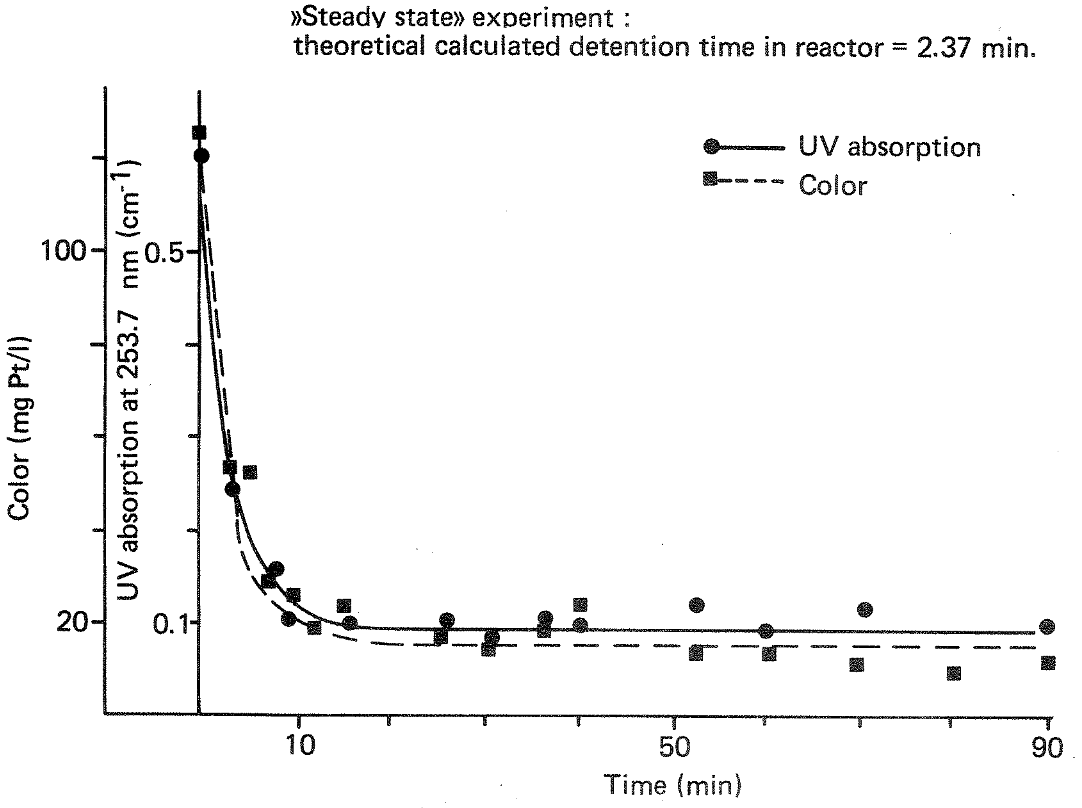


Figure 62. Results from a steady state experiment.

The water flow was 0.171 l/min. (theoretical detention time equal to 2.37 min.).

Experiments were run with varying aluminum dosages. In the first phase of the experiments, the Al-plates were weighed. The electrochemical aluminum dissolution is proportional to the current, and, when applying a certain voltage to the cell, aluminum ions start going into solution. The current increases until it reaches steady state after approximately 10 minutes. The calculated amount of aluminum dissolved was determined according to equation 18b.

Calculated amount Al dissolved, W_c (mg);

Faraday's law: $$W_c = \frac{I \cdot t \cdot M \cdot 10^3}{Z \cdot F} \tag{18a}$$

where I = current (A)

t = time (142 sec)

M = molecular weight, Al: 27

Z = charge, Al: 3

F = 96,500, Faraday's constant

$$W_c = I \cdot t \cdot 0.093 \tag{18b}$$

The effect of raw water pH on overall humus removal was evaluated. In these experiments, the raw water was always adjusted to the desired pH value one hour prior to starting the experiments in order to ensure the same conditions.

Different types of aluminum alloys have been used in the experiments. In the first forty-three experiments, the aluminum plates from Alcoa, Seattle, were used;

Type I Al: Al > 95.75%

Si < 0.25%, Fe < 0.4%, Cu < 0.1%, 0.05% < Mn < 0.2%,

5.6% < Mg < 4.5%, 0.05% < Cr < 0.2%, Zn < 0.1%,

others < 0.15%.

In the next twenty experiments, aluminum plates, also from Alcoa, Seattle, with the following characteristics were used:

Type II Al: Al > 96.5%

Si < 0.6%, Fe < 0.7%, 0.05% < Cu < 0.2%,

1.0% < Mn < 1.5%, Zn < 0.1%, others < 0.15%.

A third type of aluminum plates was used in the last part of the experiments. This aluminum type was developed in connection with experiments run at the Norwegian Defense Research Institute. High purity aluminum (Al > 99.998%) was used and 0.12% Sn was added which gave the plates following characteristics:

Type III Al: Al > 99.87%, Sn = 0.12%

In a few series of experiments, a continuous flow reactor containing one Al-anode and two graphite cathodes was used to evaluate the effect of the aluminum dissolved from the Al-cathodes. In a few experiments only two Al-electrodes were used, in order to evaluate the effect of the electrode spacing. Also the specific conductivity of the solution was varied in a few experiments by addition of table salt.

In one series of experiments, a detailed electrochemical reactor study was performed in parallel with a jar test. Water from Hellerudmyra was treated with both processes using a chemical dosage of 6 mg Al/l. The treated water was analyzed for: pH, color, specific conductivity, and Ca, Mg, Fe, Al, Na, K, Mn, Cu, Pb, NO_3, SO_4, Cl, and F.

4.2 Conventional Coagulation Experiments

Conventional coagulation experiments were carried out with a Phipps & Bird multiple stirrer containing six paddlers. Freshly mixed aluminum sulfate (5 g alum/l of $Al_2(SO_4)_3 \cdot 14.3\ H_2O$) was added and the pH adjusted immediately after with either H_2SO_4 or NaOH (see Figure 63).

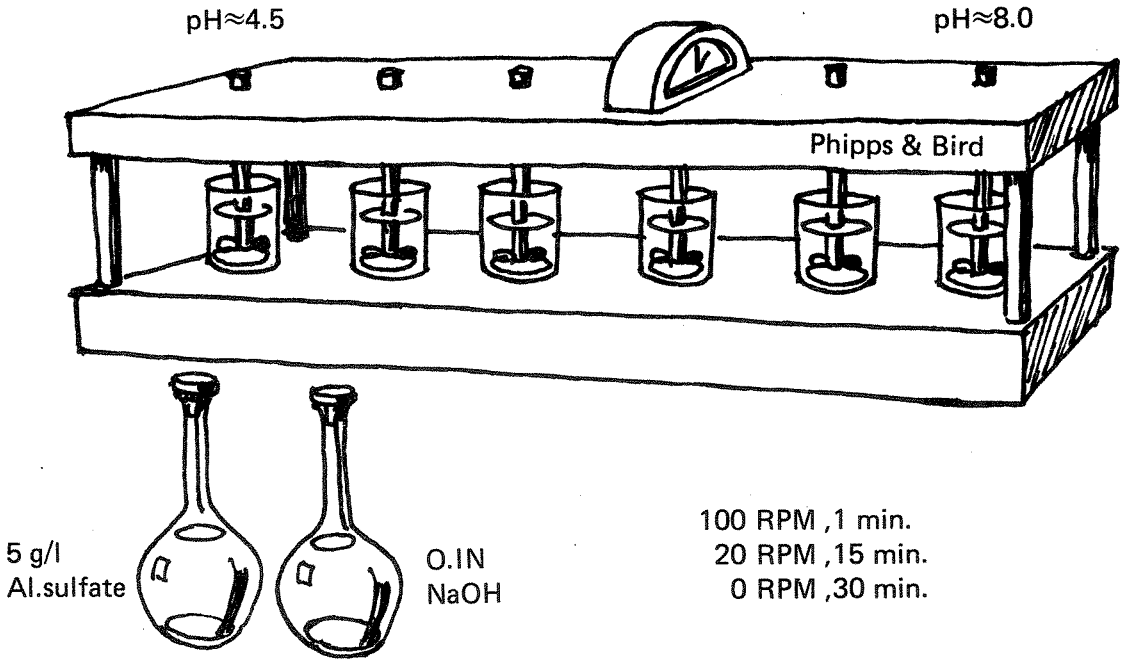


Figure 63. The laboratory mixer used in the coagulation experiments.

Most of the studies were conducted with waters from Tjernsmotjern and Hellerudmyra. Some experiments were performed with water from

Småputten and a few with water from Dragsjøen. In one series of experiments, water from Hellerudmyra was diluted with a dilution water of approximately the same composition as water from Hellerudmyra except for the organic carbon content. The dilution water was composed of the following solutions;

7.17 mg $CaSO_4$/l

1.096 mg $CaCl_2$/l

5.62 mg $NaHCO_3$/l and

1.18 mg $MgCO_3$/l,

giving the following concentrations:

Ca = 2.4 mg Ca/l

Mg = 0.24 mg Mg/l

Na = 1.6 mg Na/l

SO_4 = 4.8 mg SO_4/l

Cl = 0.71 mg Cl/l and

HCO_3 = 4.9 mg HCO_3/l.

A few series of experiments were conducted to study the influence of chemical dosage sequence; (A) dosing of Al-sulfate first immediately followed by sodium hydroxide, or (B) NaOH first immediately followed by Al-sulfate, or (C) Al-sulfate first followed 5 minutes later by NaOH dosage, or (D) mixing the two chemicals before addition. Based on the results obtained (presented in chapter 5 of this report), chemical dosing sequence (A) was used in all the experiments; Al-sulfate first immediately followed by NaOH dosing. The alum followed by NaOH was added when starting the rapid mix period (1 min), followed by 15 minutes stirring at 20 rpm and 30 minutes of sedimentation.

In one single experiment, using low alum dosage, the rapid-mix period was extended to 10 minutes, while the slow-mix and settling period remained the same. The jar-test experiments were run to provide insight on the coagulation mechanisms involved in humus coagulation with alum. The pH was adjusted between 4.5 and 8.0, and the alum dosage varied from 0.5 to 50 mg Al/l (∿5-500 mg alum/l).

4.3 Pilot Scale Experiments with the Electrochemical Reactor

A scaled up electrochemical reactor was used for the pilot scale experiments. The reactor design was based on experimental results from the laboratory model, and a modified version was built at the Aqua Care Company in Bergen. The first set of drawings sent to Bergen is presented in Figure 64, while Figure 65 gives details of the skimmer. Based on the laboratory experiments, the skimmer design was determined to be an important aspect of the reactor. A set of 84 Al-plates with a 3 mm separation distance was suggested, and, to simplify the production of the plates, they were constructed according to Figure 66. A 5 mm plexiglass plate with 2 mm tracks was placed on the bottom of the reactor in order to keep the exact distance between the plates. The size of the Al-plates perfectly fitted the size of the electrochemical reactor in order to avoid water short-circuiting on each side of the Al-plates, but forcing it up and down between the plates. The reactor was designed as a series flow reactor (Figure 67), and

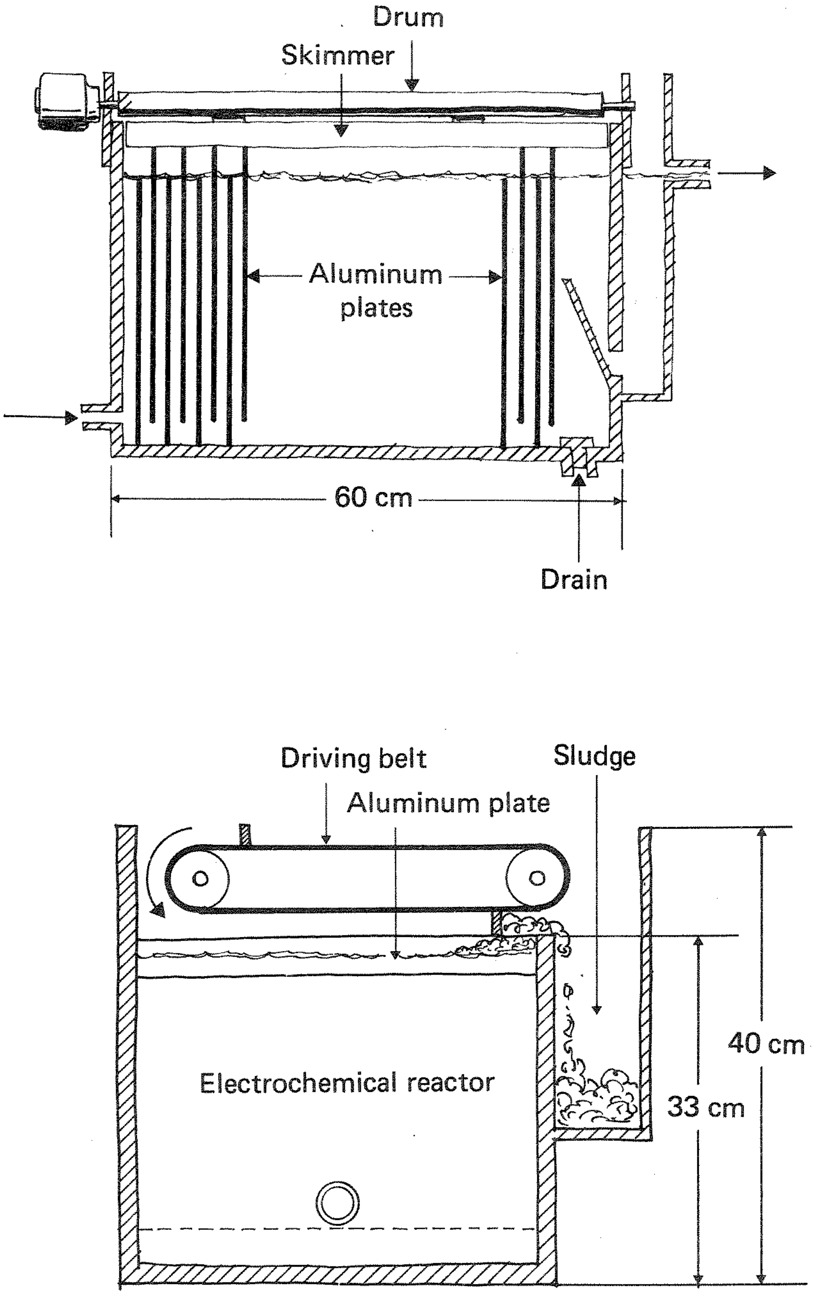


Figure 64. Preliminary design of an electrochemical reactor treating 700 l/h.

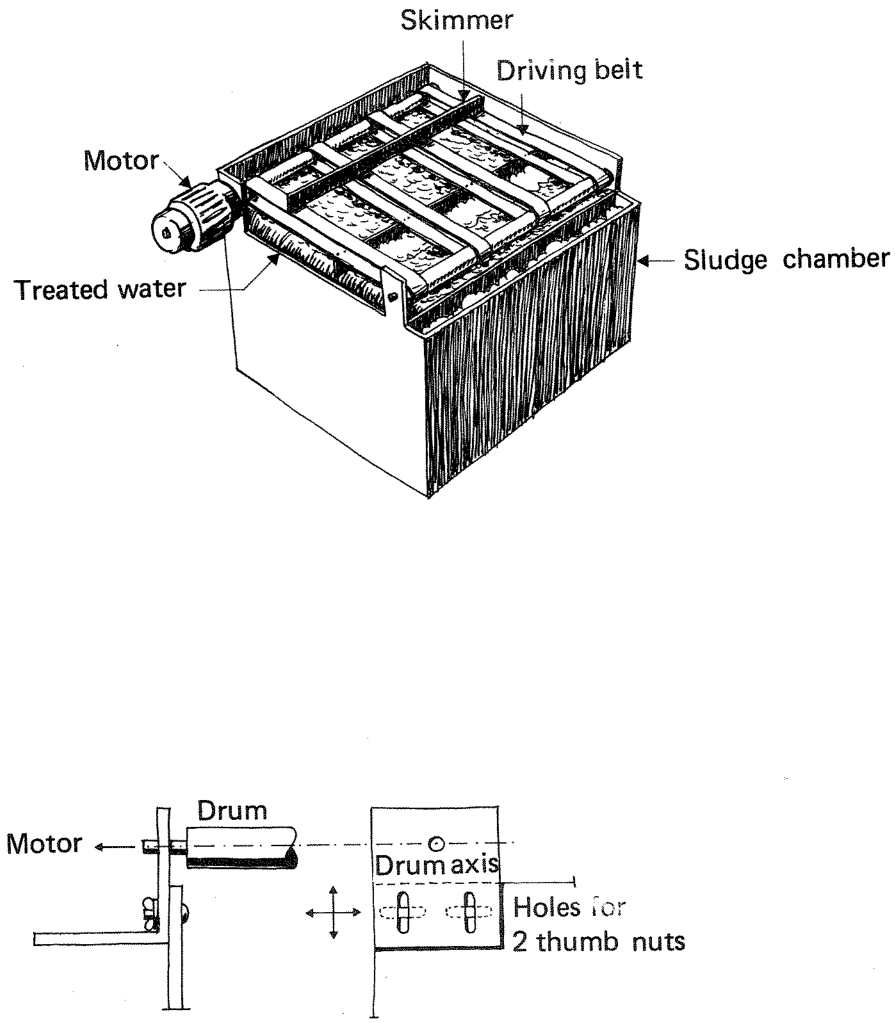


Figure 65. Preliminary design of the skimmer on top of the reactor.

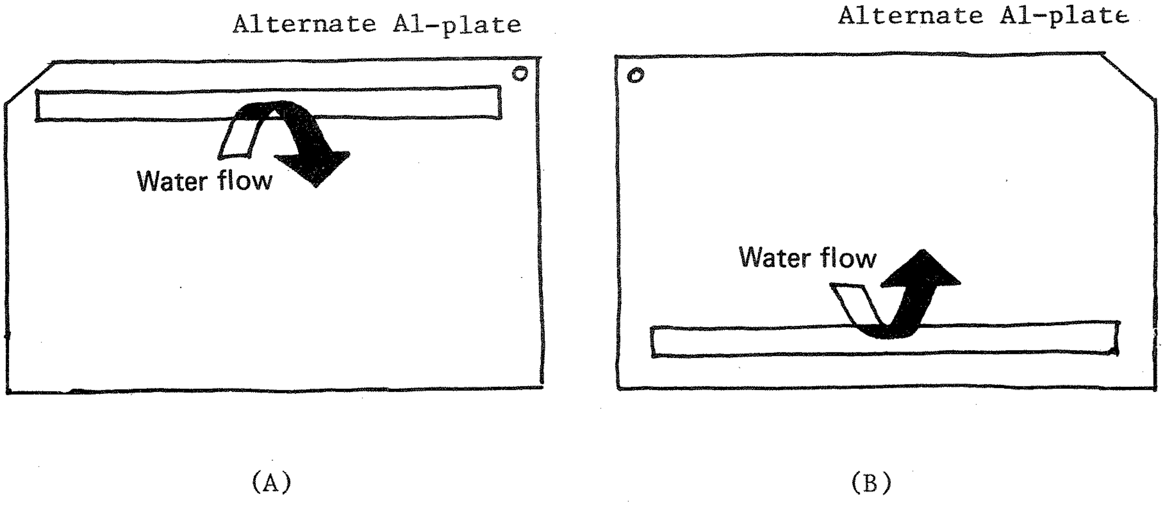


Figure 66. Design of the Al-plates in the electrochemical reactor.

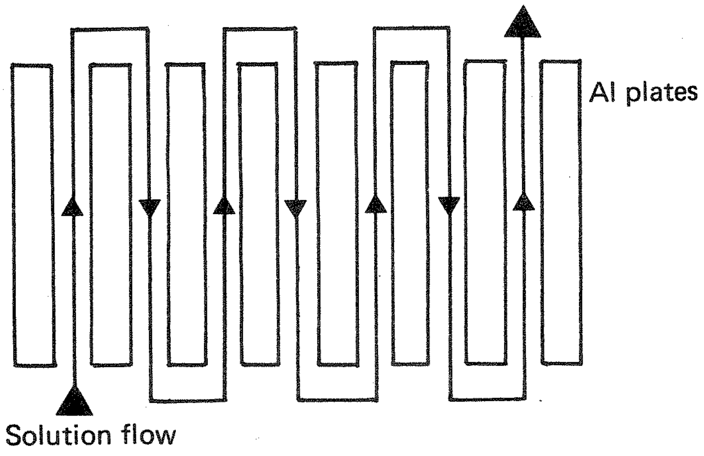


Figure 67. The electrochemical reactor was designed as a series solution flow reactor.

the electrodes were arranged with monopolar connections, see Figure 68. Alternate electrodes were connected to the opposite power supply terminals, giving a number of individual reactor units electrically in parallel with one another. In this system each unit operates at the same voltage, the total current being the sum of the individual unit currents. Every second Al-plate, type A in Figure 66, was connected to one power supply terminal through an aluminum stick going through the holes in the upper right corner, while type B, Figure 66, was connected through the holes in the upper left corner.

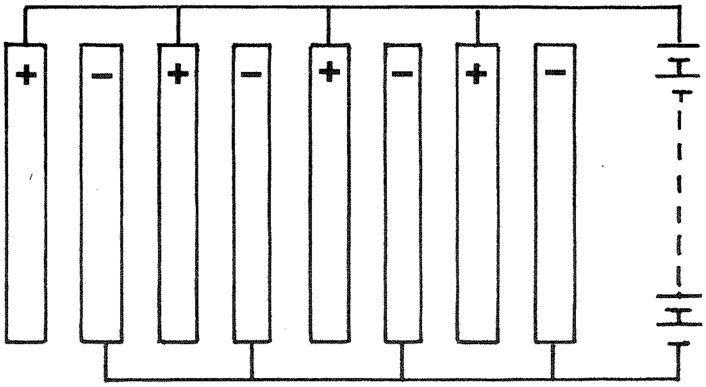


Figure 68. The electrochemical reactor was designed with monopolar connection of the electrodes.

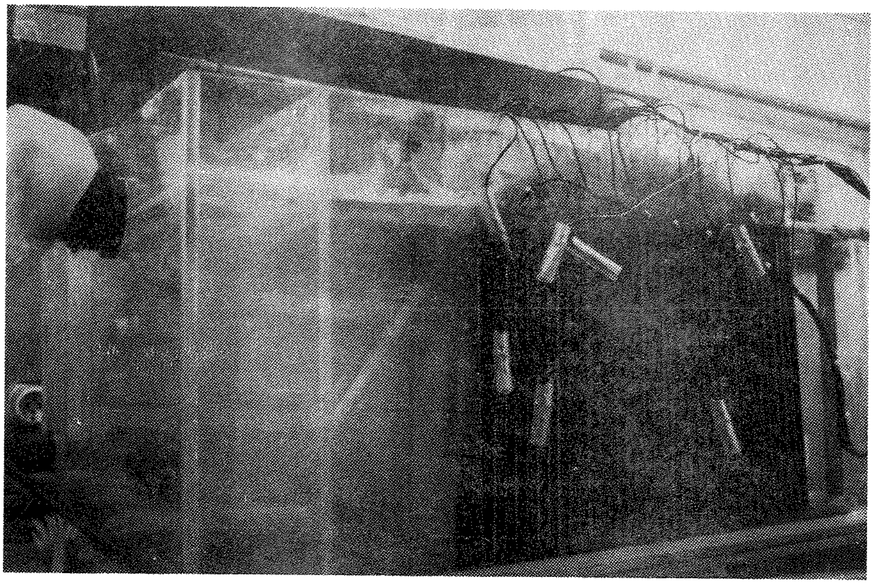
Skimmer construction did not follow the drawings. It was simplified by using a windshield-wiper belonging to a bus with a time regulator for regulation of the scraping intervals. This system was not found satisfactory, because the collector did not go between the plates to remove accumulating sludge. Sludge accumulated quickly between the plates resulting in higher potential drop and circuiting water flow.

Figure 69 contains photos of the initial pilot scale experiments. Several of the primary design criteria were changed by the time this setup was built.

1) Half of the Al-plates were taken out of the system, reducing the unit to 42 plates.
2) The distance between the Al-plates was increased to 10 mm, allowing insertion of a 10 by 10 mm plexiglass square rods between the Al-electrodes to maintain uniform plate spacing.
3) The use of aluminum rods through the holes in the Al-plates were quickly shown to be an unsatisfactory electrical conduction system because of corrosion in the holes. Clips were added to ensure good connections.
4) The system was studied without a sludge collector, resulting in sludge accumulation, thus creating hydraulic and electrical problems.
5) A frame was constructed in order to lift all the Al-plates at once out of the electrochemical reactor.

Based on these first experiments, which were performed using tap water, a few observations were made:

1) Sludge was transported all the way to the chamber for effluent water, and a large amount of sludge floated there, resulting in sludge leaving the electrochemical reactor with the water (see Figure 70A).
2) The maximum possible hydraulic loading was dictated by the head loss through the Al-plates, resulting in water leaving through the sludge chamber.



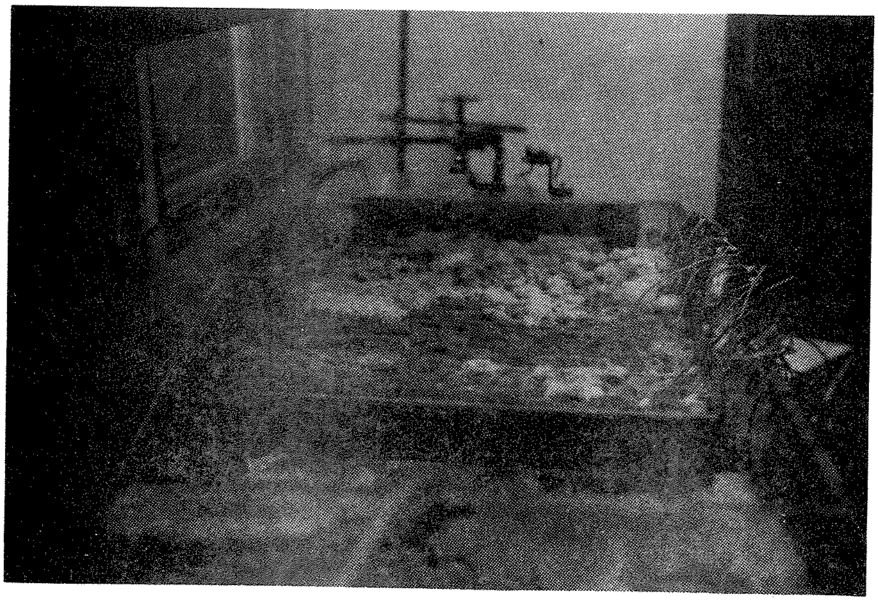
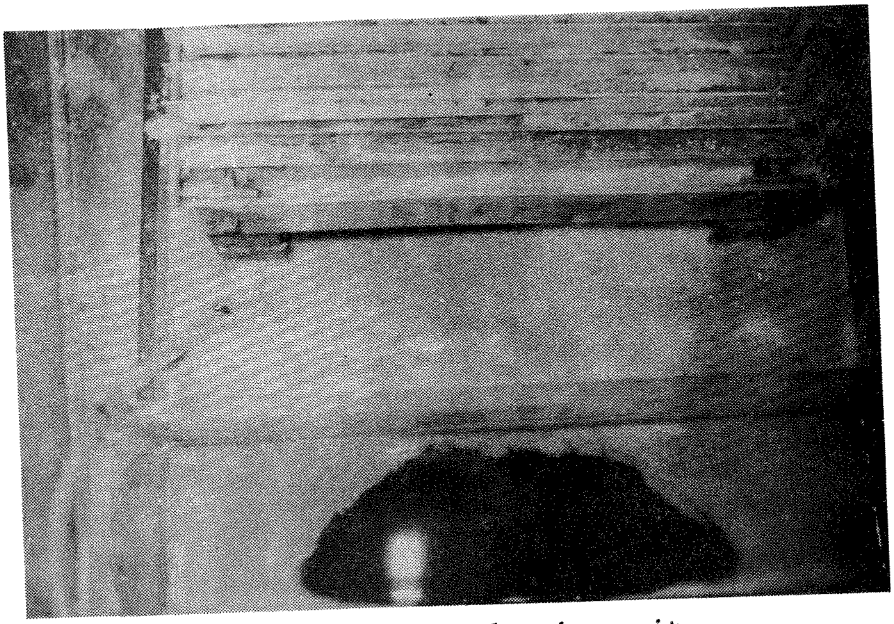
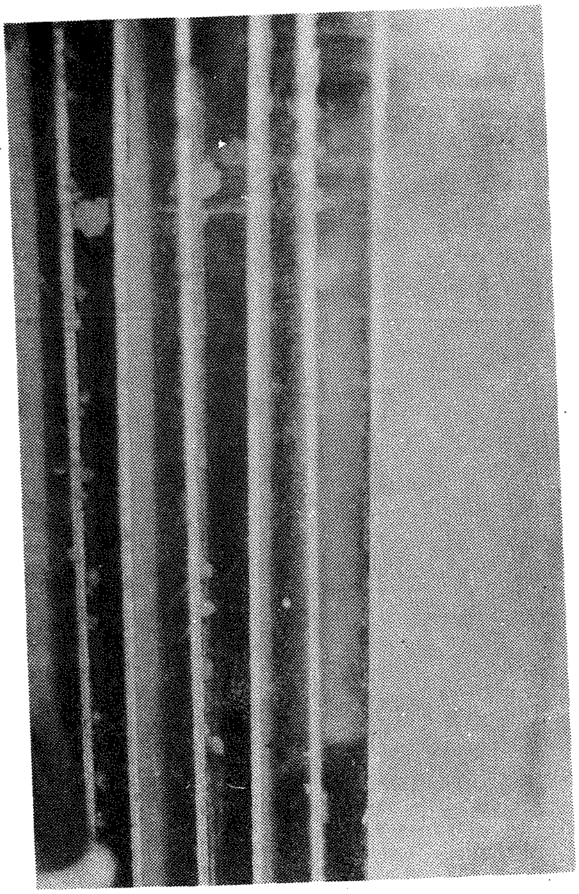


Figure 69. Photos from the initial pilot scale experiments.



(A) Sludge leaving unit



(B) Sludge accumulating between the Al-electrodes

Figure 70. Photos of observations from the electrochemical pilot scale study.

3) Low hydraulic loading resulted in sludge accumulation between the Al-electrodes (see Figure 70B).

4) A 24 V DC power supply with a current maximum of 20 A proved effective for the electrolysis process.

Based on these results, a few different designs of the Al-electrodes were tested.

A) Insulation of one side of the electrodes with varnish, in order to prevent Al and hydrogen gas production and using twice the distance between the Al-electrodes not insulated, was tried to prevent sludge formation between the electrodes where water was flowing in the opposite direction of the sludge (Figure 71). This design did not seem to improve the flotation properties of the sludge.

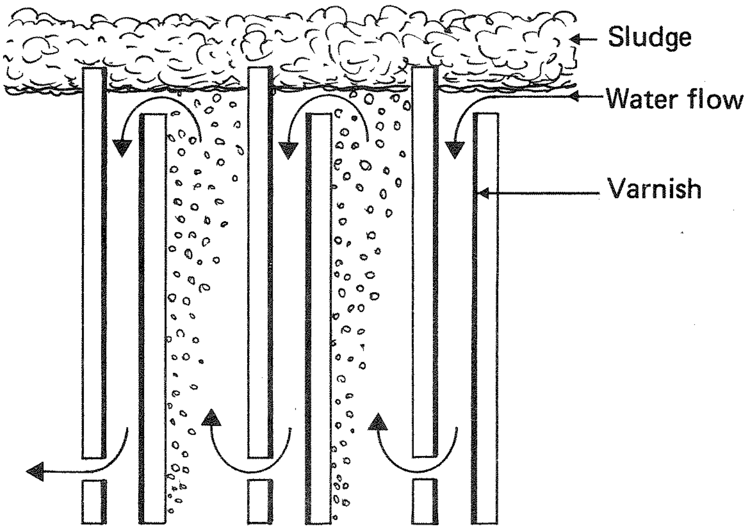


Figure 71. Experimental arrangement of the Al-electrodes.

Single space and varnish insulated Al-electrodes when water is flowing downwards, and double space, where water is flowing in the same direction as the sludge.

B) Another set of aluminum electrodes were tested, see Figure 72, in order to prevent water from flowing in the opposite direction of the sludge. This design showed clearly that the sludge was forced all through the system, and the main part of the sludge flotated in the last part of the electrochemical reactor. The sludge at this point was very heavy and had a high water content compared to the sludge produced in previous runs.

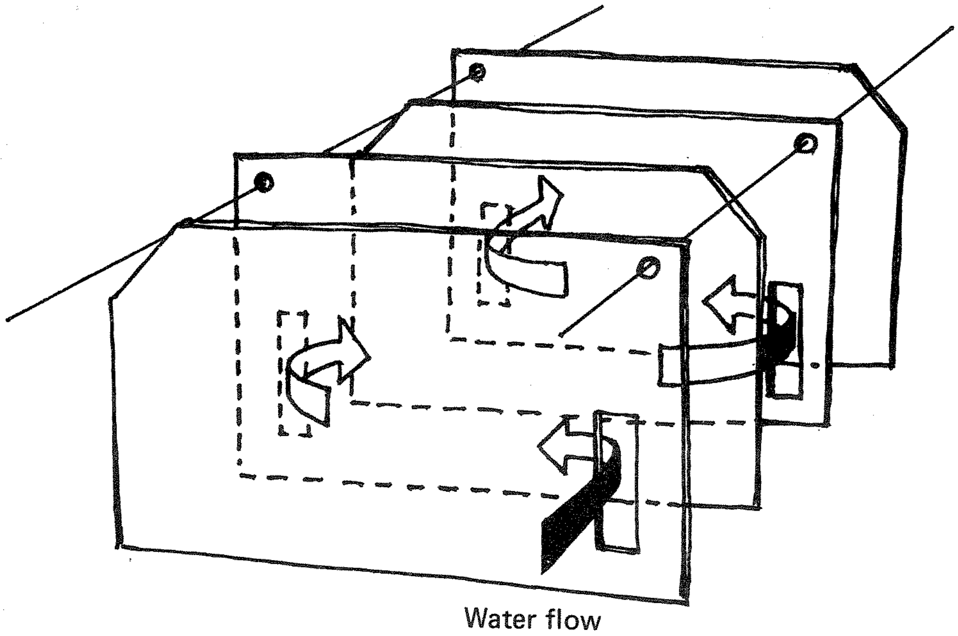


Figure 72. Experimental arrangement of Al-electrodes.

Water in this arrangement never flows in the opposite direction of the sludge.

C) The first set of Al-electrodes was tried in a modified version (Figure 73). The upper split was increased in order to allow higher head loss through the system and thus higher water flow.

This last design of Al-electrodes proved successful, probably due to two aspects; namely, the larger water surface between the Al-

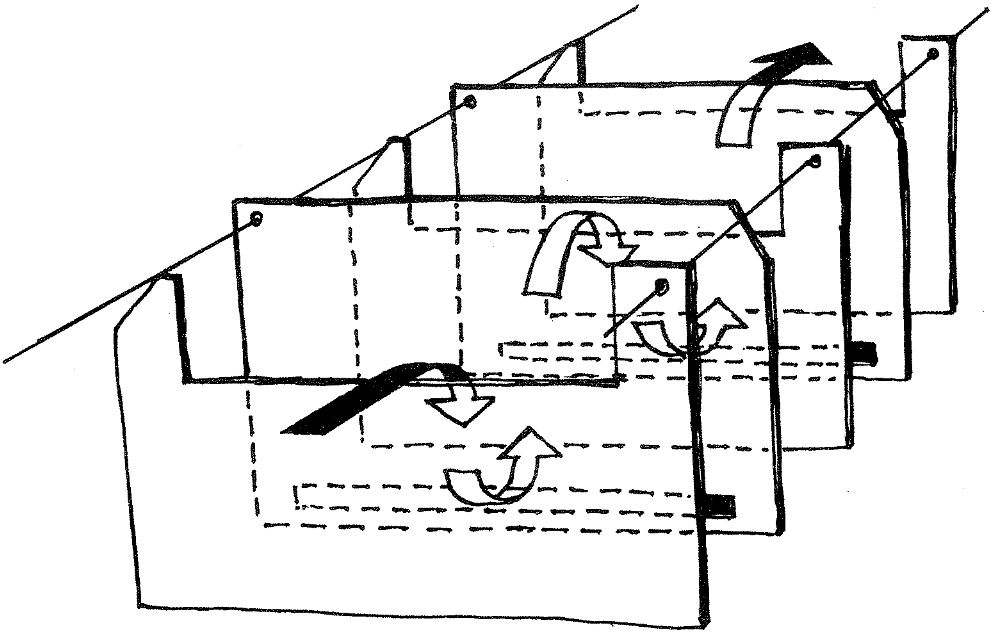


Figure 73. A modified version of the originally produced Al-electrodes proved successful.

electrodes enabling a better flotation of the sludge; and the higher water velocity through the system. This design of the Al-electrodes was used in the ensuing research.

In regard to sludge collection, an open water surface without Al-electrodes would simplify the system. A set of experiments was performed with a parallel flow reactor. These experiments stressed the importance of keeping a high enough water velocity to avoid sludge accumulation between the electrodes, and also stressed the problems involved in construction of a system giving equal hydraulic loading between all Al-plates. Based on these experiments, the series flow reactor was chosen as the one nearest a good solution of design for small flow systems.

The next problem to be solved before further experiments could be carried out, was to build a skimmer. The original drawings (Figure 65) for design were used with few changes. Most important was the use of a long brush; gear and chains were also used, see Figure 74.

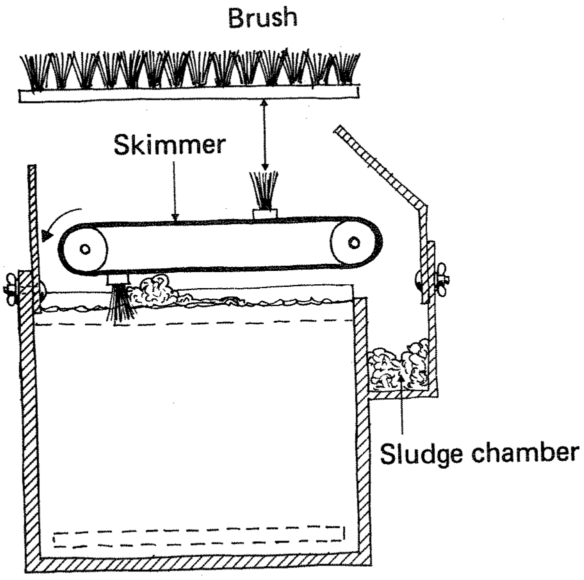


Figure 74. The new version of the skimmer using a brush to ensure cleaning between the Al-electrodes.

The last change done was in the effluent chamber, see Figure 75.

The rest of the pilot scale experiments were done with the modified electrochemical reactor (see Figure 76). The hydraulic loading of the reactor during the experiments was intended to be approximately 600-700 l/h. The raw water used was pumped through a 50 m long pipe from Småputten into a small research station where it was electrochemically treated. The most important part of this study was the sludge production study, and practical aspects in

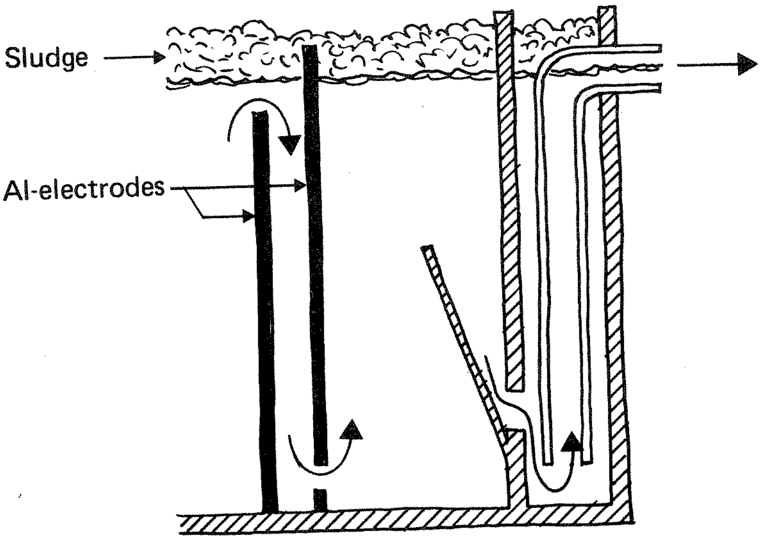


Figure 75. Details of arrangement for effluent water to reduce sludge loss.

regard to optimization of the flotation process. Only water from Småputten was used in these experiments.

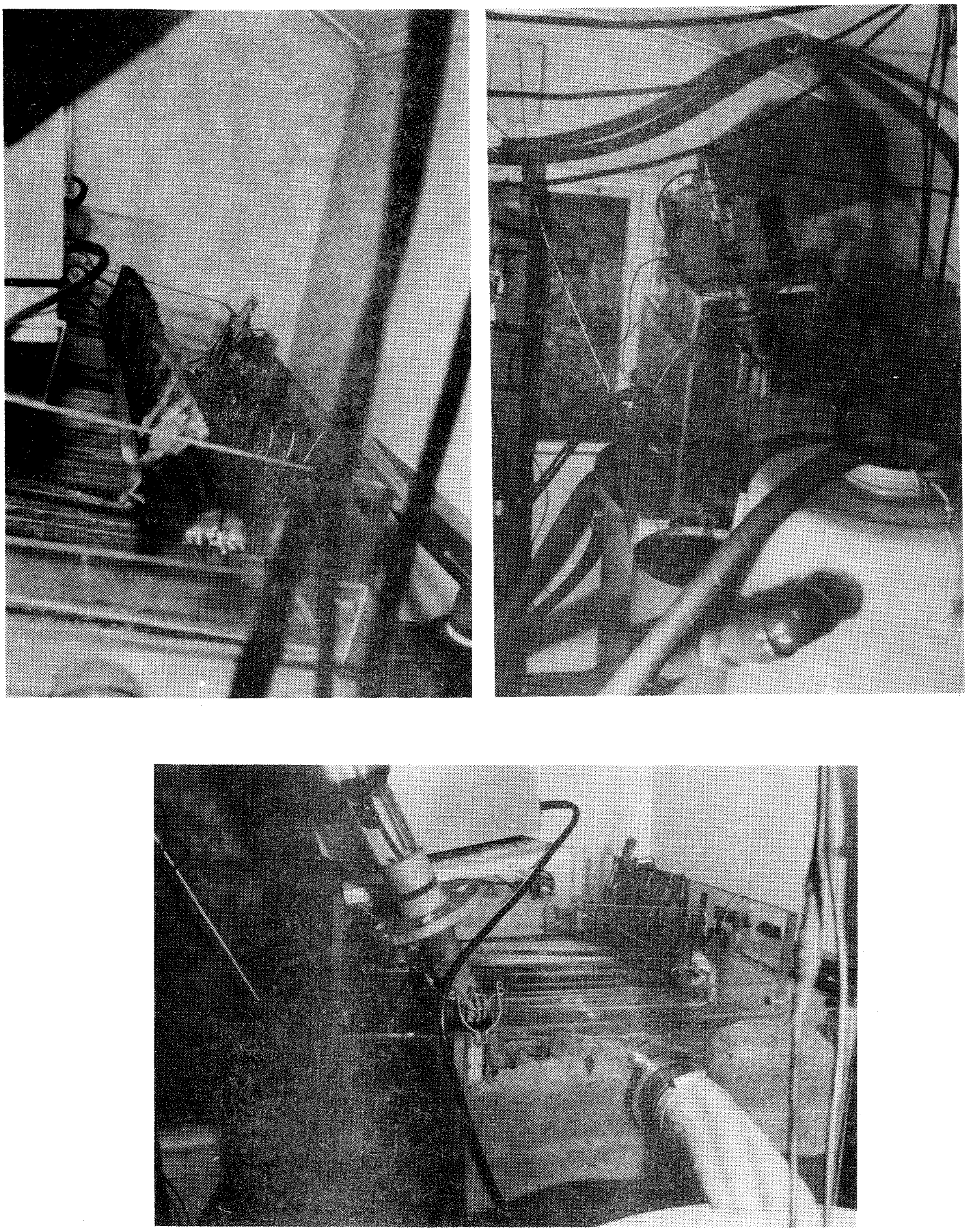


Figure 76. Photos of the modified electrochemical reactor used in the pilot scale experiments.

5. RESULTS AND DISCUSSION

5.1 Parameters for Determination of Aquatic Humus Concentration

Three different parameters were used to determine the concentration of aquatic humus; total organic carbon (TOC), UV absorption at 253.7 nm, and color. Color was determined on both filtered (GF/C) and unfiltered samples without pH adjustment of the samples. The relationship between TOC and UV absorption was determined for treated and untreated water from the sources studied (Figure 77), as was also the relationship between color and UV absorption (Figure 78). The following relationships were found from Figure 77:

Småputten TOC = 19.9 UV abs + 2.4 (r^2 = 0.99)
Tjernsmotjern TOC = 18.7 UV abs + 2.7 (r^2 = 0.94)
Hellerudmyra TOC = 18.6 UV abs + 1.6 (r^2 = 0.97).

Use of all the data gives following relationship:

TOC = 19.1 UV abs + 2.3 (r^2 = 0.93).

The relationship found between TOC and UV absorption is similar to those found by Gong & Edzwald (1981) for the Grasse River in upper New York. The great seasonal variation of the organic carbon content of this river made it possible to determine the correlation between non volatile total organic carbon (NVTOC) and UV absorption (254 nm) for raw water only, giving

Grasse River raw water; NVTOC = 20.2 UV abs + 0.4 (r = 0.91).

Including the data for treated water (at various sites in the treatment plant for this water) gave

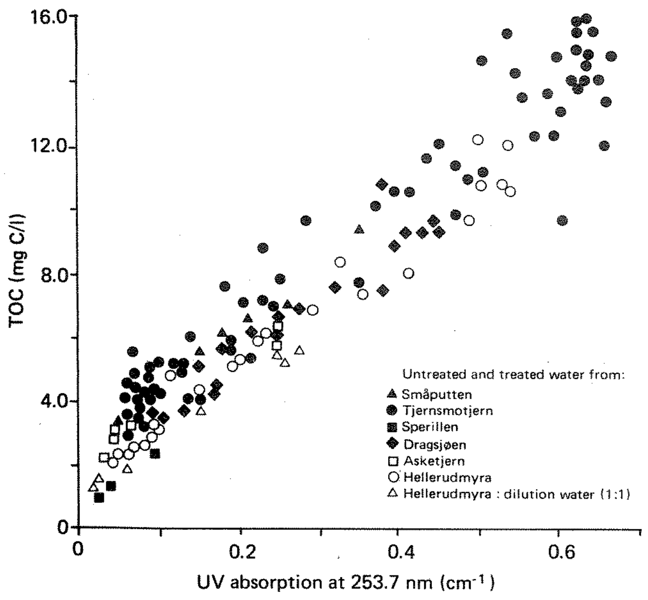


Figure 77. The relationship between total organic carbon (TOC) and UV absorption for treated and untreated water of all the different sources studied.

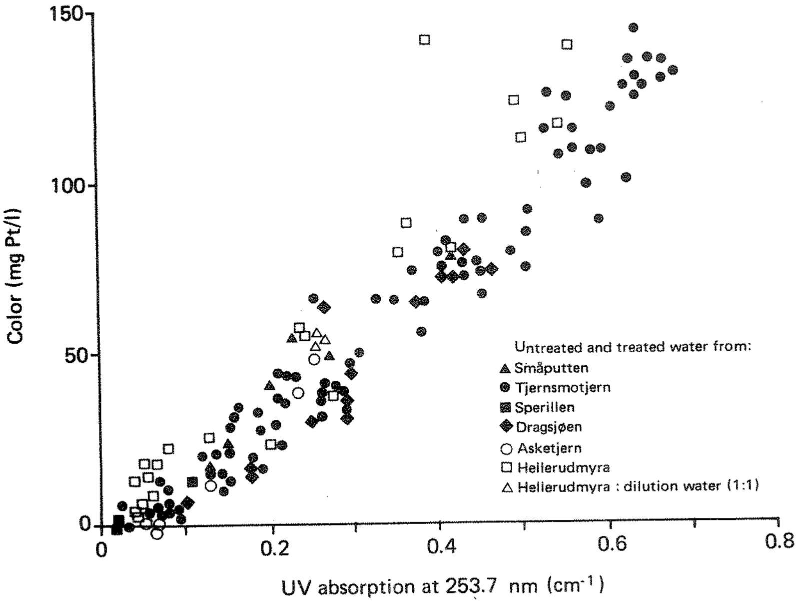


Figure 78. The relationship between color and UV absorption for treated and untreated water of all the sources studied.

NVTOC = 18.2 UV abs + 1.6 (r = 0.87).

This last correlation is almost identical to the one found for Hellerudmyra. The good correlation found for all our sources studied indicates that UV absorption can be used as a good predictor of TOC for these water sources.

The relationship between color (measured at various pH's) and UV absorption was as follows (Figure 78);

Småputten Color = 216 UV abs - 6.4 (r^2 = 0.97)
Tjernsmotjern Color = 208 UV abs - 9.2 (r^2 = 0.93)
Hellerudmyra Color = 244 UV abs - 7.6 (r^2 = 0.93).

Also color is a good surrogate parameter for UV absorption and thus also for TOC. In some of the experiments, color and UV absorption have therefore been the two only parameters used for determination of aquatic humus concentration.

5.2 Electrochemical Process

The electrochemical process was studied in detail using the laboratory scale equipment. While all the different types of raw waters were used in the experiments, Tjernsmotjern was the one primarily studied.

5.2.1 Dissolution of Aluminum

The theoretically calculated amount of Al dissolved was compared with the weighed amount dissolved (Figure 79) for various temperatures. The results agreed very well, without showing any dependence on the raw water temperature, although this varied between 5°C and 19°C.

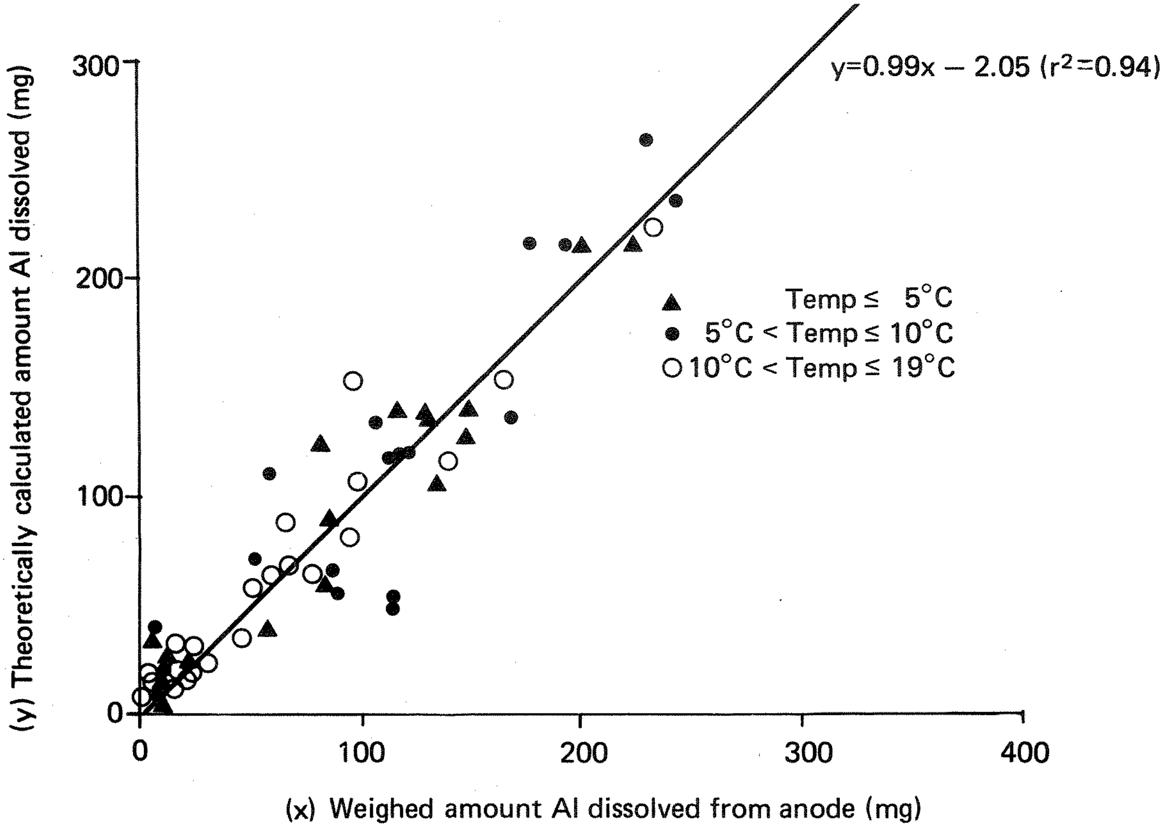


Figure 79. Theoretically calculated amount Al dissolved as a function of weighed amount Al dissolved from the anode at various temperatures.

The theoretically calculated amount of Al dissolved (y) as a function of the weighed amount Al dissolved from the anode (x) gave following relationship, when using data for all water temperatures;

$y = 0.99x - 2.05$ ($r^2 = 0.94$).

Early in the experiments it was found that the Al-plates required a very long drying period before weighing, and some of the difference between the two values could be because of this fact. A hair-drier was used to dry the Al-electrodes in order to minimize this error.

The Al dissolution was calculated according to Faraday's law, after equation 18b;

$W_c = I \cdot t \cdot 0.093$

where $I \cdot t$ = the charge (Coulombs)

W_c = mg Al dissolved from the anode.

Both the anodes and the cathodes were weighed in the first part of the experiments, and Al was found to dissolve also from the cathode. In Figure 80 the total amount of Al dissolved is presented as a function of the charge. Data are presented for the three different types of aluminum used in the experiments. A linear regression was calculated based on all the data,

Total amount dissolved = 32.8 + 0.096 charge ($r^2 = 0.75$)

No significant difference in dissolution could be seen between the three types of aluminum used. At a charge of 1000 Coulombs, 93 mg Al is dissolved according to Faraday's law, but based on the experiments,

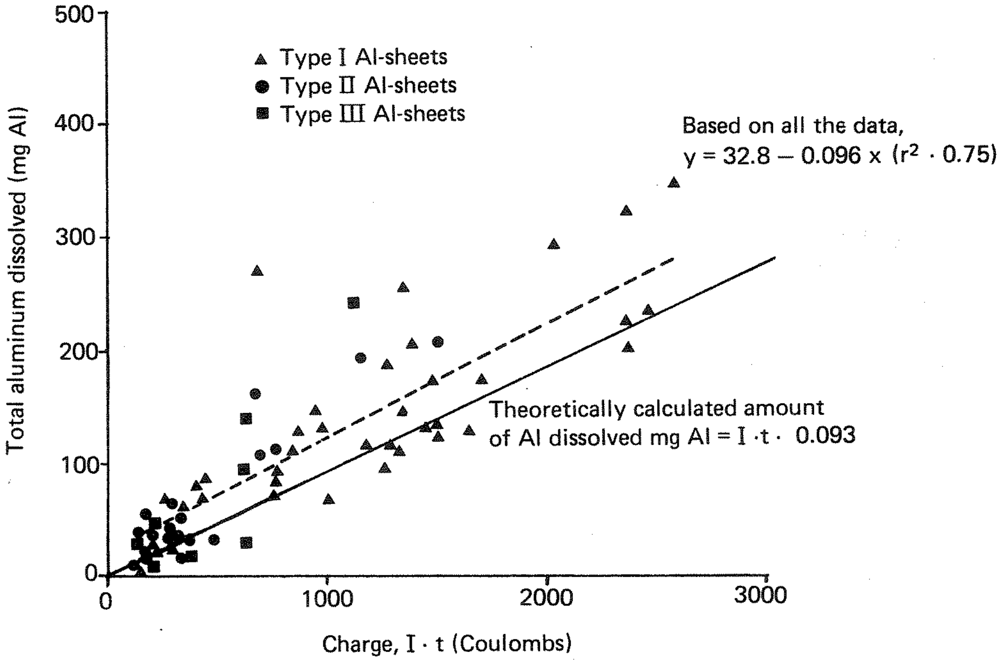


Figure 80. Total amount of dissolved aluminum as a function of the charge using three different types of aluminum.

129 mg Al is dissolved, i.e. 38 percent more than calculated. Using Figure 79, when 93 mg Al is dissolved based on theoretical calculations, 96 mg Al is dissolved from the anode, i.e. 33 mg is dissolved from the cathode. There is a variation in the data in Figure 80 as indicated by r^2 being equal to only 0.75, and there is some uncertainty bound to the actual numbers, but they show clearly that corrosion is occurring at the cathode. The great variation in the numbers is probably due to several factors, 1) different types of raw water with different pH values have been used; 2) in some of the experiments the current direction has been changed prior to the start; and 3) the current has changed during the experiment, being lower in the beginning, before stabilizing at a value.

It was important to determine whether the Al dissolved from the cathode participated in the coagulation process. Knowing that pH was higher at the cathode than at the anode, aluminum complexes such as $Al(OH)_4^-$ might be present and the Al would not be active in the coagulation process. It was therefore thought to be important to find the pH in the solution near the cathode. The dissolution of Al at the cathode was thought to be due to chemical dissolution. In one set of experiments using only two electrodes with a 13 mm separation distance, raw water from Tjernsmotjern with a pH of 6-6.5 was used. Litmus paper was used to determine pH since pH electrodes were disturbed by the applied voltage on the Al-electrodes. Near the anode pH was found to be 5.5 to 6.0 and near the cathode 8 to 8.5. To estimate the effectiveness of the Al dissolved from the cathode in the coagulation process, a set of coagulation experiments, using water from Tjernsmotjern, was run using a small electrolytic cell with one aluminum anode and two graphite cathodes. A comparison of these results with those previously obtained, has been made in Figure 81.

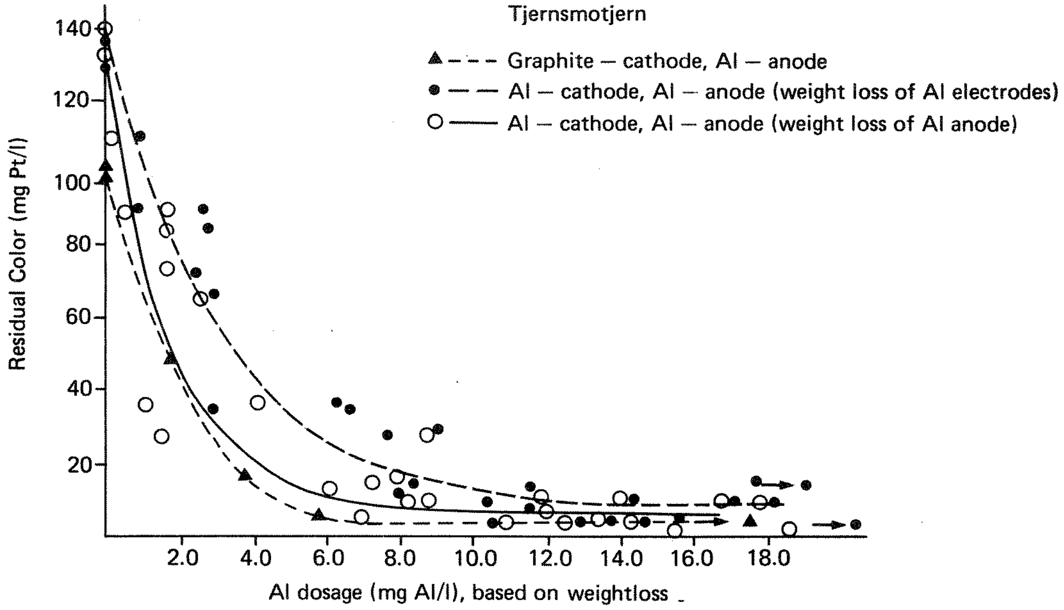


Figure 81. Residual color of water from Tjernsmotjern as a function of Al-dosage based on weight loss of the electrodes.

A comparison of results from the laboratory reactor (assuming that 1) only Al dissolved from the anode is active in the process, and 2) Al dissolved from the cathod also is active) with results from a reactor consisting of one Al-anode and two graphite cathodes.

The aluminum dosage calculated from the previously obtained results is based on weight loss. One curve is made based on only the Al dissolved from the anode. Another curve is made based on the Al dissolved from both electrodes. Figure 81 shows that to obtain a residual color of, for example, 20 mg Pt/l, an Al dosage around 4 mg Al/l is sufficient. The Al dissolved from the cathode has no effect on the coagulation process.

In the later part of the results, the aluminum dosage is presented as the charge. The calculations are based on the fact that samples were taken after 45 minutes, and the water flow was 0.171 l/min in all experiments, so that the calculated amount of Al dissolved from the anode, equals;

$$W_c = I \cdot t \cdot 0.093 = I \cdot 45 \cdot 60 \cdot 0.093 = 251 \cdot I \text{ (mg Al)}$$

The Al dosage equals thus

$$\frac{W_c \quad \cdot \text{ mg Al}}{45 \text{ min} \cdot 0.171 \text{ l/min}} = \frac{251 \cdot I}{45 \cdot 0.171} = \underline{32.6 \cdot I \text{ mg Al/l}}$$

$$\text{or } \frac{I \cdot t \cdot 0.093}{45 \cdot 0.171} = \underline{I \cdot t \cdot 0.012 \text{ mg Al/l}}$$

5.2.2 Necessary Potential

The applied voltage over the electro-chemical cell was measured during the last part of the experiments. Based on the assumption that the solution resistance is the major resistance in the system, the measured potential is presented in Figure 82 as a function of the calculated IR drop (the potential caused by the solution resistance), based on equation 19, which says,

$$\eta_{IR} = I \cdot \left(\frac{d}{A\kappa}\right) \text{ (Volts)} \qquad (19)$$

where I = the current,

d = the distance between the electrodes,

A = the surface area of the active anode, and

κ = the specific conductivity.

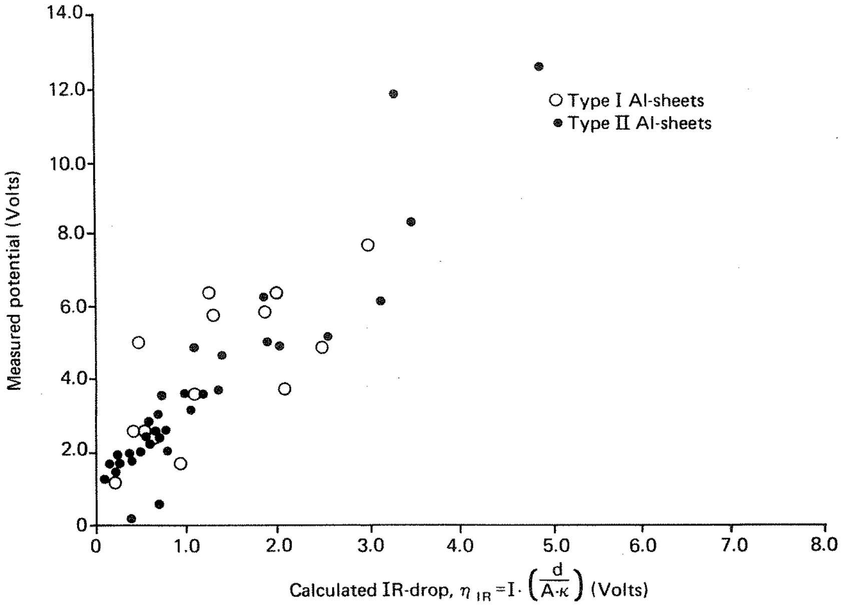


Figure 82. The measured potential in the system as a function of the calculated potential caused by the resistance in the solution (IR-drop).

Figure 82 shows that there exists a linear relationship between the two parameters, and that when the calculated IR-drop is reduced towards zero, there exists a limiting potential around 1 volt. This could be due to the mass transfer and the kinetics of the electrolytic process. The data are presented with different symbols for the two different types of Al-plates used. No significant difference on the applied voltage is seen for the two types of aluminum.

The data in Figure 82 scatter around a straight line. The variance is probably due to an effect noticed by Hanaeus (1979). When the reactor is shut down, the down time is important in regard to the potential needed to obtain a certain current. Increasing the down time will increase the potential needed. In our system, this routine varied.

In some cases one experiment followed immediately after another, and in other cases the reactor was emptied and shut down for several days. It was therefore interesting to run one set of experiments where the specific conductivity was varied over a wide range, and the distance was varied (using only two electrodes). A series of experiments using raw waters with each of the four specific conductivities studied was run continuously, and the reactor was only shut down for a short time when the raw water and the distance between the electrodes were changed. The results are presented in Figure 83. The results do not

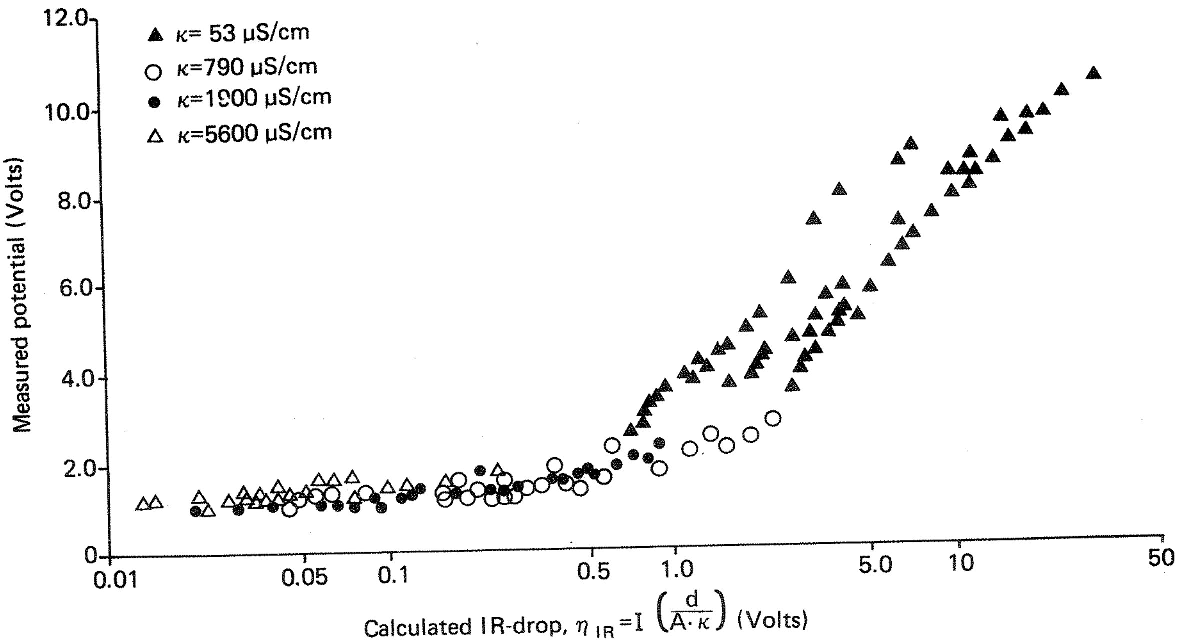


Figure 83. The measured potential of the laboratory reactor as a function of the IR-drop.

Potential developed by varying distance between the two Al electrodes and the specific conductivity of the solution.

vary as much as in Figure 82. The only significant variation seen was for the lowest specific conductivity when the distance between the electrodes varied. The figure illustrates clearly that when the IR-drop is reduced below one volt, the measured potential stays constant at approximately 1.3 volts. The minimum measured potential could perhaps have been reduced if the mass transfer of ions was improved by, for example, increasing the water velocity. This was not studied for our system.

The current density, i/a, where i is the current in mA and a the active surface area of the anodes in cm^2, is presented as a function of the applied voltage (V) in Figure 84. Strokach (1975) suggested a current density of 1-2 mA/cm^2 as the most economical. In our system, the current density used was much lower.

5.2.3 Coagulation of Aquatic Humus

Due to the hydrogen gas formation at the cathode, pH increased during the electro-chemical process, and the importance of pH on the coagulation process made it necessary to run a series of experiments adjusting the pH in the raw waters. Due to the low alkalinity of these waters, the pH of the samples changed during storage. In the first part of the experiments, the pH was measured at various times after finishing the experiments. The results in Figure 85 for raw water with no pH adjustment, show great variation. In the experiments where pH in the raw water was adjusted, the pH in treated waters was measured shortly after finishing each experiment. Raw water from

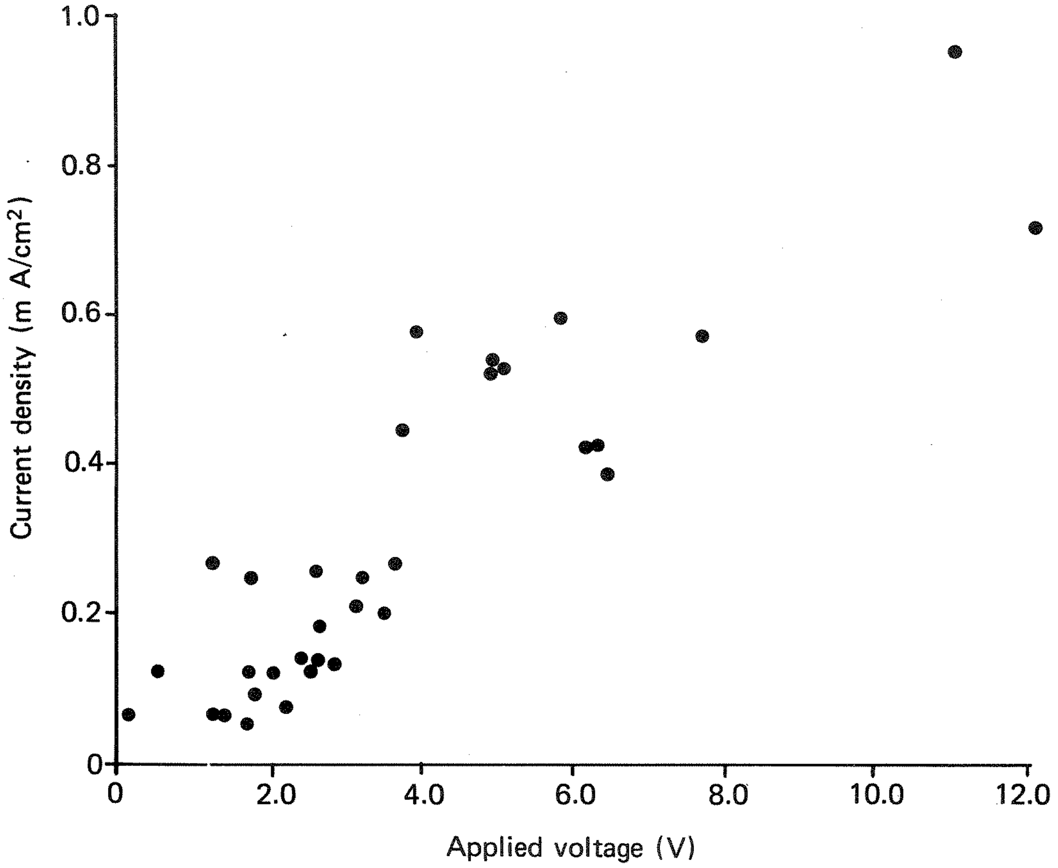


Figure 84. The current density as a function of the applied voltage (water from Tjernsmotjern).

Tjernsmotjern was used. By the time a charge of 500 Coulombs was attained (6 mg Al/1), the pH had reached its maximum value, 7.7, for raw water with an initial pH of 6-6.5 (natural water).

To illustrate the importance of the raw water pH on the removal efficiency of the humus, the results of the coagulation studies performed, are presented in Figures 86, 87 and 88, as residual TOC,UV absorption and color, respectively, as a function of the charge. Variation in the raw water pH between 3.9 and 6.0 (natural water pH)

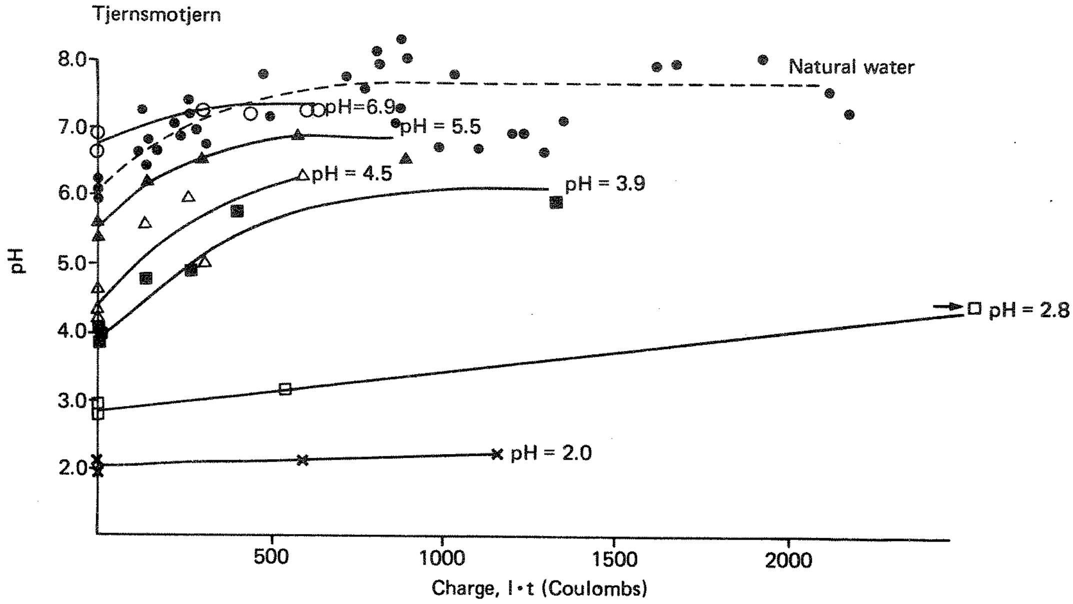


Figure 85. Increase of pH during electrochemical treatment of raw water with different initial pH value as a function of the charge.

Water source: Tjernsmotjern

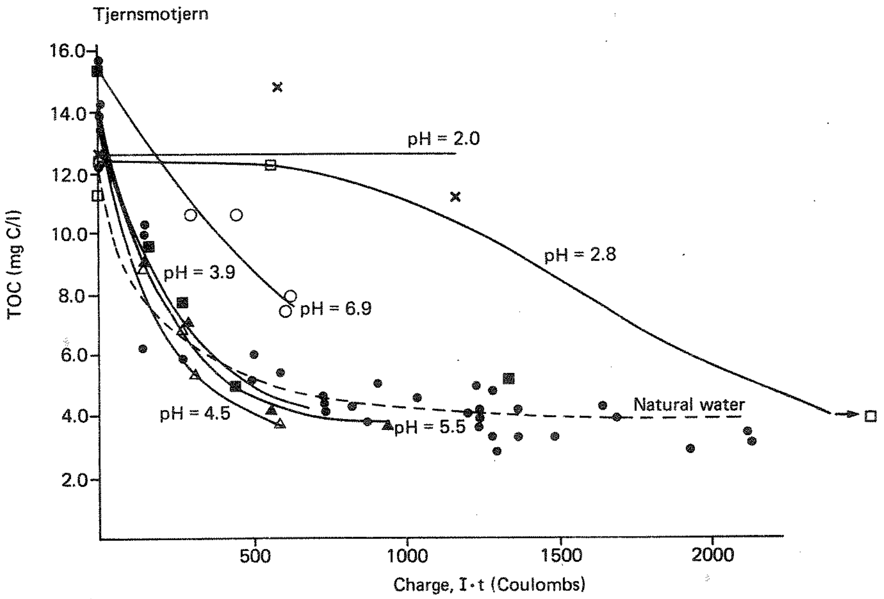


Figure 86. Residual TOC as a function of charge for raw water from Tjernsmotjern with various initial pH values.

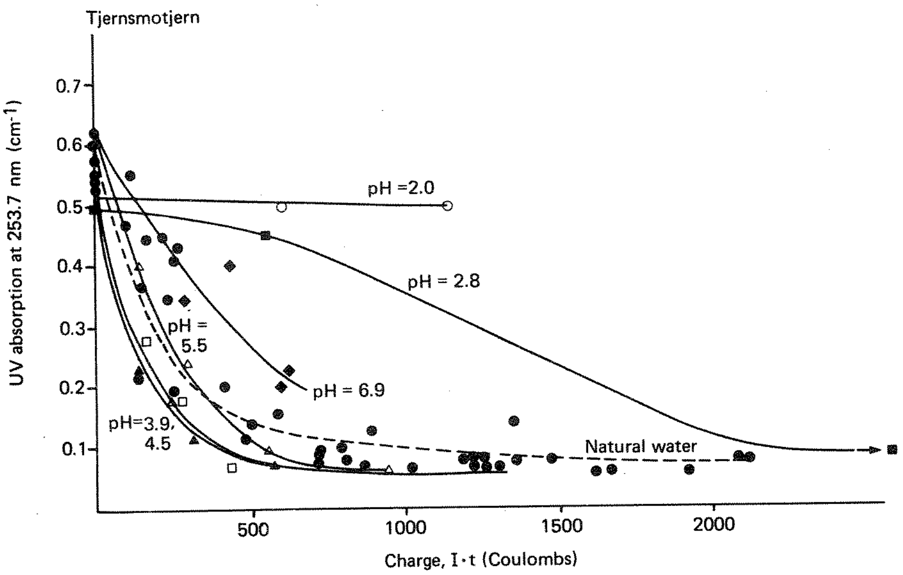


Figure 87. Residual UV absorption as a function of charge for raw water from Tjernsmotjern with various initial pH values.

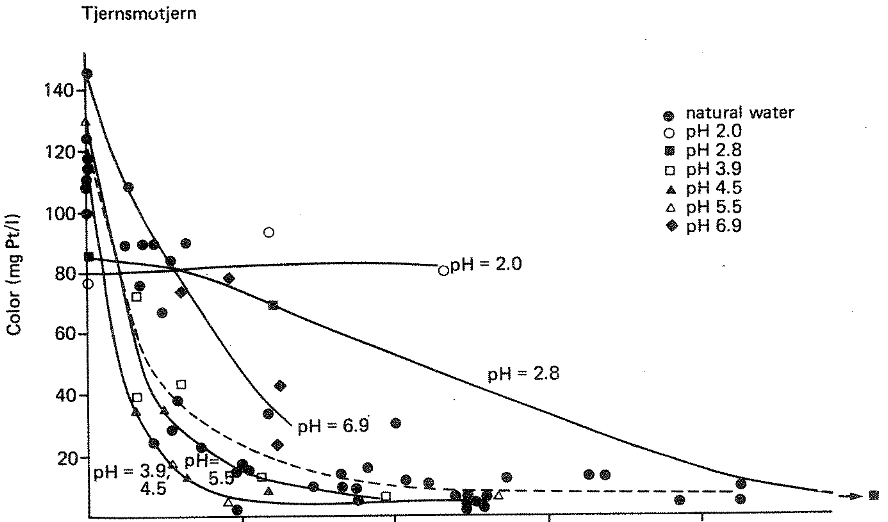


Figure 88. Residual color as a function of the charge for raw water from Tjernsmotjern with various initial pH values.

has no influence on the removal of organics at various charges (Al-dosages). This is clearly illustrated in Figure 86. The results in Figure 87 indicate some difference, the raw water with the lowest pH values needing less chemicals to obtain maximum organics removed (measured as UV absorption) than the natural raw water. The same result is emphasized in Figure 88, showing color as a function of the charge. Color, however, as shown in Figure 55, increases with increasing pH. The results presented in Figure 86 using TOC for organics determination are therefore more reliable.

The importance of temperature was also evaluated. The raw water temperature varied between 2°C and 19°C which is approximately the temperature range obtained in Norwegian surface waters during one year. It was difficult to keep the temperature at a certain degree centigrade, and the results were separated into temperature ranges, 1) less or equal to 5°C, 2) more than 5°C and less than or equal to 10°C, and 3) more than 10°C and less than or equal to 19°C. Residual TOC as a function of charge is presented in Figure 89, illustrating no difference between the results obtained at various temperatures. As previously discussed, Mohtadi & Rao (1973) studied the effect of temperature on coagulation with aluminum sulfate of bentonite and kaolinite clays dispersed in distilled water. They showed that the optimum pH for a given degree of flocculation varied with the temperature.

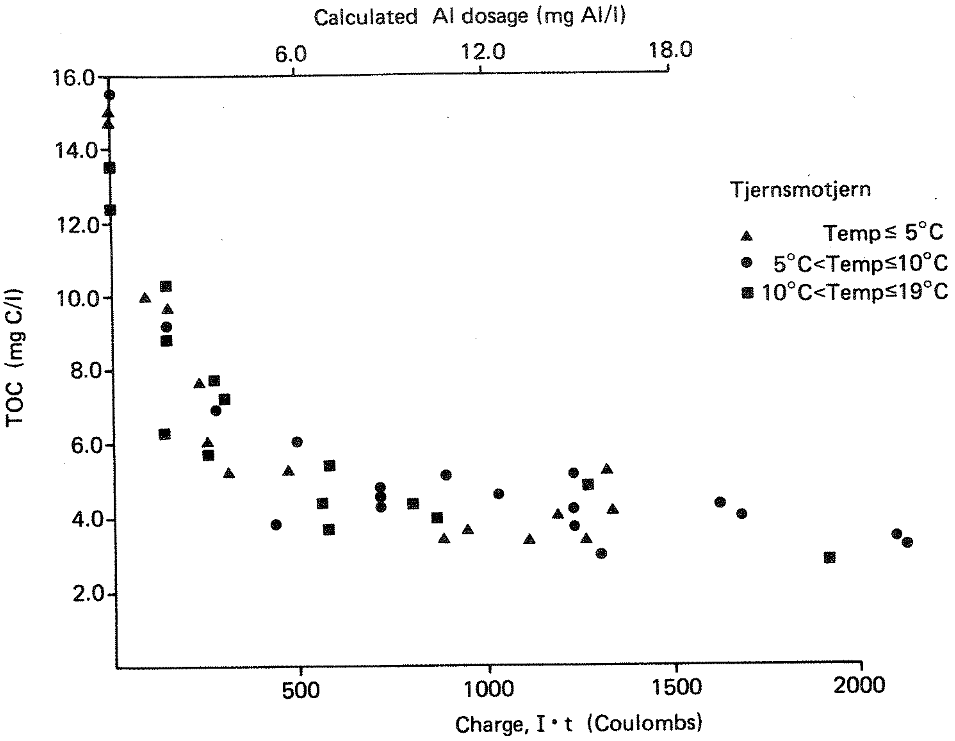


Figure 89. Residual total organic carbon (TOC) as a function of charge for water from Tjernsmotjern with different initial temperature values.

Hedberg (1974) showed by laboratory experiments that a decrease of the temperature reduced the sedimentation rate.

In our system, all samples were filtered (GF/C) before analyzing and no effect of temperature was found.

As previously mentioned, other water sources have been studied as well. The UV absorption as a function of charge for water from Hellerudmyra is presented in Figure 90, and from Småputten in Figure 91. The concentration of aquatic humus, measured as TOC, and the pH for water from Småputten varied a lot during the experimental period. Experiments were therefore performed for two different raw

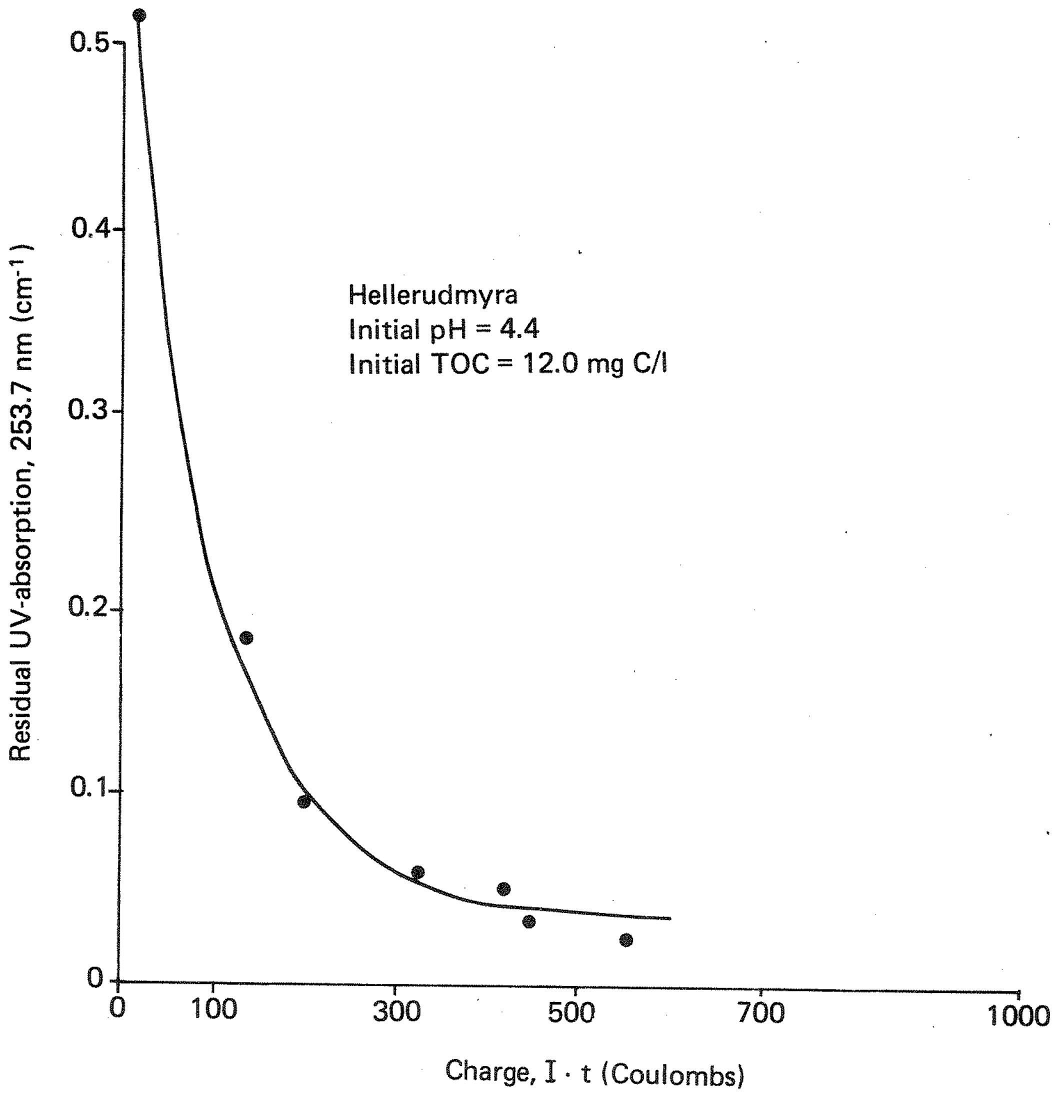


Figure 90. Residual UV absorption, 253.7 nm (cm^{-1}), as a function of charge for water from Hellerudmyra.

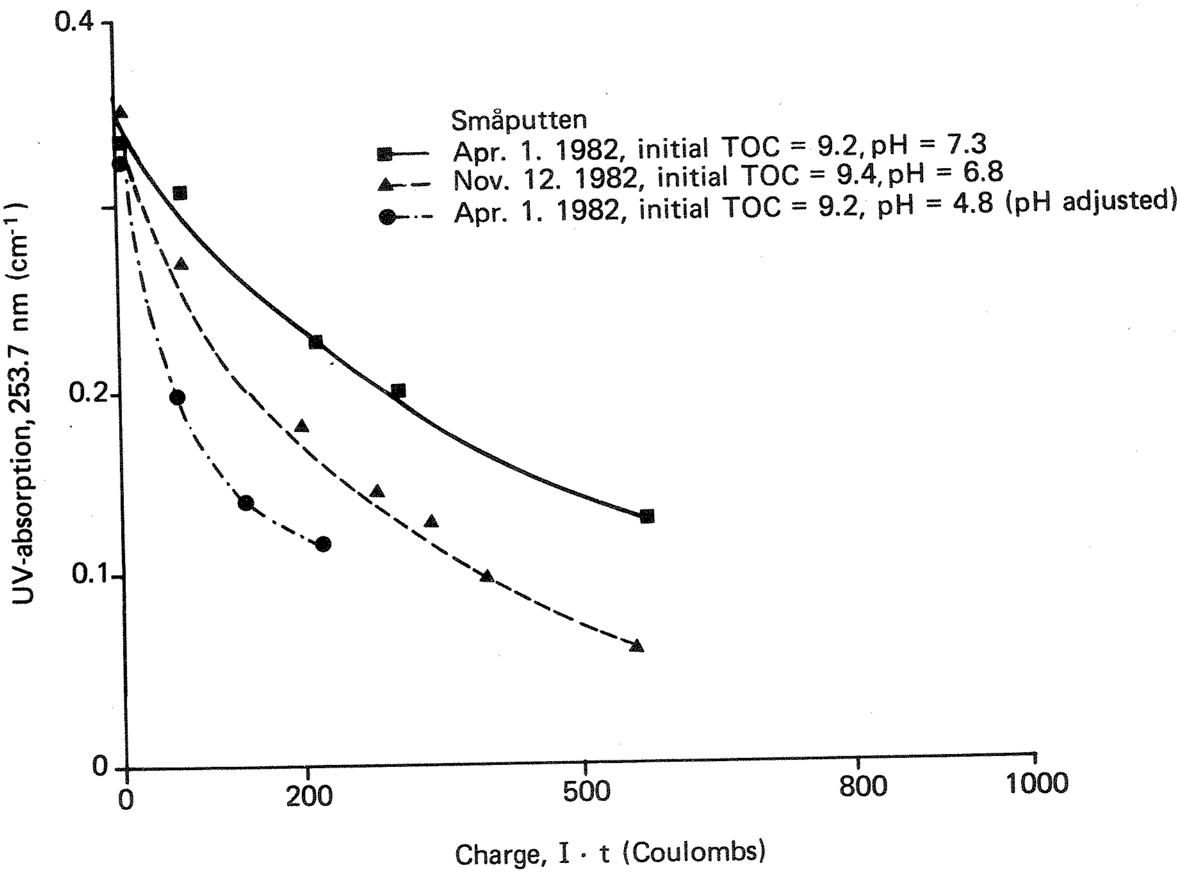


Figure 91. Residual UV absorption, 253.7 nm (cm^{-1}), as a function of charge for water from Småputten.

waters, collected on November 12 and April 1. Water from April 1, the sample with highest TOC and pH, was pH adjusted to 4.8 to see how this affected the results.

In previous results, pH adjusted water from Tjernsmotjern indicated that at pH 6.9, the pH of the raw water influenced the results, and more chemicals were needed to obtain the same results. In

Norway, the surface waters usually have pH lower than 6.0. Småputten had a higher pH value. During the winter the raw water pH was 7.3. Figure 91 illustrates clearly that pH adjustment has great influence on the amount of chemicals needed to obtain the same TOC removal.

5.2.4 Obtainable TOC Removal

Based on Figures 89 and 90 and the rest of the data presented in Appendix A, the optimum removal of aquatic humus is summarized in Table 21. The results in Table 21 show that obtainable humus removal varies from one water source to another. The humus removal measured as total organic carbon (TOC) removal varies from 57 to 82 percent, while the UV absorption removal varies from 70 to 94 percent, and the color removal varies from 92 to 100 percent. Several authors have shown that higher color removal can be obtained by coagulation than TOC removal.

Alexander & Christman (1977) showed that the fulvic acid fraction of the naturally occurring organics (humus) contain organics of lower molecular weight than the humic acid fraction. Babcock and Singer (1979) showed that the humic acid fraction contributed more to color per mg C than the fulvic acid fraction. A sample of 10 mg C/l contributed a color of 410 and 110 Pt-Co units for the humic and fulvic acid fractions, respectively. They also showed that coagulation of humic and fulvic acid resulted in 85 and 15 percent carbon removal and 99 and 90 percent color removal, respectively.

Gel filtration for determination of the relative molecular weight distribution of the organics in water from Tjernsmotjern, Hellerudmyra

Table 21. A summary of results from coagulation of aquatic humus from various water sources, using electrolytic aluminum addition.

Water sources Data	Tjernsmotjern	Dragsjøen	Asketjern	Sperillen	Hellerudmyra	Småputten
TOC (mg C/l):						
Raw water	14.0	9.5	6.2	2.3	11.0	9.2
Treated water	4.0	3.0	2.2	1.0	2.0	3.4
% removal	71	68	65	57	82	63
UV-absorption (cm^{-1}):						
Raw water	0.60	0.43	0.25	0.089	0.52	0.35
Treated water	0.060	0.073	0.032	0.027	0.032	0.056
% removal	90	83	87	70	94	84
Color (mg Pt/l):						
Raw water	125	76	45	10	110	64
Treated water	5.0	5.0	0	0	1	5
% removal	96	93	100	100	99	92
Chemical dosage:						
Charge (Coulombs)***	700	500	400	200	450	540
Al (mg Al/l) ***	8.5	6.1	4.8	2.4	5.5	6.6
Al dosage/mg C removed (mg Al/mg C)	0.85	0.94	1.2	1.8	0.61	1.13
Applied potential (V)	*5.0	** ~3.0	** ~3.0	** ~2.2	8.3	1.2
pH:						
Raw water	6.1	6.0	5.8	6.9	4.4	6.8
Treated water	8.0	7.7	7.0	7.8	6.5	7.4
Specific conductivity (μS/cm):						
Raw water	45	43	35	29	33	102
Treated water	43	33	35	25	17	100

*Estimated from Figure 98 (not registered)

**Estimated from Figure 99.

***See text, page 185.

and Småputten, showed clearly (Figure 57 and Table 20) that Hellerudmyra contained the highest fraction of high-molecular weight organics while Småputten contained the highest fraction of lower-molecular weight organics.

Our results (Table 21) showed highest TOC removal was achieved with water from Hellerudmyra (82 percent TOC removal) and lowest with water from Småputten (63 percent TOC removal). This corresponds with the Babcock & Singer (1979) results, where 85 and 15 percent carbon removal was achieved from humic acid and fulvic acid, respectively. Highest percent carbon removal can be achieved for coagulation of the organics with the highest molecular weight.

Several authors have discussed the chemical demand for various size fractions of the organics. Rashid (1971) determined the ability of a number of di- and trivalent metal ions to coagulate various molecular weight fractions of humic acid. He showed that the lower-molecular weight fractions complexed 2 to 6 times more than did the high-molecular weight fractions. Randtke & Jepsen (1980) showed that fulvic acid exerted a higher coagulant demand than humic acid.

The chemical demand in our experiments has been determined as aluminum dosage per mg C removed (mg Al/mg C). The results were presented in Table 21. Our results correspond with the literature data. Småputten had the highest chemical demand of the three sources (1.13 mg Al/mg C) and Hellerudmyra the lowest (0.61 mg Al/mg C). Use of the Narkis & Rebhun (1977) approach was difficult. To determine the chemical demand from the potentiometric titration curves, the degree of ionization of the organics must be known, i.e. the pH of coagulation and the charge of the aluminum compounds at the same pH.

5.2.5 Detailed Electrochemical Reactor Study Compared with Conventional Treatment

In one study raw water from Hellerudmyra was treated both electrochemically and conventionally. Six mg Al/1 was added to both, and the conventionally treated water pH adjusted with NaOH to 6.0. The results are presented in Table 22.

The organic carbon concentration of the treated waters measured as color is the same when using the two methods. The main differences between the results obtained through treatment with these processes are the pH and the specific conductivity. The high specific conductivity of water treated conventionally is due to the addition of sulfate. The sulfate concentration is approximately ten times higher for water receiving 6 mg Al/1 as aluminum sulfate than for water receiving 6 mg Al/1 by electrolytic addition. The high pH in the electro-chemical process results from the hydrogen gas formation at the cathode. This gives high residual Al concentrations for the electro-chemically treated water compared with conventionally treated water. The raw water iron and aluminum concentrations are relatively high, 130 and 290 μg/1, respectively. Both Al and Fe belong, according to Gjessing (1976), to the elements forming inner complexes with the aquatic humus. The removal of humus will thus also lead to removal of these elements. This theory fits very well our results,

Table 22. Results from a detailed electrochemical reactor study compared with conventional treatment.

Process Parameters		Water Quality		
		Raw water	Electrochemically treated	Conventionally treated
Color	(mg Pt/l)	80	3	3
pH		4.8	7.0	5.9
Spec. cond.	(μS/cm)	35	20	114
Ca	(mg/l)	1.08	0.76	1.09
Mg	(mg/l)	0.27	0.14	0.24
Fe	(μg/l)	130	10	20
Al	(μg/l)	290	330	40
Na	(mg/l)	1.05	1.63	1.49
K	(mg/l)	0.32	0.41	1.87
Mn	(μg/l)	34	20	32
Cu	(μg/l)	37	16	23
Pb	(μg/l)	1.9	<0.5	0.5
NO_3	(μg/l)	<10	<10	<10
SO_4	(mg/l)	4.6	2.4	32
Cl	(mg/l)	1.3	1.2	2.6
F	(mg/l)	<0.1	<0.1	<0.1

except for the high residual Al-concentration from the electrochemically treated water. The aluminum in water from Hellerudmyra is in the form of strong alumino-organic complexes, while the treated water aluminum probably is free aluminum or monomeric inorganic complexes. This means that the high Al-concentration of electrochemically treated water is due to the high pH of the water causing the formation of the $Al(OH)_4^-$ ions.

5.3 The Conventional Coagulation Process

The conventional coagulation process was studied using jar test equipment. To gain an appreciation for coagulation mechanisms involved, the process was studied for various pH and aluminum dosages.

5.3.1 The Sequence of Chemical Addition

The sequence of chemical addition also was studied. Four sequence modes were used:

(A) $Al_2(SO_4)_3$ added first immediately followed by NaOH addition.

(B) NaOH addition immediately followed by $Al_2(SO_4)_3$ addition.

(C) $Al_2(SO_4)_3$ mixed with NaOH before addition.

(D) $Al_2(SO_4)_3$ added first 5 minutes later NaOH added.

Both Hellerudmyra and Tjernsmotjern waters were studied using 10.8 and 14.4 mg Al/l dosages. The results are presented in Table 23.

In one jar-test using water from Hellerudmyra, the $Al_2(SO_4)_3$ and NaOH were mixed before addition, the same as case (C) in Table 23. The results from this study were compared with the one obtained when the $Al_2(SO_4)_3$ was added first, immediately followed by NaOH addition

Table 23. Effects of chemical addition sequence on color removal in jar tests.

(A) Al-sulfate first immediately followed by NaOH.
(B) NaOH first immediately followed by $Al_2(SO_4)_3$.
(C) $Al_2(SO_4)_3$ + NaOH mixed before addition.
(D) $Al_2(SO_4)_3$ added first, 5 minutes later NaOH added.

Al-dosage (mg Al/l)	sequence	Hellerudmyra Residual concentration				Tjernsmotjern Residual concentration			
		Final pH	UV abs.	Color Unfiltered	Color Filtered	Final pH	UV abs.	Color Unfiltered	Color Filtered
10.8	(A)	5.5	0.053	9	5	5.9	0.066	16	3
	(B)	5.4	0.043	9	3	6.0	0.065	18	3
	(C)	5.7	0.186	100	35	6.1	0.240	64	44
	(D)	5.4	0-050	15	3	6.0	0.060	18	3
14.4	(A)	7.0	0.064	15	5	6.5	0.102	21	14
	(B)	7.5	0.071	34	8	6.3	0.090	19	5
	(C)	7.5	0.355	100	80	6.4	0.326	100	60
	(D)	6.9	0.107	136	20	6.5	0.102	21	6

(see Figure 92).

From Table 23 and observations in Figure 92 it was found that mixing of $Al_2(SO_4)_3$ and NaOH before addition, case (C), does not result in an effective coagulation process. Probably $Al(OH)_{3(s)}$ is formed before the chemicals are added to the water, and the humus is not destabilized. When the pH was adjusted five minutes after aluminum sulfate dosing, case (D), the sedimentation was not as good as for case (A) and (B) for water from Hellerudmyra. This was especially true for the highest aluminum-dosage. The discussion of these results is complicated by the fact that the pH was not exactly the same in all

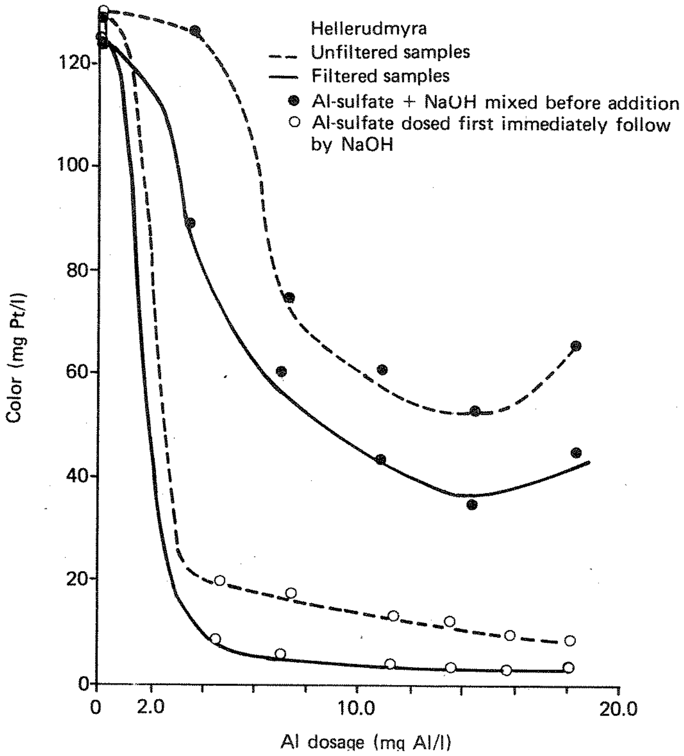


Figure 92. Residual color versus aluminum dosage using two modes of addition of chemicals.

the samples, but the Al-dosages, in all cases, were higher than the critical coagulation concentration at the various pH levels. The critical coagulation concentration will be further discussed later in this chapter. The Al-dosage of 10.8 mg/l for Tjernsmotjern was run twice to check the reproducibility of the results, which proved to be very good. There seems to be no large difference between the cases where Al was added first, compared with the cases where NaOH was added first, except at alkaline pH levels, (see Hellerudmyra, 14.4 mg Al/, case (B) in Table 23). As long as the pH adjustments did not result in an alkaline pH, there seemed to be no difference between cases (A) and (B). In all further experiments, sequence mode (A) was used, $Al_2(SO_4)_3$ added first, immediately followed by NaOH addition.

5.3.2 Coagulation Mechanisms Involved in Aquatic Humus Removal

The results from the coagulation experiments are presented as residual color as a function of pH, for the three raw waters studied. All data are given in Appendix B. The results from Tjernsmotjern are presented in Figure 93; the results from Hellerudmyra are in Figure 94; and the results from Småputten are in Figure 95. The colloidal charge was determined for water from Tjernsmotjern and from Hellerudmyra. The optimum pH for color removal lies between 5.0 and 6.0 for all three water sources. Figures 93 and 94 show clearly that the optimum pH range gets wider with increasing alum dosages, mainly in the alkaline pH range. Table 24 summarizes these results.

Table 24 shows that the optimum pH range for Tjernsmotjern and Hellerudmyra is almost identical. At an alum dosage of 10.8 mg Al/1, optimum pH ranges 4.8-6.8 and 4.7-6.8 were obtained for Tjernsmotjern and Hellerudmyra, respectively. The optimum pH range for Småputten is not as marked as for the two others.

The pH for zero point of charge for various Al-dosages is presented in Table 25.

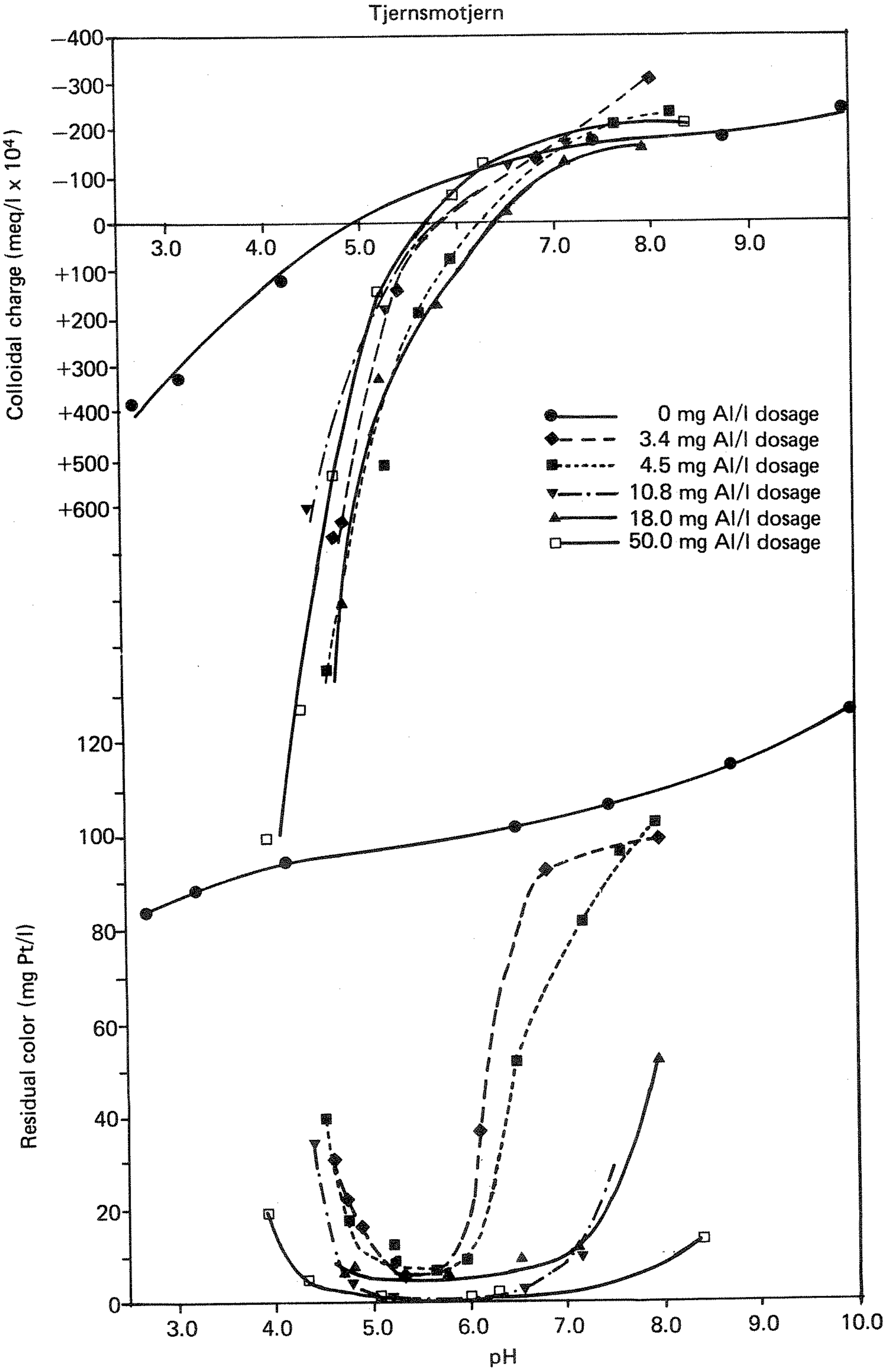


Figure 93. Results from coagulation experiments with water from Tjernsmotjern. Residual color and colloidal charge as a function of pH.

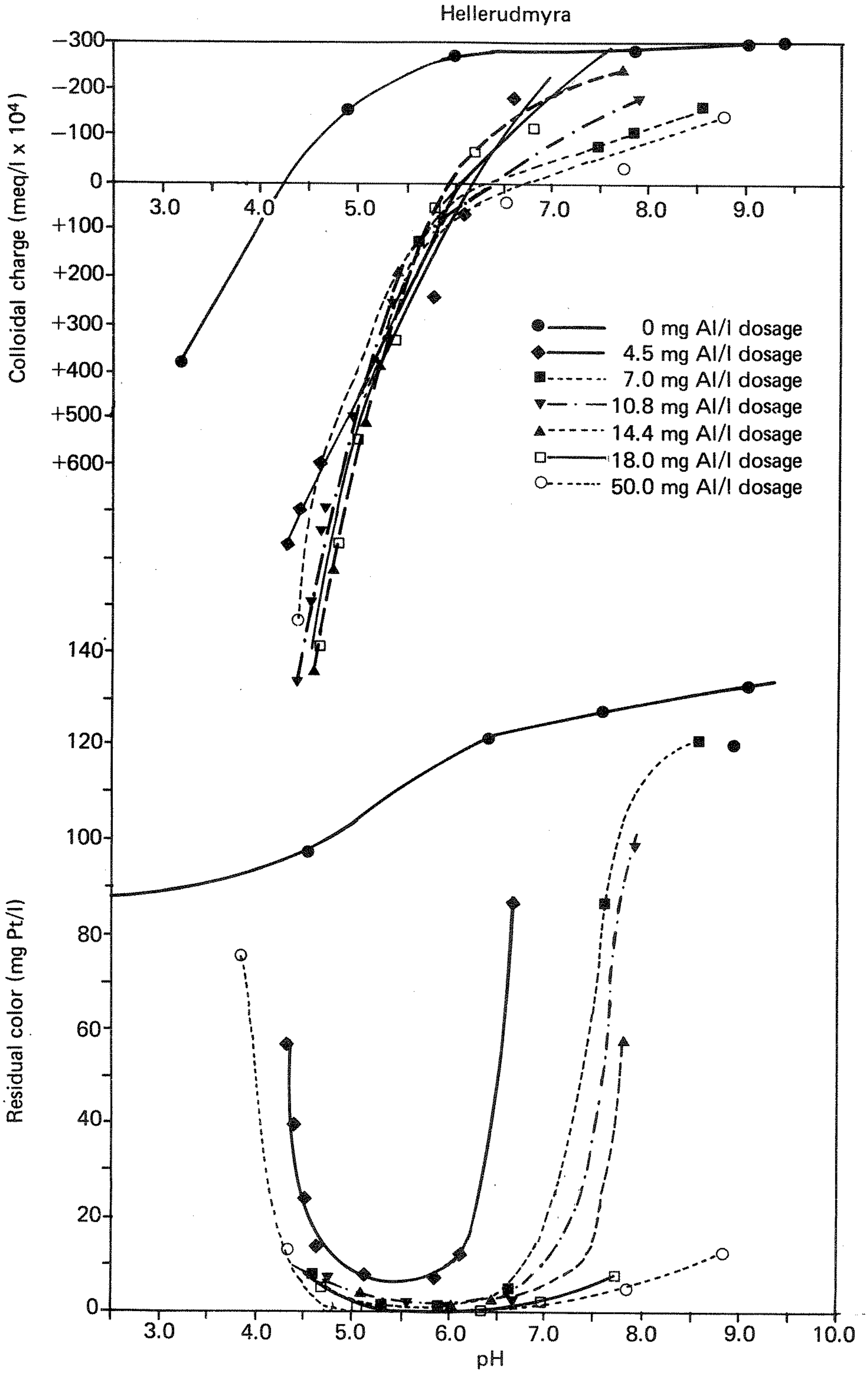


Figure 94. Results from coagulation experiments with water from Hellerudmyra. Residual color and colloidal charge as a function of pH.

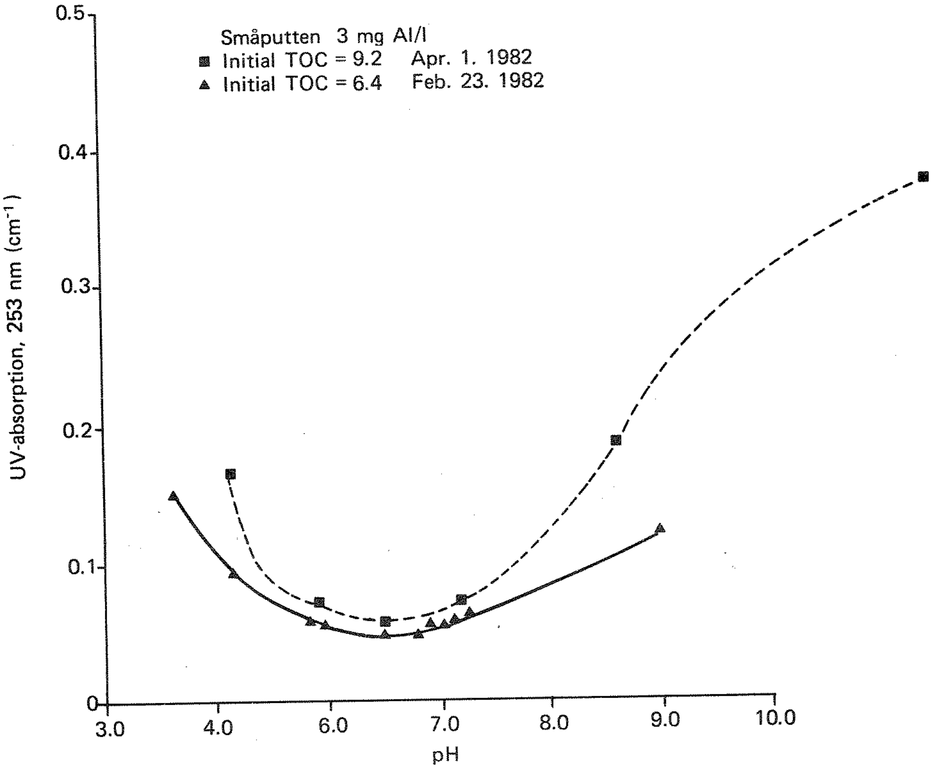


Figure 95. Results from coagulation experiments with water from Småputten. Residual UV absorption as a function of pH.

Table 24. pH range for optimum color removal at various Al-dosages.

Raw water	Al-dosage (mg Al/l)	Optimum pH range
Tjernsmotjern	3.4	5.1 - 5.9
	4.5	5.0 - 6.0
	10.8	4.8 - 6.8
	18.0	4.6 - 7.0
	50.0	4.3 - 7.8
Hellerudmyra	4.5	5.0 - 6.0
	7.0	4.8 - 6.6
	10.8	4.7 - 6.8
	14.4	4.7 - 6.9
	18.0	4.6 - 7.4
	50.0	4.5 - 7.8
Småputten	3.0	4.8 - 6.4

Table 25. The pH for zero point of charge for various Al-dosages for water from Hellerudmyra and Tjernsmotjern.

Raw water	Al-dosage (mg Al/l)	The pH for zero point of charge
Tjernsmotjern	0	4.9
	3.4	5.8
	4.5	6.2
	10.8	5.8
	18.0	6.2
	50.0	5.7
Hellerudmyra	0	4.2
	4.5	6.1
	7.0	6.3
	10.8	6.3
	14.4	5.9
	18.0	6.0
	50.0	6.7

Due to some uncertainty in the analytical technique, these small differences in the pH values for zero point of charge are not significant. For colored waters the titration end point was difficult to find exactly, and several parallel samples had to be run. This is further discussed in Appendix 5. For Tjernsmotjern, when the Al-dosage varies between 3.4 and 50.0 mg/l, the pH of zero point of charge equals approximately 6.0, and for Hellerudmyra approximately 6.3. Both pH values are within the optimum pH range for color removal.

Residual color as a function of alum dosage was determined from Figures 93 and 94. Residual UV absorption as a function of alum dosages was also determined. The results are presented in the following figures; Figures 96 and 97 present data from Tjernsmotjern, Figures 98 and 99 present data from Hellerudmyra, and Figures 100 and 101 the data from Småputten. The results from Småputten (Figure 100), presenting color as a function of Al-dosage for the highest initial TOC concentration, look misleading. The color analyses for this series are unusual. The necessary alum dosage to obtain maximum UV/color/TOC removal, and the pH value giving the lowest possible Al-dosages for the three sources, are summarized in Table 26.

The necessary Al-dosage to obtain maximum TOC removal, calculated as mg Al/mg C removed, was shown to be highest for Småputten (0.69 and 0.97 mg Al/mg C removed), and lowest for Hellerudmyra (0.63 mg Al/mg C removed). There are very small differences in chemical demand for the three water sources. The curves (Figure 96 through 101) are based on relatively few data points resulting in an uncertainty in

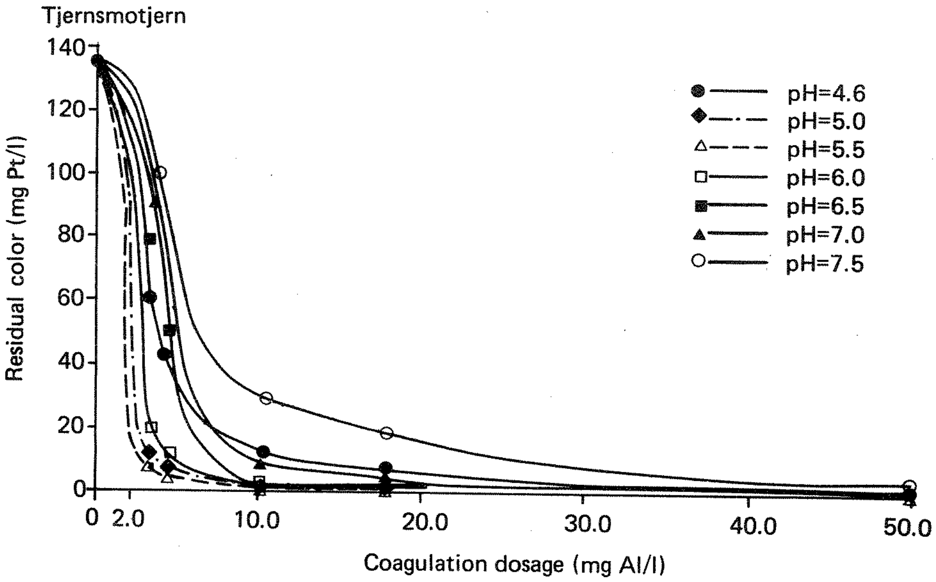


Figure 96. Residual color as a function of coagulation dosage for various pH values (Tjernsmotjern).

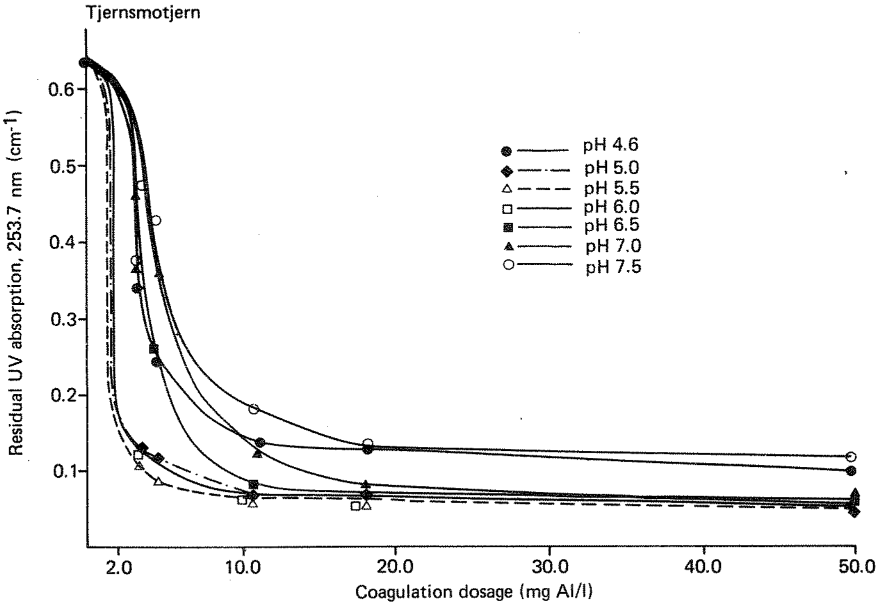


Figure 97. Residual UV absorption as a function of coagulation dosage for various pH values (Tjernsmotjern).

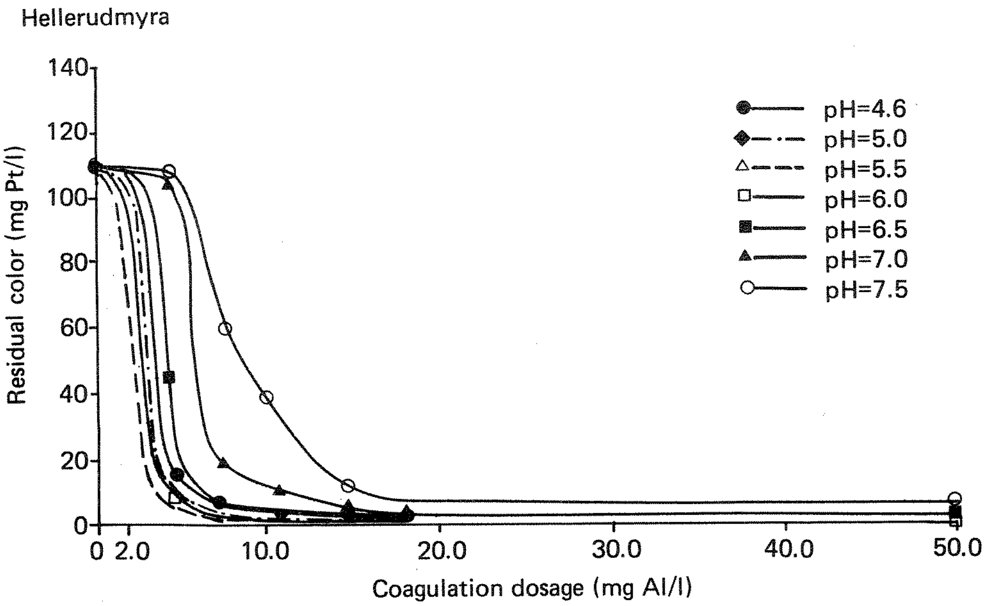


Figure 98. Residual color as a function of coagulation dosage for various pH values (Hellerudmyra).

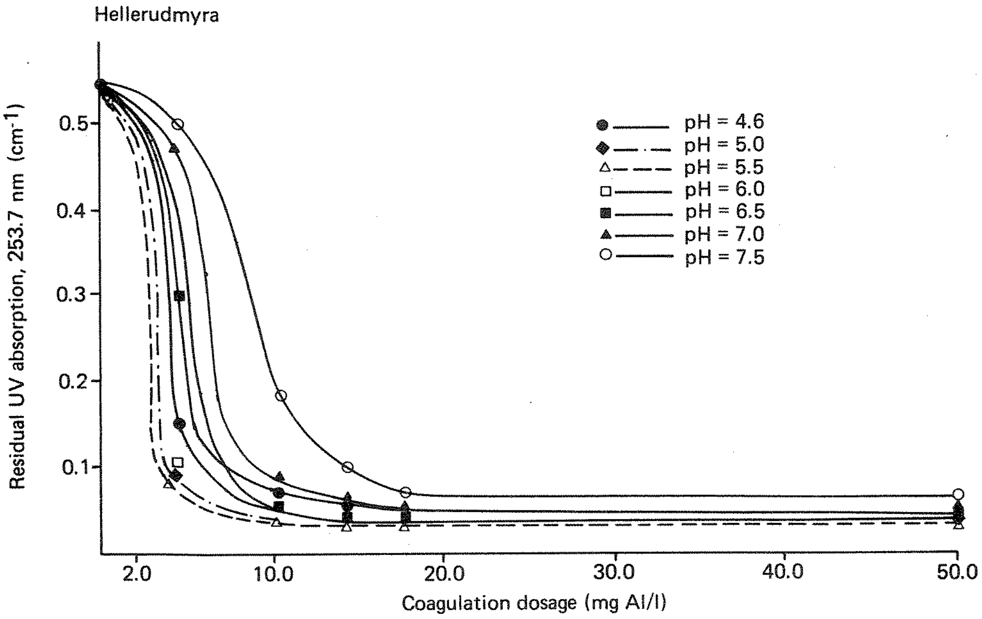


Figure 99. Residual UV absorption as a function of coagulation dosage for various pH values (Hellerudmyra).

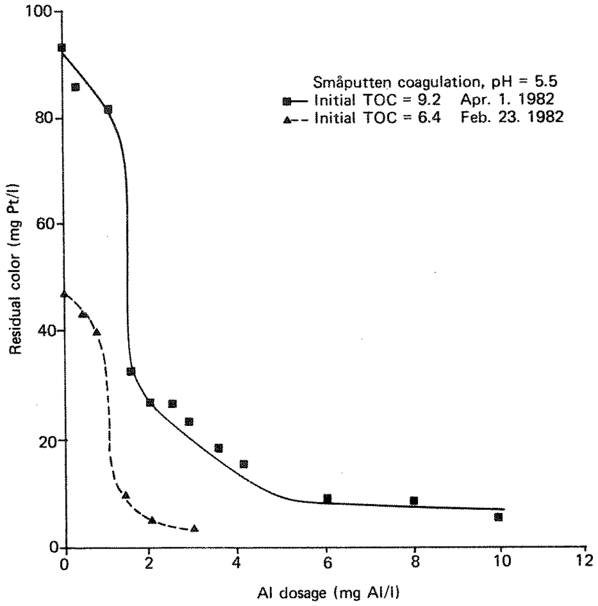


Figure 100. Residual color as a function of Al-dosage (Småputten).

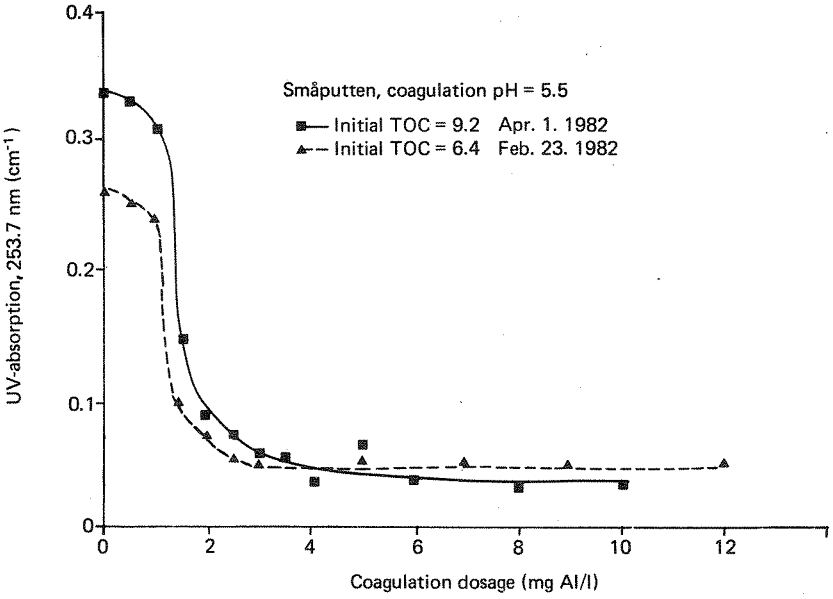


Figure 101. Residual UV absorption as a function of Al-dosage (Småputten).

Table 26. Minimum Al-dosage for maximum TOC removal.

Raw water	Al-dosages for maximum TOC removal (mg Al/l)	pH	TOC * removal (mg C/l)	Relative Al-dosage mg Al/mg C removed
Tjernsmotjern	8	5.5	10.5	0.76
Hellerudmyra	6.0	5.5	9.4	0.63
Småputten, 9.2 mg C/l	3.9	5.5	5.6	0.69
Småputten, 6.4 mg C/l	2.8	5.5	2.9	0.97

* TOC is calculated from Figure 92.

determination of the necessary Al-dosages. To get an understanding of the coagulation mechanisms involved, the results for maximum TOC removal from this research are included in the curve presented by Amirtharajah & Mills (1980), Figure 102. The Al-dosages giving maximum TOC removal varied between 2.8 mg Al/l (Småputten) and 50 mg Al/l (Tjernsmotjern & Hellerudmyra), being equal to log molar Al concentrations of -3.98 and -2.73, respectively, and pH in the range of 5.0 to 6.0 and 4.4 to 7.8, respectively.

The coagulation results obtained using the electro-chemical process give approximately the same results. According to Amirtharajah & Mills (1980), maximum humus removal is achieved partly in the restabilization zone and partly in the sweep coagulation zone. For the three water sources studied, no restabilization was ever observed. The boundaries for the restabilization zone have not been established for the humus "colloids", but the results from these tests indicate that coagulation of aquatic humus differs from the one occurring with

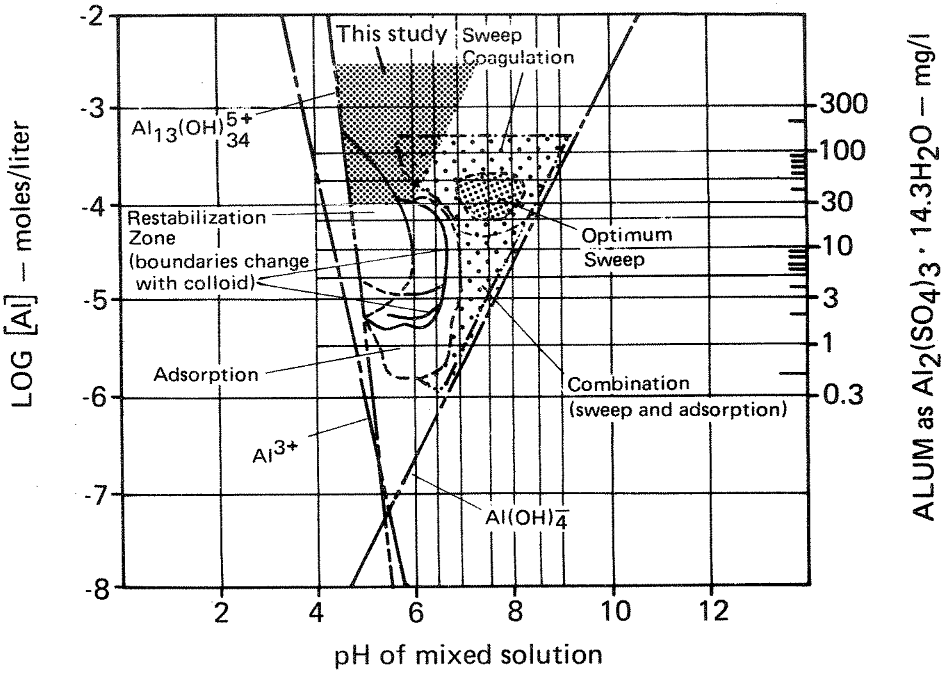


Figure 102. Mechanisms involved in coagulation of various surface waters using alum as coagulant (Amirtharajah & Mills, 1980).

The shaded area in the upper left central portion of the diagram marks the three water sources in this study with high content of aquatic humus.

clay minerals in regard to restabilization. Edzwald (1981) studied humic acid and showed that restabilization occurred. The naturally occurring organics are more complex than the humic acid fraction of the same humus. Narkis & Rebhun (1977) showed that restabilization occurred for the humic acid fraction using a cationic polyelectrolyte as coagulant.

The critical coagulation concentrations at various pH levels for the three water sources were established from Figures 97, 99, and 101. The critical coagulation concentration is defined here as the Al-dosage used to reduce the UV absorption to one half of the raw water concentration. The critical coagulation concentrations for various pH values are summarized in Table 27.

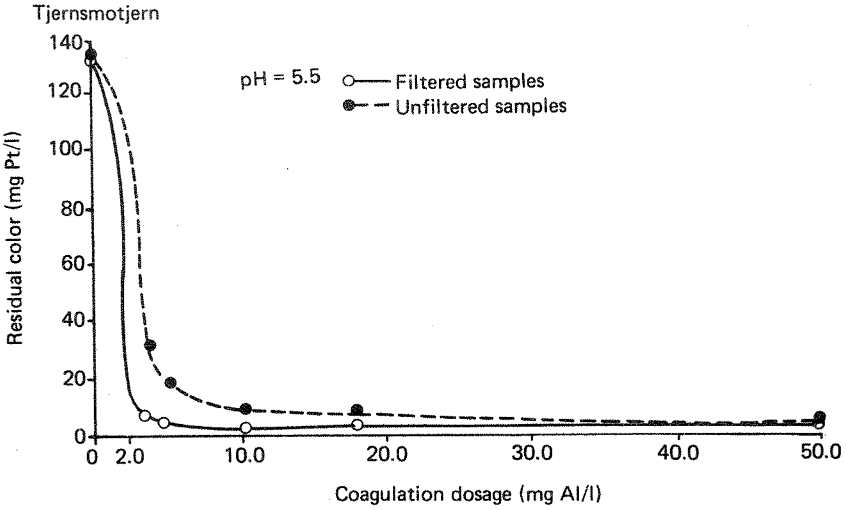
Table 27. Critical coagulation concentrations at various pH values for raw waters with high contents of aquatic humus.

Raw water		Critical coagulation concentration		pH
	TOC mg C/l	mg Al/l	log (Al) moles/l	
Tjernsmotjern	14.6	4.2	-3.81	4.6
	14.6	1.9	-4.15	5.0
	14.6	1.8	-4.18	5.5
	14.6	2.0	-4.13	6.0
	14.6	3.9	-3.84	6.5
	14.6	5.2	-3.72	7.0
	14.6	5.3	-3.71	7.5
Hellerudmyra	12.4	5.3	-3.71	4.6
	12.4	2.0	-4.13	5.0
	12.4	1.9	-4.15	5.5
	12.4	2.8	-3.98	6.0
	12.4	3.6	-3.88	6.5
	12.4	8.2	-3.16	7.0
	12.4	9.6	-3.45	7.5
Småputten	9.2	1.5	-4.26	5.5
	6.4	1.2	-4.35	5.5

Edzwald (1980) summarized the coagulation of humic acid with alum as being accomplished through two mechanisms of destabilization, by charge neutralization and by precipitation:

> Destabilization by charge neutralization resulting from specific chemical interaction between positively charged aluminum species and the negatively charged groups on the humic colloids would be accomplished over a narrow pH range (pH 4 to 6) and a stoichiometric relationship between the raw water humic concentration and the optimum coagulant dosage would be observed.
>
> As the alum dosage is increased precipitation may occur; however, destabilization via this mechanism may include incorporation of humic material within aluminum hydroxide floc or co-precipitation as aluminum humate. High alum dosages are required above pH 6 to achieve 'sweep floc' effect in which the humic material is incorporated in the floc.

As previously mentioned, coagulation of naturally organic carbon (aquatic humus) from our three water sources, never resulted in restabilization. In case only the turbidity of the samples were affected, the color measured on both filtered and unfiltered samples is presented as a function of charge for both Tjernsmotjern and Hellerudmyra. See Figure 103. No restabilization is observed. Restabilization is accompanied by charge reversal, which is only observed for increasing pH values and not with increasing alum dosages at constant pH. Sweep coagulation mechanisms seem to dominate in the systems studied in this research. The $\{Al^{3+}\}\ \{OH^-\}^3/K_s$ ratio at pH 5.0 and $\{Al^{3+}\} = 10^{-4}$, using $K_s = 10^{-31.6}$, is equal to only 4.0. To ensure very rapid precipitation, the ratio should be higher than 100 according to O'Melia (1972). At pH 6.0 and $\{Al^{3+}\} = 10^{-4}$, the ratio is about 4000 and thus rapid precipitation is expected. The precipitation is not rapid at high Al-dosages and low pH.



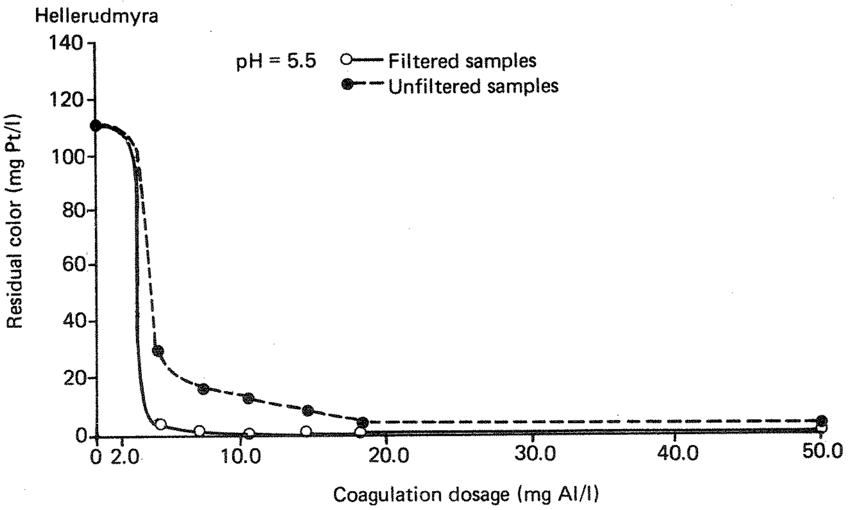


Figure 103. Residual color analyzed on filtered and unfiltered samples as a function of the coagulation dosage.

Water sources: Tjernmotjern and Hellerudmyra.

At $\{Al^{3+}\} = 10^{-2.73}$ and pH = 4.4, the ratio is 1.2, but the organic carbon is also effectively removed at this pH. At the lowest pH and Al-dosages giving effective carbon removal, the adsorption destabilization might dominate, but no restabilization occurs and sweep coagulation follows immediately when increasing either Al-dosage and/or pH.

5.3.3 Residual Al-Concentrations

In a series of experiments the aluminum concentration of the treated water was measured to determine the optimum pH for low residual aluminum concentrations. The drinking water standard for Al-concentration in Al-treated water in Norway is 0.1 mg Al/1. The results obtained from the coagulation experiments with water from Tjernsmotjern, Hellerudmyra, and Småputten are presented in Figures 104, 105, and 106, respectively. The necessary Al-dosages, at various pH levels to obtain lower residual Al-concentration than 0.1 mg Al/1, are summarized in Table 28.

Table 28. Necessary Al-dosages at various pH levels to obtain residual Al-concentrations lower than 0.10 mg Al/1.

Raw water	pH	Al-dosage (mg Al/1)
Tjernsmotjern	5.5	>16
	6.0-6.5	>10
	7.0	>16
Hellerudmyra	5.5	4-30
	6.0	>10
	6.5	>12
	7.0	>18
Småputten	5.5	> 3

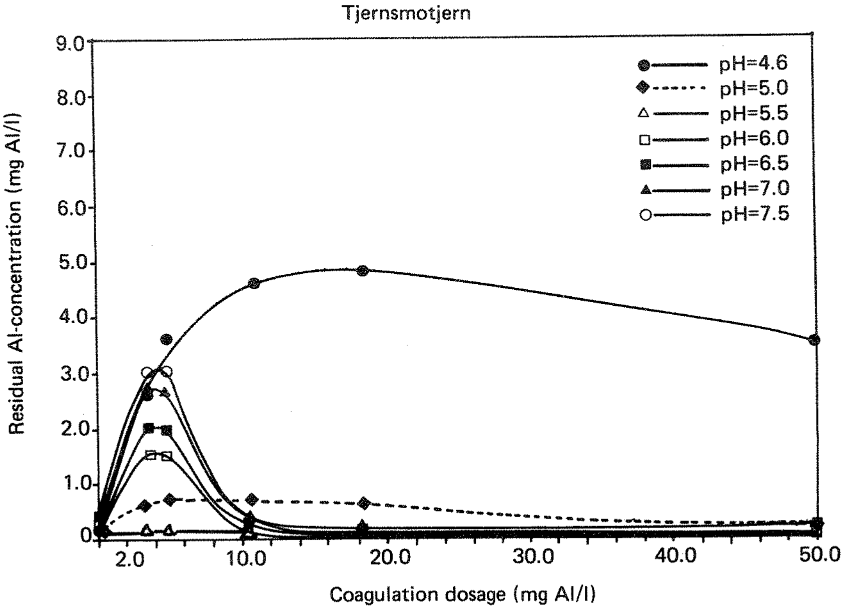


Figure 104. Residual aluminum concentration as a function of coagulation dosage for various pH values (Tjernsmotjern).

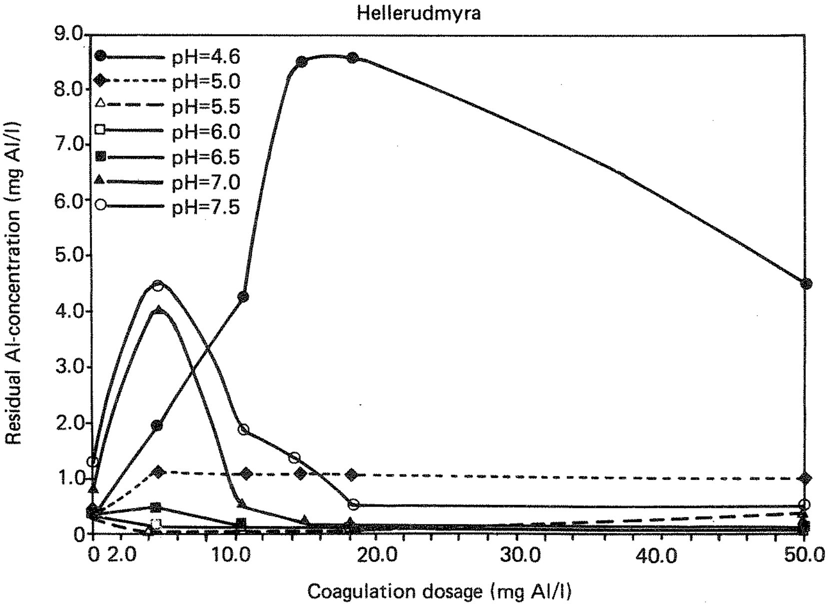


Figure 105. Residual aluminum concentration as a function of coagulation dosage for various pH values (Hellerudmyra).

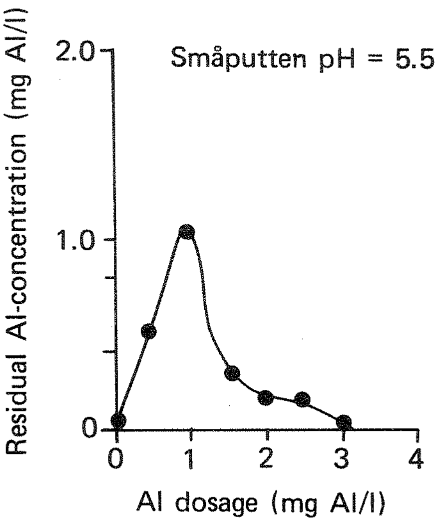


Figure 106. Residual Al-concentration for various Al-dosages at pH 5.5 (Småputten).

The residual Al-concentrations as log molar Al-concentrations for Tjernsmotjern, Hellerudmyra, and Småputten are presented in Figures 107, 108, and 109, respectively. The critical coagulation concentrations found are also marked in Figures 107 and 108. In all three figures, the following aluminum equilibrium equations were used:

$Al(OH)_{3(s)} \overset{<----}{---->} Al^{3+} + 3\ OH^-$ $\log K_{SO} = -31.6$ (Hayden & Rubin, 1974)

$Al(OH)_{3(s)} + H_2O \overset{<----}{---->} Al(OH)_4^- + H^+$ $\log {}^*K_{S4} = -12.34$ (Hayden & Rubin, 1974)

$K_{SO} = (Al^{3+})\ (OH^-)^3 \quad = -10^{-31.6}$

$K_W = (H^+)\ (OH^-) \quad = 10^{-14}$, where $(OH^-) = 10^{-4}\ (H^+)^{-1}$

$(Al^{3+}) = 10^{-31.6} \cdot 10^{14 \cdot 3} \cdot (H^+)^3$

$\log\ (Al^{3+}) = 10.4 - 3\ pH$ first line

${}^*K_{S4} = (AlOH_4^-)\ (H^+) = 10^{-12.34}$

$\log\ (AlOH_4^-) = -12.34 + pH$ second line

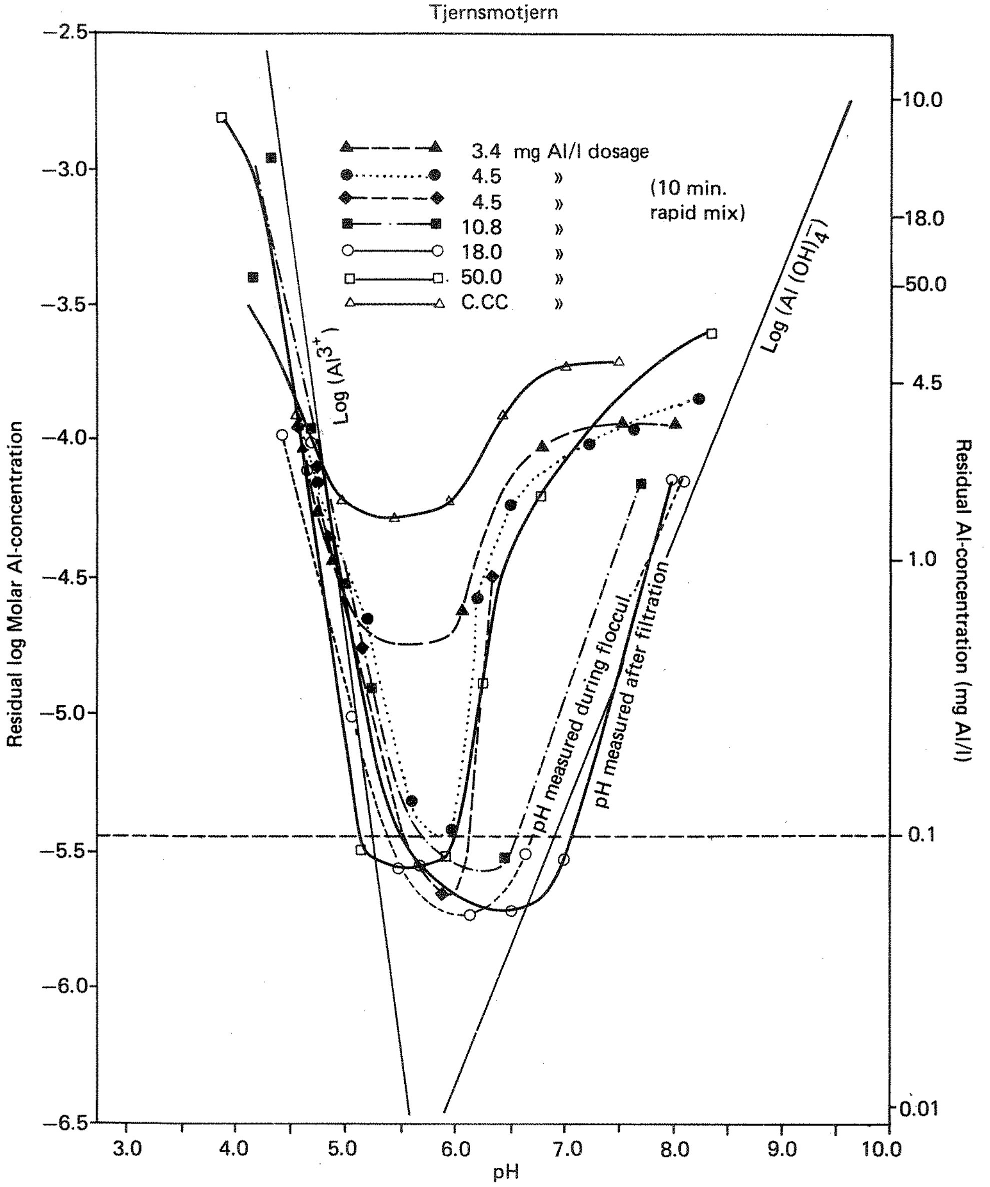


Figure 107. Residual Al-concentration (log scale) as a function of pH for various Al-dosages (Tjernsmotjern).

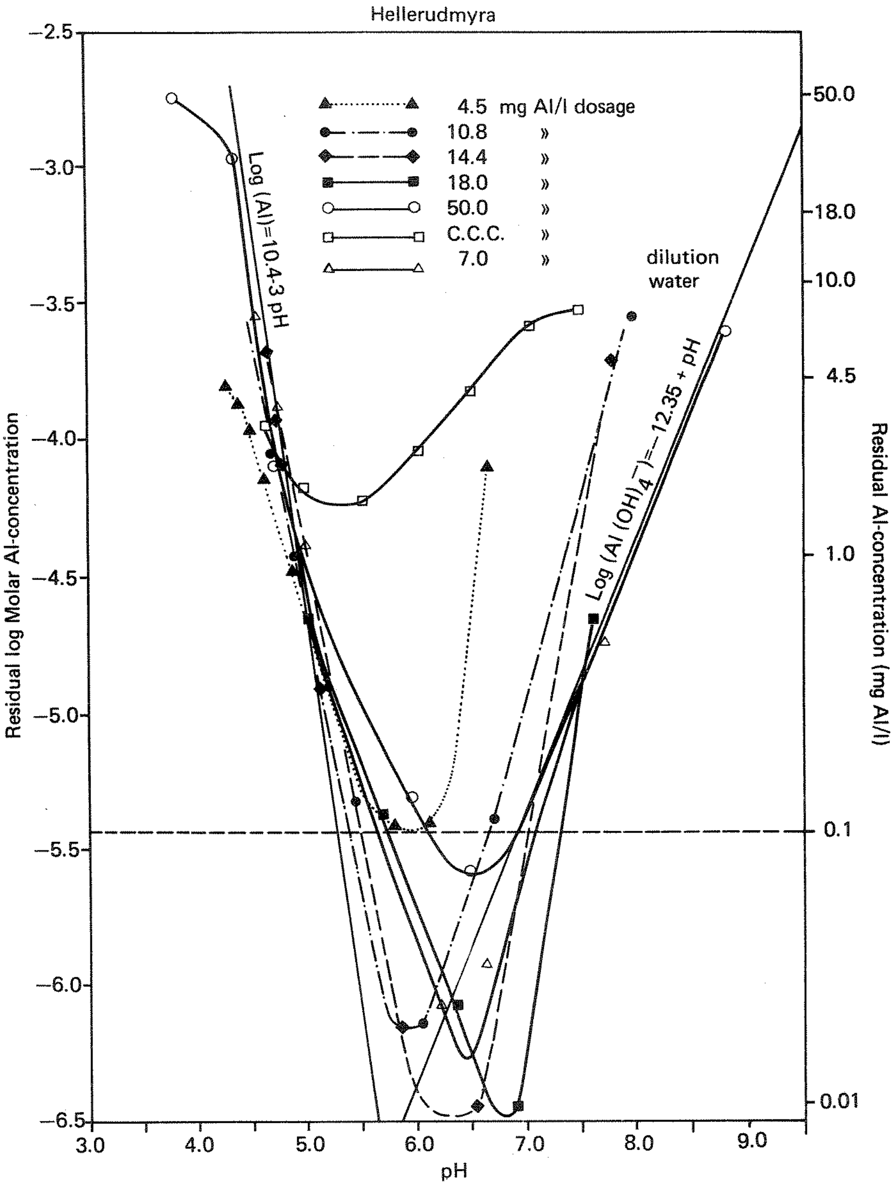


Figure 108. Residual Al-concentration (log scale) as a function of pH for various Al-dosages (Hellerudmyra).

No additional hydrolysis species have been included. The total soluble Al-concentration in the acid pH range follows the log molar $\{Al^{3+}\}$ line well for all three sources. For Tjernsmotjern at low Al-dosages, 3.4 and 4.5 mg Al/l and high dosage, 50 mg Al/l at pH values higher than approximately 6.0, the equilibrium between $\{Al(OH)_4^-\}$ and $Al(OH)_{3(s)}$ was not reached. The residual Al-concentration was higher than expected. The residual aluminum concentrations increased rapidly for low and high alum dosages when pH was higher than 6.0. The colloidal charge curve in Figure 93 showed that pH = 6.0 was the pH for zero point of charge for all Al-dosages. Increasing pH resulted in negative colloidal charges. For pH values higher than 6.0 and Al-dosages 3.4 and 4.5, optimum humus removal has not been achieved. See Figure 97. The higher than expected residual Al-concentration, according to the $Al(OH)_{3(s)}$-equilibrium curve is probably due to complexation of Al and the humus molecule. The result obtained for an Al-dosage of 50 mg Al/l is difficult to explain.

For Hellerudmyra the same result was seen for the low alum dosage (4.5 mg Al/l). Figure 99 illustrates that optimum humus removal is not obtained at an Al-dosage of 4.5 mg Al/l.

The residual Al-concentrations from the coagulation experiment, using dilution water for Hellerdumyra and an alum dosage of 7.0 mg Al/l, follow well the $Al(OH)_{3(s)}$ equilibrium curve, knowing the difficulties in finding the exact pH-values. At an alum dosage of 7.0 mg Al/l and pH higher than 6.5 in Figure 99, the residual organic carbon would still be high and, for Hellerudmyra water, the residual

Al-concentration versus pH would probably not have followed the $Al(OH)_{3(s)}$ curve as the dilution water does. Complexation between aluminum and humus seem to play an important role at pH-values higher than 6.0

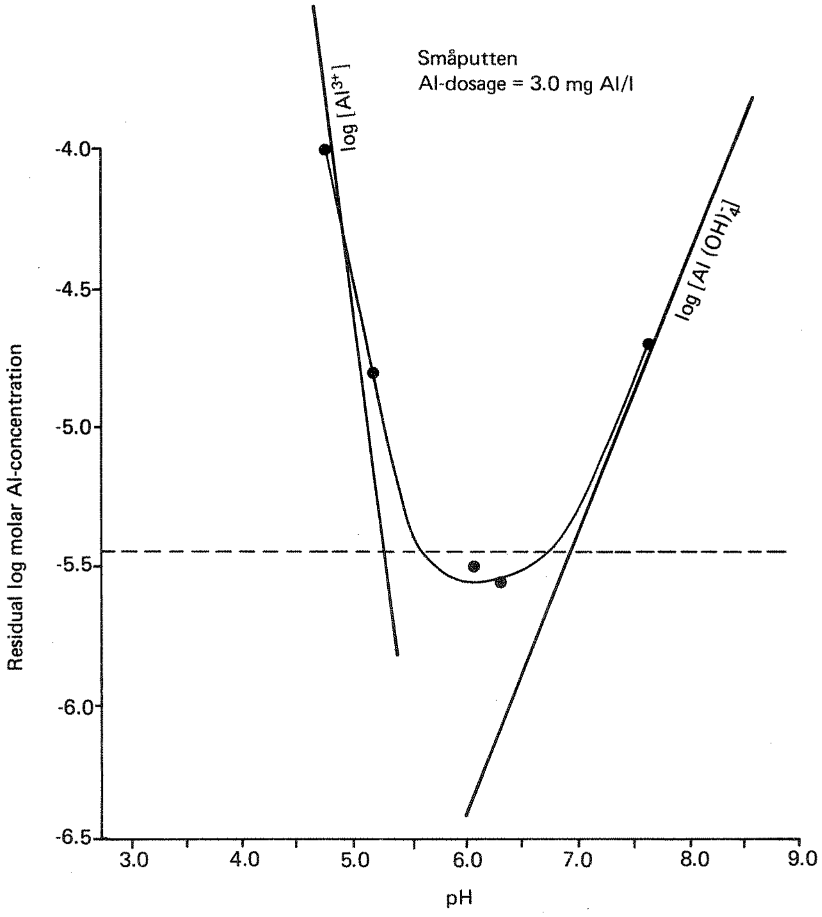


Figure 109. Residual Al-concentration (log scale) as a function of pH for various Al-dosages (Småputten).

The residual Al-concentration for coagulated water from Småputten was determined for an alum dosage of 3 mg Al/l only, and for this dosage the curve followed the $Al(OH)_{3(s)}$ equilibrium curve. The pH range for residual Al-concentrations lower than 0.1 mg Al/l for the three sources is summarized in Table 29.

Table 29. pH range for residual Al-Concentrations lower than 0.1 mg Al/l at various Al-dosages.

Raw water	Al-dosage (mg Al/l)	pH range
Tjernsmotjern	4.5	5.8 - 5.9
	10.8	5.7 - 6.5
	18.0	5.5 - 7.0
	50.0	5.1 - 6.0
Hellerudmyra	4.5	5.8 - 6.1
	10.8	5.4 - 6.7
	14.4	5.5 - 7.0
	18.0	5.7 - 7.3
	50.0	6.0 - 6.8
Småputten	3.0	5.5 - 6.8

Except for the very high alum dosage (50 mg Al/l), the optimum pH range increased with increasing dosages.

A comparison of residual Al-concentration and color versus pH was done for low and high alum dosage for water from Tjernsmotjern (Figure 110) and Hellerudmyra (Figure 111). The figures illustrate that the optimum pH range for residual Al-concentrations is slightly different from the one for residual color.

A raw water sample, Tjernsmotjern, and one treated water sample (alum dosage: 5 mg Al/l, pH adjusted to 6.0) were analyzed in order to fractionate the various aluminum complexes (Müller, 1982; Naas, 1982). The results obtained are summarized in Table 30.

The results, although varying to some extent, especially on the total Al concentration, show clearly that the raw water contains mainly monomeric aluminum organic complexes. The low residual

Al-concentration of treated water made it impossible to verify, with available equipment, whether the treated water contained primarily

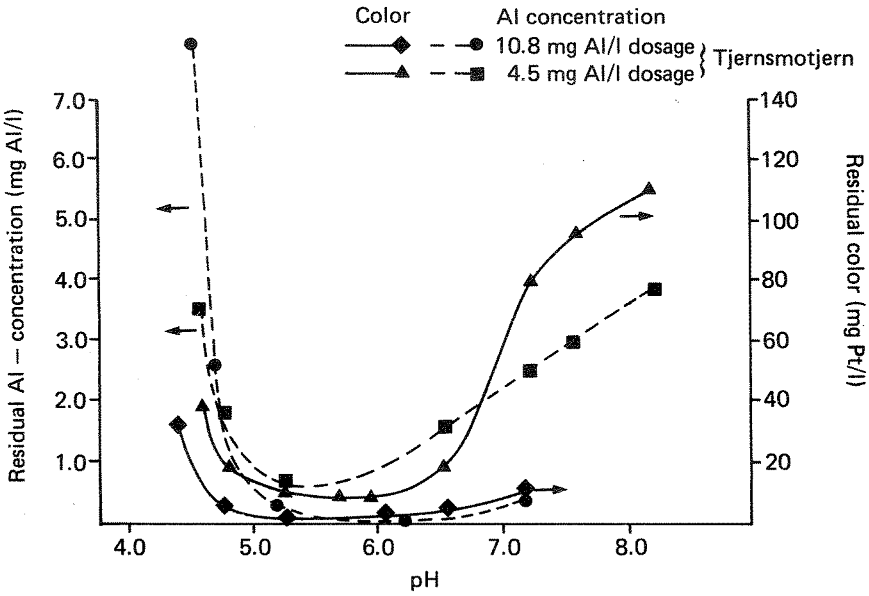


Figure 110. Residual Al and color verus pH for coagulated Tjernsmotjern water.

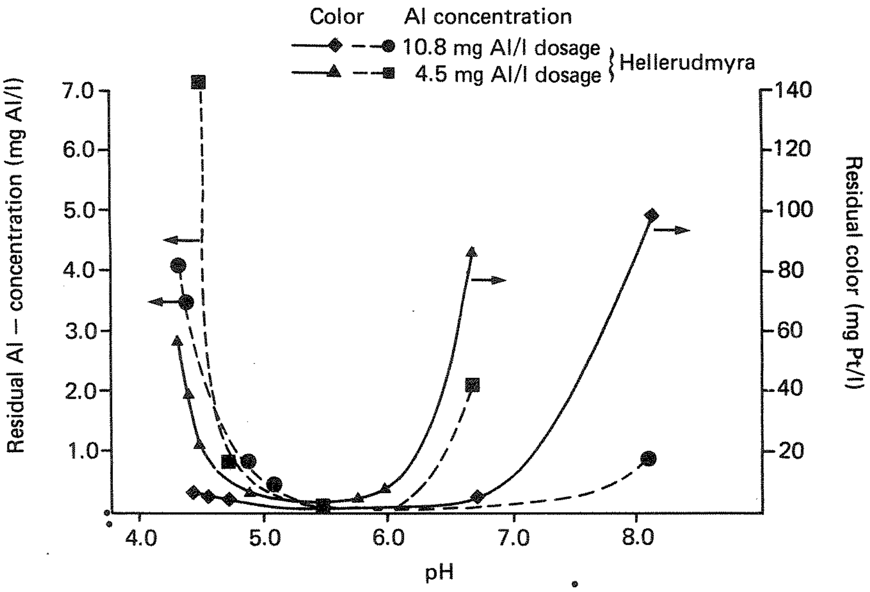


Figure 111. Residual Al and color versus pH for coagulated Hellerudmyra water.

Table 30. Determination of various fractions of the aluminum complexes in raw and treated water.

Water sample Al-fractions, various methods	Tjernsmotjern raw water	Treated water 5 mg Al/l, pH = 6.0
	(µg Al/l)	(µmg Al/l)
Total Al:		
Henriksen & B.-Paulsen (1975)	240	20
Müller (1982)	181	
Naas (1982)	174	<20, the detection limit for the analytical method.
Alumino-organic complexes:		
Müller (1982)	113	
Naas (1982)	108	
Free Al monomeric complexes:		
Müller (1982)	$\sim 5^1$	
Naas (1982)	0	
Colloidal polymeric Al (strong alumino organic complexes):		
Müller (1982)	63	
Naas (1982)	66	

[1] Estimated by Müller (1982).

free Al-monomeric complexes. A modified version of the Müller (1982) method will probably be worked out for routine use, and this will hopefully clarify some of these questions.

5.3.4 Obtainable TOC Removal

Based on Figures 97, 99, and 101, the optimum removal of aquatic humus, obtained by jar-tests from the three main sources studied, is summarized in Table 31.

Table 31 illustrates that almost identical results in respect to TOC removal was obtained in the jar-tests compared with those observed from the electro-chemical reactor study. The maximum TOC removal varied from one water source to the other, probably due to the different chemical characteristics of the aquatic humus in the various water sources.

5.3.5 The Importance of Humus Concentration

Only one series of experiments was performed to study the importance of humus concentration. Water from Hellerudmyra was diluted 1:1, and the pH adjusted to 6.5. The results are presented in Figure 112. There exists, obviously, a relation between humus concentration and necessary Al-concentration to reach maximum removal of organics. The stoichiometric relationship between color or humic acid with Al-dosage has previously been discussed by several authors, and not much time has been spent on this aspect in this project. The results obtained are summarized in Table 32.

Table 31. Maximum total organic carbon and color removal with conventional alum coagulation.

Water sources Data	Tjernsmotjern	Hellerudmyra	Småputten	
*TOC (mg C/l)				
Raw water	14.3	11.6	9.2	6.4
Treated water	3.8	2.2	3.6	3.5
% removal	73	81	61	45
UV-absorption (cm^{-1})				
Raw water	0.64	0.55	0.34	0.26
Treated water	0.068	0.045	0.05	0.05
% removal	89	92	85	81
Color (mg Pt/l)				
Raw water	135	110	93	48
Treated water	5	0	10	4
% removal	96	100	89	92
Chemical dosage, (mg Al/l)				
Al dosage/mg C removed	>7.0	>6.0	>3.9	>2.8
mg Al/mg C	0.67	0.63	0.69	0.97
pH				
Raw water	6.1	4.5	7.3	6.8
Treated water, pH regulated	5.5	5.5	5.5	5.5

* Estimated from Figure 77.

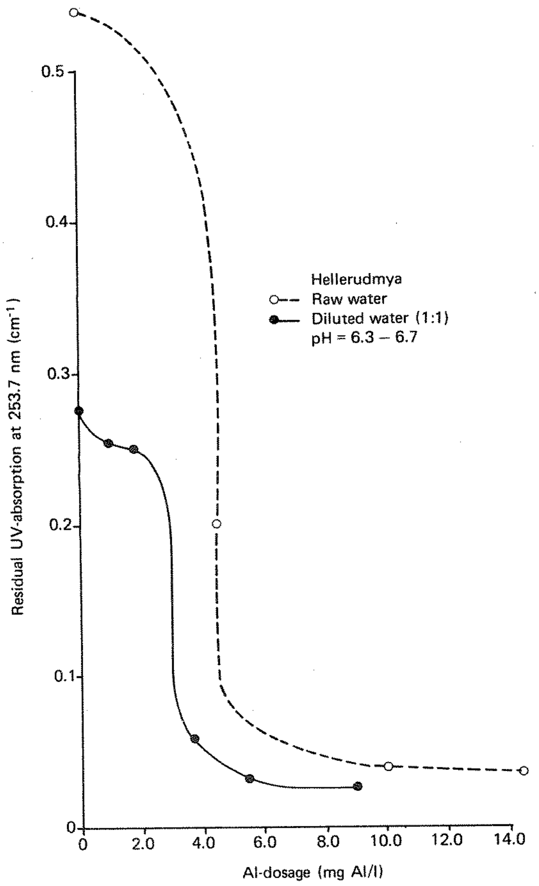


Figure 112. The influence of humus concentration on residual organics as a function of Al-dosage.

Table 32. Results from experiments on coagulation of diluted and undiluted water from Hellerudmyra.

Water type / Results	Hellerudmyra	
	Undiluted	Diluted (1:1)
TOC (mg C/1)		
Raw water	11.6	4.4
Treated water	2.3	1.2
Critical coagulation concentration (CCC) (mg Al/1)	4.5	3.0
Dosage for maximum TOC removal (mg Al/1)	11.0	7.0
Critical coagulant demand[1] (mg Al/mg) C	0.39	0.68

[1] CCC/TOC raw water.

According to Table 32, the necessary Al-dosage to obtain maximum TOC removal does not seem to be a straight stoichiometric ratio with the TOC concentration of naturally occurring organics. This result is based on one single series of experiments using only one dilution, 1:1. The critical coagulant demand for diluted water is approximately doubled compared with undiluted water.

5.3.6 The Importance of pH

The importance of pH has been stressed by many researchers and was discussed in the literature review. Semmens & Field (1980) showed in Figure 23 the relationship between pH measured before flocculation and after filtration.

In this study pH was measured during flocculation and after filtration, and similar results were obtained (Figure 113).

Which one of the pH values is used in the presentation of the results, is of importance. This is shown in Figure 107 presenting log molar Al concentration as a function of pH (water from Tjernsmotjern). The pH measured after filtration has been used in all further discussion of the results.

An additional study was performed to observe the immediate changes of pH during chemical addition. The pH was measured continuously during the rapid mix and slow mix periods when treating water from Tjernsmotjern and Hellerudmyra. Relatively low and high doses of aluminum, 4.5 mg Al/1 and 10.8 mg Al/1, were used. For each of the two dosages, pH was adjusted to 5-5.5 and 6.8-7.9. The results

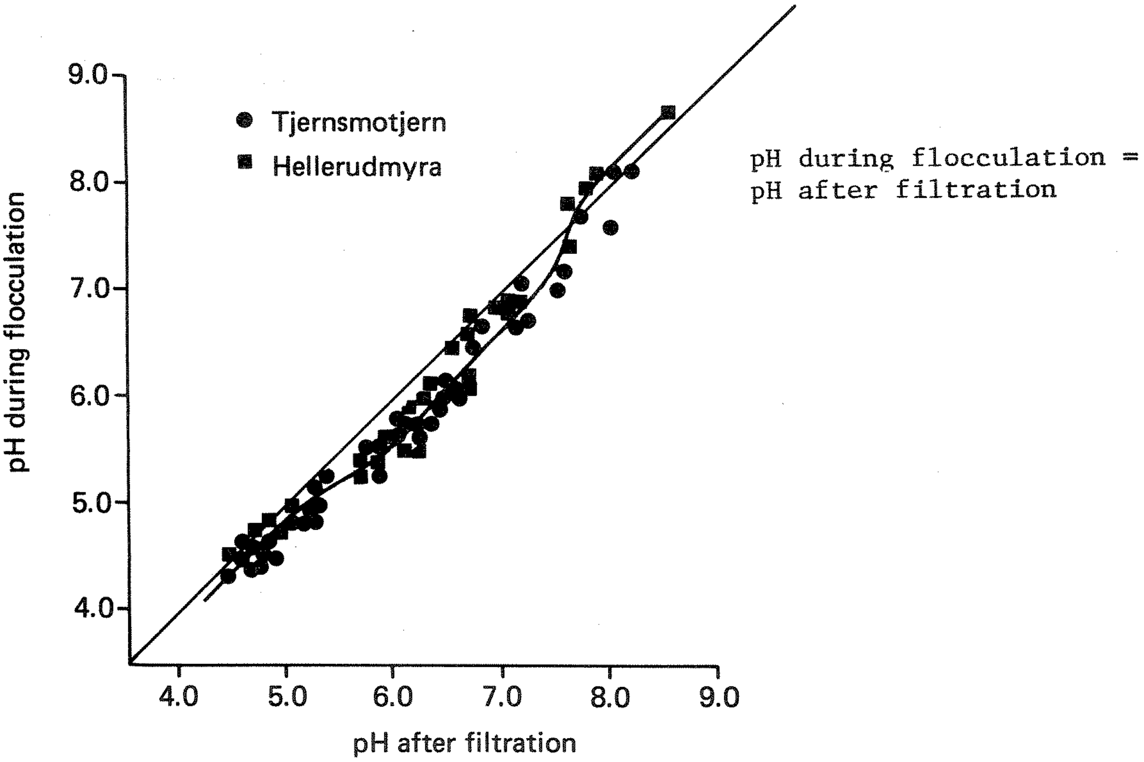


Figure 113. Relationship between pH measured during flocculation and after filtration.

are presented in Figure 114 where the dashed line represents Hellerudmyra with an initial pH of 4.5, and the other curves represent Tjernsmotjern with an initial pH of approximately 6.1. Aluminum was added at time zero and NaOH after approximately 7.5 seconds. When water from Tjernsmotjern was mixed with aluminum, the pH immediately shifted to 4.6-4.7 while the Hellerudmyra water reached

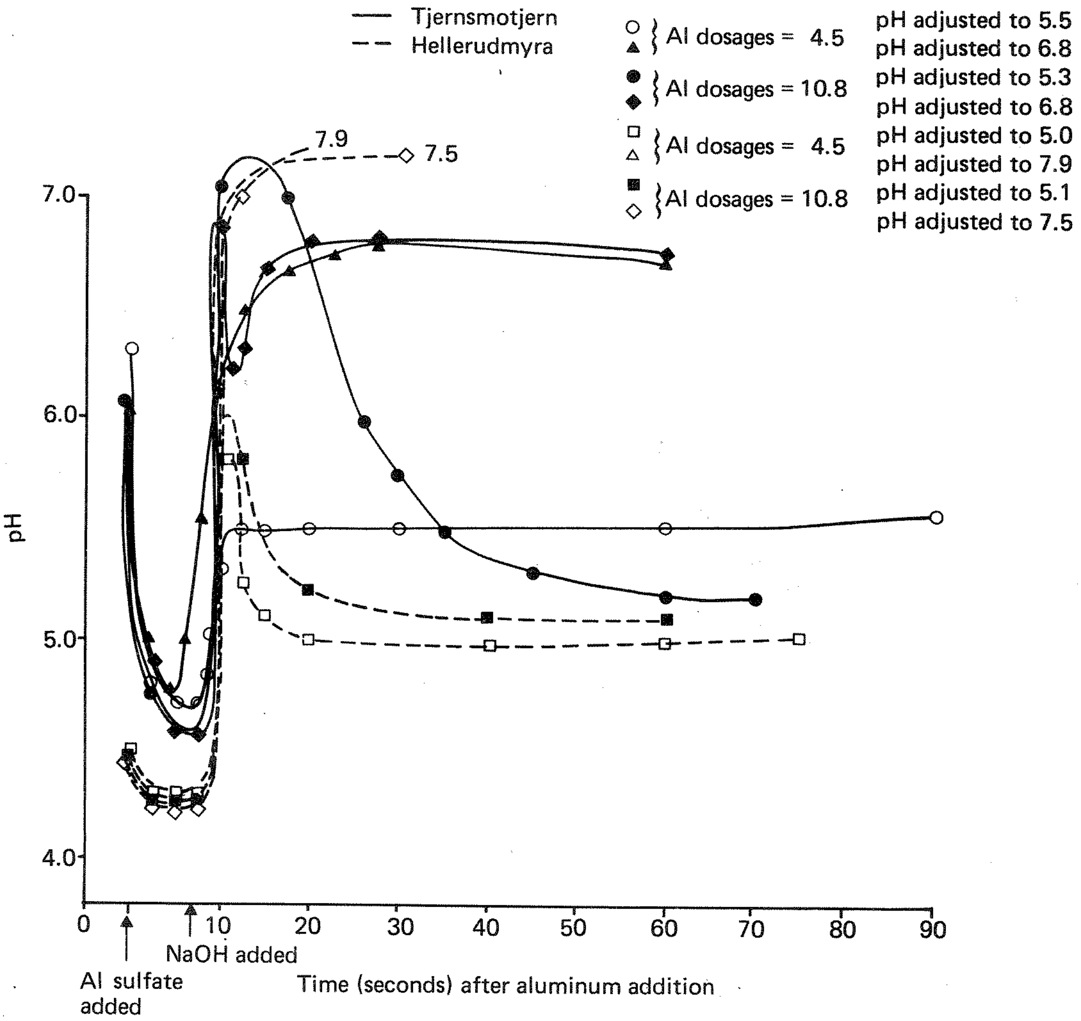


Figure 114. Results from continuous measurements of pH changes during chemical addition.

a pH of 4.2-4.3. For both water samples pH was immediately changed to the desired value when NaOH was added. For these raw waters the pH was reduced to 4.2 and 4.5 for Hellerudmyra and Tjernsmotjern, respectively. At these low pH values no $Al(OH)_{3(s)}$ was formed, but Al^{3+} and various aluminum hydroxides were expected. Addition of NaOH resulted in an immediate pH increase. In cases where the adsorption destabilization mechanisms dominate, rapid mixing will be crucial at the moment of pH adjustment.

5.3.7 The Importance of Rapid-Mix Parameters

Several authors have discussed rapid mixing. The major consideration has been uniform dispersion of the coagulant with the raw water in order to avoid break up of flocs and improper mixing. The Amirtharajah & Mills (1980) study was previously discussed, and the most important conclusion from this study was that when adsorption destabilization conditions dominate, the rapid mixing (determined as a G value) is of major importance. According to Amirtharajah & Mills (1980), the adsorption - destabilization mechanism predominates at low Al-dosages and pH < 6.5. One series of experiments increasing the rapid mixing period from one minute to ten minutes, was run using water from Tjernmotjern using an Al-dosage of 4.5 mg Al/l. UV-absorption and Al-concentration as a function of pH were determined (see Figure 115). Using standard jar test equipment means that the G value is only around $100s^{-1}$, which is low for rapid mixing. In respect to organics removal, determined as UV-absorption, the longest rapid mixing period gave slightly better result. In respect to

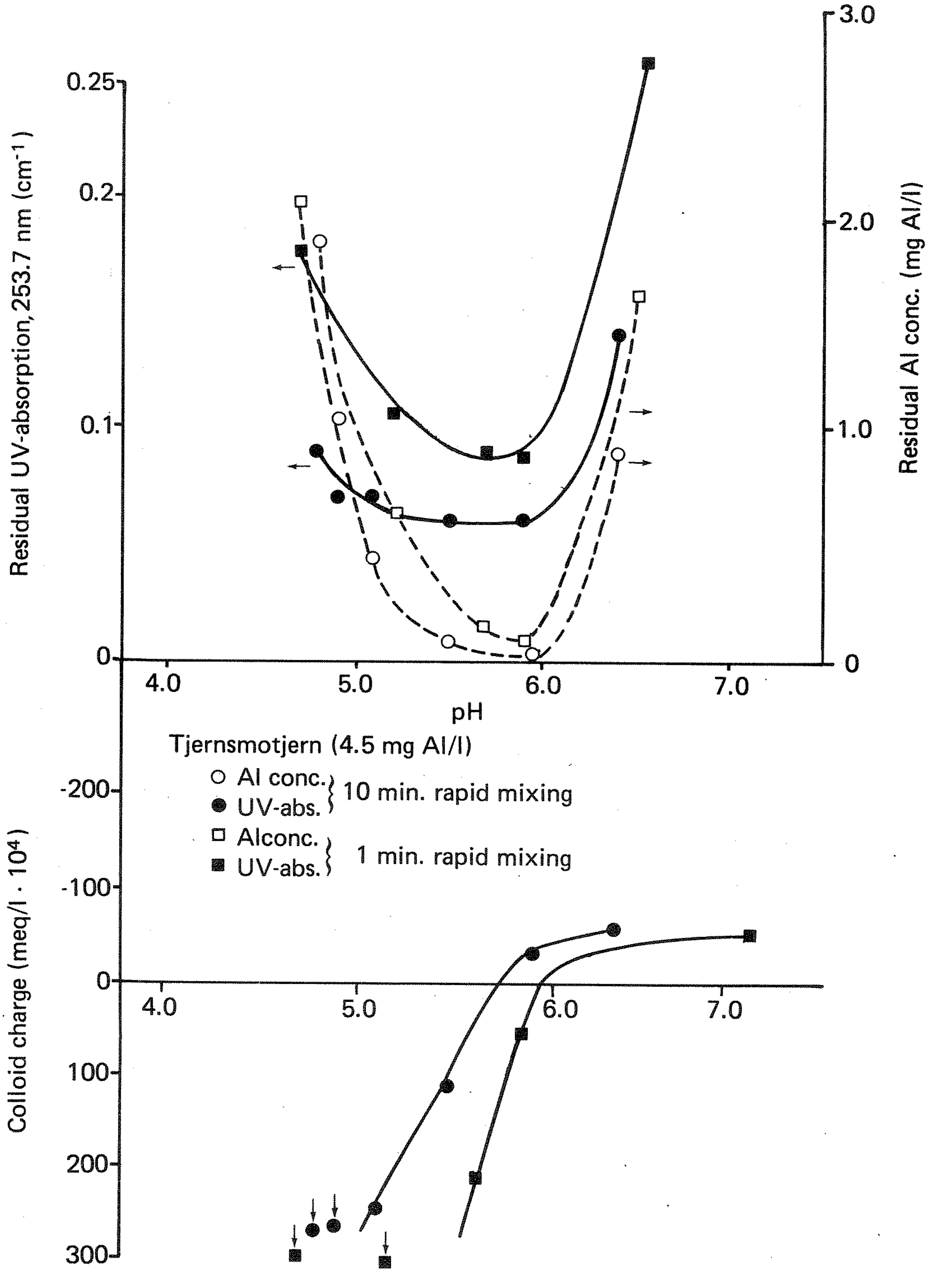


Figure 115. The effect of rapid mixing time on coagulation of water from Tjernsmotjern.

residual Al-concentrations, the optimum pH area was slightly wider. The results in Figure 115 indicate that increased mixing time has no significant effect on the efficiency of organics removal. Increasing the G value to high mixing intensities might, however, give another result.

5.4 Practical Experience with the Electrochemical Process

The pilot scale experiments started up with the intention of doing experiments with a complete treatment plant including the electrochemical unit and a dual media pressure filter. See Figures 116 and 117, which illustrate the interior of the trailer. The trailer was placed by a small lake, Småputten, located only 5 km north from NIVA's laboratory facilities in Oslo. A 50 m long pipe, surrounded by a heating conductor and insulated by styrofoam to ensure that no freezing occurred during winter time, was merged into the lake at 2 m depth. The electro-chemical process was started up treating 600 liter per hour. The head loss developed through the pipes resulted in decreased pumping capacity and, in the last period of experiments, only 250 l/h of water was treated. No pH adjustment of the water was performed and no attempt was made to optimize the treated water quality. The major aspect of the pilot scale experiments was to gain practical experience regarding design for a full scale unit.

5.4.1 Hydraulic Aspects

As previously discussed, the reactor probably giving the best results within reasonable time, would be the series flow reactor. Originally, the reactor was thought to be able to treat 600-700 l/h of water. Based on Figure 41 and equations 6 and 7 (Fair et al., 1968), the G-value of the system was calculated.

For (n-1) equally spaced over- and under-baffles with velocities v_1 and v_2 in the channel and baffle slots, the loss of head approached (equation 7);

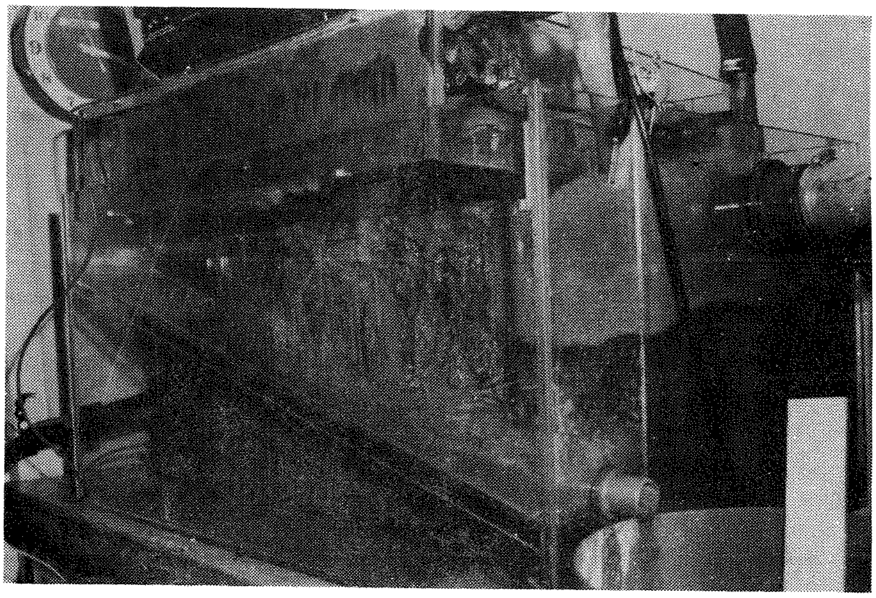


Figure 116. Photo of the electrochemical process at the pilot scale water treatment station.

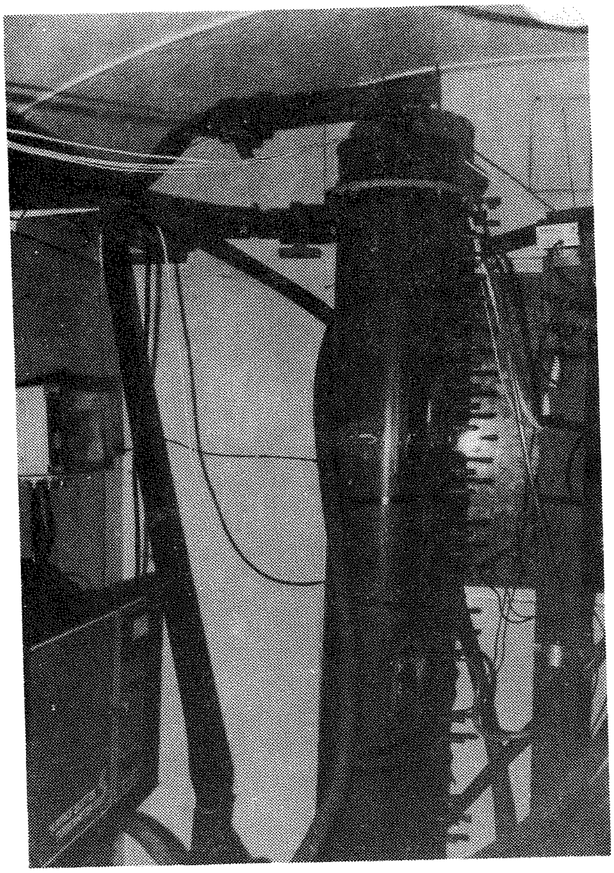


Figure 117. Photo of the dual media pressure filter at the pilot scale water treatment station.

$n\ v_1^2/2g + (n-1)\ v_2^2/2g$ in addition to normal channel friction:

$$\Delta h_f = \frac{1}{40} \cdot \frac{L}{D_h} \cdot \frac{v^2}{2g} \qquad (18)$$

where $D_h = \frac{4 \cdot a \cdot b}{2(a+b)}$, the hydraulic reactor diameter

a = width of the reactor

b = the distance between the Al-electrodes

L = (n-1) · l = length of the water flow path

n = number of Al-electrodes

l = the water depth.

Various water velocities were investigated, and the total loss of head calculated;

$$\Delta h_{tot} = n \cdot v_1^2/2g + (n-1)\, v_2^2/2g + \frac{1}{40} \cdot \frac{n \cdot l}{D_h}\, v_2^2/2g \qquad (19)$$

The G value for each water velocity was calculated according to equation 6;

$$G_{tot} = \left(\frac{Q \cdot \rho_1 \cdot g \cdot \Delta h_{tot}}{V \cdot \mu}\right)^{\frac{1}{2}}$$

The detailed calculations are performed in Appendix 4 and are summarized in Table 33.

The G values found when using this method are very low compared with proposed values for rapid mixing units. Amirtharajah (1978) suggested a velocity gradient equal to 900 for a contact time of 30 seconds. The experiments clearly showed that reduction in the hydraulic loading, i.e. decreasing the velocity of the water passing the electrodes, rapidly caused sludge accumulation between the electrodes. As the sludge accumulated, the current decreased, i.e. the resistance increased.

Another interesting visual observation was that some of the hydrogen gas shortcircuited between the walls and the electrodes, instead of passing through the reactor with the water flow. In

Table 33. Various hydraulic conditions of the electrochemical pilot scale study.

System studied	Observations	G-velocity gradient (sec^{-1})	$\overline{Gt}$	Water velocity cm/sec	Hydraulic capacity l/h
Electrochemical pilot scale unit 42 Al-electrodes, 10 mm distance	Very serious sludge accumulation. Current efficiency decrease	2.2	1202	1.0	144
Electrochemical pilot scale unit 42 Al-electrodes, 10 mm distance	Sludge accumulated between the Al-electrodes	5	2740	2.3	330
Electrochemical pilot scale unit 42 Al-electrodes, 10 mm distance	Worked well. An initial decrease in current, but then constant	10.8	5890	4.9	706

order to get an idea of how the water passed through the system, detention time experiments were performed using Rhodamine and table salt. The results are presented in Figure 118. The reactor volume was 94 l. It was easily seen that the table salt solution was not equally distributed through, due to the high viscosity of the salt solution. In the Rhodamine experiment the detention time agreed well with the theoretically calculated value. Shortcircuiting of the water was therefore thought to be minimal.

Based on these observations, the water velocity was found to be a very important parameter. To reduce sludge accumulation and ensure a rapid distribution of the dissolved aluminum into the bulk solution, the water velocity must at least be higher than 5 cm/sec (Table 33). This aspect is a very important design criteria. The distance between the Al-electrodes can be reduced and the height increased in order to ensure a high water velocity still keeping the same anode surface.

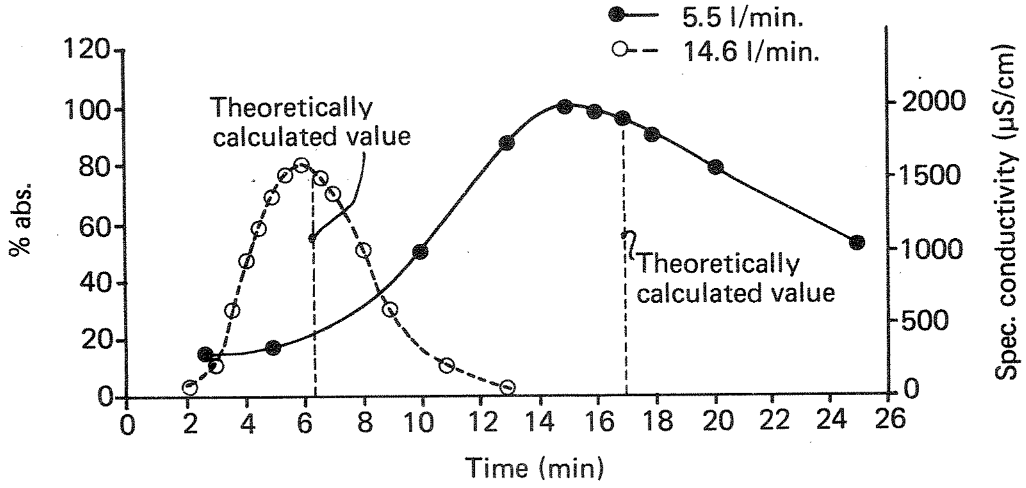


Figure 118. Detention time experiments with the electrochemical reactor.

5.4.2 Current Technical Aspects

The electrochemical unit is composed of a number of individual reactor units in parallel, where each unit operates at the same voltage, the total current being the sum of the individual units

$$I = U \cdot \sum_{i=1}^{n-1} \frac{1}{R_i} \tag{20}$$

where I = the current (A)

U = the voltage (V)

R = the resistance (Ω)

n = the number of electrodes.

The system could also have been arranged as a number of individual reactor units in series, where each unit operates at the same current, the total voltage being the sum of the individual units. Such a unit would, however, need to work at a higher voltage than is preferred when designing a simple water treatment unit. A D.C. power supply of 24 V exists as a commercial inexpensive unit and is not dangerous in use. As previously discussed, Russian literature suggests a current density range of 1-2 mA/cm^2 to be most economical. During the experiments, a 24 V D.C. power supply was used. The applied voltage varied between 6.5 and 12 V, and the current varied between 4 and 12 A. The active anode area in the electrochemical reactor was $41 \cdot 30 \cdot 40\ cm^2 = 49{,}200\ cm^2$, giving a current density range of 0.08 to 0.24 mA/cm^2. Due to the design of this pilot unit, it was not possible to work within the desired current density range of 1-2 mA/cm^2. In the design of a new unit or in further research, the number of Al-electrodes can be reduced, or the size of each can be reduced. If 12 A is used, a current density of 1 mA/cm^2 and each electrode having an area of 30 by 40 cm, the number of electrodes needed are;

$$n = \frac{\frac{12000\ mA}{30 \cdot 40\ cm^2}}{1\ mA/cm^2} + 1 = \underline{11}.$$

As previously mentioned, the current efficiency decreased with time when the sludge accumulated between the Al-electrodes. The results are presented in Table 34.

It is clearly shown in Table 34 that the water velocity is important. The resistance is kept fairly constant as long as the water velocity is higher than 3.0 cm/sec., although an initial increase from 0.57 to 0.61 to 0.73 is observed, which could be due to an initial build up of $AlO_{3(s)}$ or $Al(OH)_{3(s)}$ on the electrodes. This might have been avoided if the water velocity were higher than 5 cm/sec, which was previously observed. In these experiments the amount of aluminum dissolved was

For 4 A → $W_c = 4 \cdot t \cdot 0.093 = 0.372 \cdot t$ (mg)

at 4 A the water velocity was 1 cm/sec,

giving 2.4 l/min.,

giving an Al-dosage of $\frac{0.372 \cdot 60}{2.4} = \underline{9.3\ mg\ Al/l}$.

For 14 A and 8.6 l/min,

→ $W_c = 1.302 \cdot$

→ Al-dosage of $\frac{1.302 \cdot 60}{8.6} = \underline{9.0\ mg\ Al/l}$.

Table 34. Current efficiency results from electrochemical pilot scale study.

Time after starting the experiments (hours)	Visual observations	Water velocity (cm/sec)	Spec-cond. (µS/cm)	Applied voltage, U (V)	Current, I (A)	Calculated resistance U/I (Ω)	* $\frac{d}{A \cdot \kappa}$ (Ω)
0		3.6	87	8.0	14	0.57	0.23
22.5		3.6	87	11.0	18	0.61	0.23
47	Some sludge accumulation observed	2.4	87	9.5	13	0.73	0.23
70		3.3	87	9.5	13	0.73	0.23
119		3.3	84	9.5	13	0.73	0.24
137	Some sludge still between the electrodes	3.3	87	9.5	13	0.73	0.23
161		3.4	86	6.5	8	0.81	0.23
185		3.6	85	6.5	7.5	0.87	0.24
	The electrolyzer was taken out of use for approximately 200 hours, due to an exhibition, before starting it up again.						
0		3.0		11.5	12	0.96	
75	Sludge accumulated	Gradually decreasing ↓		8	16	0.50	
124.5	More sludge			11	11	1.0	
170.5	" "			11	10	1.1	
221	" "			11	8.5	1.3	
	Turned the current direction.						
0	Large amounts of sludge	2.1		11	12	0.92	
	Some of the sludge between the electrodes was removed.						
0		2.7		9	12	0.75	
48	Sludge	2.8		12	10	1.2	
135	Full of sludge	1.0		12	4	3.0	

* A = active anode area = 49,200 cm^2, κ= spec. cond. (µS/cm) 10^{-6},

d = distance between the electrodes = 1 cm.

5.4.3 Water Quality Aspects

No optimization of Al-dosage versus treated water quality was done in these pilot scale experiments. The results are presented in Table 35. Maximum possible removal of color (i.e. TOC) was obtained in all cases. The Al-dosage was high in all cases. The turbidity of treated water was high in all cases.

In addition to the usual parameters for determination of humus removal, a series of other parameters was analyzed to see if any other raw water characteristics were affected by the electro-chemical process. See Table 36.

The only parameters affected were;

- the organic carbon determined as color and UV-absorption,
- the pH, and
- the Al-concentration.

The residual Al-concentration exceeded the allowable drinking water regulations for Norway (SIFF, 1976).

5.4.4 Sludge Production

The sludge production was measured by the sludge volume, the total suspended solids and the volatile suspended solids. Due to the small volume of sludge collected, the sludge was collected only every second or third day. The characteristics of sludge collected are presented in Table 37. The volume of water treated is presented in the same table. The amount of aluminum added was calculated. The theoretically calculated amount of $Al(OH)_{3(s)}$ produced was based on

Table 35. Results from pilot scale experiments with the electrochemical process.

Water source: Sm̊putten.

Day	Coagulation condition			Water Quality						
	Al-dosage (mg Al/1)	pH raw water	Spec. cond. (μS/cm)	Color mg(Pt/1) raw water	Color mg(Pt/1) treated water	UV-abs. (cm^{-1}) raw water	UV-abs. (cm^{-1}) treated water	pH treated water	Turbidity (NTU) raw water	Turbidity (NTU) treated water
March 18	12.6	6.4	87	73	3	0.31	0.031	6.8	1.0	15
" 19	9.2	6.6	84		3		0.041	7.1		9.7
" 21	9.2	6.6	84	75	3	0.32	0.027	7.0	1.0	18
" 22	9.2	6.6	87	78	5	0.32	0.032	6.9	1.6	22
" 23	5.5	6.6	86	75	6	0.32	0.044	6.9	1.2	18
" 24	4.8	6.6	85	73	6	0.31	0.041	7.0	2.5	22
Apr. 5	13.3	6.6	103		3			~7.0		High
" 7	9.8	6.6	86		0			~7.0		"
" 9	9.3	6.6	87		0			~7.0		"
" 11	8.6	6.6	86		1			~7.0		"
" 13	10.3	6.6	92		1			~7.0		"
" 19	9.3	6.6	86		5			~7.0		"

Table 36. Results from electrochemical study (pilot scale).

Water source: Småputten.

Parameters		Residual concentrations	
		Raw water	Treated water
Al-dosage	(mg Al/l)	0	8.1
Color	(mg Pt/l)	73	6
UV-abs.	(cm^{-1})	0.31	0.041
Spec. cond.	(µS/cm)	87	85
pH		6.6	7.0
PO_4	(µg/l)	0.5	0.5
NO_3	(µg/l)	<10	<10
SO_4	(mg/l)	10	10
Cl	(mg/l)	6	6
Ca	(mg/l)	11	10.7
Mg	(mg/l)	2.1	2.0
Al	(µg/l)	55	800
Fe	(µg/l)	590	610
Na	(mg/l)	3.9	4.0
K	(mg/l)	0.80	0.80
Mn	(µg/l)	610	620
Cu	(µg/l)	4.5	3.2
Pb	(µg/l)	1.8	1.7

Table 37. Sludge characteristics of collected sludge from electrochemical treatment

Volume of water treated (m^3)	Sludge characteristics			
	Volume collected (l)	Total susp. solids (mg/l)	Volatile susp. solids (mg/l)	Amount collected (g)
20.3	7	21272	14145	149
34.2	16	18545	11974	298
8.6	15	17115	11526	257
24.2	2.5	10819	6636	27
18.0	15	13400	9170	201
17.2	12	4490	3280	54
17.6	16	16600	11800	266

the solubility reaction;

$$Al^{3+} + 3\ OH^- \rightleftarrows Al(OH)_{3(s)}$$

which says that one mole Al^{3+} produces one mole of $Al(OH)_{3(s)}$, and thus

$$1\ g\ Al^{3+} \text{ gives } \frac{1}{27} \cdot 78\ g = 2.89\ g\ Al(OH)_{3(s)},$$

where 27 is the molecular weight of Al and 78 the molecular weight of $Al(OH)_{3(s)}$. The residual Al-concentrations were high. In the detailed study of the process, the residual Al-concentration was equal to 0.8 mg/l, for an Al-dosage of 4.8 mg/l. For Al-dosages higher than 5 mg Al/l, the residual Al-concentration was assumed to be approximately 1 mg Al/l. The Al^{3+} concentration producing sludge was calculated as the difference between Al dosed and the estimated residual Al-concentration. The total amount produced $Al(OH)_3$ was found to be much higher than the amount of sludge collected. For example, the day when 149 g sludge was collected, based on the mass of aluminum dosed, 580 g $Al(OH)_3$ should have been produced. In addition 114 g carbon was removed and mass of all the other elements (H, O, N, metals) bound to the humus also were removed. The amount of sludge collected by the skimmer was very low compared with the total amount produced. The flotation process and the sludge collection system were not optimized in order to prevent sludge from leaving the system. In the last part of the experimental period, large amounts of sludge were leaving the electrochemical unit and a few treated water samples were analyzed for total suspended solids (TSS) concentrations. Values of around 200 mg TSS/l were found. It was not possible to make meaningful mass balances for this unit because of periodical sludge accumulation in the system.

5.4.5 Other Practical Aspects of Importance for Design

With regard to design of a full scale unit, several important factors have already been mentioned, such as the hydraulic aspects and the electrical current aspects. The importance of improving the skimming process was stressed both in regard to the water quality and the sludge production. Another aspect not previously mentioned, is design of the Al-electrodes. The amount of Al in the electrodes should at least last for one year of water treatment when using 10 mg Al/l. A chemical dosage of 10 mg Al/l should cover most different types of water. The thickness of the electrodes can be increased from two to five mm.

6. SUMMARY AND CONCLUSIONS

The purpose of this research has been to seek an understanding of the basic principles involved in coagulation of naturally occurring organics (aquatic humus), using aluminum as coagulant. The maximum possible removal of organic carbon was evaluated. The objective was also to study the electrochemical process for aluminum addition and to derive design criteria for this process.

The total organic carbon content of several water sources showed good correlation with UV absorption and color. Using all data for untreated and treated water from various sources, the following relationships were obtained:

$$\text{Color} = 223 \text{ UV absorption} - 7.4 \quad (r^2 = 0.92)$$

$$\text{TOC} = 19.1 \text{ UV absorption} + 2.3 \quad (r^2 = 0.93).$$

Both color and UV absorption measured at 253.7 nm can be used to estimate TOC. TOC is, today, probably the best available parameter for determination of the humus concentration. Raw waters from Tjernsmotjern, Hellerudmyra, and Småputten were studied. These raw waters varied in composition, both in respect to concentration of total organic carbon and in respect to the molecular size distribution of the organics. Hellerudmyra contained the highest fraction of high-molecular weight organics while Småputten contained the highest fraction of lower-molecular weight organics. Also pH for the three sources varied a great deal. Water from Hellerudmyra had a pH of approximately 4.4, while Tjernsmotjern had a pH of approximately 6.0, and Småputten had a pH of around 6.8.

A laboratory unit was used to study the electrochemical process in detail. The amount of aluminum dissolved from the anodes was both weighed and determined theoretically according to Faraday's law, and the following relationship was found:

$$\begin{array}{l}\text{Theoretically calculated amount}\\ \text{Al dissolved (mg)}\end{array} = 0.99 \begin{array}{l}\text{weighed amount}\\ \text{Al dissolved}\\ \text{from anodes}\end{array} - 2.05$$

$(r^2 = 0.94)$.

Although the raw water temperature varied between 5 and 10°C, no influence was exhibited on the coagulation efficiency. Using raw water with a pH of 6-6.5, the pH near the anode was 5.5-6.0 and near the cathode 8.0-8.5. Aluminum was found to dissolve from the cathode because of the high pH. Three types of electrodes with different Al-composition were studied with no difference in the results. The Al dissolved from the cathode did not participate in the coagulation process and was looked upon as a loss of aluminum. The applied potential over the electrochemical cell was studied, showing a linear relationship with the calculated IR-drop. When the IR-drop was reduced towards zero, the applied potential was reduced to a limiting value of approximately 1.3 V. The current density used varied between 0.1 and 0.6 with a few values up to 1 mA/cm^2. The applied voltage varied from 1 to 8 V. Only a few times did the applied voltage exceed 11 V.

The hydrogen gas formatinon at the cathode resulted in increased pH of the solution. A series of experiments were performed to evaluate the effect of adjusting the pH of the raw water. For raw water with an initial pH of 6 to 6.5, the treated water pH increased to 7.7. When the raw water pH varied between 3.9 and approximately 6.0, the same water quality, measured as total organic carbon, was obtained for the same Al-dosage. For higher pH values $\geq$ 6.8, it was shown that higher Al-dosages were needed to obtain the same results. The maximum total organic carbon removal (TOC) varied from 57 to 82 percent from one water source to the other. Also UV absorption and color removal varied. The UV absorption varied between 70 and 94 percent, while the color removal varied between 92 and 100 percent. The highest TOC removal was obtained for the raw water source containing the highest fraction of high-molecular weight organics, 82 percent for Hellerudmyra, while coagulation of the water from Småputten, containing the highest fraction of lower-molecular weight organics only resulted in 63 percent TOC removal.

A comparison of treated water quality from the electro-chemical process and the conventional coagulation process was done. Several parameters were analyzed. The major differences were, 1) higher pH of treated water from the electrochemical process, 2) higher specific conductivity of the conventionally treated water due to high sulfate concentrations, and 3) high residual Al-concentrations from the electrochemical treatment due to the high pH of treated water.

The conventional treatment process was studied in several series of experiments varying pH and aluminum dosage. The sequence of chemical addition was studied, and no major difference was seen between the case where alum was added first immediately followed by

NaOH addition, or when NaOH was added first immediately followed by alum, as long as the pH adjustment did not result in alkaline pH values. The optimum pH range was shown to get wider with increasing alum dosage, and in all cases a pH of 5.5 was the optimum for efficient coagulation. When coagulating water containing aquatic humus, no restabilization was observed, and the mechanisms involved in the coagulation seemed mainly to be sweep coagulation. The efficiency of the coagulation process was dominated by the efficiency of the $Al(OH)_{3(s)}$ precipitation. The residual Al-concentrations followed the equations for the solubility of $Al(OH)_{3(s)}$ in respect to Al^{3+} and $Al(OH)_4^-$. No other hydrolysis species were included. For high humus concentrations and low caogulant doses the residual Al-concentrations at pH values higher than 6.0 were higher than expected probably because of complexation between aluminum and humus. The optimum pH range, with respect to the residual Al-concentration, increased with increasing alum dosages, except for the highest dosage studied, 50 mg Al/l. The optimum coagulation pH, with respect to aluminum concentrations, were slightly different from the one for color. The humus concentration was shown to be important with respect to the amount of coagulant needed. The critical coagulant demand defined as critical coagulant concentration divided by TOC concentration of raw water (mg Al/l/mg C/l) for 1:1 diluted water was approximately doubled compared with undiluted water. When colloidal particles are enmeshed in a precipitate, an increase in the concentration of colloidal material results in reduced coagulant demand. The importance of pH was stressed in the results, and the difference in pH values observed on the samples measured during flocculation and the ones measured after filtration, complicated the discussion of exact pH values. The importance of rapid mix parameters such as the G value and rapid mixing time, was discussed, and in one series of experiments using low alum dosage, the rapid mix time was increased and the results were slightly improved. The maximum possible TOC removal using the conventional coagulation process was the same as for the electro-chemical process, as was UV absorption and color removal. The only difference registered was the lower chemical demand for Tjernsmotjern and Småputten, the water sources with highest pH. For Tjernsmotjern, with an initial pH in some cases equal to 6.5, the Al0dosage needed was 0.85 and 0.67 mg Al/mg C removed for electrochemical and conventional treatment, respectively for Småputten, with an initial pH of 6.8, 1.13 and 0.69 mg Al/mg C removed, respectively.

The pilot scale experiments with the electrochemical process stressed the importance of keeping a minimum water velocity between the electrodes in order to prevent sludge accumulation. The required minimum water velocity was 5 cm/sec. The electrical connections on the electrodes must be replaced out of the water to avoid corrosion. Current densities in the range of 1-2 mA/cm^2 can be applied, and the electrode surface area can be reduced compared to our experiments. The residual Al-concentrations obtained were too high for raw waters with high pH and when using high aluminum dosages. The importance of optimizing the flotation process and the sludge collection system was stressed both in respect to sludge accumulation between the electrodes and in respect to the turbidity of treated water. The ease of operation of this process was also stressed. All the experience in respect to design of a prototype of the electrochemical process is summarized under design recommendations (chapter 7).

7. DESIGN RECOMMENDATIONS

The design recommendations for the electrochemical unit are based on limited experience, but ongoing research will probably clarify many of the questions.

o Detention time can, according to the literature and this research, be short, and will not be the limiting factor for design. A high degree of organics removal can be achieved even at detention times less than one minute.

o The necessary flotation surface after passing through the Al-electrodes was shown to be of major importance. An open surface without Al-electrodes in the last part of the electrochemical unit, with a surface loading of 6 m/h, is suggested to ensure proper flotation (see Figure 119).

o The water velocity between the electrodes was found to be of major importance in regard to mixing, and a minimum value of 5 cm/sec was suggested, while 10 cm/sec would give a higher degree of security.

o The electrode distance is of importance both in regard to the water velocity between the electrodes and the solution resistance. A distance of 5 mm is suggested.

o The electrode life is important in regard to practical applications. The electrodes should at least last for one year of water treatment. An aluminum addition of 10 mg Al/l should cover most different types of water, and can be used to determine necessary electrode thickness.

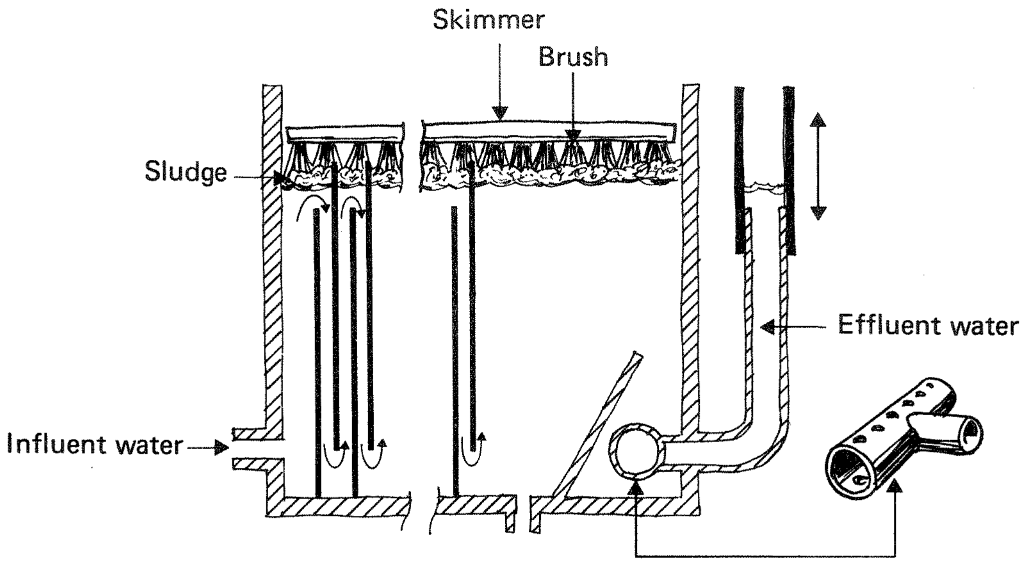


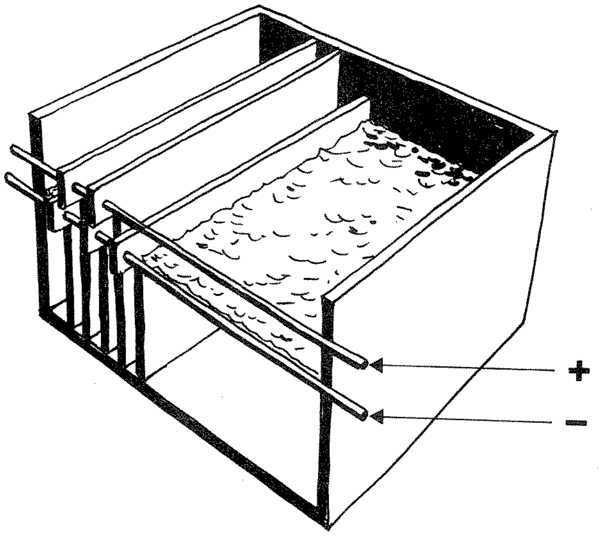
Figure 119. Design recommendation for the electrochemical unit.

o The <u>electrode thickness</u> should be sufficient to ensure one year of electrode life. An electrode thickness of 5 mm can easily be used.

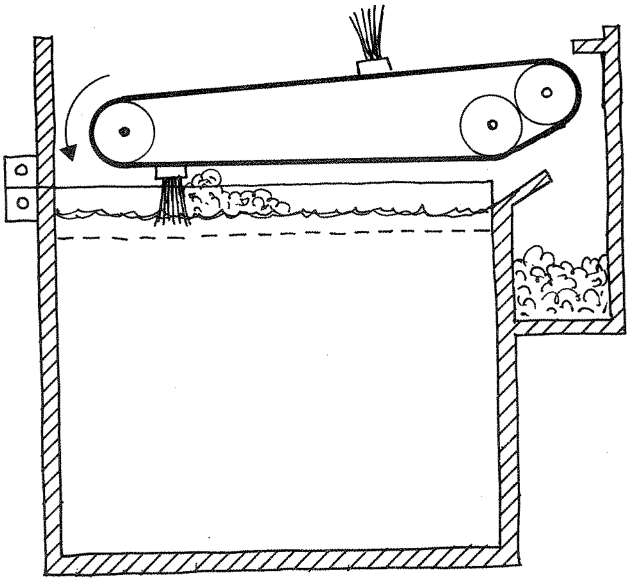
o <u>Corrosion control</u> is important. The current connections need to be located outside the electrochemical unit to avoid corrosion (see Figure 120A).

oThe <u>Al-composition</u> of the electrodes is suggested to be commercial Al-quality with 99.5% Al content. Long time experience might, however, indicate that certain Al-compositions are better in order to avoid cavitation.

o The <u>skimmer design</u> is important. As much as possible of the water surface must be reached by the skimmer (see Figures 119 and 120B). Locating the current connections outside the treatment unit



(A) Details of the current connection system



(B) Details of the skimmer arrangement

Figure 120. Design recommendation for the electrochemical process.

is a major improvement in regard to skimming (see Figure 120A).

o The current density can easily vary between 0.5 and 2.0 mA/cm^2.

o The power supply should avoid using a high potential system. A 24 VDC power supply which is inexpensive and not dangerous is suggested.

o A filtration unit needs to be located downstream from the electro-chemical process. At the present state of the art, the electrochemically treated water have high suspended solids concentrations and a filtration unit will be of importance.

o pH adjustment will be needed for raw waters with pH higher than 6.0 for optimum TOC removal. pH adjustment will also be necessary to ensure low residual Al-concentrations.

8. FURTHER WORK

There is a need for further work in several of the areas touched in this dissertation.

Analytical Methods:

o The accuracy of the colloidal charge method used on colored waters needs to be tested. A comparison of Zeta potential and colloidal charge for colored water, treated with various Al-dosages, at various pH values would be worth evaluating.

Basic Principles of Al-Coagulation of Humus:

o Further studies using diluted humus water would clarify the coagulant dose demand dependence upon humus concentration.

o A study of how the rapid mixing intensities (determined as the G-value) influence the removal of organics and the residual Al-concentrations at various Al dosages and pH would clarify whether adsorption destabilization is involved in coagulation of humus or if enmeshment in the precipitate is the sole mechanism occurring.

Electrochemical Process:

o The optimum pH area needs to be found in regard to organics removal, turbidity removal and residual Al-concentrations. It is important to determine whether the raw water can be pH adjusted to a pH value between 4 and 5 to ensure optimum conditions.

o The possibility of using an electroplating cathode as the last cathode in the electro-chemical cell to avoid high residual Al-concentrations and to produce $H_{2(g)}$ for optimizing the flotation should be tried.

o The importance of the Al-composition of the electrodes both in regard to avoiding Al-loss from the cathodes and in respect to cavitational corrosion of the anodes should be studied on a long term basis.

o The possibility of using Fe-electrodes should be evaluated.

o The influence of intermittent operation of the electrochemical unit with respect to initial potential, organics and turbidity removal efficiency and lifetime of the Al-electrodes is important operational aspect.

o The effect of higher water velocities (>5 cm/sec) on the mass transfer of aluminum and on the hydraulic conditions in the reactor need to be studied.

o The effect of high current densities (high aluminum doses) on mass transfer of aluminum and sludge flotation at various water velocities needs to be studied.

o The optimum skimming process both in regard to design and frequency needs to be further evaluated.

o Different raw waters should be studied. An interesting raw water would be an oil-water mixture which the flotation process would be of major advantage. Inert electrode materials might be an advantage in some cases.

o An economic evaluation of the electrochemical process needs to be done. This evaluation should be based on the complete process involving coagulation, flocculation and separation. Whether the separation also should include filtration depends on the efficiency of the flotation process.

The electrochemical process should be studied as one part of a complete water treatment plant treating various types of raw waters. A regulation system ensuring the best possible treated water quality needs to be developed, and the sludge collection system must be developed. In a development project in close cooperation with Aqua Care (Bergen), the intention is to develop a small package plant based on the electrochemical process, granular media filtration and UV-disinfection. A small package plant comparable to Figure 121 will be developed during 1982 to obtain operational experience with this system.

Other interesting process combinations of the electrochemical unit needs to be studied, such as combining the electrocoagulation and electroflotation with disinfection. Addition of, for example, $CaCl_2$ might have several advantages, such as increasing the specific conductivity of the raw water and causing disinfection because of $Cl_{2(g)}$ formation. This system should be studied.

Another interesting process combination would involve oxidation of organics. Addition of H_2O_2 to an electrochemical cell (lead-lead dioxide), similar to the study of Hemphill & Rogers (1973) would be very interesting both in respect to oxidation of organics from surface water, and organics in municipal and industrial sewage.

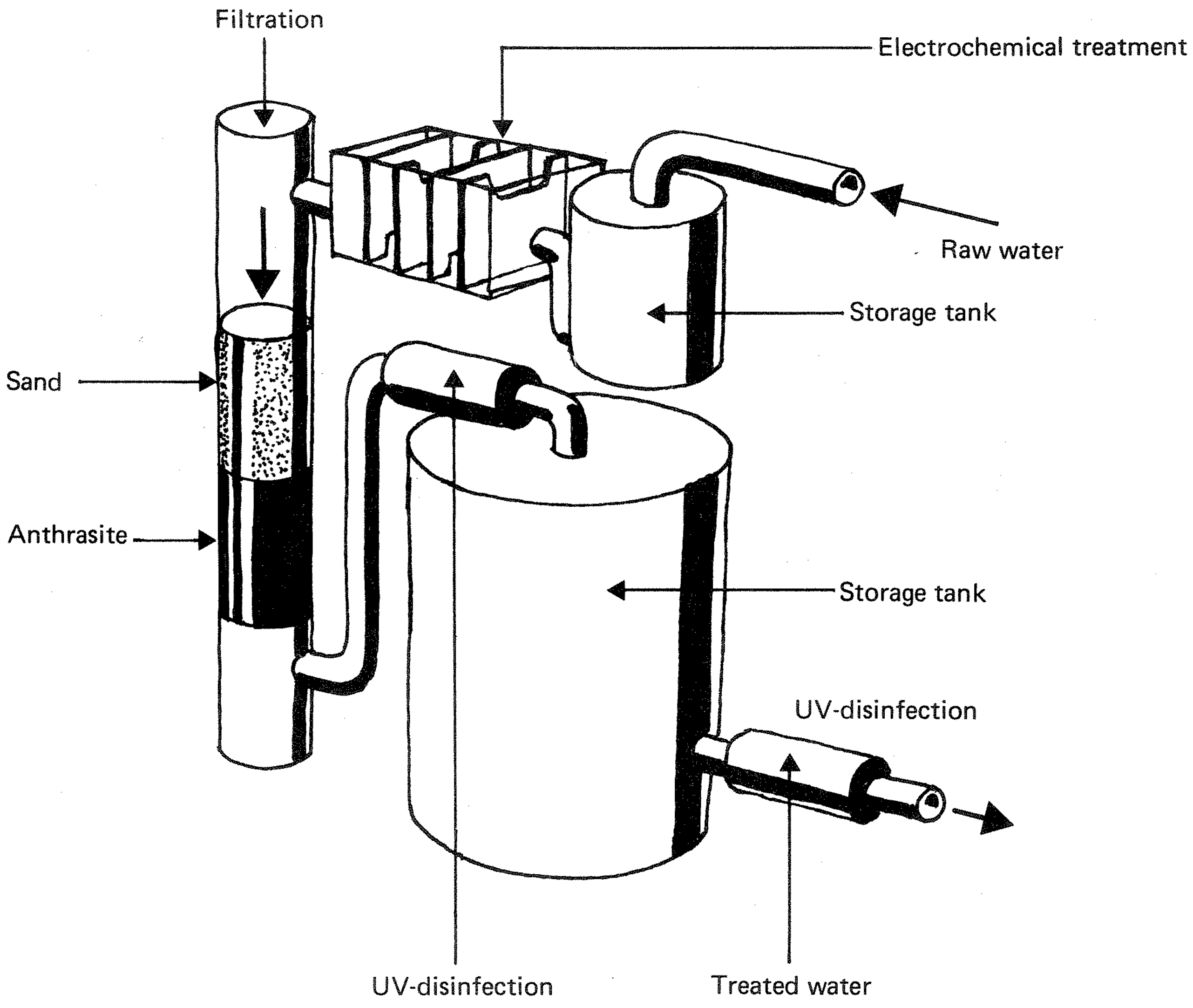


Figure 121. Principle sketch of a future package plant for water treatment, - a development project by Aqua Care (Bergen).

8. LITERATURE REFERENCES

Adin, A., Baumann, E.R. and Cleasby, J.L., (1979); The Application of Filtration Theory to Pilot Plant Design. Journal of American Water Works Association, 71:1:17.

Adin, A. and Rebhun, M., (1974); High-Rate Contact Flocculation - Filtration with Cationic Polyelectrolytes. Journal of American Water Works Association. 66:2:109.

Alberts, J.J., Schindler, J.E. and Miller, R.W., (1974); Elemental Mercury Evolution Mediated by Humic Acid. Science. 184:895.

Alexander, H.J. and Christman, R.F., (1976); Review of the Chemical Composition of Naturally Occurring Organics. Not published.

Amirtharajah, A., (1978); Design of Flocculation Systems. Chapter 11, Water Treatment Plant Design for the Practicing Engineer (R.L. Sanks, editor), Ann Arbor Sci., Publishers Inc. Ann Arbor, Michigan.

Amirtharajah, A., (1978); Design of Rapid Mix Units. Chapter 8, Water Treatment Plant Design for the Practicing Engineer, (R.L. Sanks, editor), Ann Arbor Sci., Publishers, Inc., Ann Arbor, Michigan.

Amirtharajah, A. and Mills, K.M. (1980); Rapid Mix Design for Mechanisms of Alum Coagulation. Journal of American Water Works Association, 1980 Annual Conference Proc. p. 201.

Anderson, C.T. and Maier, W.J., (1979); Trace Organic Removal by Anion Exchange Resins. Journal of American Water Works Association, 71:5:278.

ASCE, AWWA and CSSE, (1969); Water Treatment Plant Design. (New York: American Water Works Association, Inc.).

Babcock, D.S. and Singer, P.C., (1979); Chlorination and Coagulation of Humic and Fulvic Acids. Journal of American Water Works Association, 71:3:148.

Ballard, T.M., (1971); Role of Humic Carrier Substances in DDT Movement Through Forest Soil. Soil Science Society American Proceedings 35:1:145.

Beck, E.C., Giannini, A.P. and Ramirez, E.R., (1974); Electrocoagulation Clarifies Food Wastewater. Food Technology, (Feb.).

Bellar, T.A., Lichtenberg, J.J. and Kroner, R.C., (1979); The Occurrence of Organohalides in Chlorinated Drinking Water. Journal of American Water Works Association, 71:11:703.

Berglind, L., Gjessing, E. and Skipperud Johansen, E., (1979); Removal of Organic Matter from Water by UV and Hydrogen Peroxide. Presented at Conference for Oxidation Techniques in Drinking Water Treatment, Karlsruhe, F.R.G., EPA 570/9-79-020, p. 510, CCMS 111.

Berglind, L. and Gjessing, E., (1981); Fjerning av humus ved H_2O_2-Tilsetning og UV-bestråling. Norwegian Institute for Water Research, F-80415, VA-10/81.

Bersillon, J.L., Brown, D.W., Fiessinger, F., and Hem, J.D., (1978); Studies of Hydroxyaluminium Complexes in Aqueous Solution. Jour. Research U.S. Geolog. Survey, 6:325.

Black, A.P. and Christman, R.F., (1963a); Chemical Characteristics of Fulvic Acids. Journal of American Water Works Association, 55:7:897.

Black, A.P. and Christman, R.F., (1963b); Characteristics of Colored Surface Waters. Journal of American Water Works Association, 55:6:753.

Black, A.P., Rice, O. and Bartow, E., (1933); Formation of Floc by Aluminium Sulfate. Industrial & Engineering Chemistry, 25:811.

Black, A.P., Singley, J.F., Whittle, G.P., and Maulding, J.S., (1963); Stoichiometry of the Coagulation of Color-Causing Organic Compounds with Ferric Sulfate. Journal of American Water Works Association, 55:10:1347.

Bonilla, C.F., (1947); Possibilities of the Electronic Coagulator for Water Treatment. Water and Sewage, March, p. 21.

Bratby, J., (1980); Coagulation and Flocculation. Upland Press Ltd., Croydon CR 1 LB, England.

Bronsted, J.V. and Volquartz, K.Z., (1928); Z. Phys. Chem., 134:97.

Brosset, C., Biedermann, G. and Sillen, L.G., (1954); Studies on the Hydrolysis of Metal Ions XI. The Aluminum Ion, Al^{3+}, Acta Chem. Scand.., 8:10:1917.

Bull, R.J., (1979); Health Effects of Alternative Disinfectants and their Reaction Products. Presented at the 99th Annual Conference of the American Water Works Association, San Francisco (June 24-28).

Burrows, W.D., (1977); Aquatic Aluminum Chemistry: Chemistry, Toxicology and Environmental Prevalence, Critical Reviews in Environmental Control, 7:167.

Camp, T.R. and Stein, P.C., (1943); Velocity Gradients and Internal Work in Fluid Motion. Journal of Boston Society Civil Engineers, 30:219.

Camp, T.R., (1968); Floc Volume Concentration. *Journal of American Water Works Association*, 60:6:656.

Canter, K.P., Hoover, R., Masen, T.J. and McCable, L.J., (1978); Association of Cancer Mortality with Halomethanes in Drinking Water. *Journal of National Cancer Institute*, 61:679.

Cantor, K.P. and McCabe, L.J., (1978); Epidemiologic Approach to the Evaluation of Organics in Drinking Water. *Water Chlorination, Environmental Impact and Health Effects*, *Volume 2*; Edited by Jolley, R.J., Gorchev, H. and Hamilton Jr., D.H. Ann Arbor Science. Ann Arbor, Michigan.

Carlberg, G.E., Drangsholt, H., Martinsen, K., and Olufsen, B., (1980); Analyse av haloformer, polysykliske aromatiske hydrokarboner og klorete hydrokarboner i utvalgte drikkevannskilder. *Central Institute for Industrial Research*, 780806-1.

Christman, R.F. et al., (1980); Chemical Identification of Aquatic Humic Chlorination Products. Prepared for publication in Water Chlorination. Environmental Impact and Health Effects.

Christman R.F. and Oglesby, R.T., (1971); Microbial Degradation and the Formation of Humus. *Lignins*. Chapt. 18. Editors: Sarkanen, K.V. and Ludwig, C.H. Wiley - Interscience, New York.

Clarke, J. and Davis, Jr., M.W., (1969); Color Removal from Kraft Mill Bleachery Waste of the Chlorination Stage. *Tappi*. 52:10:1923.

Collier, W.R., (1912); Description of plants at Oklahoma City, Okla and Santa Monica, Calif. *Engineering Record*, 66:55.

Committee Report, (1967); Report on Color Problem. Report for 1966. *Journal of American Water Works Association*, 59:8:1023.

Committee Report, (1979); Organics Removal by Coagulation: A Review and Research Needs. *Journal of American Water Works Association*, 71:10_588.

Committee Report, (1980); The Status of Direct Filtration. *Journal of American Water Works Association*, 72:7:405.

Costello, J.J., (1980); Postprecipitation in Distribution Lines Following Water Treatment. American Water Works Association 1980 Annual Conference Proc. p. 149.

Cross, B.T., (1972); Organic Pollutants in water. *Water Treatment and Examination*, 21:3:213.

Culp, R.L., (1977); Direct Filtration. *Journal of American Water Works Association*, 69:7:375.

Damhaug, T., (1980); Driftsundersøkelse av vannbehandlingsanlegg. Norwegian Institute for Water Research. F-80417, VA 12/80.

Dawson, H.J., Hrutfiord, B.F., Zasoski, K.J. and Ugolini, F.C., (1981); The Molecular Weight and Origin of Yellow Organic Acids. Soil Science, 132:3:19.

Dempsey, B.A., O'Melia, C.R. and Christman, R.F., (1979); Factors Affecting the Transport and Fate of Humic Substances and Associated Pollutants. Research Proposal to the Water Resources Research Institute of the University of North Carolina (Feb. 16).

Dickson, W., (1978); Some Effects of the Acidification of Swedish Lakes. Verh. Internat. Verein, Limnol., Stuttgart, 20:10:851.

Dobbs, R.A., Wise, R.H. and Dean, R.B., (1972); The Use of Ultra-Violet Absorbance for Monitoring the Total Organic Carbon Content of Water and Wastewater. Water Research, 6:10:1173.

Dobolyi, E., (1978); Experiments Aimed at the Removal of Phosphate by Electrochemical Methods. Water Research, 12:12:1113.

Driscoll, C.T., (1980); Chemical Characterization of Some Dilute Acidified Lakes and Streams in the Adirondack Region of New York State. Ph.D. dissertation Cornell University.

Driscoll, C.T., Baker, Jr. J.P., Bisogni, Jr. J.J. and Schofield, C.L., (1980); Effect of Aluminum Specification on Fish in Diluted Acidified Waters. Nature, 284:3:161.

Drozdova, T.V., (1968); Role of Humic Acid in Concentrating Rare Elements in Soil. Soviet Soil Science, 10:1393.

Dybwad, T.M., (1968); Elektrolytisk kloakkrenseanlegg for 1000-2000 personer. Tekniske og økonomiske vurderinger og resultater. Vann, 4:114.

Edzwald, J.K., (1978); Coagulation of Humic Substances. Presented at AIChE Mtg., Atlanta, Ga.

Edzwald, J.K., (1979); A Preliminary Feasibility Study of the Removal of Trihalomethane Precursors by Direct Filtration. Report of the Drinking Water Research Division, EPA, Cincinnati, Ohio (febr.)

Edzwald, J.K., (1980); Coagulation-Sedimentation-Filtration. Processes for Removing Organic Substances from Drinking Water. Prepared for EPA Monograph, Control of Organic Substances in Water and Wastewater, Prepublication copy, Aug.

Edzwald, J.K., (1981); Personal Communication.

Edzwald, J.K., Haff, J.D. and Boak, J.W., (1977); Polymer Coagulation of Humic Acid Waters. Journal of Environmental Engineering Division, 103:12:989.

Eidsness, F., (1974); Organic Contaminants in Drinking Water. Willing Water, 18:12.

Eikebrokk, B., (1982); Direct Filtration of Colored Surface Water. Doctoral Dissertation under preparation, NTH, Trondheim.

Evans, S. and Maalman, T.F.J., (1979); Removal of Organic Acids from Rhine River Water with Weak Base Resins. Environmental Science and Technology, 13:6:741.

Everhard, W.H. and Freeman, R.A., (1973); Toxic Effects of Aqueous Aluminum to Rainbow Trout - EPA-R3-73-0116.

Fair, G.M., Geyer, J.C. and Okun, D.A., (1968); Water and Wastewater Engineering, Volume 2, Water Purification and Wastewater Treatment and Disposal. Chapt. 26, John Wiley and Sons, Inc., New York.

Flaig, W., (1963); The Chemistry of Humic Substances. Report of the FAO/IAEA Technical Meeting, p. 103.

Flaig, W., (1964); Effect of Micro-organisms in the Transformation of Lignin to Humic Substances. Geochimica et Cosmochimica Acta. 28:1523.

Frink, C.R., (1960); Reactions of the Aluminum Ion in Aqueous Solutions and Clay Suspensions. Ph.D. dissertation Cornell University.

Frink, C.R. and Peech, M., (1963); Hydrolysis of the Aluminum Ion in Dilute Aqueous Solutions. Inorganic Chemistry, 2:3:473.

Fulton, G.P., (1977); In Defense of Conventional Water Filtration. Public Works, 5:86.

Fulton, G.P., (1980); New York City's Pilot Plant Filter Studies. Part two. Public Works, 5:85.

Fuoss, R.M. and Strauss, U.M., (1948); Electrostatic Interaction of Polyelectrolytes and Simple Electrolytes. Journal of Polymer Science, 3_602.

Føyn, E., (1950); Elektrolytisk kloakkrensing. Regionalplankomiteen for Oslo-området. Foredragshefte nr. 5. Mars.

Føyn, E., (1953); Elektrolytisk kloakkrensing i teknisk målestokk. Forsøksdriften på Huk. Teknisk Ukeblad, 19:3.

Føyn, E., (1980); Etter 20 år på "is": Tid for revurdering av den elektrolytiske renseprosess. Teknisk Ukeblad, 15a:4:48.

Gadkari, S.K., Raman, V., Gadkari, A.S. and Mirchandani, N.W., (1980); Studies of Direct Filtration of Raw Water. Indian Journal of Environmental Health. 22:1:57.

Gayer, K.H., Thompson, L.C. and Zajick, O.T., (1958); The Solubility of Aluminum Hydroxide in Acidic and Basic Media at 25°C. Canadian Journal of Chemistry, 36:9:1268.

Ghassemi, M. and Christman, R.F., (1968); Properties of Yellow Organic Acids of Natural Waters. Limnology and Oceanography, 13:583.

Gjessing, E.T., (1968); Elektrolytisk rensing av humus-vann; Internt notat, mai. Norwegian Institute for Water Research.

Gjessing, E.T., (1970); Reduction of Aquatic Humus in Streams. Vatten, 1:12.

Gjessing, E.T., (1971a); Some Factors Affecting on the Stability of Aquatic Humus. Vatten, 2:135.

Gjessing, E.T., (1971b); Effect of pH on the Filtration of Aquatic Humus Using Gels and Membranes. Schweizerische Zeitschrift für Hydrologie, 33:2:592.

Gjessing, E., (1972); "Black Sand" - Sandkorn overtrukket med MnO_2 for fjerning av humus. Norwegian Institute for Water Research, K-14/69 (March).

Gjessing, E.T., (1973); Gel- and Ultramembrane Filtration of Aquatic Humus: A Comparison of the two Methods. Schweizerische Zeitschrift für Hydrologie, 35:2:286.

Gjessing, E.T., (1976); Physical and Chemical Characteristics of Aquatic Humus. Ann Arbor Science, Ann Arbor, Michigan.

Gjessing, E.T., (1979); Vannforsyning i Norge. Forsknings- og utredningsbehov. NTNF (March).

Gjessing, E.T., (1980); Water Treatment Considerations. Aquatic Humus. Presented at IAWPR Post Conf. in Alberta, June.

Gjessing, E.T., (1981); Handlingsprogram 1981-1986, Drikkevannsrapport 1. NTNF's Utvalg for drikkevannsforskning.

Gjessing, E.T., (1981); The effect of aquatic humus on the biological availability of cadmium. Arch. Hydrobiol. 91:2:144.

Gjessing, E.T. and Berglind, L., (1981); Adsorption of PAH to aquatic humus. Arch. Hydrobiol. 1:92:24.

Gjessing, E.T. and Gjerdahl, T., (1972); Electromobility of aquatic humus: fractionation by the use of the isoelectric focusing technique. Proc. int. Meeting Humic Substances. Nienwersling, Pudoc, Wageningen.

Gjessing, E.T. and Lee, G.F., (1967); Fractionation of Organic Matter in Natural Waters on Sephadex, Columns, Environmental Science and Technology, 1:631.

Glaser, H.T. and Edzwald J.K., (1978); Removal of Naturally Occurring Color from Water Supplies by Coagulation - Direct Filtration. Proc. 98th, American Water Works Association's Annual Conf., Atlantic City, NJ.

Glaser, H.T. and Edzwald, J.K., (1979); Removal of Organic Matter in Natural Waters on Sephadex, Columns. Environmental Science and Technology, 1:631.

Glazer, H.T. and Edzwald, J.K., (1979); Coagulation and Direct Filtration of Humic Substances with Polyethylenimine. Environmental Science and Technology, 13:3:299.

Glembotskiy, V.A., Mamakov, A.A. and Sorokina, V.N., (1973); The size of Gas Bubbles formed under Elektroflotation Conditions. Electrochemistry in Industrial Processing and Biology, 5:59.

Gong, B. and Edzwald, J.K., (1981); Seasonal Evaluation of Organics Removal at a Conventional Water Treatment Plant. Aqua, p. 0300.

Greenland, D.J., (1971); Interaction Between Humic and Fulvic Acids and Clays. Soil Science, 111:1:34.

Griffith, J.D. and Williams, R.G., (1972); Application of Jar-Test Analysis of Phoenix, Ariz. Journal of American Water Works Association, 64:12:825.

Hahn, H.H., (1968); Effects of Chemical Parameters Upon Rate of Caogulation, unpublished Ph.D. dissertation. Harvard University, Cambridge, Mass.

Hahn, H.H. and Stumm, W., (1968); Coagulation by Al(III), Chapter 9 in Adsorption from Aqueous Solution. Advances in Chemistry, 79:91.

Hahn, H.H. and Stumm, W., (1968); Kinetics of Coagulation with Hydrolyzed Al(III). The Rate-Determining step. Journal of Colloid and Interface Science, 28:9:1.

Hall, E.S. and Packham, R.F., (1965); Coagulation of Organic Color with Hydrolyzing Coagulants. Journal of American Water Works Association, 57:9:1149.

Halle, O., (1979); Ionebytting for fjerning av humus fra drikkevann. Hovedoppgave i renseteknikk, D-1-79-7. The Norwegian Institute of Technology, University of Trondheim.

Hanna, G.P., Jr. and Rubin, A.J., (1970); Effect of Sulfate Ions in Coagulation with Aluminum (III). Journal of American Water Works Association, 62:5:315.

Hanaeus, J., (1976); Elektrolytisk dosering vid kemisk fällning av ytvatten. Del 1: Litteraturstudie. Chalmers Tekniska Högskola, Göteborg, Publikasjonsserie B, 76:5.

Hanaeus, J., (1979); Elektrolytisk dosering vid kemisk fällning av ytvatten. Chalmers Tekniska Högskola, Gøteborg, Publikation B 79:1.

Hartford, W.H., (1942); Chromic Acid Anodic Baths Interpretation of Glass Electrode Measurements. Industrial & Engineering Chemistry, 34:8:920.

Hassett, J.P. and Anderson, M.A., (1979); Association of Hydrophobic Organic Compounds with Dissolved Organic Matter in Aquatic Systems. Environmental Science and Technology, 13:12:1526.

Hayden, P.L. and Rubin, A.J., (1974); Systematic Investigation of the Hydrolysis and Precipitation of Aluminum (III). Chapter 9, Aqueous-Environmental Chemistry of Metals, (A.J. Rubin, editor) Ann Arbor Sci. Publishers, Inc., Ann Arbor, Michigan.

Hedberg, T., (1973); Elektrolytisk dosering av aluminium vid kemisk rening av vatten. Vatten, 73:2:145.

Hedberg, T., (1974); Studium av flockningsprocessen. Del 1: Teoretisk Bakgrunn. Publikationsserie B 75:3, Chalmers Tekniska Högskola, Göteborg.

Hedberg, T., (1975); Studium av flockningsprocessen. Del 2: Undersøkningar. Publikationserie B, 75:2. Chalmers Tekniska Höskola, Göteborg.

deHek, H., Stol, R.J., and de Bruyn, P.L., (1978); Hydrolysis, Precipitation Studies of Aluminum (III) Solutions 3. The Role of the Sulfate Ion. Journal of Colloid and Interface Science, 64:3:72.

Hem, J.D., (1968); Graphical Methods for Studies of Aqueous Aluminum Hydroxide, Fluoride and Sulfate Complexes. U.S. Geol. Survey Water Supply Paper, No. 1827 B.

Hem, J.D. and Robertson, C.E., (1967); Form and stability of aluminum hydroxide complexes in dilute solution, U.S. Geolog. Surv. Water Supply Pap. No. 1827 A, pp. 55.

Hemphill, L. and Rogers, R., (1973); Electrochemical Degradation of Domestic Wastewater. Proceedings 28th Industrial Waste Conference. Purdue University, 5:214.

Henriksen, A., (1966); An automatic method for determining iron in natural water. Vattenhygien, 22:1:2.

Henriksen, A., (1967); Application of the auto-analyzer in routine water analysis. Technicon Symposia, New York 1966. Automation in Analytical Chemistry. New York, Mediad Incorp., 1:658.

Henriksen, A. and Bergmann-Paulsen, I-M., (1974); An automatic method for determining sulfate in natural soft water, Vatten, 30:2:2.

Henriksen, A. and Bergmann-Paulsen, I-M., (1975); An automatic method for determining aluminum in neutral waters. Vatten, 31:4:339.

Henriksen, A. and Selmer-Olsen, A.R., (1970); Automatic methods for determining nitrate and nitrite in water and soil extracts. Analyst, 95:601.

Herer, D.O. and Woodard, F.E., (1976); Electrolytic coagulation of lignin from kraft mill bleach plant wastewaters. Tappi, 59:1:134.

Hiisvirta, L., (1981); THM-concentrations in Finland. The World's Record? Note, The National Board of Health, Finland.

Holden, W.S., (1956); Electrolytic Dosing of Chemicals. Proceedings of the Society for Water Treatment and Examination, 5:120.

Hudson, Jr., H.E., (1976); Dynamics of Mixing and Flocculation. Proc. of the 8th Annual Public Water Supply Conference. University of Illinois, Dept. of Civil Engineering, p. 41.

Hudson, Jr., H.E. and Wolfner, J.P., (1967); Design of Mixing and Flocculating Basins. Journal of American Water Works Association, 59:10:1257.

Hutchison, W.R. and Foley, P.D., (1974); Operational and Experimental Results of Direct Filtration. Journal of American Water Works Association, 66:2:79.

Hutchison, W.R. (1976); High-Rate Direct Filtration. Journal of American Water Works Association, 68:6:292.

Ishibashi, T., (1980); Electron - Microscopic Study on Organic Colour in Water. *Aqua*, 1:0003.

Ito, T. and Yui, N., (1954); Hydrolysis Constant of Aluminum Ion in Chloride Solutions. *Chemical Abstracts*, 48:10:5613.

Jackson, T.A., (1975); Humic Matter in Natural Waters and Sediments. *Soil Science*, 119:1:56.

Jeffcoat, W.B. and Singley, J.E., (1975); The Effect of Alum Concentration and Chemical-Addition Times on Coagulation. *Journal of American Water Works Association*. 67:4:177.

Johansen, M., (1978); Humus og Aluminium; Notat *Norwegian Institute for Water Research*, Feb. 22nd.

Jones, J.R.E., (1964); *Fish and River Pollution*. London, Butterworths, p. 203.

Jonsson, N.Å., Jähkel, S. and Perman, G., (1969); Undersökning av kontaktkoagulering i flerbäddsfilter medest elektrolytisk dosering av aluminiumjoner. *Chalmers Tekniska Högskola*, Göteborg. Publikation 69:5.

Josephson, J., (1982); Humic Substances Outlook. *Environmental Science and Technology*. Under Preparation.

Kaiser, K.L.E. and Lawrence, J., (1979); Polyelectrolytes: Potential Chloroform Precursors. *Science*, 196:1205.

Kavanaugh, M.C., (1978); Modified Coagulation for Improved Removal of Trihalomethane Precursors. *Journal of American Water Works Association*, 70:11:613.

Kawamura, S., (1973); Coagulation Considerations. *Journal of American Water Works Association*, 65:6:417.

Kawamura, S., (1976); Consideration on Improving Flocculation. *Journal of American Water Works Associaiton*, 68:6:328.

Kawamura, S. and Tanaka, Y., (1966); Applying Colloid Filtration Techniques to Coagulant Dosage Control *Water and Sewage Works*, 9:348.

Kirk, T.K., Higuchi, T. and Chang H.-M., (1980); *Lignin Biodegradation: Microbiology, Chemistry and Potential Applications*. Volume I and II. CRC Press Inc., Boca Raton, Florida.

Kisla, T.C. and McKelvey, R.D., (1978); Color Removal from Softwood Kraft Pulp Bleach Plant Effluent by Polyamines. *Environmental Science and Technology*, 12:2:207.

Kodama, H. and Schnitzer, M., (1966); Effects of Interlayer Cations on the Adsorption of a Soil Humic Compound. Science, 153:70.

Kodama, H. and Schnitzer, M., (1968); Effects of Interlayer Cations on the Adsorption of a Soil Humic Compounds by Montmorillonite. Soil Science, 106:1:73.

Kononova, M.M., (1966); Soil Organic Matter. Its Nature, Its Role in Soil Formation and in Soil Fertility, second English ed. Pergamon Press, New York.

Koottatep, S., (1979); Removal of Humic Substances from Natural Waters by Reverse Osmosis. Thesis for the degree of Doctor of Engineering. Div. of Hydraulic and Sanitary Engineering, the University of Trondheim, The Norwegian Institute of Technology.

Koroleff, F., (1970); ICES. Interlab No. 3.

Kostychev, P.A., (1886); Soils of the Chernozem Region of Russia, Part 1. The Formation of Chernozem.

Kubota, H., (1956); Properties and Volumetric Determination of Aluminum Ion. Thesis, Univ. of Wisconsin.

Kölle, W., (1979); Resin Treatment Improves High Color Groundwater. Water and Sewage Works. 126:1:68.

Leach, J.M., Mueller, J.C. and Walden, C.C., (1976); Biodegradability of Toxic Compounds in Pulp Mill Effluents. B.C. Research. Vancouver.

Letterman, R.D. and Logsdon, G.S., (1976); Survey of Direct Filtration Practice: Preliminary Report. Presented at American Water Works Association Annual Conference, New Orleans, LA (June).

Letterman, R.D., Quon, J.E. and Gemmell, R.S., (1973); Influence of Rapid-Mix Parameters on Flocculation. Journal of American Water Works Association, 65:11:716.

Lind, C.J. and Hem, J.D., (1975); Effects of Organic Solutes on Chemical Reactions of Aluminum. U.S. Geol. Survey Water-Supply Paper, 1927-G.

Lipowicz, M., (1981); Rapid oxidation destroys organics in wastewater. Chemical Engineering, Nov. 2.

Logsdon, G.S., (1978); Direct Filtration - Past, Present, Future. Civil Engineering - ASCE, 7:68.

Logsdon, G.S., Clark, R.M. and Tate, C.H., (1978); Costs of Direct Filtration to Meet Drinking Water Regulations. Presented at American Water Works Association Annual Conference, Atlantic City, NJ (June 25).

Lovelock, J.E., Maggs, R.J. and Wade, R.J., (1973); Halogenated Hydrocarbons in and over the Atlantic. Nature, 241:194.

Malachesky, P.A., 1976; Aluminum. Encyclopedia of Electrochemistry of the Elements. Vol. VI, Marcel Dekker, Inc., New York & Basel, Bard, A.J., Editor.

Mallevialle, J., (1979); Transformation of Humic Acid by Ozone. Presented at Conference of Oxidation Techniques in Drinking Water Treatment, Karlsruhe, F.R.G. EPA-570/9-79-020, p. 291. CCMS 111.

Mangravite, Jr., FC., Buzzell, T.D., Cassell, E.A., Matijevic, E. and Saxton, G.B., (1975); Removal of Humic Acid by Coagulation and Microflotation, Journal of American Water Works Association, 67:2:88.

Mathur, S.P. and Paul, E.A. (1966); A Microbiological Approach to the Problem of Soil Humic Acid Structures. Nature, 212:5062:646.

Marson, H.W., (1965); Electrolytic Sewage Treatment. The Engineer, 4:591.

Matijevic, E., (1973); Colloid Stability and Complex Chemistry. Journal of Colloid and Interface Science, 43:2:217.

Matijevic, E., Janauer, G.E. and Kerker, M., (1964); Removal of Charge of Lyophobic Colloids by Hydrolyzed Metal Ions: Aluminum Nitrate. Journal of Colloid Science, 19:333.

Matijevic, E. and Stryker, L.J., (1966); Coagulation and Reversal of Charge of Lyophobic Colloids by Hydrolyzed Metal Ions. III Aluminum Sulfate. Journal of Colloid and Interface Science, 22:68.

May, H.M., Helmke, P.A. and Jackson, M.L., (1979); Gibbsite solubility and thermodynamic properties of hydroxy-aluminum ions in aqueous solution at 25°C. Geochimica et Cosmiochimica Acta, 43:861.

McCooke, N.J. and West, J.R., (1978); The Coagulation of a Kaolinite Suspension with Aluminum Sulphate. Water Research, 12:793.

Miljøministeriet, (1980); Bekendtgjørelse nr. 6 af 4. jan.

Miller, L.B., (1925); A Study of the Influence of Anions Upon the Properties of the Floc. Public Health Reports, 40.

Miller, H.C. and Knipe, W., (1963); Electrochemical Treatment of Municipal Wastewater. Final Report. U.S. Public Health Service. Div. of Water Supply and Pollution Control. Contract No. PH 86-62-113.

Miller, G.W., Rice, R.G., Robson, C.M., Scullin, R.L., Kühn, W. and Wolf, H., (1978); An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies. Executive Summary. U.S. EPA-600/8-78-081.

Moffett, J.W., (1968); The Chemistry of High-Rate Water Treatment. Journal of American Water Works Association, 60:11:1255.

Mohtadi, M.F. and Rao, P.N., (1973); Effect of Temperature on Flocculation of Aqueous Dispersions. Water Research. Vol. 7, p. 747.

Monscvitz, J.T., Rexing, R.G., Williams, R.G. and Heckler, J., (1978); Some Practical Experiences in Direct Filtration. Journal of American Water Works Association, 70:10:584.

Moore, G.N., (1977); Interaction of Fulvic Acid and Kaolinite During Coagulation. Presented at American Water Works Association Convention.

Mortensen, J.L., (1963); Complexing of Metals by Soil Organic Matter. Soil Science Soc. Amer. Proc., 27:2:179.

Mueller, H.M. and Conley, W.R., (1981); Alternative Processes for Small Water Treatment Plants. Water and Pollution Control, 2:21.

Müller, L., (1982); A modification of standard colorimetric procedure to determine various Al-complexes in waters with high content of aquatic humus. Hovedfagsarbeide, under preparation. The University of Oslo.

Naas, A., (1982); Driscoll's method for determination of various Al-complexes in waters with high content of aquatic humus. Hovedfagsarbeide, under preparation. The University of Oslo.

Narkis, N. and Rebhun, M., (1975); The Mechanism of Flocculation Processes in the Presence of Humic Substances. Journal of American Water Works Association, 69:6:325.

NAS, (1977); Drinking Water and Health. Part I, Chapters 1-5. The National Research Council, National Academy of Sciences, Washington, D.C.

Nickel, J.B., (1945); Fundamental Techniques for Running Jar-Tests. Journal of American Water Works Association, 37:11:1207.

Nissenbaum, A. and Kaplan, I.R., (1972); Limnology and Oceanography, 17:4:570.

Nissenbaum, A. and Swaine, D.J., (1976); Organic Matter - Metal Interactions in Recent Sediments: the role of humic substances. Geochimica et Cosmochimica Acta, 40:809.

Nusbaum, P.E. and Riedinger, A.B., (1978); Water Quality Improvement by Reverse Osmosis. From: Water Treatment Plant Design for the Practicing Engineer, Chapter 26, ed. Sanks, R.L. Ann Arbor Science, Publishers Inc., Ann Arbor, Michigan.

Oden, S., (1919); Humic Acids. Kolloidchem. Beih. (Ger.) 11:75.

Oliver, B.G., (1978); Chlorinated Non-volatile Organics Produced by the Reaction of Chlorine with Humic Material. Canadian Research, 11:6:21.

Oliver, B.G. and Shindler, D.B., (1980); Trihalomethanes from the Chlorination of Aquatic Alga. Prepared for Environmental Science and Technology.

O;Melia, C.R., (1972); Coagulation and Flocculation, Chapter 2. Physicochemical Processes for Water Quality Control, (W.J. Weber Jr., editor). Wiley-Interscience. New York, NY, p. 61.

O'Melia, C.R. and Stumm, W., (1967); Theory of Water Filtration. Journal of American Water Works Association, 59:11:1393.

Ong, H.L. and Bisque, R.E., (1968); Coagulation of Humic Colloids by Metal Ions. Soil Science, 106:220.

Organization for Economic Cooperation and Development (OECD), (1980); Control of Organochlorinated Compounds in Drinking Water (an Evaluation of Alternative Options), Paris, March 26, (restricted to the members of the Water Management Group).

Packham, R.F., (1964); Studies of Organic Colour in Natural Water. Spring Meeting of Society for Water Treatment and Examination, London.

Packham, R.F., (1965); Studies of Organic Color in Natural Waters, Proc. Soc. Water Treat. Exam., 13:316.

Perdue, E.M., Beck, K.C. and Renter, H.J., (1976); Organic Complexes of Iron and Aluminum in Natural Waters. Nature, 260:4.

Peters, C.J. and Perry, R., (1980); The Formation and Control of Trihalomethanes in Water Treatment Processes. Presented on IAWPR post conference in Albert (June).

Pickett, D.J., (1979); Electrochemical Reactor Design. Chemical Engineering Monographs 9. Elsevier Scientific Publ. Company. New York.

Poon, C.P.C., (1973); Electrochemical Process for Sewage Treatment. Proc. 28th Ind. Waste Conf. Purdue Univ. Ext. Series. W. Lafayette, Ind. May 1, p. 281.

Poon, C.P.C. and Brueckner, T.G., (1975); Physicochemical treatment of wastewater-seawater mixture by electrolysis. Journal of Water Pollution Control Federation, 47:1:66.

Randtke, S.J. and Jepsen, C.P., (1980); Chemical Pretreatment for Activated-Carbon Adsorption. Presented in preliminary form at the Annual Conference of the American Water Works Association.

Randtke, S.J., Thiel, C.E., Liao, M.Y. and Yamaya, C.N., (1981); Removal of Soluble Organic Contaminants by Lime-Soda Softening. Draft Copy submitted to Journal of American Water Works Association, September.

Rashid, M.A., (1971); Role of Humic Acids of Marine Origin and their Different Molecular Weight Fractions in Complexing di- and tri-valent Metals. Soil Science, 111:5:298.

Raupach, M., (1963); Austeriche Journal of Soil Research, 1:36.

Research Committee (1967) Report on Color Problem; Journal of American Water Works Association, 59:8:1023.

Rogne, Å.K.G., Haraldsen, S. and Gjessing, E., (1981); Rapport om laboratorieforsøk med UV-H_2O_2 oksydasjon av humus. Norwegian Institute for Water Research, Notat dec. 23.

Romslo, R., (1968); Prosjektering og beregning av et elektrolytisk kloakkrenseanlegg for mellom 100 000 og 200 000 personer. Vann, 68:4:119.

Rook, J.J., (1974); Formation of Haloforms During Chlorination of Natural Waters. Water Treatment and Examination, 23:2:234.

Rova, G. and Källander, L., (1972); Elektrolytisk dosering av aluminium. Chalmer Tekniska Högskolla, Göteborg. Publikation, 72:12.

Rubin, A.J. and Kovac, T.W., (1974); Effect of aluminum (III) hydrolysis on alum coagulation. Chapter 8. Chemistry of Water Supply Treatment and Distribution. (Edited by Rubin, A.J.) Ann Arbor Science Publ. Ann Arbor, Michigan.

Saatçi, A.M. and Oulman, C.S., (1980); The Bed Depth Service Time Design Method for Deep Bed Filtration. Journal of American Water Works Association, 72:9:524.

Sadek, S.E., (1970; An Electrochemical Method for Removal of Phosphates from Waste Waters. Federal Water Quality Administration. Dept. of Interior. PB-217, 673, Feb.

Sarkanen, K.V. and Ludwig, C., (1971); Lignins. Wiley Interscience, New York.

Scheuch, L.E. and Edzwald, J.K., (1979); Removal of Color and Chloroform Precursors from Low Turbidity Waters by Direct Filtration. Presented at the Annual Conference of American Water Works Association, San Francisco, CA.

Schnitzer, M., (1976); The Chemistry of Humic Substances. Environmental Biochemistry, vol. 1 (J.O. Nriagu, editor). Ann Arbor Science, Ann Arbor, Michigan.

Schnitzer, M. and Hansen, E.H., (1970); Organo-Metallic Interaction in Soils. An Evaluation of Methods for the Determination of Stability Constants of Metal-Fulvic Complexes. Soil Science, 109:6:333.

Schnitzer, M. and Khan, S.V., (1972); Humic Substances in the Environment. Marcel Dekker, Inc., New York.

Schnitzer, M. and Kodama, H., (1966); Montmorillonite: Effects of pH on Its Adsorption of a Soil Humic Compound. Science, 153:70.

Schofield, R.K. and Taylor, A.W., (1954); The Hydrolysis of Aluminum Salt Solutions. Journal of Chemical Society, 12:4445.

Seip, H.M., (1980); Complexes of Aluminum in the pH-range 4-6. Note, Central Institute for Industrial Research, Norway.

Semmens, M. and Field, T.K., (1980); Coagulation: Experiences in Organics Removal. Journal of American Water Works Association, 72:8:476.

Shapiro, J., (1957); Chemical and Biological Studies on the Yellow Organic Acids of Lake Water, Limnology and Oceanography, 16:2:1.

Shea, T.G., Gates, W.E. and Argman, Y.A., (1971); Experimental Evaluation of Operating Variable in Contact Flocculation. Journal of American Water Works Association, 63:1:41.

Shin, Y.-O., Chodan, J.J. and Wolcott, (1970); Adsorption of DDT by Soils, Soil Fractions and Biological Materials. Journal of Agriculture and Food Chemistry, 18:6:1129.

SIFF, (1976); Kvalitetskrav til vann. Ny revidert utgave, november.

Simmon, V.F. and Tardiff, R.G., (1978); The Mutagenic Activity of Halogenated Compounds Found in Chlorinated Drinking Water. Water Chlorination Environmental Impact and Health Effects, Vol. 2. Edited by Jolley, R.J., Gorchero, H. and Hamilton, Jr., D.H., Ann Arbor Science. Ann Arbor, Michigan.

Smith, R.W. and Hem, J.D., (1972); Effect of Aging on Aluminum Hydroxide Complexes in Dilute Aqueous Solutions, U.S. Geol. Surv. Water-Supply Paper No. 1827 D.

Snoeyink, V.L. and Jenkins, D., (1980); Water Chemistry. John Wiley & Sons Inc., New York.

Sontheimer, H., (1978); Flocculation in Water Treatment. Presented in The Scientific Basis of Flocculation, Ives, K.J. (ed.). NATO Advanced Study Institute's Series Sÿthoff and Noordhoff, Alphenaan den Rÿn - The Netherlands.

Standard Methods for the Examination of Water and Wastewater, (1975) 14th Ed. American Public Health Assoc., Inc., New York.

Stevens, A.A., (1979); Formation of Non-Polar Organochloro Compounds as Byproducts of Chlorination. Presented at Conference for Oxidation Techniques in Drinking Water Treatment, Karlsruhe, F.R.G. EPA-570/9-79-020, CCMS 111.

Stevens, A.A. et al. (1980); Study of Organic Byproducts of Disinfection. Inhouse. Task 19, EPA Quarterly Report.

Stevens, A.A., Slocum, C.J., Seeger, D.R. and Robeck, G.G., (1976); Chlorination of Organics in Drinking Water. Journal of American Water Works Association, 68:11:615.

Stevenson, F.J., (1979); Nature of Divalent Transition Metal Complexes of Humic Acids are Revealed by a Modified Potentiometric Titration Method. Soil Science, 123:1:10.

Stevenson, F.J., (1976); Divisions-3-Soil Microbiology and Biochemistry. Stability Constants of Cu^{2+}, Pb^{2+} and Cd^{2+} Complexes with Humic Acids. Soil Science Soc. Am. J., 40:665.

Strokach, P.P., (1975); The Prospects of Using Anodic Dissolution of Metal for Water Purification. Electrochemistry in Industrial Processing and Biology, Eng. Transl. No. 4, Jul./Aug., p. 55.

Strokach, P.E., Stipehenko, V.A., Kul'skiy, L.A. and Belaya, V.P., (1973); A Study of Water Purification in an Electrolyser with an Aluminum Anode. Electrochemistry in Industrial Processing and Biology, Eng. Transl., No. 4, Jul./Aug., p. 39.

Stuart, F.E., (1946); Electronic Principle of Water Purification. Journal of the New England Water Works Association, 60:3:236.

Stuart, F.E., (1946); Electronic Water Purification. Progress Report on the Electronic Coagulator - A New Device Which Gives Promise of Unusually Speedy and Effective Results. Water and Sewage, 5:24.

Stumm, W. and Morgan, J.J., (1970); Aquatic Chemistry, Wiley - Interscience, New York, p. 230.

Stumm, W. and Morgan, J.J. (1962); Chemistry Aspects of Coagulation. Journal of American Water Works Association, 54:8:971.

Stumm, W. and Morgan, J.J., (1970); An Introduction Emphasizing Chemical Equilibria in Natural Waters. Wiley-Interscience, New York.

Stumm, W. and O'Melia, C.R., (1968); Stoichiometry of Coagulation, Journal of American Water Works Association, 60:5:514.

Symons, J.M. et al., (1975); National Organics Reconnaissance Survey for Halogenated Organics. Journal of American Water Works Association, 67:11:634.

Symons, J.M. et al., (1976); Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes. U.S. EPA-WSERL, Cincinnati.

Symons, J.M. and Stevens, A.A., (1979); Physical-Chemical Pretreatment for the Removal of Precursors. Presented for the Conference for Oxidation Techniques in Drinking Water. Treatment Karlsruhe, F.R.G. EPA-570/9-79-020, p. 195, CCMS-111.

Szabo, Z., Czanyj, L.J. and Kavai, M., (1955); Determination of the Solubility Products of Metal Hydroxide. Precipitates: I. Reaction of Aluminum Ions with Hydroxide Ion. Z. Anal. Chem., 146:401.

Szalay, A., (1969); Arkiv för Mineralogi och Geologi, 5:23.

Tate, C.H., Lang, J.S. and Hutchinson, H.L., (1977); Pilot Plant Tests of Direct Filtration. Journal of American Water Works Association, 69:7:379.

Tejera, N.E. and Davis, Jr., M.W., (1970); Removal of Color and Organic Matter from Kraft Mill Caustic Extraction Waste by Coagulation, Tappi, 53:10:1031.

The Engineer, (1884); 4:316.

Thiele, H., Affeldt, H. and Ryhiner, G., (1960); Ion Exchange of Humins by Equilibrium Dialysis and Swelling. Scientific Proceedings of the Royal Dublin Society, Series A, 1:4:81.

Thompson, C.G., Singley, J.E. and Black, A.P., (1972a); Magnesium Carbonate: A Recycled Coagulant, I. Journal of American Water Works Association, 64:1:11.

Thompson, C.G., Singley, J.E. and Black, A.P., (1972b); Magnesium Carbonate: A Recycled Coagulant, II, Journal of American Water Works Association, 64:2:93.

Thorsen, T., (1981); Drikkevannsrensing med omvendt osmose. SINTEF, STF 21 A81029, The Norwegian Institute of Technology, University of Trondheim.

Thurman, E.M. and Malcolm, R.L., (1981); Structural Study of Humic Substances. New Approaches and Methods. Presented at Symposium on Terrestrial and Aquatic Humic Materials, Chapel Hill, North Carolina, Nov.

Thurman, E.M. and Malcolm, R.L., (1979); U.S. Geological Survey Water Supply Paper, 1871-G.

Thurman, E.M., Wershaw, R.L., Malcolm, R.L. and Pinkney, D.J., (1981); Molecular Size of Aquatic Humic Substances. Paper Submitted to Organic Geochemistry, July.

Treweek, G.P., (1979); Optimization of Flocculation Time Prior to Direct Filtration. Journal of American Water Works Association, 71:2:96.

US EPA, (1979); National Interim Primary Drinking Water Regulations; Control of Trihalomethanes in Drinking Water, Final Rule, Federal Register, Nov. 20.

U.S. Patent, (1889); 389, 101.

U.S. Patent, (1909); 937, 210.

van Olphen, H., (1977); An Introduction to Clay Colloid Chemistry, Wiley-Interscience, John Wiley & Sons, Inc. Second ed., New York.

van Dijk, H., (1971); Cation Building of Humic Acids. Geoderma 5:53.

Vetter, K.J., (1967); Electrotechnical Kinetics. Theoretical and Experimental Aspects. Academic Press, New York.

Vik, E.A., (1980); Filtering av avløpsvann. Forsøk i pilot- og laboratorieskala. Norwegian Institute for Water Research.

Vråle, L. and Jorden, R.M., (1971); Rapid Mixing in Water Treatment. Journal of American Water Works Association, 63:1:52.

Våland, T. and Nilsson, G., (1976); The Electrochemical Behavior of Al in Na-Acetate Buffers. Corrosion Science, 16:591.

Walker, J.D., (1971); Instomix for Instantaneous and Uniform Blending of Coagulants in Water Treatment. Chicago Bridge & Iron Co. Tech. Bull. No. CBT 5525. Oak Brook, Ill.

Weber, Jr., W.J., (1972); Physiochemical Processes for Water Quality Control. Wiley-Interscience, John Wiley & Sons, Inc. New York.

Weÿman-Hane, G., (1971); Elektrolytisk dosering av aluminium vid Kemisk Rening av Vatten. Chalmers Tekniska Högskola, Göteborg, Publikation B 71:2.

Wershaw, R.L., Burcar, P.J. and Goldbert, M.C., (1969); Interaction of Pesticides with Natural Organic Material. Environmental Science and Technology, 3:271.

Westall, J.C., Zachary, J.L. and Morel, F.N.M., (1976); Mineql. a computer program for the calculation of chemical equilibrium composition of aqueous systems, Dept. of Civil Engr. MIT, Techn. Note No. 18.

Wetzel, R.G., (1976); Limnology, Ch. 17 W.B. Saunders Co., Philadelphia.

Wiese, G.R. and Healy, T.W., (1975); Heterocoagulation in Mixed TiO_2-Al_2O_3 Dispersions. Journal of Colloid and Interface Science, 52:9:3.

Williams, K.W., (1974); Solute-Gel Interactions in gel filtration. Lab. Pract. 20:667.

Wilson, D.E. and Kinney, P., (1977); Effects of Polymeric Charge Variations on the Proton-Metal Ion Equilibra of Humic Materials. Limnology and Oceanography, 22:2:281.

Wright, R.F., Conroy, N. Dickson, W.T., Harrman, R., Henriksen, A. and Schofield, C.L., (1980); Acidified lake districts of the world: a comparison of water chemistry of lakes in southern Norway, southern Sweden, southwestern Scotland, the Adirondack Mountains of New York and southeastern Ontario. Proc. Int. Conf. ecol. impact acid precip., Norway, SNSF project.

Öztürk, Y.F., (1971); Slow Sand Filtration of Surface Water Containing Humus (Filtration of Impounded Water and Impounded - Microstrained - Ozonized Water). Norwegian Institute for Water Research, T-4/69 (Dec.).

APPENDIX 1

WATER QUALITY RESULTS FROM THE ELECTROCHEMICAL REACTOR STUDY.

	COAGULATION CONDITION						WATER QUALITY							
Raw water:	Al-dosage (mg Al/l)						TOC mgP/l		UV-abs (cm^{-1})		Color (mgPt/l)		pH	
TJERNSMOTJERN:	Theor. calcul.	Measured	Charge (coulomb)	Temp. oC	Spec.cond. uS/cm	Appl. Voltage	Raw water	Treated water	Raw water	Treated water	Raw water	Treated water	Raw water	Treated water
pH adjusted	7.1	70.3	585	2.5	300	1.2	12.6	14.8	0.59	0.50	126	93	2.0	2.15
- " -	14.1	74.4	1160	3-6	246	5.0	11.2	11.1	0.50	0.48	99	80	2.0	2.25
- " -	6.6	17.5	548	2.5	42	1.7	12.4	12.2	0.57	0.45	131	70	2.8	3.10
- " -	32.6	42.3	1000	2.5	71	0.6	11.3	4.0	0.50	0.085	115	5	2.8	4.4
- " -	1.7	1.6	143	5	75	1.4	14.8	9.7	0.59	0.28	110	35	3.9	4.8
- " -	3.2	8.2	267	15.5	79	1.7	9.7	7.7	0.60	0.18	120	17	3.9	5.0
- " -	4.9	10.4	405	6	64	2.6	14.2	3.9	0.64	0.071	130	5	3.9	5.8
- " -	16.9	12.8	1330	3.5	61	5.8	15.6	5.2	0.62	0.060	120	7	3.9	6.0
- " -	1.8	1.6	145	17	69	1.3	16.2	8.8	0.63	0.23	130	41	4.5	5.6
- " -	7.1	11.9	585	17	62	2.6	14.7	3.7	0.63	0.073	120	8	4.5	6.3
- " -	3.1	3.8	260	17	59	2.0	14.1	5.8	0.62	0.19	140	34	4.5	6.0
- " -	3.8	13.0	310	5	72	2.6	14.6	5.2	0.63	0.12	130	11	4.5	5.0
- " -	1.7	1.2	140	16	56	-	14.0	9.1	0.62	0.400	129	75	5.5	6.2
- " -	3.5	6.9	290	18.5	55	2.8	14.0	7.0	0.66	0.240	135	44	5.5	6.6
- " -	6.8	11.6	560	17	56	3.2	15.1	4.3	0.62	0.098	130	13	5.5	6.9
- " -	11.4	24.1	945	3.5	48	6.2	14.0	3.6	0.66	0.063	135	5	5.5	6.6
- " -	3.6	1.7	295	16	63	2.8	15.6	10.6	0.63	0.390	145	74	6.9	7.2
- " -	5.4	4.1	450	16	67	3.5	15.9	10.6	0.62	0.410	123	80	6.9	7.2
- " -	7.3	19.8	602	17	63	3.6	15.6	7.4	0.64	0.210	123	25	6.9	7.3
- " -	7.5	17.7	621	18	42	3.7	16.1	7.9	0.61	0.250	120	43	6.9	7.0
	1.3	0.8	108	2.5-3	48	-	12.9	9.9	0.650	0.470	138	90	6.1	6.5
	3.0	2.8	235	3	51	-		7.7		0.350		68		6.9
	10.4	10.7	865	4-5	44	-		3.3		0.089		5		7.2
	12.1	9.0	1000	15-9	54	3.7		-		-		30		6.8
	13.4	16.9	1110	3-4	56	-		3.3		0.086		11		6.8
	14.0	15.5	1230	8.5-9	43	-		5.0		0.087		3		6.8
	14.5	13.5	1200	3.5	52	4.9		4.0		0.081		6		7.0
	15.3	14.4	1270	3.5	47	7.7		3.3		0.078		4		7.0
	15.7	12.7	1300	5.5	54	-		2.9		0.071		6		6.7
	16.3	14.3	1350	4-5	46	-		4.1		0.140		12		7.2
	25.5	25.6	2105	8	43	11.0		3.4		0.081		5		7.6
	25.6	23.7	2115	5.5	55	-		3.2		0.081		9		7.3
	1.6	3.0	135	12	30	-	14.3	6.3	0.560	0.220	115	36	6.2	7.3
	1.8	2.5	145	10.5	30	-		10.2		0.370		75		6.8
	3.1	7.7	255	5	34	-		5.9		0.190		28		7.4
	3.4	6.4	280	10.5	30	-		7.0		0.210		38		7.0
	5.8	26.1	475	3-5.5	30	-		5.2		0.120		16		7.8
	6.1	8.3	500	10	32	-		6.0		0.140		16		7.2
	7.0	6.7	585	17	29	-		5.4		0.160		35		7.6
	9.7	8.1	805	16.5	32	-		-		0.095		14		8.0
	9.8	10.4	810	17	30	-		4.3		0.086		10		8.1
	10.1	11.7	720	5-9	30	-		4.4		0.092		10		7.6
	10.5	18.0	865	15	26	-		3.8		0.071		9		8.3
	10.9	17.2	900	7.5	32	-		5.0		0.131		16		8.1
	12.4	11.7	1025	7.0	29	-		4.6		0.066		12		7.8
	19.6	29.7	1625	8.0	27	-		4.3		0.063		13		8.0
	20.0	29.3	1670	10.0	29	-		4.0		0.058		13		8.0
	23.2	24.6	1920	17.0	24	-		2.9		0.060		5		8.1
	24.0	24.5	1280	17.0	30	-		4.8		0.070		3		6.4
	1.5	1.1	122	15.5	54	1.7	15.2	15.0	0.64	0.560	130	110	6.6	6.7
	2.1	2.8	170	15.5	50	2.2		11.7		0.450		90		6.7
	3.2	2.7	264	14	51	2.5		10.5		0.410		85		7.2
	3.7	6.3	305	20	57	2.4		-		-		-		-
	7.0	4.7	216	18	53	1.8		11.0		0.453		90		7.3

APPENDIX 1 (Cont.)

	COAGULATION CONDITION						WATER QUALITY							
Raw water:	Al-dosage (mg Al/l)						TOC mgP/l		UV-abs. (cm^{-1})		Color (mgPt/l)		pH	
	Theor. calcul.	Mea-sured	Charge (coulomb)	Temp. °C	Spec.cond. uS/cm	Appl. Voltage	Raw water	Treated water	Raw water	Treated water	Raw water	Treated water	Raw water	Treated water
Asketjern:														
	11.4	21.1	945	3.5	40	6.2	6.2	2.9	0.250	0.050	42	3	5.8	7.2
	19.3	28.5	1580	2.5	37	12.6		2.2		0.032		0		6.5
	1.6	5.4	135	9.0	44	0.1		3.1	0.250	0.064	39	1	6.3	6.9
	3.3	4.2	270	5.5	42	0.5		3.1		0.046		0		6.8
Dragsjøen:														
	10.6	14.9	980	3-4.5	54	-	9.6	4.4	0.430	0.170	76	22	6.1	7.3
	15.7	13.7	1295	18.5	33	-		2.9		0.073		5		7.7
Hellerudmyra:														
	1.8	6.3	140	20	24	2.0	10.8	5.1	0.500	0.186	105	39	4.4	5.4
	2.3	2.5	195	20	24	2.9	-	3.2	-	0.101	110	26	4.3	5.5
	4.0	3.4	350	20	25	4.6	10.8	3.5	0.500	0.061	105	23	4.4	5.7
	4.0	-	310	20	22	4.8	-	4.9	0.523	0.120	110	26	-	6.4
	5.4	-	430	20	18	-	-	3.3		0.056		11	-	6.6
	5.5	12.6	310	20	29	5.9	10.8	-	0.500		105	15	4.4	5.1
	6.3	6.5	620	-	18	6.4	11.0	2.0	0.540	0.038	117	2	4.5	6.5
	7.7	9.5	620	20	20	8.3		2.2		0.011	110	3	4.3	6.5
Småputten:														
pH adjusted	0.8		70	~15	230	~2.0			0.377	0.208	108	58	~4.8	5.8
- " -	1.6		135	~15	230	~2.0				0.146		34	4.8	5.9
- " -	2.5		210	~15	230	~2.0				0.125		34	4.8	5.9
	0.7		50	~15		1.3			0.301	0.252	52	47	6.2	6.6
	1.2		80	~15		1.4				0.244		46		6.5
	1.6		110	~15		1.6				0.248		48		6.5
	3.3		230	~15		2.0				0.187		30		6.5
	0.9		65	~15		1.9			0.301	0.260	53	44	6.7	7.0
	1.3		95	~15		1.7				0.208		34		6.9
	1.9		135	~15		1.4				0.190		30		6.9
	2.4		175	~15		2.0				0.158		26		6.8
	2.9		205	~15		-				0.197		34		7.0
	3.8		270	~15		-				0.180		31		7.0
	6.5		540	~15		2.5	5.9	2.5	0.260	0.049	50	5	6.7	6.8
	0.9		68	1	102		9.6	7.1	0.350	0.260	64	52	6.8	7.2
	1.9		140		100			6.6		0.210		44		7.2
	2.9		205		100			6.1		0.180		34		7.3
	3.8		270		100			5.5		0.150		30		7.2
	4.8		340		100			5.2		0.130		21		7.3
	5.8		405		100			4.4		0.097		11		7.2
	7.7		540		99			3.4		0.056		5		7.4
	0.8		68	~15	87	~2.0			0.337	0.310	94	82	7.3	6.6
	2.4		205	~15	87	~2.0				0.223		60		6.6
	3.6		295	~15	87	~2.0				0.201		56		6.7
	7.8		645	~15	87	~2.0				0.128		40		6.8
Sperillen:														
	7.1	8.5	560	17	25		2.3	1.0	0.089	0.027	10	1	6.9	7.6
	21.7	22.3	1700	17	24			1.2		0.031		1		7.8

APPENDIX 2

CURRENT TECHNICAL DATA FOR THE LABORATORY SCALE ELECTROCHEMICAL REACTOR.

Current (mA)	Specific conductivity (us/cm)	Distance between the electrodes (cm)	Applied Voltage	Calculated Voltage due to solution resistance $^{*}\eta_{IR}$
28	53	1.3	3.4	2.4
31			3.6	2.7
33			4.0	2.9
34			4.2	2.9
37			4.4	3.2
42			4.8	3.6
45			5.0	3.9
47			5.3	4.1
53			5.2	4.6
60			5.8	5.2
70			6.4	6.1
77			6.7	6.7
86			7.0	7.4
98			7.5	8.5
118			7.9	10.2
133			8.1	11.5
138			8.4	11.9
161			8.7	13.9
185			9.1	16.0
202			9.3	17.5
240			9.7	20.7
356			11.0	30.8
1300		1.3	12.7	112
30		0.8	3.7	1.6
36			3.9	1.9
37			4.0	2.0
37			4.1	2.0
37			4.2	2.0
38			3.8	2.0
39			4.4	2.1
51			4.7	2.7
59			4.9	3.1
61			5.2	3.3
65			5.6	3.5
78			5.9	4.2
124			7.3	6.6
192			8.4	10.2
206			8.4	11.0
221			8.7	11.8
287			9.3	15.3
340			9.6	18.1
449		0.8	10.1	23.9
42		0.3	2.7	0.72
43			2.6	0.71
44			2.9	0.75
46			3.1	0.78
50			3.2	0.83
53			3.4	0.87
57			3.6	0.94
67			3.8	1.1
76			4.2	1.3
81			4.0	1.3
88			4.4	1.5
95			4.5	1.6
112			4.9	1.9
125			5.2	2.1
152			6.0	2.5
189			7.3	3.1
243			8.0	4.0
415			8.7	6.9
440	53	0.3	8.9	7.3
39	790	1.3	1.3	0.23
45			1.3	0.26
51			1.4	0.30
76			1.5	0.44
271			2.3	1.6
342			2.6	2.0
409		1.3	2.9	2.4
45		0.8	1.2	0.16
52			1.2	0.19
58			1.3	0.21

APPENDIX 2 (Cont.)

Current (mA)	Specific conductivity (us/cm)	Distance between the electrodes (cm)	Applied Voltage	Calculated Voltage due to solution resistance $^{*}\eta_{IR}$
75	790	0.8	1.3	0.27
96			1.4	0.34
127			1.5	0.45
161			1.7	0.57
246			1.9	0.88
325			2.2	1.2
393		0.8	2.5	1.4
41		0.3	1.2	0.046
44			1.3	0.050
49			1.3	0.056
56			1.3	0.064
75			1.3	0.086
153			1.5	0.17
216			1.6	0.25
330			1.9	0.38
544	790	0.3	2.3	0.62
46	1900	1.3	1.1	0.11
70			1.2	0.17
89			1.3	0.21
101			1.4	0.24
116			1.4	0.28
162			1.5	0.39
185			1.6	0.45
214			1.7	0.52
248			1.8	0.60
343			2.0	0.83
376		1.3	2.3	0.91
43		0.8	1.1	0.064
46			1.1	0.068
51			1.1	0.076
64			1.2	0.095
82			1.3	0.12
162			1.4	0.24
253			1.6	0.38
340			1.8	0.50
490		0.8	2.1	0.73
45		0.3	1.1	0.021
62			1.1	0.029
87			1.1	0.040
135			1.2	0.063
200			1.3	0.093
270			1.4	0.13
485	1900	0.3	1.8	0.22
45	5600	0.8	1.1	0.023
55			1.2	0.028
63			1.2	0.032
67			1.2	0.034
75			1.2	0.038
83			1.2	0.042
91			1.3	0.046
106			1.3	0.053
119			1.3	0.060
158			1.3	0.080
198			1.4	0.10
230			1.5	0.12
320			1.6	0.16
486		0.8	1.8	0.24
44		0.3	1.1	0.0071
45			1.1	0.0072
49			1.1	0.0078
52			1.1	0.0084
56			1.1	0.0091
66			1.1	0.011
84			1.2	0.014
95			1.2	0.015
134			1.3	0.022
195			1.3	0.032
225			1.4	0.036
268			1.5	0.043
376			1.6	0.060
400			1.6	0.064
479	5600	0.3	1.7	0.077

* $\eta_{IR} = \frac{I \cdot d}{A \cdot \kappa}$, where I=current (ampère), d=distance between the electrodes (cm) A=active surface area (cm^2), κ=spec.conductivity us/cm, here 280 cm^2

APPENDIX 3

WATER QUALITY RESULTS FROM THE CONVENTIONAL COAGULATION STUDY

	COAGULATION CONDITION		WATER QUALITY							
HELLERUDMYRA	Al.sulfate-dosage (mg Al/l)	pH	TURB (NTU)	TOC (mg C/l)	UV-abs. 253.7nm (cm^{-1})	Color (mg Pt/l)		pH	Al (mg Al/l)	Colloid charge (meq/l.10^4)
						Unfiltr.	Filtr.			
Raw water	0	6.5		12.4	0.498	131	113	6.5		
Al.sulfate + NaOH mixed before addition	4.5	5.8		9.2	0.409	128	92	6.2		
	7.2	5.5		6.9	0.292	75	61	6.1		
	10.8	5.8		6.1	0.225	61	44	6.1		
	14.4	5.5		5.4	0.201	53	35	6.2		
	18.2	6.0		6.2	0.229	66	45	6.4		
Al.sulfate + NaOH mixed before addition	14.4	4.1		8.2	0.409	120	80	4.2		
	14.4	4.4		4.3	0.146	31	15	4.5		
	14.4	4.6		3.0	0.090	24	6	4.7		
	14.4	4.8		2.2	0.060	12	2	5.0		
	14.4	8.0		9.8	0.483	148	125	8.3		
	14.4	9.6		10.7	0.532	145	140	9.8		
Raw water:	0	6.5		12.4	0.498	131	113	6.5		
	4.5	5.8		9.2	0.409	128	92	6.2		
	4.5	5.6		2.8	0.081	20	9	5.8		
	4.5	4.2			0.328	121	58	4.3	4.10	+ 688
	4.5	4.4			0.268	88	40	4.4	3.60	+ 760
	4.5	4.5			0.192	52	24	4.5	2.80	+ 772
	4.5	4.6			0.140	42	15	4.6	1.90	-
	4.5	4.8			0.070	29	7	4.8	0.90	+ 596
	4.5	4.8			0.060	36	9	5.1	0.47	+ 488
	4.5	5.4			0.060	27	9	5.8	0.10	+ 240
	4.5	5.8			0.070	40	12	6.1	0.10	+ 61
	4.5	6.5			0.357	155	88	6.7	2.10	- 196
	6	6.0					3.0	5.9		
	7.2	4.9		2.5	0.066	19	7	5.1		
	7.2	5.5		6.9	0.292	75	61	6.1		
	10.8	4.4			0.076	24	8	4.6	7.20	+1070
	10.8	4.6			0.060	19	7	4.7	2.30	+ 888
	10.8	4.8			0.051	18	5	4.8	0.90	+ 728
	10.8	5.3			0.037	14	3	5.5	0.12	+ 180
	10.8	5.8			0.040	10	7	6.1	0.02	+ 280
	10.8	6.8			0.051	15	5	6.7	0.11	- 8
	10.8	8.1			0.387	143	100	7.9	6.90	- 176
	11.3	5.0		2.4	0.059	14	4	5.1		
	13.5	6.0		2.3	0.053	14	4	6.0		
	14.4	4.6			0.071	18	9	4.7	5.40	+1060
	14.4	4.7			0.059	15	7	4.8	3.30	+ 912
	14.4	4.9			0.048	10	5	4.9	2.20	+ 712
	14.4	5.2			0.050	13	7		0.34	+ 400
	14.4	5.6			0.032	9	4	5.9	0.02	+ 40
	14.4	6.4			0.036	9	4	6.6	0.01	- 144
	14.4	8.0			0.233	162	58	7.8	5.00	- 228
	15.8	5.9		2.0	0.051	4	4	6.0		
	18.0	4.6			0.063	13	6	4.7	4.30	+ 980
	18.0	4.7			0.044	9	4	4.8	1.70	+ 752
	18.0	5.0			0.040	7	3	5.0	0.59	+ 524
	18.0	5.4			0.020	10	7	5.4	0.11	+ 328
	18.0	6.0			0.032	7	2	6.3	0.03	- 64
	18.0	6.1		2.2	0.053	10	4	6.6		
	18.0	6.8			0.043	7	2	6.9	<0.01	- 124
	18.0	7.8			0.068	26	8	7.6	0.60	- 284
	50.0	4.1			0.387		77	3.80	48.0	-
	50.0	5.0			0.044		1.0	4.70	2.0	+ 528
	50.0	4.4			0.120		13	4.38	30.0	+ 960
	50.0	6.0			0.040	6.0	3.0	6.58	0.15	+ 48
	50.0	6.4			0.040	6.0	5.0	7.75	0.075	- 40
	50.0	8.9			0.080	17.0	11.5	8.83	6.70	- 148
Diluted water: (1:1)	0				0.233	52	48	5.90	0.160	- 48
	0			5.7	0.276	55	55	5.5		
	0.9	5.9		5.3	0.254	58	54	6.4		
	1.8	6.0		5.5	0.250	70	58	6.5		
	3.6	6.1		1.8	0.059	28	6	6.7		
	5.4	6.2		1.3	0.032	12	1	6.7		
	9.0	5.8		1.2	0.026	11	0	6.3		
	13.5	8.7		3.8	0.152	80	33			
	7	4.7			0.086	19	6.5	4.78	2.00	+ 700
	7	5.2			0.058	22	2.5	5.25	0.35	+ 240
	7	7.4			0.365	155	88	7.62	3.00	- 72
	7	8.7			0.502	125	122	8.60	5.60	- 167
	7	4.7			0.056	40	5.5	4.65	3.90	+ 792
	7	5.3			0.025	23	0	5.62	0.25	+ 120
	7	6.6			0.036	6	0	6.70	0.035	- 81
	7	8.1			0.081	65	13	7.97	1.45	- 120

APPENDIX 3 (Cont.)

	COAGULATION CONDITION		WATER QUALITY							
TJERNSMOTJERN	Al.sulfate dosage (mg Al/l)	pH	TURB. (NTU)	TOC (mg C/l)	UV-abs. 253.7 nm (cm^{-1})	Color (mg Pt/l)		pH	Al (mg Al/l)	Colloid charge (meq/l.10^4)
						Unfiltr.	Filtr.			
Raw water	0	6.2	0.64	12.6	0.550	130	110	6.2		
Al.sulfate + NaOH mixed before addition	0.9	5.5	3.2	11.5	0.470	130	90	5.9		
	1.8	5.5		11.5	0.430	130	81	5.9		
	4.5	4.9	4.8	7.1	0.280	125	26	5.2		
	9.0	4.0	3.9	5.2	0.096	65	7	5.1		
	18.0	5.9	4.2	5.7	0.190	83	4	6.5		
Raw water	0	6.3			0.360	65.0			0.250	- 98
10 min. mixing at 100 RPM	4.5	4.8			0.090	22.0	6.5	4.75	1.900	+ 550
	4.5	4.9			0.070	7.5	5.5	4.87	1.05	+ 458
	4.5	5.1			0.070	7.0	2.0	5.20	0.450	+ 221
	4.5	5.4			0.060	9.5	3.0	5.52	0.100	+ 90
	4.5	5.7			0.060	10.0	2.5	5.90	0.060	- 10
	4.5	6.4			0.140	81.0	24.0	6.35	0.900	- 30
	2.3	5.9		9.7	0.389	110	70	6.4		
	3.4	4.6			0.252	68	31	4.7	2.30	+ 676
	3.4	4.7			0.201	51	21	4.8	1.50	+ 640
	3.4	4.9			0.155	40	16	4.9	1.00	+ 548
	3.4	5.8			0.208	123	36	6.1	0.65	+ 260
	3.4	6.7			0.440	131	92	6.8	2.40	- 132
	3.4	8.1			0.481	125	98	8.0	3.00	- 304
	3.4	5.3			0.116	41	6	5.3	0.37	+ 128
	4.5	4.5			0.312	80	48	4.6	3.60	+ 960
	4.5	4.5			0.179	36	19	4.7	2.00	+ 792
	4.5	4.9			0.120	23	11	5.2	0.63	+ 512
	4.5	5.1			0.110	35	12	5.2	1.05	+ 520
	4.5	5.4			0.090	31	8.5	5.7	0.175	+ 200
	4.5	5.6			0.090	26	8.0	5.9	0.090	+ 96
	4.5	6.0			0.260	170	51	6.5	1.60	+ 260
	4.5	6.7			0.387	155	80	7.2	2.50	- 64
	4.5	7.2			0.432	150	95	7.6	2.90	- 208
	4.5	8.1			0.509	135	110	8.2	3.90	- 222
	4.5	5.6		4.0	0.097	21	10	6.2		
	7.2	5.8		3.5	0.073	16	6	6.3		
	10.8	5.4		3.7	0.060	14	3	5.9		
Raw water	0	7.0		12.7	0.469	100	95			
	10.8	4.2		7.3	0.314	110	40	4.4		
	10.8	4.4		4.0	0.125	25	9	4.7		
	10.8	4.5		3.3	0.075	19	6	4.8		
	10.8	4.8		3.2	0.081	17	5	5.0		
	10.8	6.0		4.1	0.091	14	8	6.5		
	10.8	7.7		7.2	0.216	140	41	7.7		
Raw water	0			15.3	0.565	105	100	4.7		- 428
	10.8	4.4		5.2	0.119	23	8	4.7		+ 727
	10.8	4.8		4.5	0.081	15	5	5.0		+ 260
	10.8	5.3		4.3	0.075	13	3	5.9		+ 70
	10.8	6.0		5.3	0.111	20	10	6.6		+ 70
	10.8	7.0		11.4	0.325	160	60	7.5		- 70
	10.8	7.6		11.8	0.425	140	83	8.0		- 280
	10.8	4.4			0.276	80	33	4.4	8.00	+ 609
	10.8	4.7			0.089	19	5	4.7	2.70	+ 548
	10.8	5.2			0.066	10	<1	5.2	0.32	+ 188
	10.8	6.7			0.076	10	3	6.5	0.05	+ 122
	10.8	7.1			0.116	30	9	7.2	0.27	+ 152
	14.4	5.5		3.0	0.051	9	1	5.8		
	18.0	5.8		3.0	0.060	9	5	6.2		
	18.0	4.5			0.088	14	6	4.7	2.9	+ 888
	18.0	4.7			0.086	11	8	4.8	1.6	+ 716
	18.0	5.1			0.071	10	8	5.2	0.27	+ 340
	18.0	5.5			0.073	10	8	5.8	0.08	+ 192
	18.0	6.2			0.076	11	9	6.5	0.05	- 8
	18.0	6.7			0.085	12	10	7.1	0.09	- 124
	18.0	8.1			0.202	148	50	7.9	2.6	- 156
	50.0	4.1			0.190	35	19.0	3.92	42.5	+1320
	50.0	4.3			0.100	15.4	5.0	4.30	18.5	+1040
	50.0	5.2			0.050	3.5	1.0	5.15	0.065	+ 148
	50.0	5.9			0.060	3.0	1.5	5.95	0.065	- 52
	50.0	6.3			0.070	5.0	3.0	6.25	0.300	- 120
	50.0	8.6			0.120	18.0	12.5	8.35	6.300	- 200

APPENDIX 3 (Cont.)

	COAGULATION CONDITION		WATER QUALITY						
Raw water: SMÅPUTTEN	Al.sulfate dosage (mg Al/l)	pH	TURB. (NTU)	TOC (mg C/l)	UV-abs. 253.7 nm (cm^{-1})	Color (mg Pt/l)		pH	Al (mg Al/l)
						Unfiltr.	Filtr.		
Raw water	0	6.7		5.9	0.260	50			
	3	5.7		2.4	0.051	24	5	6.1	
	5	5.4		2.1	0.036	55	3	5.7	
	7	5.5		1.9	0.036	15	2	5.8	
	9	5.5		1.8	0.037	12	2	5.9	
	12	5.4		2.0	0.035	11	2	5.8	
Raw water	0			6.4	0.264	45	44	6.6	0.080
	0.5	5.6		5.9	0.252	45	42	5.8	0.540
	1.0	5.6		3.3	0.240	48	40	5.9	1.080
	1.5	5.5		2.8	0.097	66	10	5.9	0.260
	2.0	5.5		2.1	0.071	60	5	5.8	0.190
	2.5	5.4		2.1	0.056	24	3	5.7	0.210
Raw water	0	6.6	1.1		0.337	93,5	-		
	0.5	5.6	1.3		0.328	72	86	5.8	
	1.0	5.6	2.0		0.310	69	82	5.7	
	1.5	5.6	1.8		0.143	63	32	6.0	
	2.0	5.7	1.7		0.086	76	28	6.0	
	2.5	5.7	2.0		0.076	79	28	6.0	
	3.0	5.7	1.7		0.058	82	24	6.0	
	3.5	5.5	1.3		0.056	84	19	6.0	
	4.0	5.6	1.2		0.036	82	15	5.9	
	5.0	5.7	1.1		0.066	66	27	5.9	
	6.0	5.6	0.3		0.039	77	10	5.8	
	8.0	5.5	0.8		0.034	91	12	5.8	
	10.0	5.5	0.4		0.039	58	6	5.7	
	3.0	4.1	0.6		0.162	82	24	4.3	
	3.0	4.9	0.6		0.066	85	13	4.9	
	3.0	5.5	1.1		0.056	85	22	5.7	
	3.0	6.2	0.7		0.076	81	24	6.3	
	3.0	7.6	1.8		0.187	53	60	7.1	
	3.0	10.4	1.0		0.280	65	108	10.1	
	3.0	5.5		-	0.048	29	3	6.0	0.090
	3.0	5.8		1.9	0.048	25	2	6.1	0.070
	3.0	8.0		3.8	0.119	35	15	7.7	0.690
	3.0	5.0		2.0	0.056	28	3	5.3	0.590
	3.0	4.1		3.1	0.094	27	8	4.7	1.860
	3.0	3.7	0.73		0.143	33	17	3.9	
	3.0	4.9	1.70		0.056	31	3	5.1	
	3.0	5.9	2.0		0.059	33	3	6.2	
	3.0	6.0	1.7		0.056	29	1	6.3	
	3.0	6.1	2.0		0.060	36	3	6.4	
	3.0	6.1	1.7		0.070	28	11	6.8	

APPENDIX 3 (Cont.)

	COAGULATION CONDITION		TREATED WATER							
Raw water: DRAGSJØEN	Al.sulfate-dosage (mg Al/l)	pH	TURB (NTU)	TOC (mg C/l)	UV-abs. 253.7 nm (cm^{-1})	Color (mg Pt/l)		pH	Al (mg Al/l)	Colloid charge (meq/l·10^{4})
						Unfiltr.	Filtr.			
	0	6.0	4.1	9.6	0.43	131	81	-		- 280
	0.9	5.2	4.2	9.2	0.40	150	73	5.7		- 234
	1.8	5.1	7.3	7.0	0.25	190	66	5.0		- 22
	4.5	4.7	7.5	6.3	0.25	205	33	4.5		+ 234
	9.0	4.6	7.1	6.8	0.25	168	51	4.4		+ 254
	18.0	4.5	6.0	7.0	0.27	175	42	4.3		+ 454
	0.9*	5.7	3.8	9.4	0.41	137	77	5.8		- 234
	1.8*	5.5	5.3	7.7	0.32	136	66	5.4		- 118
	4.5*	5.3	5.2	5.7	0.18	91	33	5.0		+ 106
	9.0*	5.3	5.5	5.0	0.15	107	14	5.2		+ 64
	18.0*	5.3	4.0	3.7	0.095	72	10	5.1		+ 144
	0.9	5.7	3.9		0.41	125	75	5.9		- 184
	1.8	4.8	6.1		0.24	130	26	5.2		+ 26
	1.5	4.4	4.9		0.24	86	30	4.3		+ 254
	9.0	4.3	5.8		0.24	95	30	4.3		+ 466
	18.0	4.2	5.0		0.27	100	39	4.2		+ 502
	0.9*	5.5		7.5	0.38	120	65	5.6		
	1.8*	5.1		6.3	0.29	126	48	5.4		
	4.5*	4.7		4.5	0.17	90	16	4.7		
	9.0*	4.5		3.7	0.13	60	15	4.6		
	18.0*	5.7		4.0	0.15	110	23	6.3		

* Al.sulfate + NaOH mixed before addition.

APPENDIX 4

CALCULATION OF G VALUES FOR THE ELECROCHEMICAL PROCESS.

System 1, the pilot scale unit, 42 Al electrodes with an electrode distance of 1 cm. The volume between the electrodes, V= 3.0,1.4· 42 l = 50.4 l

The water depth in v_2 direction equaled 1.5 cm, $Q_{max}=9.2\cdot10^{-5}$ m^3/sek.

v_1 is crossing a surface of, $0.1\cdot4=\underline{0.4}$ dm^2

$$\Rightarrow v_1=\frac{9.2\cdot10^{-5}}{0.4\cdot10^{-2}}=\underline{2.3\cdot10^{-2}}\ \text{m/sek.}\ (2.3\ \text{cm/sek.})$$

v_2 is crossing a surface of, $0.15\cdot4=\underline{0.6\ dm^2}$

$$v_2=\frac{9.2\cdot10^{-5}}{0.6\cdot10^{-2}}=1.5\cdot10^{-2}\ \text{m/sek.}\ (1.5\ \text{cm/sek.})$$

$$D_h=\frac{0.4\cdot4\cdot0.01}{2\cdot(0.01+0.4)}=\underline{0.02}\ \text{m}$$

$$\Delta h_t=(n-1+\frac{1}{40}\cdot\frac{L}{D_h})\cdot v_2^2/2g+n\cdot v_1^2/2g=(42+\frac{1}{40}\cdot\frac{43.0.3}{0.02})\cdot\frac{(1.5\cdot10^{-2})^2}{2.9.8}+$$

$$\frac{43\cdot(2.3\cdot10^{-2})^2}{2.9.8}=0.00183\ \text{m}=\underline{18.3\cdot10^{-4}}\ \text{m}$$

$$G=\sqrt{\frac{Q\cdot\rho_1\cdot g\cdot\Delta h_t}{V\cdot\mu}}=\sqrt{\frac{9.2\cdot10^{-5}.10^3.9.8\cdot18.3\cdot10^{-4}}{50.4\cdot10^{-3}\cdot1.3.10^{-3}}}=5$$

$$\Rightarrow\bar{G}t=5\cdot\frac{50.4\cdot10^{-3}}{9.2.10^{-5}}=\underline{2740}$$

System 2, the pilot scale unit. The maximum water flow was increased.

$Q_{max}=\underline{19.6\cdot10^{-5}}$ m^3/sek.

$\Rightarrow v_1=\underline{4.9\cdot10^{-2}}$ m/sek. $v_2=\underline{3.2.10^{-2}}$ m/sek.

$\Delta h_t=\underline{84.1.10^{-4}\text{m}}$ $\Rightarrow$ $6=\underline{10.8}$ $\Rightarrow$ $\bar{G}t=\underline{5892}$

System 3, same unit, the pumping capacity reduced the water flow.

Qmax= 144 l/h = $4\cdot10^{-5}$ m^3/sek.

$\Rightarrow$ $v_1=\underline{1.10^{-2}}$ m/sek., $v_2=\underline{0.67}$ m/sek.

$\Delta h_t=\underline{3.5.10^{-4}}$m $\Rightarrow$ G=2.2 $\Rightarrow$ $\bar{G}t=\underline{1202}$

APPENDIX 5

DISCUSSION ON THE COLLOIDAL CHARGE ANALYSIS

Some of the problems associated with the method will be described here.

For some samples the endpoint has been more difficult to determine than for others. Several parallel samples had to be titrated in order to find an exact value. Both glycol chitosan and methyl glycol chitosan were used. Glycol chitosan was preferred. According to Kawamura and Tanaka (1966) , glycol chitosan is a polyamine with each monomer unit having one NH_2 group. It is a weak base. We could not see how this affected the results.

Another problem registered was the biological growth observed in the glycol chitosan. This fungi growth can be avoided by storage in refrigerator.

Another problem observed was the difficulties associated with the dissolution of the glycol chitosan (GC). In order to make a homogeneous solution, we had to filter the solution through GF/C filter. The gelatinous consistence of the solution complicated the filtration. The GC was by an other occasion freeze dried to simplify the dissolution, without success. Raw water and treated water samples were analysed for colloidal charge. Both filtered and unfiltered samples were analysed without showing any difference in the results.

The method is very interesting, but there are several aspects, as mentioned, making it hard to discuss the results. The method should be further investigated in regard to colored waters. Use of other chemicals and indicators might give better results in respect to the end-point detection.

VITA

Eilen Arctander Vik, born February 12, 1952.

Education

1971	Holtet High School, Oslo, Norway.
1975	Chemical Engineer, Technical University of Trondheim, Norway.
1980	Master of Science in Engineering. University of Washington, Seattle, Washington, USA.

Professional Societies

Norwegian Society of Chartered Engineers (NIF)
Norwegian Society for Water Conservation and Water Hygiene
American Water Works Association (AWWA)

Experience

1980-1982 Norwegian Institute for Water Research (NIVA), Oslo, Norway.

During this period I was working full-time on my research project, treatment of potable water containing humus by electrolytic addition of aluminum. The work was done with Arild S. Eikum and Egil T. Gjessing of NIVA as supervisors.

1979-1980 I was on leave from Norwegian Institute for Water Research (NIVA) for 15 months, doing graduate work at the University of Washington, Seattle, Wash. I finished the M.Sc. degree in June 1980 and continued on a doctoral program. I completed my general examination in Dec. 1980. During this period in Seattle I concentrated my work on potable water research.

1976-1979 Norwegian Institute for Water Research (NIVA), Oslo, Norway.

From 1976 to 1979 I was the principal investigator in several projects on advanced wastewater treatment, including biological and chemical treatment, using activated sludge, biodisc, trickling filter, and chemical treatment with conventional aluminum sulfate addition, and physical treatment using filtration. I was also involved in a project investigating the experience from use of simultaneous precipitation. The work on filtration was carried out in close cooperation with the Nordic Research Group in NORDFORSK, "Operation of Treatment Plants".

Publications

1. Vik, E.A. og Lundar, A. (1977): Biologisk rensing med fastsittende kulturer i kombinasjon med kjemisk felling. NIVA 0-40/71-K, PRA 2.1, juli.

2. Vik, E.A. (1977): Bruk av biorotor/rislefilter med etterfølgende felling, aktuelle biologiske rensetrinn i Norge? NIVA's årbok, 143-150.

3. Vik, E.A. (1978): Filtrering av avløpsvann fra kloakkrenseanlegg. Resultater fra pilotforsøk på Hovemoen renseanlegg. HPB-17/76 NTNF's Utvalg for drift av renseanlegg, april.

4. Vik. E.A. (1978): Basis for research and preliminary results on wastewater filtration. NIVA's årbok, 89-95.

5. Vik, E.A. (1978): Summary of preliminary results on wastewater filtration. VANN No. 4, 287-296.

6. Vik, E.A. (1979): Filtrering av avløpsvann fra kloakkrenseanlegg. Erfaringer fra kloakkrenseanlegg med filtrering i England, Sverige og Danmark. HPB-17/76, NTNF's Utvalg for drift av renseanlegg, september.

7. Vik, E.A. og Lygren, E. (1979): Filtrering av avløpsvann fra kloakkrenseanlegg. Forsøk i halvteknisk målestokk. HPB-17/76 NTNF's Utvalg for drift av renseanlegg, november.

8. Vråle, L. og Vik, E.A. (1979): Driftsresultater fra norske simultanfellingsanlegg. NIVA C2-28, VA-2/79, juli.

9. Vik, E.A. (1979): Bruk av direktfiltrering for fjerning av partikulært materiale og patogene organismer (Giardia lamblia). Notat XT-25 NIVA, desember.

10. Vik, E.A. (1980): Rapid Granular Media Filtration. Notat XT-25 NIVA, mars.

11. Vik, E.A. (1980): Important Aspects of Water Treatment in USA. University of Washington, NIVA XT-25, VA-10/80, juli.

12. Vik, E.A. (1981): Treatment of Potable Water Containing Humus by Electrolytic Addition of Aluminum Followed by Direct Filtration. Research Proposal, NIVA F-80415, VA-1/81.

13. Fiksdal, L., Vik, E.A., Mills, A., and Staley, J.T. (1982): Nonstandard methods for enumerating bacteria in drinking water. JAWWA.74:6:313.