Department of Civil & Environmental Engineering University of Delaware

SEPARATION OF COLLOIDAL PARTICLES FROM GROUNDWATER BY CROSS-FLOW ELECTRO-FILTRATION PROCESS FOR IMPROVING THE ANALYSIS OF LEAD (YEAR III)



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## SEPARATION OF COLLOIDAL PARTICLES FROM GROUNDWATER BY CROSS-FLOW ELECTRO-FILTRATION PROCESS FOR IMPROVING THE ANALYSIS OF LEAD (YEAR III)

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## TABLE OF SYMBOLS

A:	Area, m <sup>2</sup> .
C:	Number of particles per unit volume, m <sup>-3</sup> .
$ ilde{C}_i$ :	Initial number of particles per unit volume at $x = 0$ , $m^{-3}$ .
$\tilde{C}_{L}$ :	Final number of particles per unit volume at $x = L$ , $m^{-3}$ .
$\tilde{C}_x$ :	Number of particles per unit volume at x position, $m^{-3}$ .
d <sub>p</sub> :	Particle diameter, m.
E:	Electric field strength, V/m.
E <sub>m</sub> :	Mean electric field strength, V/m.
f:	Fraction.
L:	Length, m.
N:	Total number of particles.
p:	Perimeter, m.
Q:	Volumetric flow rate, m <sup>2</sup> /s.
$Q_c$ :	Volumetric flow rate of concentrate, $m^3/s$ .
$Q_{f}$ :	Volumetric flow rate of filtrate, m <sup>3</sup> /s.
q:	Charge, C.
${\widetilde{q}}_{\scriptscriptstyle vi}$ :	Charge density, $C/m^3$ .
$\widetilde{q}_{_{vL}}$ :	Initial charge density at $x = 0$ , C/m <sup>3</sup> .
$\widetilde{q}_{\scriptscriptstyle vx}$ :	Final charge density at $x = L$ , $C/m^3$ .
q <sub>vx</sub> :	Charge density at x position, $C/m^3$ .
r:	Radius, m.
r <sub>I</sub> :	Inner radius, m.
r <sub>o</sub> :	Otter radius, m.
$\widetilde{V}$ :	Voltage, V.
v <sub>p</sub> :	Particle velocity, m/s.
v <sub>r</sub> :	Velocity at x direction, m/s.
v <sub>t</sub> :	Terrminal velocity, m/s.
V <sub>X</sub>	Velocity at x direction, m/s.
X:	Distance from bottom of CFEF to control surface, m.
η:	Removal efficiency.
ε:	Dielectric constant, $C^2/J \cdot m$ .
$\epsilon_0$ :	Permittivity constant, $8.85 \times 10^{-12} \text{ C}^2/\text{J} \cdot \text{m}$ .
ε <sub>r</sub> :	Dielectric constant of medium.
μ:	Dynamic viscosity, kg/m·s.
к:	Conductivity, mho.
ρ:	Density, kg/m <sup>3</sup> .

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## **EXECUTIVE SUMMARY**

Soil contamination by heavy metals in general and lead in particular is a potential pollution problem for the underlying ground water. Like most heavy metals, lead in the soil-water system is mostly associated with solid particulates, especially colloids which covers particle size from 0.01 to 10  $\mu$ m. Since the particulate material is small, it is easily disturbed and often introduced into water samples during sampling operations. This is especially true for new monitoring wells, as the particulates are unstable and present at abundant quantities. In contrast, this group of fine particulates generally does not occur in supply wells. The presence of fine particulates in water samples of monitoring wells can trigger unnecessary site investigation.

NJDEP (New Jersey Department of Environmental Protection) has used a low flow purging technique to minimize the introduction of particulates in groundwater samples. This technique is effective, but it is slow (with a pumping rate of 0.5 to 5 mL/min) and therefore is rather expensive. Filtration is another way to separate the soluble from the insoluble (particulates) fraction of lead in groundwater samples. However, there is concern that the filter (currently only 0.45  $\mu$ m filters are used.) will collect the colloidal materials. This will not only exclude the naturally occurring colloids in the analysis of lead in groundwater, but also cause great difficulties in the filtration process.

The major goal of this research project was to develop an innovative solid-liquid separation technique for the determination of heavy metal in groundwater exemplified by lead. The technique should be capable of separating the naturally occurring colloids into several size fractions with ease. The following were specific objectives: 1) to design and operate a crossflow electro-filtration (CFEF) process for the separation of naturally occurring colloids from the groundwater. An instrument based on the principle of cross-flow electro-filtration process was to be constructed and operated. The CFEF unit will eliminate all problems associated with conventional dead-end filtration process; 2) to study the major factors controlling the operation of the crossflow electrofiltration process. Factors such as filtration rate, applied field strength, influent water quality; membrane type and characteristics that may affect the performance of the CFEF unit were to be evaluated. Performance of the CFEF process were to be assessed in terms of effluent quality, rejection, flux rate, and backwash; 3) to study the use of the crossflow electrofiltration (CFEF) as a means to improve lead determination in the groundwater. The effectiveness of the CFEF process on the speciation of lead in groundwater was to be compared with low-flow-purging technique and conventional bailer sampling method.

Naturally occurring colloidal particles of interest are generally negatively charged. In the presence of an electrostatic field, the particles can be collected on the surface of a countered electrode. A prototype cross-flow electro-filtration system (CFEF) was constructed to separate colloidal particles at selected size and surface charge levels. The CFEF module consisted of an external tube, an inner cathodic filter membrane (circular shape), and a co-centric anodic rod. The cathode/filter and the anode collector were connected to a d.c. power supply that provided the electric field. By adjusting the applied field across the cathode and the anode, it is possible to differentiate the colloidal particles into various size and surface charge fractions. The external tube has a diameter of 8.9 cm, the inner filter has a diameter of 3.0 cm and the co-centric piece is

a 0.5-cm stainless piece. The total module is 22.5 cm long and has a total filtration surface area of 212 cm<sup>2</sup>. A power supply (Model: E861, Consort, Belgium) with a maximum output of 600 volts d.c. at 1 amp was used to provide the electric field across the membrane. The CFEF filter unit is fed from a Milipore<sup>TM</sup> cross flow module, model ProFlux M12. Pressure sensors were installed at the inlet and outlet of filtrate and concentrate. A computer with necessary software was used to control the filtration rate and flow direction and continually record the pressure of inlet and outlet streams.

Two model colloid particles,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, and naturally colloidal particles collected from New Jersey wells were selected in this research. The particles were chosen primarily for their size and surface charge characteristics. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was obtained from the Degussa Company (Darmstadt, Germany). The colloidal silica (SiO<sub>2</sub>) was obtained from the Nissan Chemical Industries, Ltd. (Chiba, Japan). The naturally occurring colloids were collected from the well waters sampled with low-flow-purging, bailer, and high-flow-purging techniques at the Denzer-Schaefer site, Toms River, New Jersey.

Experiments were conducted to evaluate the performance of the CFEF module under various conditions specifically, solid concentration, and applied voltage. The suspension pH was altered to pre-selected values using NaOH (0.1 M) or HCl (0.1 M). No other chemical dispersants were added. The following performance characteristics were evaluated: (1) clogging, (2) flux production, (3) quality of flux, and (4) backwash frequency. The degree of filter clogging can be measured in terms of several properties including pressure drop and water quality of the filtrate, i.e. turbidity. During the course of the filtration, the pressure of the system was monitored continuously. Laboratory experiments were run under the following conditions: (1) filtration rate, (2) particle concentration, (3) initial electrostatic field applied, and (4) pH. The filtration rate was from 2.4 to  $14.2 \text{ cm}^3/\text{cm}^2$ -min, the particle concentration was from 50 to 427 mg/L, and the electrostatic field strength applied was from 0 to 156.5 V/cm.

Each experiment was run until both filtrate and concentrate turbidity (i.e. total solid concentration) reached a "steady state" - since a true steady state was not always reached, for the sake of practicality, it was taken when the turbidity was reduced by less than 2 % over a tenminute period. If the filtrate and concentrate turbidity were not stabilized by this time, the experiment was continued until a steady flow in the rejection stream was achieved. During filtration experiments, samples were withdrawn periodically from both the filtrate and the concentrate streams. The pH and the conductivity of the feed tank, the concentrate and the filtrate streams were monitored during filtration. The pressure and pumping rate were continuously monitored by a PC (personal computer). The temperature of the suspension solution (influent) was maintained at approximately 25°C during each test.

Results indicate that the prototype CFEF unit functions properly. There is no clogging problem encountered and therefore no need to backwash the CFEF unit under the experimental conditions of this study. Naturally occurring particles collected from water samples are negatively charged under the pH condition of the groundwater. The pH<sub>zpc</sub> was approximately 1 to 2. The surface charge of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is positive under acidic condition. The pH<sub>zpc</sub> of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 9.2. All particle samples appear to be monodispered. The average particle size of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and naturally occurring particles were in the range of 300 to 727 nm. For  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, in the concentration range between 50 and 200 mg/L, there is no distinct difference in solid removal efficiency. The removal rate of nano-sized colloidal particles increased as the applied electrostatic field strength increased. Naturally occurring particles collected from groundwater samples were mixed with model colloidal silica (SiO<sub>2</sub>) to prepare a bimodal particle size

distribution system. Results indicate that the proportion of larger particle size (i.e. naturally occurring particles) decreased as the electrostatic field strength increased. On the other hand, the proportion of smaller particle (i.e. colloidal silica) increased as the electrostatic field increased. Base on the results, it is clear that we can successfully separate particles of different size using the CFEF module.

Many authors have attempted to describe the mathematical aspect of cross-flow filtration using both the film theory and the resistance-in-series model. However, these authors did not include the transportation of charged particles in describing the characteristics of the CFEF. The analysis of particle trajectories of nano-sized colloids in a filter chamber is of great importance in the design and operation of crossflow electrofiltration system. A mathematical model to predict the transport of nano-sized particles in CFEF unit was developed. A sensitivity analysis of the transport model was conducted as to assess the effect of pertinent parameters, such as particle size, surface charge, and applied electric field strength on model behavior. The model results agree well with those obtained experimentally. Based on model and experimental results, it is possible to predict the separation of the naturally occurring particles by adjusting the pH (or surface charge) and/or applied electrostatic field of the CFEF unit.

Well water samples were taken from both #10 and #5S wells at the Denzer-Schaefer site, Toms River, New Jersey. Low-flow-purging, bailing, and high-flow-purging techniques were used. The flow rate of low-flow-purging and the high-flow-purging were 0.1 and 5 L/min, respectively. As expected, results indicate that water-sampling methods can strongly affect the particle size distribution, total solid content and ultimately the total lead concentration. Apparently the disturbance caused by bailing and high-flow-purging brings about high total solid concentration in the water samples. Results also show that lead is closely associated with colloid. The larger the concentration of total solid the greater was the lead concentration in the water samples. The water samples were filtered using the CFEF unit at various field strength (which controls particle size) and pH (which controls surface charge). Generally, the lead concentration increases with increase in applied field strength, that is, the smaller the particles the greater the metal concentration content is regardless of sampling method.

The form of lead associated with the colloidal material was further characterized using sequential chemical extraction procedures, which further separate the particulate lead into several fractions including exchangeable, carbonate, Fe/Mn oxide, organic and residual phases. The particles in well water samples were separated into several size fractions using the cross-flow electro-filtration process (CFEF). The distribution of lead in these particles was analyzed by the sequential chemical extraction method also. The results show that the distribution of lead in the above fractions (Pb speciation) is similar among the three well water samples. For well #5S and #10 water samples, two features of the lead data are obvious. A small percentage of the total lead was in the easily mobile, exchangeable or bound to carbonate fractions. At other extreme, greater than 80% of the lead was found in the residual or the organic fraction. Results also show that lead concentrations increase with increasing electrostatic field. Clearly, this indicates that the distribution of lead in particles of different size is different. The CFEF process can be an important technique for the speciation of various chemical constituents in natural water, i.e., groundwater. Moreover, CFEF is able to separate naturally colloidal particles without operational difficulties such as clogging; the most common operational problem of filtration is eliminated.

Results presented in this research project provide insight into the performance and the separation mechanism of the CFEF module, and lead speciation in groundwater system. There is

great prospect to replace current slow-purging technique with this CFEF process in groundwater monitoring for the purpose of site remediation. It is first to characterize the particles in the water sample of interest for particle size distribution and surface charge (e.g. zeta potential measurements). Given the size of particles to be included in the analysis for total concentration of chemical constituents, one can calculate the threshold field strength necessary for the separation of particles of this specific size fraction. Once this threshold electrical field strength is identified for specific groundwater system, the CFEF module can be readily deployed.

However, in order to fully deploy this system, further improvement of the CFEF module and continued data collection are needed. The following are but three possible future research needs. (1) **Improvement of the CFEF module**. The current version of the CFEF module can only be operated with partial automation of flow rate control. The operation of the CFEF module by and large is not completely automatic. The current CFEF unit can be upgraded for total automation. For examples, on-line monitoring devices, e.g. turbidity meter, size analysis equipment, and conductivity meter etc can be added. (2) **Scaling down the size of the CFEF module**. The dimension of the whole CFEF system is  $110 \times 70 \times 90$  cm (LxWxH). This is too large to carry around for field work. Based on the mathematical model developed in this research, it is possible to successfully predict the transport of particles in the CFEF unit. A scale-downed CFEF unit would prove to be handy for field applications. (3) **Field demonstration.** More field data collection and demonstration is necessary as to establish the long-term performance and reliability of the CFEF module. Information on the distribution of total chemical constituents as a function of applied field strength will be useful to further verify the theoretical calculations.

#### CHAPTER 1

## INTRODUCTION

## **1.1** Rationale and Scope of Research

Chemical constituents in water can be readily divided into soluble (or dissolved) and insoluble (or particulate) fractions. This is done generally by filtering the water sample through a filter membrane of specific cut-off pore size (currently 0.45  $\mu$ m pore size). Due to the small size, colloids tend to clog the filter media, form filter cake and render filtration difficult or even impossible. Furthermore, deposition of colloids on the filter will increase the chemical concentration, e.g. lead, in the particulate fraction (Horowitz et al. 1996).

Numerous studies have demonstrated that the presence of colloidal materials in groundwater may facilitate the transport of organic and inorganic contaminants (Sheppard et al. 1979; Means and Wijayaratne 1982; Takayanagi and Wong 1983; Chiou et al. 1986). Colloidal materials having a diameter in the range of 0.01 to 10 µm may originate from macromolecular components of dissolved organic carbons, such as humic acids, biological materials, and micro-emulsions of non aqueous phase liquids (NAPL) and weathering products. The effects of colloidal materials on the transport and the distribution of contaminants in the saturated zone depend on the nature of interactions between the contaminants and the colloids, the groundwater, and the soil matrix. As a general rule, metals tend to attach onto negatively charged colloids.

Conventional groundwater sampling procedures stress speedy pumping and rely on filtration to separate the particulate matters, or the insoluble chemical species of interest. The validity of the such samples is therefore questionable (Kearl et al. 1992). Vigorous bailing of groundwater samples may increase oxygen concentrations and disturb particles and colloids in the influence zone. This agitation of the monitoring well may generate additional colloids or particulate associated with organic and inorganic chemicals of concern. It is generally accepted that the water in the well casing may not be representative of the formation water, so it needs to be purged prior to water samples collection. Traditional sampling methods rely on purging and sampling with bailers or high speed pumps to remove 3-5 well casing volumes. This can lead to excessive drawdown, accelerated groundwater flow, aeration of well water, stirring up of sediments in the well, and abrasion of the well casing. Following the purge, there is a cursory evaluation of water quality stability, usually pH, temperature, and specific conductivity (Puls and Barcelona 1996). This sampling practice tends to disturb colloidal materials and bring them into water samples. The water is generally filtered, especially for metal analysis, then analyzed for dissolved constituents of interest. Current technique uses 0.45-µm filters to separate the soluble from the particulate chemical constituents (U.S. Environmental Protection Agency 1983; APHA et al. 1989; ASTM 1995). According to this current method, particles collected will include colloidal materials between 0.01 and 0.45 µm and exclude the 0.45- to 10-µm portion of colloids in the determination of soluble lead. It is difficult to filter groundwater that contains particles in the submicron size range. Moreover, a number of factors associated with the filtration process such as the pore size (e.g., diameter), type of membrane, sample volume, and concentration of suspended particles can produce significant variations in the determination of "dissolved" metals (i.e. Fe, Al, Cu, Zn, Pb, Co, and Ni). The bulk of these variations result from the inclusion/exclusion of colloidally associated elements in the filtrate, although dilution and sorption/desorption from filters also may be factors. Thus, dissolved trace element concentrations quantified by analyzing filtrates generated by processing the whole water sample through similar pore-sized filters may not be the same as or comparable to those being filtered (Horowitz et al. 1996).

Low-flow-purging sampling was developed to allow the collection of samples while causing as little disturbance in the well and the surrounding formation as possible, and the collection of water samples while continuously observing stability parameters during purging. In this manner, representative unfiltered samples can be collected. The major feature of the low-flow-purging method is the velocity at which water enters the pump intake and that is imparted to the formation pore water in the immediate vicinity of the well screen (Puls and Barcelona 1996). Soil contamination by lead can cause potential groundwater pollution problems. Lead in solid-water systems is mostly associated with the solids, i.e. colloidal or particulate state. During site investigation water samples are taken from monitoring wells for chemical analysis, e.g., lead. Particulate materials in water can range from 1 to 5,000  $\mu$ m whereas, colloidal materials range from 0.01 to 10  $\mu$ m. There is an overlap of particles in the size range of 1 to 10  $\mu$ m that has resulted in the rejection of filtered data. This complicates the process in segregating dissolved and particulate matter. An investigation of the overlap pore size may result in protocol that would allow the use of filtered samples in site investigations. It is proposed that lead contaminated groundwater samples from wells containing high particulate levels be subjected to a series of filtration using filters in the size range of from 0.45 to 10  $\mu$ m. An acceptable filtering procedure would be one that eliminates the presence of artificially introduced particulate materials while still allowing naturally occurring colloid materials to be included in the chemical analysis of water.

Traditional methods depend on speed pumping and bailing. This sampling practice tends to disturb colloidal materials and bring them into water samples. The water is generally filtered, especially for metal analysis, then analyzed for dissolved constituents of the interest. Current technique uses 0.45-µm filters to separate the soluble from the particulate chemical constituents (U.S. Environmental Protection Agency 1983; APHA et al. 1989; ASTM 1995). This will include colloidal materials between 0.01 and 0.45 µm and exclude the 0.45- to 10-µm portion of colloids in the determination of soluble lead. Finally, the use of the term "soluble" to describe the chemical concentrations associated with filtered water is obviously misleading and should be discontinued (Horowitz et al. 1996). Moreover, it is difficult to filter groundwater that contains particles in the submicron size range. Although the low-flow-purging technique can minimize the introduction of particulates into groundwater samples, it is also slow and expensive.

In order to characterize the lead speciation in groundwater, it is necessary to separate the colloids into various size fractions then analyze the lead content in each individual fraction

separately. Specifically, it is necessary to separate the colloidal materials over the size range of 0.01 to 10  $\mu$ m without any operational difficulty.

#### **1.2 Literature Review**

## **1.2.1** Groundwater Sampling Technique

## 1.2.1.1 Background

Environmental groundwater monitoring is a relatively new practice. The earliest work borrowed information and methods from the field of water supply well monitoring. However, the water quality monitoring goals for water supply wells are much different from most of monitoring wells. With time, it became apparent that water well practices did not always satisfy the special requirements of environmental monitoring. One of the greatest disparities is in the water-bearing units. Water supply wells tap the best available aquifer, whereas, environmental monitoring wells are located in the critically impacted geologic area, usually irrespective of its actual ability to produce water.

One of the issues of sampling these formations is the role of colloids with respect to contaminant transport. Low-flow-purging sampling was developed for collecting water samples that are as undisturbed and representative as possible without filtration, thereby giving true and accurate information regarding water quality, including the colloidal content.

The goal of groundwater sampling is to collect water samples that are as representative of the groundwater as possible. The contribution to water samples from turbidity made by conventional well purging and water sampling techniques has generated much interest in the environmental sector. Vigorous removal of groundwater in a typical monitoring well will likely mobilize otherwise stable particulates and may also create artificial colloids by changes in dissolved gases or the breakup of larger colloids.

The traditional bailer sampling or pumping may increase the concentration of colloidassociated metals and hydrophobic organic compounds in groundwater samples. Alternative approaches to groundwater sampling suggest a procedure to minimize the introduction of otherwise immobile colloids into wells by slow and prolonged pumping. Low-flow-purging sampling was developed to allow for the collection of water samples while causing as little disturbance in the well and the surrounding formation as possible, and the collection of water samples with continuous observations of stability parameters during purging. In this manner, ideal representative unfiltered samples can be collected. The major feature of the low-flow-purging method is the velocity at which water enters the pump intake and is imparted to the formation (Puls and Barcelona 1996). However, this technique is slow and expensive.

#### **1.2.1.2** Hydrogeological Effects on Samples

While traditional sampling techniques can adversely affect the quality of collected water samples because of the presence of artificially generated turbidity. Additionally hydrogeological effects also can confound our understanding of the true contaminant distributions and concentrations.

Mixing water, both the contaminated and the uncontaminated, in both the subsurface and the monitoring well can occur when purging and sampling are improperly performed. This problem is manifested further with longer well screens, higher pump rates, bailing, and when variable stratigraphy exists across the screened interval. Long well screens tend to distribute the contaminant concentration over the vertical screen dimension, i.e., over the screen length. This is because traditional sampling techniques simultaneously pull water from all zones that the screen intersects, both contaminated and uncontaminated. This may be satisfactory if the desired result is a concentration integrated over a fairly large volume of the aquifer. It yields little information, however, about plume thickness or contaminant concentration gradients within the actual plume.

The problem can be worsened by stratigraphic variations that result in zones of high natural groundwater flow layered with less permeable zones across the screened interval. In these

situations, the water is transferred preferentially into the well casing from the higher permeability flow zones, whether or not these are the zones of maximum contaminant.

#### **1.2.1.3** Colloidal Transport

Numerous studies have demonstrated that the presence of colloidal materials in groundwater may facilitate the transport of organic and inorganic contaminants (Sheppard et al. 1979; Means and Wijayaratne 1982; Takayanagi and Wong 1983; Chiou et al. 1986; Puls et al. 1991). Colloidal materials with diameter in the range of 0.01 to 10 µm may originate from macromolecular components of dissolved organic carbon, such as humic substances, biologic materials, and micro-emulsions of non-aqueous phase liquids (NAPLs), or from inorganic mineral precipitates and weathering materials. The effect that colloidal materials may have on the distribution and transport of contaminants in the saturated zone depends on the highly charged colloids.

Conventional groundwater sampling procedures stress speed in purging and sampling and rely on filtration to remove turbidity. The representation of the resulting samples is questionable. Vigorous bailing of groundwater samples to develop and sample wells may increase oxygen concentrations and alter redox potentials as well as physically disturb particles and colloids in the influence zone of the well. The agitation of a monitoring well during bailing (in conjunction with other physical/chemical effects) may generate additional colloids or particulates with adsorbed organic and inorganic chemicals of concern.

## 1.2.1.4 Traditional Methods

It is generally accepted that the water in the well casing may not be representative of the formation water, so it needs to be purged prior to collection. Traditional methods stress speed and tendency of maintaining the status quo. Traditional sampling methods rely on purging and sampling using bailers or high-speed pumps to removal 3 to 5 well casing volumes. This can lead to excessive drawdown, accelerated groundwater flow, aeration of water in the well, stirring

up of sediments, and abrasion of the well casing. Following the purge, there is a cursory evaluation of water quality stability – usually pH, temperature, and specific conductance – which have been shown to be poor indicators of the actual variation between "stagnant" well water and "fresh" formation water.

Finally, the water samples are collected; these samples need to be filtered to remove the excess turbidity. Usually, only samples required water quality analysis are filtered. Filtration is done using a default pore filter size (typically 0.45  $\mu$ m) that is the mid-size range of colloids. This default particle size does not take into account site-specific factors, which might include contaminant transport by colloids larger than 0.45  $\mu$ m or the presence of organic contaminants on colloids. Figure 1.1 shows the process flow scheme of the traditional groundwater sampling methods.

#### 1.2.1.5 Low-Flow-Purging Sampling Protocols

Low-flow-purging sampling technique was developed to allow for the collection of water samples while causing as little disturbance in the well and the surrounding formation as possible. In order to enable the collection of water samples, continuous observations of stability parameters during purging is needed as to obtain representative unfiltered samples.

Low-flow-purging sampling is somewhat misleading, because the important factors are the velocity at which water enters the pump intake and how water imparts the formation. It does not necessarily relate to the rate at which water is discharged from the pump. Water level drawdown in the well during purging and sampling provides the best indication of the degree of stress imparted by the sampling process. Therefore, the change in water level is an indicator of stabilization of the well water.

The pumping rate should be stable and specific to the well being sampled. The pump discharge should be set at a rate that minimizes drawdown. Typically, flow rate is 0.1 to 0.5 L/min, but for coarser formations higher flow rates are allowable as long as little or no drawdown is desirable.



Figure 1.1 Traditional groundwater sampling methods for soluble chemical constituents.

Low-flow-purging should be done with the pump intake located in the middle or slightly above the middle of the screened interval. These methods often bring about groundwater stabilization with the removal of 1 to 3 well volumes. In formations of high-hydraulic-conductivity and with dedicated equipment, the well may stabilize as soon as the water in the pump is purged, because natural groundwater flow is constantly purging the water in the well and the low-flow-purging method creates little or no mixing in water above the screen.

Water quality stabilization is determined by observing the trends of a number of parameters that are measured and evaluated in the field during purging. Water quality stabilization is achieved when these specific parameters remain constant. It is not necessary to have or even consider "purging" and "stabilization" as separate steps. Measurements of field parameters can begin as soon as the pumping rate is stabilized. Stabilization of field parameters include pH, specific conductance, redox potential, dissolved oxygen, temperature, and turbidity. Of these, pH and temperature are the two parameters to reach stabilization first, and turbidity is the last parameter to stabilize. Many regulators use 10 NTU (nephelometric turbidity units) as the stabilization criterion, even though natural turbidity in groundwater at a site may be much higher than 10 NTU.

Low-flow-purging sampling can be performed using either dedicated or portable equipment. The advantages of dedicated equipment include low disturbances in the well (which is an overall goal of the method), less purge water, less decontamination, and less setup time. However, dedicated equipment requires a high initial investment. Low-flow-purging sampling data may be comparable to historical data collected by traditional methods from a site. Although the sample collection method should be linked to the data, **h**e data from the two methods can probably be correlated, and the necessity for using low-flow-purging method should be re-examined. However, if the data collected by low-flow-purging methods are different from historical data collected by traditional methods are different from historical data should be noted as questionable.

However, low-flow-purging sampling is neither simple nor ecnomic. It is likely that sampling will take more field time, more accessory equipment, and more documentation. Naturally occurring colloidal particles in sample water are often produced by various processes during the well purging procedure (Ryan and Gschwend 1990; Puls et al. 1991; Kearl et al. 1992; Backhus et al. 1993). The aforementioned process can increase in shear as a result of the increased flow velocity in response to pumping, the surging effect in the well screen from the introduction of the pump, scraping the sides of the well bore, agitating sediments settled at the bottom of the well, and chemical changes in response to pumping (Gibs et al. 2000).

#### **1.2.2 Low-Flow-Purging Sampling Protocols**

#### **1.2.2.1** Sampling Recommendation

Water samples should not be taken immediately following well development. Sufficient time should be allowed for the groundwater flow regime in the vicinity of the monitoring well to stabilize and to approach chemical equilibrium with the construction materials of the well. The lag time will depend on site conditions and methods of installation but often exceeds one week.

Well purging is nearly always necessary to obtain water samples flowing through the geologic formations in the screened intervals. Rather than using a general but arbitrary guideline of purging three casing volumes prior to sampling, it is recommended that an in-line water quality measurement device (e.g., flow-through cell) be used to establish the stabilization time for several parameters (e.g., pH, specific conductance, redox, dissolved oxygen, and turbidity) on a well specific basis. Data on pumping rate, drawdown, and volume required for parameter stabilization can be used as a guide for conducting subsequent sampling activities.

The following are recommendations before, during and after sampling (Kearl et al. 1992; Backhus et al. 1993; Puls and Barcelona 1996; Gibs et al. 2000; Ivahnenko et al. 2001):

- 1. Use low-flow rates (< 0.5 L/min), during both purging and sampling to maintain minimal drawdown in the well;
- 2. Maximize tubing wall thickness, minimize tubing length;
- 3. Place the sampling device intake at the desired sampling point;
- 4. Minimize disturbances of the stagnant water column above the screened interval during water level measurement and sampling device insertion;
- 5. Make proper adjustments to stabilize the flow rate as soon as possible;
- 6. Monitor water quality indicators during purging;
- 7. Collect unfiltered samples to estimate contaminant loading and transport potential in the subsurface system.

#### **1.2.2.2 Equipment Calibration**

Prior to sampling, all sampling device and monitoring equipment should be calibrated according to manufacture's recommendations.

Calibration of pH should be performed with at least two buffers which bracket the expected range. Dissolved oxygen calibration must be corrected for local barometric readings and elevation.

### 1.2.2.3 Water Level Measurement and Monitoring

It is recommended that a device be used which will least disturb the water surface in the casing. Well depth should be obtained from the well logs. Measuring to the bottom of the well casing will only cause re-suspension of settled solids from the formation and require longer purging times for turbidity equilibration. Measure well depth after water sampling is completed. The water level measurement should be taken from a permanent reference point, which is surveyed relative to ground elevation.

## 1.2.2.4 Pumping Type

The use of low flow (e.g., 0.1 - 0.5 L/min) pumps is suggested for purging and sampling for all types of analyses. All pumps have some limitations and these should be investigated with respect to application at a particular site. Bailers are inappropriate devices for low flow sampling.

#### 1.2.2.4.1 General Considerations

There are no unusual requirements for groundwater sampling devices when using low flow, minimal drawdown techniques. The major concern is that the device gives consistent results and minimal disturbance of the sample across a range of low flow rates (i.e., < 0.5 L/min). Clearly, pumping rates cause minimal to no drawdown in one well could easily cause significant drawdown in another well finished in a less transmissive formation. The pump should not cause under pressure or temperature changes or physical disturbance on the water sample over a

reasonable sampling range. Consistency in operation is critical to meet accuracy and precision goals.

#### 1.2.2.4.2 Advantages and Disadvantages of Sampling Devices

A variety of sampling devices are available for low flow (minimal drawdown) purging and sampling, which include peristaltic pumps, bladder pumps, electrical submersible pumps, and gas-driven pumps. Devices, which lend themselves to both dedication and consistent operation at definable low flow rates, are preferred. It is desirable that the pump be easily adjustable and operates reliably at these lower flow rates. The peristaltic pump is limited to shallow applications and can cause degassing resulting in alteration of pH, alkalinity, and some volatile loss. Gas-driven pumps should be of a type that does not allow the gas to be in direct contact with the sampled fluid.

Clearly, bailers and other grab type samplers are ill-suited for low flow sampling since they will cause repeated disturbance and mixing of stagnant water in the casing and dynamic water in the screened interval. Similarly, the use of inertial lift foot-valve type samplers may cause too much disturbance at the point of sampling. Use of these devices also tends to introduce uncontrolled and unacceptable operator variability.

## 1.2.2.5 Pump Installation

Any portable sampling device should be slowly and carefully lowered to the middle of the screened interval or slightly above the middle (e.g., 1 - 1.5 m below the top of a 3-m screen). This is to minimize excessive mixing of the stagnant water in the casing above the screen with the screened interval zone water, and to minimize resuspension of solids, which will have been collected at the bottom of the well. These two disturbance effects have been shown to directly affect the time required for purging. There also appears to be a direct correlation between the size of portable sampling devices relative to the well bore and resulting purge volumes and times. The key is to minimize disturbance of water and solids in the well casing.

## 1.2.2.6 Filtration

Although filtration may be appropriate, it may cause a number of unintentended changes to occur (e.g., oxidation, aeration) possibly leading to filtration-induced artifacts during sample analysis and uncertainty in the results. Note that this step was avoided in this study.

### 1.2.2.7 Monitoring of Water Level and Water Quality Indicator Parameter

Check water level periodically to monitor drawdown in the well as a guide to flow rate adjustment. The goal is minimal drawdown (< 0.1 m) during purging. This goal may be difficult to achieve under some circumstance due to geologic heterogeneities within the screened interval, and may require adjustment based on site-specific conditions and personal experience. The water quality indicators monitored can include pH, redox potential, conductivity, dissolved oxygen (DO) and turbidity. The last three parameters are often most sensitive. Pumping rate, drawdown, and the time or volume required to obtain stabilization of parameter readings can be used as a future guide to purge the well. Measurements should be taken every three to five minutes if the above-suggested rates are used. Stabilization is achieved after all parameters remain constant in three successive readings. In lieu of measuring all five parameters, a minimum subset would include pH, conductivity, and turbidity or DO. Three successive readings should be within  $\pm 0.1$  for pH,  $\pm 3\%$  for conductivity,  $\pm 10$  mv for redox potential, and  $\pm 10\%$  for turbidity and DO. Trends for stabilized purging parameters are generally obvious and follow either an exponential or asymptotic change to stable values during purging. Dissolved oxygen and turbidity usually require the longest time for stabilization. The above stabilization guidelines are provided for rough estimates based on experience.

## 1.2.2.8 Sampling, Sample Containers and Preservation

Upon parameter stabilization, sampling can begin. Sampling flow rate may remain at established purge rate or may be adjusted slightly to minimize aeration, bubble formation, turbulent filling of sample bottles or loss of volatizes due to extended residence time in tubing. Typically, flow rates less than 0.5 L/min are appropriate. The same device should be used for

sampling as was used for purging. Sampling should occur in a progression from the least to the most contaminated well. Generally (e.g.,  $Fe^{2+}$ ,  $CH_4$ ,  $H_2S/HS^-$ , alkalinity) parameters should be sampled first. The sequence in which samples for most inorganic parameters are collected is immaterial unless filtered (dissolved) samples are desired.

The appropriate sample container will be prepared in advance of actual sample collection for the analyses of interest and include sample preservative where necessary. Water samples should be collected directly into this container from the pump tubing. Immediately after a sample bottle has been filled, it must be preserved as specified in the site. Sample preservation requirements are based on the analyses being performed. It may be advisable to add preservatives to sample bottles in a controlled setting prior to entering the field in order to reduce the chances of improperly preserving sample bottles or introducing field contaminants into a sample bottle while adding the preservatives.

After a sample container has been filled with groundwater, a cap is screwed on tightly to prevent the container from leaking. A sample label is filled out. The samples should be stored inverted at 4°C.

#### **1.2.2.9** Blanks

The following blanks should be collected:

- Field blank: One field blank should be collected from each source water (distilled/deionized water) used for sampling equipment decontamination or for assisting well development procedures.
- Equipment blank: One equipment blank should be taken prior to the commencement of field work, from each set of sampling equipment to be used for that day.
- Trip blank: A trip blank is required to accompany each volatile sample shipment. These blanks are prepared in the laboratory by filling a 40-mL volatile organic analysis (VOA) bottle with distilled/deionized water.

## 1.2.3 Cross-Flow Electro-Filtration Process

#### 1.2.3.1 Filtration

Filtration is pressure-driven separation process. The task of separating solids from liquids is important in nearly every field of industrial production including waste water treatment and environmental protection, mineral processing industry, i.e., coal and ore, basic chemicals and synthetic fertilizer, dye and pigment chemistry, biotechnology, biomedicine, food industry, and drinking water treatment (Iritani et al. 1992; Weber and Stahl 2002).

Filtration is an accepted technique for separation of solid-liquid system. However, one of the major bottlenecks in the application of the filtration process is the flux decline due to membrane fouling. Such flux decline is mainly to the formation of highly resistant filter cake caused by accumulation of the colloidal or the proteinanceous solutes on the membrane surface (Iritani et al. 1991; Iritani et al. 2000). The formation of these layers reduces the permeate flux and can make the process uneconomic to operate due to either low permeate fluxes or the need to replace membranes too frequently. In order to maintain a high filtration rate for an extended period of time, therefore, it would be necessary to prevent a continuous buildup of solutes on the filtering surface. Various techniques have been developed to reduce or prevent polarization and fouling. Indeed, various ingenious techniques have been developed for reducing the amount of cake forming; including crossflow filtration (Iritani et al. 1991), dynamic filtration with rotating cylindrical membrane (Murase et al. 1989), upward and inclined filtration (Iritani et al. 1991; Iritani et al. 1992; Iritani et al. 2000). Crossflow filtration is a technique developed to minimize accumulation of the dispersed phase on the membrane.

## 1.2.3.2 Cross-Flow Filtration

Crossflow membrane filtration was originally deployed to reduce concentration polarization by utilizing hydrodynamic forces to hinder solute deposition at the membrane surface. This technique was developed by Zhevnovatyi (Turkson et al. 1989/90). In 1970 Bechhold found by experiments that in the filtration of colloidal and very fine suspensions a flow parallel to the filter medium increases the filtrate volume before the filter medium is blocked due to a compact layer formation. Bechhold used a stirred filtration cell to create the shear flow across the filter media (Altmann and Ripperger 1997). The cross-flow filtration technique involves the feed stream being pumped at a relatively high velocity parallel to a membrane surface. This helps to reduce the concentration polarization by thinning the boundary thickness and by assisting in sweeping away the filter cake or gel layer film (filter cake refers to colloidal particles and gel layer to macromolecules). Today crossflow filtration is a standard operation in many medical and technical applications. A flow parallel to the filter medium reduces the formation of the layer and keeps it at a low level. So it is possible to get a quasi-stationary filtrate flow for a long time (Altmann and Ripperger 1997).

The crossflow filtration is influenced by a great number of parameters, e.g. crossflow velocity, transmembrane pressure, membrane resistance, layer resistance, size distribution of the suspended particles, particle form, agglomeration behavior and surface effect of the particles etc (Altmann and Ripperger 1997).

Crossflow filtration was conceived as a means of removing liquid from a suspension rapidly by preventing cake formation at the filter surface. Cake formation prevented by using adequate crossflow velocities to induce high shear rates across the filter septum; crossflow velocities of 3 m/s were quite usual in the earlier days of crossflow filtration, but the failure of the shear generated by these velocities to increase permeate (filtrate) rates has led industry to use increasingly higher crossflow velocities until today when 4 to 7 m/s is quite usual (Wakeman and Tasleton 1991).

In the crossflow filtration, the suspension flows parallel over the membrane, and the permeate flows normally through the membrane because of the transmembrane pressure. Particles flow into the direction of the membrane, too, where they are retained and form the filter cake. Particle deposition on the layer is mostly an irreversible process (Altmann and Ripperger 1997). Adhesive and friction forces are dominating on a deposited particle. The effect can be concluded from experiments: the build-up of the layer is a continual process, while the removal

of the layer only takes place by removing large agglomerates or large layer fragment (Altmann and Ripperger 1997). Only large particles, agglomerate and layer fragments can be detached from the layer (Altmann and Ripperger 1997). The filter cake increases the flow resistance and considerably reduces the specific permeate rate. It could be shown that fine particles are deposited at the membrane even for high crossflow velocities (Altmann and Ripperger 1997). Fine particles increase the resistance, which in turn decreases the permeate rate further.

Because the flow resistance increases with decreasing particle size, the mechanical filtration of fine particle suspensions is time-consuming. When the formation rate of these layers is reduced, the permeate flux, dramatically increases and can make the process uneconomic to operate due to either low permeate fluxes or the need to replace membranes too frequently. In many instances these high shear rates do not prevent contamination of the surface and can actually further decrease permeation rates (Wakeman and Tasleton 1991; Altmann and Ripperger 1997). However, because of the limitations of achieving sufficiently high crossflow velocities and the inevitability of membrane/solute interactions, concentration polarization can still take place.

Various other techniques, including the use of abrasives and filter aids, backwashing and backpulsing, flow reversal and pulsed crossflows have been devised to reduce the effects of the fouling layers. These techniques generally lead to reduced membrane lifetime or to complicate the filter operating cycle, both of which are undesirable (Wakeman and Tasleton 1991).

The other techniques to reduce these foulants (Radovich and Sparks 1980) including using turbulence promoters, chemically modifying the membrane surface, or employing additional force field (e.g. electric field or acoustic) inside the filter. Coupling of two or more force fields can enhance the permeate flux. Rotating membranes (Rushton and Zhang 1988; Park et al. 1994), crossflow electro- (Henry et al. 1977; Wakeman and Tarleton 1987; Bowen et al. 1989; Bowen 1992; Bowen and Sabuni 1994; Wakeman and Sabri 1995; Akay and Wakeman 1996) or acoustic (Muralidhara et al. 1985; Muralidhara and Senapati 1986) and cross-flow electro-acoustic (Belfort 1987; Wakeman and Tasleton 1991; Tarleton and Wakeman 1995) filtrations

represent important applications of external force field superimposed orthogonally on the main hydrodynamic field in order to enhance permeate flux. Pulsatile flows represent an axial superimposition of two flow fields (Belfort et al. 1994). Pulsatile flows, on the other hand, can be considered to be the axial superimposition of two flow field (Burgmayer and Murray 1982; Misra and Varanasi 1991). The effect of superimposed sonic fields in enhancing permeate flux is not solute selective but that of the electric field can be solute selective (Wakeman 1998).

When particle size becomes small, the ratio of particle surface area to volume increases. It becomes advantageous to use surface properties, like surface charge, for solid-liquid separation processes. Therefore, charge characteristics of particles are known to play an important role in solid-liquid separation processes (Lo et al. 1983).

Due to the selectivity of an electric field based on particle or solutes charge sign and density, the concentration of various solutes or particles in permeate will depend on the charge structure of the solute or particles. The effect of enhancing permeate flux by an electric field can be solute or particle selective and is best suited to the filtration of charged solutes (Wakeman 1998).

Electro-filtration of aqueous dispersions can be have many applications including chemical manufacturing, water purification, food processing, medicine and radioactive industry (Veselov 1983; Il'in and Kolesnikov 2001). Electro-filtration equipment is much more efficient than settlers, which makes it possible to reduce the treatment time by a factor of 10 to 20 and decrease the area occupied by the equipment by a factor of 3 to 5 (Il'in and Kolesnikov 2001). There have been numerous reports on the use of electrochemical techniques to assist membrane processes in a preventative role by stopping membranes from becoming fouled and in a restorative role by assisting the cleaning of membranes that are already fouled, or by enabling the selective separation of species based on charge and size (Henry et al. 1977; Huotari et al. 1999; Webster et al. 2000; Zhang et al. 2000).

An applied electric field is established between the electrodes of appropriate polarity usually so that the membrane is in proximity to a negative field since most particles of interest in aqueous solution are negative charged. Crossflow membrane filtration enhanced by a d.c. (direct current) electric field, i.e., electro-filtration has been investigated from the seventies (Henry et al. 1977). The industrial adoption of crossflow filtration in the 1980's as a means of slurry dewatering recently has been focused more on using the electrophoretic effects to reduce fouling of the filter (Henry et al. 1977; Lee et al. 1980; Yukawa et al. 1983; Verdegan 1986; Wakeman and Tarleton 1987).

In electro-filtration, the accumulation of the solutes on the membrane surface is limited by the imposed electrophoretic force. Fouling can be reduced progressively by increasing the electric field strength to induce an electrophoretic velocity to the particles in the feed stream in a direction away from the filter surface. The extent of the increase in permeate rates as a result of imposing the electric field is ultimately dependent on the particle size and the charge density around its surface. In addition, the filtration rate through the filter cake is dramatically enhanced due to electroosmosis as a secondary electrokinetic phenomenon. This method is best suited to the separation of nano-sized colloids since their surface charge changes according the solution pH and ionic strength.

#### **1.2.3.3** Cross-Flow Electro-Filtration

Cross-flow electro-filtration is a hybrid separation process, which combines crossflow filtration and electrophoretic separation devices (Bier 1959; Yukawa et al. 1983; Radovich et al. 1985; Wakeman and Tarleton 1987). In crossflow filtration, a filter cake is formed on the membrane during filtration. This cake acts as an additional resistance to filtration and significantly decreases the high initial permeate flow rate thereby the efficiency of the process. Like a conventional crossflow filter, the influent flow of contaminated fluid is directed parallel to the filter media surface. In **h**is case, as particles in suspensions carry an electric charge, it is possible, by means of a suitable superposition of the crossflow filtration with an electric field, to prevent or reduce cake formation, and to considerably increase the stationary permeate rate. In cross-flow electro-filtration a d.c. electric field is applied normal to this surface. If the field is of sufficient strength and proper polarity, charged particles will migrate away from the media
surface by electrophoresis, giving rise to a clear boundary layer. Particle-free fluid can then be withdrawn through the media.

In theory, the behavior of a cross-flow electro-filtration toward charged particles should approximate that of the mythical ideal filter. Nearly complete separation should be obtained for particles of all sizes without a corresponding increase in pressure drop. From the standpoint of electrophoretic separation, it is immaterial whether the contaminant is an ion or a grain of sand, as long as it has sufficient charge. Since the contaminant does not come in direct contact with the media, no increase in pressure drop should be observed; hence cross-flow electro-filtration should be characterized by extremely long service intervals. Cross-flow electro-filtration offers great promise in reducing the fouling problems associated with charged particles and colloids (Wakeman and Tasleton 1991).

The cross-flow filtration process has been investigated extensively. Manegold was the first to study the process of combining conventional pressure filtration and electrophoresis (Manegold 1937). It was not until 1977 when Henry provided a fundamental analysis of the cross-flow electrofiltration process (Henry et al. 1977). Moulik applied an electrostatic field to microfilters and reported excellent removal of colloidal particles such as bentonite and algal cells (Moulik 1976).

Archer et al (1993) designed an electrode capable of generating non-uniform electric fields over a large surface area to separate yeast cells from water. They reported that a linear relationship between dielectrophoretic collection and pulse length over the range 0 to 100 second. Lo et al. (1983) separated  $Al_2O_3$  colloids from non-aqueous solution using cross-flow electrofiltration process. The effect of feed rate, driving pressure, and electrical field strength on the filtration rate and total solid deposition rate on the collection electrode was evaluated. Results indicate that the extent of filter fouling was greatly decreased in crossflow electrofiltration.

Majmudar and Manohar (1994) reported the separation of  $TiO_2$  from aqueous solution by electrophoretic filtration. Experiments were carried out at various voltages and flow rates. It

was observed that voltage lower than 10 V and higher than 50 V was largely inefficient in solid separation. The optimal conditions were 15 V and 200-mL/h flow rate. It was further observed that 96% separation was the maximum obtainable.

Wakeman and Sabri (1995) reported that direct current electric fields reduce cake formation in cross-flow membrane filtration. Operating parameters such as filtration pressure, cross-flow velocity, electric field gradient, pH and feed concentration can affect filter performance. Verdegan (1986) studied the separation of fine particles (<10 µm) from nonpolar liquids by crossflow electrofiltration process. He reported that crossflow electrofiltration has many distinct advantages over conventional separation processes: high removal for all particle sizes, long life, and minimal power requirement. Akay and Wakeman (1996) reported enhanced removal of a double chain cationic surfactant (diocatadecyldimethlammonium chloride) in water using the crossflow electrofiltration process. Wakeman (1998) reported electrophoretically assisted crossflow microfiltration of bovine serum albumin (BSA), ovalbumin and denatured lactalbmin. It is shown that steady state flux is higher when an electric field is applied than it is with conventional crossflow microfiltration. The flux is almost independent of the membrane pore size. Finer pore sizes enable steady state flux and rejection conditions to be reached sooner. von Zumbusch et al. (1998) reported that the alternating electric field diminished membrane fouling and hence yields a higher specific filtrate flux. The effect of the electric field was dependent on frequency (0.5-50)Hz), field strength (0-80 V-cm<sup>-1</sup>), conductivity (1-10 mS<sup>-1</sup>), and protein concentration (0.1-5 w%). Low frequency and high field strength yield the best results for electroultrafiltration with alternating current (a. c.) fields. The effectiveness of the electric field increases with rising conductivity to the point where a limiting electrolytic current is reached. Increasing protein concentration diminishes the effect of the electric field.

Houtain et al. (1999) reported that applying an electrostatic field to crossflow filtration could greatly increase the flux rate. Weigert et al. (1999) conducted the first pilot plant study on microfiltration of mineral and biological slurries with cross-flow filtration, coupled with constant and pulsed fields and reported that the specific permeate rate markedly increased compared to

that without an electrostatic field. For mineral slurry, the increase in flux rate was more than 10 fold. An estimation of the specific energy input further demonstrates the cost-effectiveness of this technique.

## **1.2.4** The Chemistry of Lead in the Environment

## **1.2.4.1** Lead in the Environment

Lead has been an important metal in human society for many thousand years. Unique physical characteristics such as low melting point, good workability and durability made lead a popular construction material in our early society. The use of lead pipe for water transmission of the Roman Empire is a significant example. Lead has also been used over the year as a glaze on pottery, in cosmetics and as a wine sweetener.

The use of lead, however, has increased dramatically since the early days of industrial revolution. Annual lead production has stabilized at a rate of 2.5 million tons per year. As many as 40 counties worldwide have workable lead deposits, with Russia, USA, Australia and Canada (ca. 60% of the total) being the four major lead producing countries. Mining, smelting and refining of lead, as well as the production and use of lead-based products tend to release lead into This takes the form primarily of either lead-laden waste streams, or the environment. atmospheric emissions in the forms of fume and dusts. A large part of the lead discharged into surface waters is rapidly incorporated into suspended and bottom sediments and most of this lead will ultimately be found in the marine sediments. Of greater concern, however, is the emission of lead into the atmosphere. The finer aerosol particles may be transported long distance from their sources before deposition onto land or sea. Although the magnitude of the resulting pollution is very small at large distances, significant concentrations in soils and vegetation can occur close to a major lead source, such as a smelter or busy highway. Most of this lead will ultimately be found in marine sediments. When incorporated in the soil, lead is of very low mobility. Hence once contaminated, the soil remained polluted with lead.

Soils contamination by lead can cause potential groundwater pollution problems. Stumm and Bilinski divided the lead species into three group: "soluble" (<  $0.001 \ \mu$ m), "colloidal" ( $0.001 \ 1 \ \mu$ m) and " particulate" (> 1  $\mu$ m) (Stumm and Bilinski 1972) (Table 1.1). Soluble lead species are free lead ion, ion pairs or organic complexes. Colloidal lead species are those bound to organic ligands of high molecular weight and those adsorbed on colloids such as hydrous oxides of Mn or Fe. Particulate lead species are those incorporated with organic particles, remains of microorganisms, and lead precipitates.

## 1.2.4.2 Aqueous Chemistry of Lead

Lead is a heavy metal with an atomic weight of 207.2. In its neutral state it contains 82 neutrons, protons and electrons. In aquatic systems Pb usually loses two of the 6p electrons giving it a net charge of +2. The remaining  $6s^2$  electrons are the outer shell electrons that exist as a lone pair of electrons. This lone pair has significant influence on the reactivity and coordination of Pb<sup>2+</sup> ions. Lead can also lose both 6s electrons under severe oxidizing conditions giving it a net positive charge of +4. Lead (IV) is not very stable in most environments; thus, the divalent form usually controls the fate of Pb in aqueous geochemical conditions. Since Pb is a strongly sorbed, its solubility is low at ambient pH, most natural waters have low concentrations of aqueous Pb. In fact, a significant amount of Pb in waterways may exist in an undissolved state, and is being transported as colloidal particles (Hem 1976).

The solution concentration of Pb in natural waters with pH nears seven is normally less than 10  $\mu$ g/L (Hem 1976). The common species of aqueous Pb in acid soils are Pb<sup>2+</sup>, organic-Pb, PbSO<sub>4</sub><sup>0</sup> and PbHCO<sup>3+</sup>, and for alkaline soils PbHCO<sub>3</sub><sup>0</sup>, PbHCO<sup>3+</sup>, organic-Pb, Pb(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>, and PbOH<sup>+</sup> (Sposito 1989). The behavior of Pb in solution is largely governed by the size (ionic radius = 1.2 Å), valence and electronegativity of the ion. These characteristics contribute to the strength and number of water molecules surrounding the Pb atom (the hydration number for Pb is between 5 to 8) (Burgess 1978). Lead is considered a type B metal, or a soft sphere ion, which

Group	Soluble		Colloidal				Particulate
Size	1 nm	-	10 nm	-	100 nm	-	1000 nm
Metal Species	Free metal ions	Inorganic ion pairs: Organic Chelates	Organic complexes	Metal species bound to high molecular weight organic material	Metal species adsorbed on colloids	Metals incorporated with organic particles and remains of living organisms	Mineral solids: Metal adsorbed on solids; Precipitates and co- precipitates
Example	Pb <sup>2+</sup>	PbHCO <sub>3</sub> Pb-EDTA	Pb-fulvic acid	Pb-humic acid	Pb-Fe(OH) <sub>3</sub> Pb-MnO <sub>2</sub>	Pb-organic solids	Pb-clay PbCO <sub>3(S)</sub>

Table 1.1Lead Speciation in Water

Ref: Stumm and Bilinski (1972).

means that the electron sheath is easily deformed by external charges making it more polarizable than type A metals. Another classification scheme (Sparks 1995) considers Pb a soft acid, which corresponds to most type B metal. The hard and soft acid classification scheme predicts that a particular acid will have a strong affinity for its respective hard or soft base. This means that Pb will have a strong affinity to form covalent bonds with soft base. Soft bases are atoms and molecules that have a low electronegativity. These Lewis bases are easily polarized and oxidized.

Many experiments have been conducted and results show that soils form strong complexes with Pb (Zimdahl and Skogerboe 1977). This strong sorption is a result of Pb forming specific bonds with functional groups on oxides, edges of clay minerals, and organic matter. In addition Pb may form precipitates with inorganic anions of C, Cl, P, and S.

Groundwater monitoring is an important part of site remediation and environmental risk assessment. However, very little is understood of the aqueous chemistry of lead. Using 0.45  $\mu$ m filters as the criteria, lead in groundwater can be divided into "dissolved" and "particulate" fractions. As mentioned above, the "dissolved" lead includes mainly free Pb(II) and its hydrolysis species, ion-pairs, and organo-lead complexes. "Particulate" lead is collection of all lead species that are associated with particulates of greater than 0.45- $\mu$ m in diameter. Chemically, "particulate" lead can be further fractionated into the following forms: (1) adsorbed

at particle surfaces, (2) present as discrete carbonate minerals or co-precipitated with major carbonate phases, (3) occluded in iron and/or manganese oxyhydroxide, (4) bound with organic matter, in either living or detritus form, (5) bound with amorphous authigenic sulfides or in more crystalline forms, or (6) bound in lattice positions in aluminosilicates, in resistant oxides or in resistant sulfides.

Lead has a strong tendency to form ion pairs, principally  $PbHCO_3^+$  and  $PbCO_3^0$  at the pH of the most waters. The formation of lead ion pairs increased the concentration of total dissolved lead in water. Lead can also form strong complexes with organic matter such as the ill-defined humic acid and fulvic acid, and increase the concentration of lead in water.

It is known that pH plays an important role on the adsorption of lead onto hydrous ferric and manganese oxides (Gadde and Laitinen 1974). This is an important linkage in the hydrogeochemical cycle of lead. Hydrous ferric and manganese oxides are readily reduced and hence become soluble under anaerobic conditions; consequently, lead will become mobilized. However, there may be concomitant formation of metal sulfides which are even less soluble than hydrous oxides of ferric and manganese. Typically three lead compounds govern the solubility of lead in water, via the following equilibrium:

$$Pb(OH)_{2(S)} \Leftrightarrow Pb^{2+} + 2OH^{-}; K_{so} = 10^{-15.5} @ 25^{\circ}C$$

$$(1.1)$$

$$PbCO_{3(S)} \Leftrightarrow Pb^{2+} + CO_3^{2-}; K_{so} = 10^{-13.2} @ 25^{\circ}C$$
 (1.2)

$$Pb_{3}(OH)_{2}(CO_{3})_{2(S)} \Leftrightarrow Pb^{2+} + 2OH^{-} + 2CO_{3}^{2-}; K_{so} = 10^{-46.8} @ 25^{\circ}C$$
(1.3)

Conceptually, the solid material can be partitioned into specific fractions (cf. (1) to (6) above); sequential extractions with appropriate reagents can then be devised to leach successive fractions "selectively" from the particulate sample.

## **1.2.5** Sequential Extraction Process

The levels of heavy metals circulating in the environment have seriously increased during the last few decades due to various localized human activities. Heavy metals in the environment is a

major pollution concern because of their toxicity and threat to human life and the environment (Purves 1985). It is important to predict the likely mobility and bioavailability of the metals in environmental systems, as these two features are closely related to the transport of heavy metal in hydrobiological systems, namely surface waters and groundwaters. Much research has been conducted on heavy metal contamination in soils from various anthropogenic sources such as industrial wastes (Gibson and Farmer 1984), automobile emissions (Fergusson et al. 1980), mining activity (Davies and Ginnever 1979), and agricultural practice (Colbourn and Thornton 1978). Metal ions are retained by solid phases through various mechanisms, namely, ion exchange, outer- and inner-sphere surface complexation (adsorption), precipitation or coprecipitation. Most studies dealing with particulate metals in the sediment, soil and water systems are concerned with total metal concentrations. Relatively few attempts have been made to evaluate the speciation of particulate metals, i.e. partitioning among the various forms in which they might exist. The analysis of total metal may give information concerning possible enrichment of different solid samples with heavy metals, but generally, and for most elements, there are no sufficient criteria for estimating their health and ecological effects (Chakrabarti et al. 1994; Ramos et al. 1994; Holm et al. 1995). The behavior of the heavy metals in the environment (e.g., bioavailability, toxicity and mobility) cannot be predicted on the basis of their total concentrations. For example, it has been reported that the levels of heavy metals in plants are determined not only by their concentrations in soil, but also by the physiochemical properties of the soil (Xian 1989). Use of the total concentration as a criterion to assess the potential effects of soil contamination implies that all forms of a given metal have an equal impact on the environment; such assumption is clearly untenable (Tessier et al. 1979). It is, in fact, the physicochemical forms of the heavy metals that govern their potential bioavailability and remobilization.

### 1.2.5.1 Mobility and Bioavailability of Heavy Metals

The mobility and bioavailability of heavy metals are strongly dependent on their specific chemical forms and ways of binding to the solid matters, e.g. soil, sediment, sludge, and naturally occurring colloidal particle (Prudent et al. 1996; Ariza et al. 2000). Geochemical forms of heavy metals in solid matter affect their solubility, which directly influences their bioavailability (Xian 1987). Once present in water courses, metals can be taken up by freshwater plants and animals or human through drinking water supplies. To evaluate the contamination of solid matters correctly, the total amount of metals must be subdivided into their different chemical forms in order to draw conclusions as to which metals are more ready to enter the biological cycle and which metals are more firmly bound and thus less likely to enter the biological process (Campos et al. 1998). Thus, it is important to evaluate the bioavailability and mobility of heavy metals to establish environmental guidelines for potential toxic hazards and to understand chemical behavior and fate of heavy metal contaminants in solids.

#### 1.2.5.2 Chemical Speciation

It is now recognized that the quantification of the chemical forms of metals in soil, sediment, and water systems is essential to estimating the mobility and bioavailability of metals in the environment. Chemical speciation determines and identifies specific chemical species or binding forms. It allows one to estimate the bioavailability and mobility of metals and to understand their chemical behavior and fate which in turn is useful to the development of environmental guidelines for potential toxic hazards (Beckett 1989). Metals in solid matter may be present in several different geochemical phases that act as reservoirs or sinks of heavy metals in the environment (Kramer and Allen 1988; Li et al. 1995). These phases include the following broad categories: specifically adsorbed, carbonate, Fe- and Mn-oxides, organic matter, and mineral lattice (Tessier et al. 1979; Salomons and Forstner 1980; Beckett 1989). All of these fractions may occur in a variety of structural forms. However, determinations of specific chemical species are difficult and often impossible. Therefore, determinations of boarder defined form, depending

on operationally-defined procedures, can be a good compromise to provide information on the environmental risks (Tiooing et al. 1985; Tipping et al. 1985; Gulmini et al. 1994). Heavy metals present in each of these fractions have different mobilization behaviors under specific environmental conditions.

Therefore, the chemical forms of these metal contaminants in soils need to be determined in order to assess their bioavailability and mobility and long-term environmental consequences. Recently, determination of the distribution of metals among these phases has been advanced by direct and indirect chemical analytical methods. Direct methods are generally of insufficient sensitivity for environmental trace analysis (e.g. NMR spectroscopy) and require specialized equipment (e.g. EXAFS) (Glidewell and Goodman 1995). Indirect analysis has been made by phase-selective chemical extractions involving single or multiple extracting reagents.

### **1.2.5.3** Sequential Extraction Analysis

Conceptually, solid matter can be partitioned into specific fractions which can be extracted selectively by using appropriate reagents. Several experimental procedures, varying in manipulative complexity, have recently been proposed for determining the speciation of particulate trace metals. The procedures can be grouped into (i) method designed to effect the separation between residual and non-residual metals only (Jackson 1958), and (ii) more elaborate methods making use of sequential extraction. The use of sequential extraction, although more time consuming, furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, and the transport of trace metals (Tessier et al. 1979).

A widely used method for the identification and availability of heavy metals in solid matter is the leaching of solid matters by means of chemical extractants. Both single extraction (Lindsay and Norvell 1978; Leschber et al. 1985; Beckett 1989) and sequential extraction have been used (Tessier et al. 1979; Slavek and Pickering 1986; Ure et al. 1993; Ramos et al. 1994; Ma and Uren 1998). Multistep sequential extraction schemes provide a more complete picture for predicting the heavy metal distribution, mobility, and bioavailability in solid matters. The reagents utilized in the sequential extraction have been chosen on the basis of their supposed selectivity and specificity towards particular physicochemical forms, although variations in reagent strength, volume, temperature and extraction time between schemes are apparent (Li et al. 1995). Generally three to nine extractants are used in a sequence in which the earlier ones are the least aggressive and the most specific, and subsequent extractants are progressively more destructive and less specific, except that coming late in the sequence there may remain only or two groups of compounds that they can dissolve (Beckett 1989; Elliott et al. 1990). Various chemical reagents have been proposed to determine the metal species in particulates (Engler et al. 1977; Gibbs 1977; Tessier et al. 1979; Forstner and Patchineelam 1980). Regardless of the specific chemicals used, these chemicals can be divided into classes of similar chemical behavior, for example:

- Concentrated inert electrolytes (desorption of electrostatically adsorbed metals);
- Weak acids (dissolution of carbonate phases; desorption of specifically adsorbed metals);
- Complexing agents (competition for metal complexes with organic functional groups; dissolution of precipitates);
- 4. Oxidizing agents (oxidation of organic mater and sulfides);
- 5. Strong mineral acids (dissolution of resistant oxides, sulfides and aluminonsolicates).

Table 1.2 gives a list of sequential extraction procedures(Chao and Theobald 1976; Engler et al. 1977; Tessier et al. 1979; Rapin and Förstner 1983).

Although the selective sequential extraction methods are useful for obtaining information on heavy metals distributions, they are controversial from both philosophical and practical standpoints. Philosophically, selective extraction requires existence of discrete phases that may be dissolved independently. Many solid samples in fact may not contain chemically or physically distinct phases; thus element "distribution" patterns produced by extraction methods may be artifactual. In addition, even when phases are discrete, there are technical difficulties associated with achieving complete and selective dissolution and recovery of trace metals from those phases (Kheboian and Bauer 1987). A number of investigators have highlighted pitfalls in the use of sequential extraction (Nirel and Morel 1990). Three major experimental problems with sequential procedures have been recognized (1) the limited selectivity of extractants, (2) the redistribution of metals during extraction process, and (3) the deficiency of a reagent dose if metal content is too high (Tessier et al. 1979; Tipping et al. 1985; Kheboian and Bauer 1987; Dudka and Chlopecka 1990; Nirel and Morel 1990). These limitations mean that sequential extraction can not be used to determine specific geochemical associations, but the approach is still of value in the assessment of soil contamination. Sequential extraction can be used to give an indication of the amounts of metals in various reservoirs which could be mobilized by changes in environmental chemistry (notably pH or Eh) (Kennedy et al. 1997).

The amount of inaccuracy introduced to sequential extraction process by resorption has been debated in the literature (Kim and Fergusson 1991), but theoretically it may lead to a significant underestimation of bioavailability. Howard and Vandenbrink (1999) evaluated the utility of a sequential extraction process for counteracting resorption during sequential extraction analysis using sediments with a wider range in composition. They indicated that significant resorption may occur during sequential extraction analysis, thereby reducing the accuracy of the method. However, this problem may be important only at very high levels of contamination (Howard and Vandenbrink 1999). Generally it is difficult to associated a given extractant reagent with a particular physicochemical phase. Instead the specificity of an extractant is operationally

defined according to what it extracts. Therefore, most validation studies have focused on the selectivity and completeness of extraction rather than the redistribution. Emphasis was also on major species rather than trace elements (Kheboian and Bauer 1987). Keeping these limitations in mind, "operational speciation" results from sequential extractions still provide useful information on metal partitioning, beyond the simple elemental concentrations which are conventionally measured (Ho and Evans 2000).

Step	Method I	Method II	Method III	Method IV
(1)	MgCl <sub>2</sub>	NH <sub>4</sub> OAc	NH <sub>4</sub> OAc	NH <sub>2</sub> OH•HCl/HNO <sub>3</sub>
(2)	NaOAc/HOAc	NaOAc/HOAc	NH <sub>2</sub> OH•HCl	NH <sub>2</sub> OH•HCl/HCl
(3)	NH <sub>2</sub> OH•HCl/HOAc	NH <sub>2</sub> OH•HCl/HOAc	H <sub>2</sub> O <sub>2</sub> /HNO <sub>3</sub>	$Na_2S_2O_4$
(4)	H <sub>2</sub> O <sub>2</sub> /HNO <sub>3</sub>	$H_2O_2/HNO_3$	$Na_2S_2O_4$	KClO <sub>3</sub> /HCl/HNO <sub>3</sub>
(5) or (6)	HF/HClO <sub>4</sub>	HNO <sub>3</sub>	HF/HNO <sub>3</sub>	HF/HNO <sub>3</sub>

 Table 1.2
 Example of Sequential Extraction Procedures

Refs: Method I: (Tessier et al. 1979); Method II: (Rapin and Förstner 1983); Method III: (Engler et al. 1977); Method IV: (Chao and Theobald 1976).

However, several researchers have addressed the limitations of sequential extraction. These limitations include the technical difficulties associated with achieving complete and selective dissolution and recovery of trace metals from those geochemical phases in soils and sediments. For example, the overlap of chemical reagents and readsorption of trace metals during extraction. Despite these inherent limitations, the sequential extraction scheme is still a very useful method for characterizing the trace metals in solid mattes (Li et al. 1995). A large number of sequential extraction procedures have been developed. Among them, the most widely used sequential extraction method was provided by Tessier et al. (1979) and was based on the fact that different forms of heavy metals retained in soils can be extracted selectively by a series of extracting reagents (Kheboian and Bauer 1987; Li et al. 1995; Ma and Rao 1997; Lo and Yang 1998; Ariza et al. 2000). Due to the above situations, this method was selected in this study.

## 1.3 Objectives

The major objective of this research is to develop an innovative solid-liquid separation technique that will allow the use of filtered water samples in site investigation. The technique should be capable of separating the naturally occurring colloids into several size fractions with ease. The following are specific objectives:

- To design and operate a cross-flow electro-filtration (CFEF) process for the separation of naturally occurring colloids from groundwater. An instrument based on the principle of cross-flow electro-filtration process is to be constructed and operated. The CFEF unit will eliminate fouling problems associated with conventional dead-end filtration process;
- 2. To study the major factors controlling the operation of cross-flow electrofiltration process. Factors such as filtration rate, applied field strength, influent water quality, and characteristics that may affect the performance of the CFEF unit will be evaluated. Performance of the CFEF process will be assessed in terms of effluent quality, rejection, flux rate, and backwash;
- 3. To study the effect of the cross-flow electro-filtration (CFEF) on the improvement of lead determination in groundwater. The effectiveness of the CFEF process on the speciation of lead in groundwater will be compared with low-flow-purging technique and conventional bailer samples.

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#### **CHAPTER 2**

# SEPARATION OF NANO-SIZED COLLOIDAL PARTICLES BY CROSS-FLOW ELECTRO-FILTRATION PROCESS

## 2.1 Abstract

The major purpose of this research is to test the hypothesis that surface property of colloidal particle, specifically surface charge can affect the separation of nano-sized colloids. Further improvement of the separation efficiency of nano-sized colloids can be achieved by applying an appropriate electrostatic field across the membrane and the collector electrode. In the presence of an electrostatic field, the particles are collected on the surface of a counter electrode. A prototype cross-flow electro-filtration system (CFEF) was designed and used. Model colloids, e.g.,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, and naturally occurring colloidal particles collected from well water in New Jersey were used to evaluate the performance of the CFEF. Results indicate that the prototype CFEF unit functions properly. There is no clogging encountered under the experimental conditions of this study. Therefore, there is no need to backwash the CFEF unit. The removal of nano-sized colloidal particles increases as the applied electrostatic field strength increases. It is possible to effectively separate the nano-sized colloidal particles by adjusting the electrostatic field strength of the CFEF unit.

## 2.2 Introduction

Separation of nano-sized particles from liquid medium by conventional techniques such as filtration is difficult because of their small size. Based on flow pattern, filtration process can be divided into two major types: dead-end and cross-flow. In the dead-end filtration mode, both the water (flux or permeate, or filtrate) and the solid (or rejection) pass through a filter medium (or membrane) in the same direction. The flux declines significantly with time due to membrane fouling which is a potential limitation to the efficient use of dead-end filtration (Iritani et al. 2000). In the cross-flow filtration mode, the feed water and the filtrate passes the membrane in a different direction, generally, at almost a right angle. The cross-flow filtration has the intrinsic

merit of minimizing the solid contact with the filter membrane. However, since the particles of interest are of micron or nano-size, further improvement of solid separation efficiency can be made by the application of an electrostatic field. In the presence of an electrostatic field, the particles can be collected on the surface of a counter electrode, usually an anode, as most particulates in water are negatively charged.

Manegold (1937) was the first to study the process of combining conventional pressure filtration and electrophoresis. It was not until 1977 that Henry provided a fundamental analysis of the cross-flow electro-filtration process (Henry et al. 1977). Moulik (1976) applied an electrostatic field to microfilters and reported excellent removal of colloidal particles such as bentonite and algal cells. Archer et al. (1993) designed an electrode capable of generating nonuniform electrostatic fields over a large surface area to separate yeast cells from water. They reported that a linear relationship between dielectrophoretic collection and pulse length over the range of 0 to 100 sec. Lo et al. (1983) separated Al<sub>2</sub>O<sub>3</sub> colloids from non-aqueous solution using the cross-flow electro-filtration process. The effect of feed rate, driving pressure, and electrostatic field strength on the filtration rate and total solid deposition rate on the collection electrode was evaluated. Results indicate that the extent of filter fouling is greatly decreased. Majmudar and Manohar (1994) studied the separation of TiO<sub>2</sub> from aqueous solution by electrophoretic filtration. Experiments were carried out at different voltages and flow rates. It was observed that a maximum separation of 96% occurred at 15 V and 200mL/h flow rate. Wakeman and Sabri (1995) demonstrated that direct current electrostatic field reduced cake formation in cross-flow membrane filtration. Operating parameters such as filtration pressure, cross-flow velocity, electrostatic field gradient, pH and feed concentration can affect filter performance. Verdegan (1986) studied the separation of fine particles (< 10  $\mu$ m) from nonpolar liquids by cross-flow electro-filtration process and reported that cross-flow electro-filtration has many distinct advantages over conventional separation processes such as high removal for all particle size, long life, and minimal power requirement. Akay and Wakeman (1996) observed an enhanced removal of a double chain cationic surfactant (diocatadecyldimethylammonium chloride) in water using the cross-flow electro-filtration process. Wakeman (1998) reported electrophoretically assisted cross-flow microfiltration of bovine serum albumin (BSA), ovalbumin and denatured lactalbumin. It is shown that the steady state flux is higher when an electrostatic field is applied than what is with conventional cross-flow microfiltration. The flux is almost independent of the membrane pore size. Finer pore sizes enable steady state flux and faster arrival of rejection conditions.

von Zumbusch et al. (1998) reported that the alternating electrostatic field diminished membrane fouling and hence yielded a higher specific filtrate flux. The effect of the electrostatic field depends on frequency (0.5 to 50 Hz), field strength (0 to 80 V/cm), conductivity (1 to 10 mS<sup>-1</sup>), and protein concentration (0.1 to 5 w%). Low frequency and high electrostatic field strength yield the best result for electroul trafiltration with alternating current fields. The effect of the electrostatic field increases with rising conductivity up to the point where a limiting electrolytic current is reached. Increasing protein concentration diminishes the effect of the electrostatic field.

Huotari et al. (1999) reported that applying an electrostatic field across cross-flow filtration can greatly increase the flux rate. Weigert et al. (1999), conducted the first pilot plant study on the microfiltration of mineral and biological slurry with cross-flow filtration, coupled with constant and pulsed fields and reported that the specific permeate rate markedly increased compared to that without an electrostatic field. For mineral slurry, the increase in flux rate was more than 10 folds. An estimation of the specific energy input demonstrates the cost-saving potential of this technique. Most of the above research is aimed at correlating the applied field strength with the hydraulic pressure difference across the filter and filter cake.

The major objective of this research was to develop an innovative solid-liquid separation technique that will allow the use of filtered water samples in site investigation. The technique should be capable of separating the nano-sized colloids. The following are specific objectives: (1) to design and evaluate the performance of a cross-flow electro-filtration (CFEF) devise and (2) to study the major factors controlling the operation of the CFEF unit using model colloid particles, e.g.,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and naturally occurring particles from well waters.

#### 2.3 Material and Experiment

#### 2.3.1 Design and Construct CFEF Module

Figure 2.1 shows the experimental apparatus and the processes flow scheme used in all laboratory experiments. The main components of the apparatus include a suspension preparation tank (or feed tank), pump, power supply, pH controller, and cross-flow electro-filtration unit (CFEF), respectively. The tank for the preparation of suspension was a 230-L plastic container equipped with circulation pump to prevent the suspended particles from settling and agglomerating. The inlet and outlet tubes on the unit were connected via polymer tubing to a peristaltic pump.

A schematic layout of the CFEF setup is shown in Figure 2.2. As indicated in Figure 2.2 the main filter unit consisted of an external tube (insulated), an inner electrically charged cathodic filter membrane, and a co-centric anodic rod. The external tube had a diameter of 8.9 cm, the inner filter has a diameter of 3.0 cm and the co-centric anode was a 0.5-cm stainless wire. The total module was 22.5 cm long and had a total filtration surface area of 212 cm<sup>2</sup>. The cathode and the anode were connected to an a. c. power supply. A stabilized power supply (Model: E861, Consort, Belgium) with a maximum output of 600 d. c. volts at 1 amp was used to provide the electric field across the membrane. To prevent and reduce membrane fouling by gas bubbles and gas generation at the electrodes by electrolysis and heat generation, the current was limited to less than 1 amp. One electrode was located downstream of the membrane support, so that bubbles were carried away in the filtrate flow. The electrode could not be placed closer than about 3 mm from membrane surface. Gas evolved from this electrode was flushed out of the module in the filtrate and the concentrate streams.



Figure 2.1 (a) Sketch of the total arrangement of the CFEF module; (b) photo of the total CFEF module.





Depending on the charge characteristics of the particle, we can alter the polarity of the collector electrode. For example, if the surface charge of colloidal particle is positive, the centric electrode will be a cathode and vice versa. The filtration experiments reported here all used Kenmore membranes, with an average pore size greater than 10 µm, and a new membrane was used for each experiment. Kenmore 10-µm pore size membranes were obtained from a local supermarket.

The CFEF filter unit is fed from a Milipore<sup>TM</sup> cross flow filter module, model ProFlux M12. A pressure sensor is installed at the inlet and the outlet of filtrate and concentrate. A computer with necessary software is used to control the filtration rate and flow direction and continually record the pressure of the inlet and the outlet streams.

#### **2.3.2** Operation of the CFEF Module

Experiments were conducted to characterize the performance of the CFEF module under various conditions specifically, solid concentration and applied voltage. The suspension was made up to a known concentration using either dry powder or slurry added to distilled water and the mixture was stirred in the feed tank for two hours to ensure a constant influent concentration prior to experiments. The dispersion was stirred in the feed tank and re-circulated continuously as to produce a homogenous mixture and to allow the particles to adsorb onto the surfaces of the rig. The suspension pH was then adjusted to the required value using NaOH or HCl. No other chemical dispersants were added.

Laboratory experiments were conducted to evaluate the performance of the cross-flow electro-filtration unit. The following operational conditions were observed: (1) clogging, (2) flux production, (3) quality of flux, and (4) backwash frequency. The degree of filter clogging can be measured in terms of several properties including pressure drop and water quality of the filtrate, i.e. turbidity. During filtration experiments, the pressure of the system was monitored continuously. Laboratory experiments were run under the following conditions: (1) filtration rate, (2) particle concentration, (3) initial electrostatic field applied, and (4) pH. The filtration

rate was from 2.4 to 14.2  $\text{cm}^3/\text{cm}^2$ -min. The particle concentrations were from 50 to 427 mg/L. The electrostatic field strength applied was from 0 to 156.5 V/cm.

Each experiment was run until both filtrate and concentrate turbidity (i.e. total solid concentration) reached a "steady state". Since a true steady state was not always reachable, for the sake of simplicity it was taken as the time when the turbidity was reduced by less than 2 % during a ten-minute period. If the filtrate and concentrate turbidity did not stabilize by this time, the experiment was continued until a steady flow rate in the filtrate stream was observed. During filtration experiments, samples were withdrawn periodically from the filtrate and the concentrate streams. The pH and conductivity of water in the feed tank, the concentrate, and the filtrate streams were monitored during filtration. The pressure and pumping rate were continuously monitored using a a software provided by the Millipore Company. The temperature of suspension was kept constant at approximately 25°C during each test.

## 2.3.3 Material and Chemical Analysis

Two model colloid particles,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, and naturally colloidal particles collected from groundwater were selected in this study. The particles were chosen primarily for their size and surface charge characteristics. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was obtained from the Degussa Company (Darmstadt, Germany). The colloidal silica (SiO<sub>2</sub>) was obtained from the Nissan Chemical Industries, Ltd. (Chiba, Japan). The naturally occurring colloids were collected from the well water sampled with low-flow-purging, bailer, and high-flow-purging techniques at the Denzer-Schaefer site, Toms River, NJ. The average particle size and size distribution were determined by dynamic light scattering (DSL) analyzer using the ZETASIZER 3000HSA (Malvern Instrument Ltd., Malvern, Worcs, U. K.). The intensity distribution is weighted according to the scattering intensity of each particle fraction. The particle scattering intensity is proportional to the square of the molecular weight (Mattison 1996). As such, the intensity distribution can be somewhat misleading, in that larger particles can dominate the distribution. In typical applications, a result that is more desirable than the intensity distribution is the volume

distribution (Jillavenkatesa et al. 2001). The volume distribution can be calculated from the intensity distribution using the Mie theory. The electrophoretic mobility of particles in the well water samples was determined by the ZETASIZER 3000HSA zeta potential meter (Malvern Instrument Ltd., Malvern, Worcs, U.K.). The colloidal particles were suspended in electrolyte, prepared with distilled and deionized water. The electrophoretic measurements of colloidal particles were done in dilute suspensions. The pH was adjusted to the target values by adding HCl (0.1 M) or NaOH (0.1 M). The upper limit for silica suspension was pH 9 to avoid dissolution of the particles. The ionic strength was in the range  $10^{-3}$  to  $10^{-1}$  mol/L. The experimental results reported in this work are the turbidity of filtrate. Suspended and colloidal particles such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, clay, silt, finely divided organic and inorganic matter cause turbidity in water. The turbidity (nephelometric turbidity units or NTU unit) of the filtrate was measured against a calibration curve using dilute water sample solutions. A linear relationship exists between turbidity and the solid concentration of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and naturally occurring colloidal particles was observed. The turbidity (NTU) was found out to correlate to the solid concentration with a linear correlation coefficient ( $\mathbb{R}^2$ ) of 0.99. The results show that all water samples have a high refractive index, which contribute turbidity to the water even at low solid concentrations. So we can use turbidity as a means to monitor the solid concentration. The turbidity was measured by a turbidimeter (Model 2100P, HACH, Colorado, USA). The removal efficiency of colloidal particles is calculated by the following expression:

$$R_{i} = \frac{T_{o} - T_{i}}{T_{o}} x100(\%)$$
(2.1)

where:

 $R_i$ : Removal efficiency at time  $t_i$ ;

T<sub>o</sub>: The turbidity of filtrate suspension at time t<sub>o</sub>;

T<sub>i</sub>: The turbidity of filtrate suspension at time t<sub>i</sub>.

#### 2.4 Results and Discussion

#### 2.4.1 Particles and Characterization

Figure 2.3 shows the pH dependence of the zeta potential (surface charge) for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and naturally occurring colloids. The average particle size of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 200 nm. According to Figure 2.3, the pH<sub>zpc</sub> for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was approximately 9.2. This value agrees well with these reported by others (Huang and Stumm 1973; Hsieh 1987). The results indicate that the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> will be positively charged at pH values less than 9. The mean particle diameters of Snowtex 20L and Snowtex ZL (SiO<sub>2</sub>) were 76 and 126 nm, respectively, which was smaller than that of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Results show that the particles appear to be monodispersed. Based on Figure 2.3, the pH<sub>zpc</sub> of colloidal silica is approximately 2.0 and that the colloidal SiO<sub>2</sub> was negatively charged at the pH values greater than 2.0.

The average particle diameter of naturally occurring colloid collected from the groundwater is 727 nm, which was greater than that of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and colloidal SiO<sub>2</sub>. The results show that the particles appear to be monodispersed. According to Figure 2.3, the pH<sub>zpc</sub> of naturally occurring colloid was approximately 1~2 that clearly indicates that these colloids were negatively charged under the pH value of well water. Results also indicate that the zeta potential is strongly dependent on pH. This suggests that H<sup>+</sup> and OH<sup>-</sup> are the potential determining ions. Table 2.1 summarizes the characteristics of colloidal particles used in this study.

#### 2.4.2 Performance Assessment of the CFEF Unit

The effects of several variables on the performance of the filter were examined using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the surrogate colloidal particles and naturally occurring colloidal particles collected from well water samples were assessed. The following operational conditions of CFEF were evaluated: clogging, flux production, quality of flux, and backwash frequency.



Figure 2.3 Zeta potential of various particles as a function of pH. (a) **g**Al<sub>2</sub>O<sub>3</sub>, (b) SiO<sub>2</sub>, and (c) naturally occurring.

Particle Type	Mean size (nm)	pH <sub>zpc</sub>	Source
γ-Al <sub>2</sub> O <sub>3</sub>	209	9.2	Degussa Company
SiO <sub>2</sub>	76 ~ 126	< 2	Nissan Chemical Industries, Ltd
Naturally occurring colloidal particles	297 ~ 1007	< 2	Naturally occurring colloids were collected from the well water with low-flow-purging, bailer, and high- flow-purging sampling techniques at the Denzer-Schaefer site, Toms River, NJ.

Table 2.1The characteristics of particles

## 2.4.2.1 Clogging

During filtration experiments the pressure of the system was monitored constantly. The initial pressures of the inlet and the outlet streams were controlled at 2 and 1 psi, respectively. At the end of all experiments, the pressure at the inlet and the outlet always remained at the same level. To evaluate long-term clogging, filtration experiments were run for two hours at a pump speed of 15% (or 0.46 L/min),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> of 100 mg/L, initial pH of 5.6 and electrostatic field strength of 96.8 V/cm (or 300 dc voltage). The results were the same as reported above. No difference between the inlet and the outlet pressure was observed.

## 2.4.2.2 Flux Production

The pumping speed (S, %) can be correlated to filtration flow rate (Q, L/min) by the equation:  $Q = -0.48 + 6.21 \times 10^{-2}$ S. Filtration flow rate can be converted to flux production by dividing the filtration flow rate by filter surface area. The flux production of the cross-flow electro-filtration unit varied from 2.4 to 14.2 cm<sup>3</sup>/cm<sup>2</sup>-min.

## 2.4.2.3 Quality of Flux

The solid concentration of the inlet is in the range of 50 to 780 mg/L. The turbidity of the inlet stream was related to solid concentration in the range of 16 to 750 NTU. After applying the electrostatic field, the turbidity of the filtrate decreased to a maximum NTU value of one.

## 2.4.2.4 Backwash Frequency

No clogging was observed in all experiments. Therefore, it was not necessary to backwash the filter under the experimental conditions.

## 2.4.3 Kinetics of Particle Separation

#### 2.4.3.1 Theoretical Aspect of CFEF System

Many models have been published for predicting fluxes in electro-filtration (Henry et al. 1977; Radovich et al. 1985; Rios et al. 1988; Bowen 1992; Bowen 1993). These models can be

divided into two major groups: resistance-in series and film theory. In this study we did not use either model directly, but a simple approach was employed by considering all forces acting on one single particle. In a cross-flow electro-filtration system, there is a balance between the electrostatic force and the hydrodynamic force exerting on the particle. When both forces exerted on the particle are balanced, the particle will remain stationary and the following equation is obtained:

$$F_e = F_d \tag{2.2}$$

where  $F_e$  is the electrostatic force and  $F_d$  is the drag force. When a charged particle with a solid charge,  $q_{p_i}$  is located in the region where an electric field of strength, E, is present, an additional force,  $F_e$ , will exert on the particle. The magnitude of this force is given by the following expression:

$$\mathbf{F}_{\mathrm{e}} = \mathbf{q}_{\mathrm{p}} \mathbf{E} \tag{2.3}$$

Next, let us consider the case of a laminar flow around a particle. Under such circumstance, the drag force can be obtained by the expression:

$$F_{d} = 3 \, pm l v_{t} \tag{2.4}$$

where  $\mu$  is the viscosity of the fluid, d is the particle diameter, and v<sub>t</sub> is the terminal velocity of the particle.

For small particles, its terminal velocity will soon be reached under the action of these forces. When an equilibrium state is reached, the terminal velocity becomes:

$$v_{t} = \frac{F_{e}}{3pmd_{p}} = \frac{q_{p}E}{3pmd_{p}}$$
(2.5)

In the CFEF system, when the particles are traveling at the terminal velocity,  $v_t$ , relative to the surrounding flow, where flow is moving at an opposite direction with velocity,  $v_r$ , then the velocity of the particle,  $v_p$ , relative to the fixed coordinate of the CFEF unit is:

$$v_{\rm p} = v_{\rm t} - v_{\rm r} = \frac{q_{\rm p}E}{3pmd_{\rm p}} - v_{\rm r}$$
(2.6)

According to the mixed flow model, it can be assumed that the flow is completely mixed in the r-direction but not in the x-direction. This makes sense, because mixing in the x-direction will move particles both up and downstream, with little effect on the removal efficiency, whereas mixing in the r-direction (radial) leads to a decrease in the removal efficiency. We then consider a section of cross-flow electro-filtration with length "dx". In this section the fraction of the particles that reach the collector electrode, Y, will be equal to the vertical distance an average particle falls due to electrostatic force in passing through the section, divided by the height of the section, which we may write as

$$Y = \frac{pdr}{A} \tag{2.7}$$

where dr is the displacement of the particle, p is the perimeter and A is the total cross-sectional area.

A particle, which enters the capture zone adjacent to the wall, will migrate a distance "dr" toward the wall while it moves a distance "dx" in the axial direction. Since the time required for moving these two distances is identical, one has:

$$dr = v_{p}dt = v_{p}\frac{dx}{v_{x}}$$
(2.8)

The change in number of particle passing this section is:

$$dN = NY = -\frac{Npdr}{A} \tag{2.9}$$

Combining equations (2.6) and (2.9) and by rearrangement, one has:

$$\frac{dN}{N} = -\frac{p}{Av_x} \left( \frac{\mathbf{q}_p \mathbf{E}}{3\mathbf{pml}_p} - v_r \right) dx$$
(2.10)

Upon integration of equation (2.10), and under the following boundary conditions, i.e.,  $N = N_i$  at x = 0 and allow  $v_t$  to vary with x, the theoretical removal efficiency becomes:

$$\boldsymbol{h} = 1 - \exp\left(-\frac{p}{Av_{x}}\left(\frac{q_{p}}{3\boldsymbol{pmd}_{p}}\int_{0}^{L}Edx - v_{r}L\right)\right)$$
(2.11)

Next, we define the mean electric field strength at the collector electrode,  $E_m$ , as:
$$E_{m} = \frac{1}{L} \int_{0}^{L} E dx \qquad (2.12)$$

Then equation (2.11) becomes:

$$\mathbf{h} = 1 - \exp(-a_1 q_p E_m + a_2 v_r) \tag{2.13}$$

where  $a_1$  is pL/3 $\pi A\mu v_x d_p$  and  $a_2$  is pL/ $v_x A$ .

According to equation (2.13) the removal efficiency enhancement due to the applied electrostatic field is dependent on the surface charge of particles in the feed solution, filtration velocity, and applied electrostatic field strength. That is, the larger the electrostatic field strength and surface charge, the greater is the removal rate of the particles. Also, the smaller the filtrate velocity, the greater is the removal efficiency of the particles at constant electrostatic field strength and surface charge. Figure 2.4 shows the free-body diagram of the particle movement in the CFEF system.



Figure 2.4 Free body diagram of particle movement in CFEF system.

## 2.4.3.2 Effect of Filtration Rate

The experiments were begun by adjusting the desired pumping speed, pH at 5.6, and a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> concentration of 100 mg/L, before applying an electrostatic field of 96.8 V/cm (or 300 voltage) to the electrodes. The removal efficiency of the colloidal particles was affected by changing the filtration velocity, as shown in Figure 2.5 when an electrostatic field is applied. Results indicate that the particle removal was 80, 64, 53, 45, and 46%, at filtration flow rate of 0.3, 0.42, 0.54, 0.66 and 0.78 L/min, respectively. From Figure 2.5, it is seen that the removal efficiency of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> decreases with filtration rate. The removal efficiency of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> decreased exponentially with respect to filtration rate to a constant value when the filtration rate was greater than 0.65 L/min.



Figure 2.5 Effect of filtration flow rate on the removal of colloidal articles. Experimental conditions: 100 mg/L g-Al2O3; initial pH = 5.6; E = 96.8 V/m.

#### 2.4.3.3 Effect of Applied Electric Field

The electrostatic attraction between colloidal particles and collector electrode increases with increasing electrostatic field strength. Figure 2.6 shows the typical turbidity changes as a function of time at various electric field values. It is clear from Figure 2.6 that the mechanism of crossflow filtration is strongly dependent on the interaction of the electric field with charged colloidal particles.

Results indicated that the removal rate of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was fast within two minutes and that the final turbidity decreased with increasing electric field. Similar kinetic profiles were also attained for SiO<sub>2</sub> and naturally occurring colloids. All data indicated strong transient state behavior, i.e., the solid concentration in filtrate changes with time. As expected, an initial period of a rapid and significant turbidity decline at constant electric field was observed and then a near-steady state of turbidity was reached. Figures 2.7 to 2.9 show the effect of electrostatic field on the removal of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and naturally occurring colloid, respectively.

When no electric field was applied, the system behavior was found to be completely different. It can be seen from Figure 2.6 that, in the absence of an electrostatic field condition (i.e., 0 volt), the final removal efficiency was about 3% after 1-min filtration time and remained at this level afterward, which means that colloidal particles do pass through the membrane under these experimental conditions. This poor removal efficiency of colloidal particles would be expected due to the relatively large pore size of the membrane (10 µm). Even after some adsorption of particles onto the pore walls the flow pore would still be considerably larger than the colloidal particles. In the absence of an electric field the removal efficiency was too low to be of interest from a practical separation point of view. But the electric field improves the removal efficiency to the extent that the process becomes potentially attractive. However, in the presence of an electric field, the steady state turbidity is constant and has a tendency to decrease. For safety consideration, we first applied electrostatic field strength at less than 16.1 V/cm (or 50 voltages).



Figure 2.6 Turbidity changes as a function of time at various electrostatic field values. Experimental condition: 427 mg/L; pH = 6.6; filtration flow rate = 0.37 L/min); Groundwater Sample = 5SIIB03.



Figure 2.7 Effect of electrostatic field on removal of **g**Al<sub>2</sub>O<sub>3</sub>. Experimental conditions: 100 mg /L ?-Al<sub>2</sub>O<sub>3</sub>; pH = 5.6; filtration flow rate = 0.3 L/min.



Figure 2.8 Effect of electrostatic field on removal of colloidal SiO<sub>2</sub>. Experimental condition: 242 mg/L; pH = 5; filtration flow rate = 0.3 L/min; SiO<sub>2</sub> Sample: Snowtex ZL.



Figure 2.9 Effect of electrostatic field on removal of naturally occurring particles. Experimental condition: 427 mg/L; pH = 6.6; filtration flow rate = 0.37 L/min; Sample: 5SIIB03.

Results clearly show that the removal efficiency increases with increasing electrostatic field (voltage). The removal of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was fast during the first 3 minutes. The final removal efficiency was 13% and 18% at electrostatic field strength of 12.9 and 16.1 V/cm (or voltage of 40 and 50 V), respectively, under a filtration flow rate of 0.37 L/min. It is clear that a high electrostatic field will enhance the removal efficiency of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. We then decreased the filtration flow rate to 0.3 L/min and adjusted the electrostatic field strength to between 16.1 and 96.8 V/cm (or voltage between 50 and 300 V). Figure 2.7 shows the removal efficiency of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under these conditions.

The results show that the removal rate of SiO<sub>2</sub> was fast during the first minute and that the removal efficiency increases with increasing electrostatic field (voltage). The final removal efficiency was 23, 46, 60, 68, 72, and 80%, respectively, at 16.1, 32.3, 48.4, 64.5, 80.6, and 96.8 V/cm (or 50, 100, 150, 200, 250, 300 V) applied electrostatic field, respectively. This is almost 27-fold increase in particle removal efficiency, which demonstrates the potential of the process. For Snowtex ZL (Figure 2.8), the final removal efficiency was 3, 21, 60, 70, 93, 97 and 98%, respectively, at electrostatic field of 0, 32.3, 64.5, 96.8, 129.0, 161.3, and 187.7 V/cm (or 0, 100, 200, 300, 400, 500, and 582V). As expected, high electrostatic field will enhance the removal efficiency.

Figure 2.9 shows the effect of electrostatic field on the removal of naturally occurring colloids. Because naturally occurring colloids are negatively charged at pH 6.6, the collector electrode was made cathodic. Results indicate that the removal rate was fast during the first 4 minutes (Figure 2.6). After 3-min filtration time, the removal efficiency of naturally occurring colloids remained at the same level afterward. The final removal efficiency was 7, 39, 62, 82, 93, 95% at electrostatic field of 0, 32.3, 64.5, 96.8, 129.1, and 156.5 V/cm (or 0, 100, 200, 300, 400, 485V), respectively, for well water sample collected by the bailing method. It is clear from

Figure 2.9 that the efficiency of crossflow filtration is strongly dependent on the interaction of the electric field with charged colloidal particles. High electrostatic field will enhance the particle removal efficiency as expected.

#### 2.4.3.4 Effect of Solid Concentration

The effect of total solid concentration at various electrostatic field values and various total solid concentrations (426 and 680 mg/L) for well water samples is shown in the Figures 2.10. The final removal efficiency was 7, 39, 54 and 65 %, respectively, at the electrostatic field of 0, 32.3, 64.5 and 96.8 V/cm (0, 100, 200 and 300 V) for well water sample collected by the low-flow-purging sampling at total initial solid concentration of 680 and 426 mg/L and at a filtration time of 10 minutes. The result shows that there is no distinct difference in the particle removal efficiency over the range of total solid concentrations studied.



Figure 2.10 Effect of solid concentration on the removal of colloidal particle. Experimental conditions: filtration flow rate = 0.28 L/min; Sample: 5SIIIL01.

## 2.4.3.5 Effect of pH

Figure 2.11 shows the effect of pH on the performance of CFEF system. The effect of pH on the percentage of particle removal was observed at the 10-minute operation time. Results show that the particle removal efficiency was 84, 72, 64, 45, and 46%, respectively, at pH 4, 5, 6, 7, and 8. It is interesting to note that the profile was parallel to the surface charge of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. As shown in Figure 2.3, the pH<sub>zpc</sub> of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is 9. Results again prove the hypothesis that crossflow electrofiltration can successfully separate the colloidal particles by manipulating their surface charge in place of zeta potential measurements.

## 2.4.4 Separation of Particles of Various Sizes Using the CFEF Module

## 2.4.4.1 Bimodal Particles Size Distribution Using the CFEF Module

Because the range of the particle size distribution of surrogate colloidal particles ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) and naturally occurring particles collected from groundwater samples are very narrow, we cannot observe the effect of particle size on solid-liquid separation using the CFEF technique. Therefore, we use naturally occurring colloidal particles collected from groundwater samples and model colloidal silica (SiO<sub>2</sub>) to prepare a bimodal distribution of particle size. Under the prevailing pH conditions of most groundwater, the surface charge of colloidal SiO<sub>2</sub> is negative. This is the same situation as naturally occurring particles collected from the well water. The mean particle sizes of colloidal SiO<sub>2</sub> and naturally occurring particle collected from well water (10IIB02) were 76 and 441 nm, respectively. We therefore prepared colloidal SiO<sub>2</sub> and naturally occurring particle suspension at different concentrations to determine the best proportion for bimodal size distribution (Figure 2.12). Before beginning any separation experiment, it is necessary to know if we can use turbidity measurement instead of solid concentration to express the particle separation efficiency, as both colloidal SiO<sub>2</sub> and naturally occurring particles were in good agreement with that of measured.



Figure 2.11 Effect of pH on the removal of colloidal particle. Experimental conditions: filtration flow rate = 0.3 L/min); E = 96.8 V/cm; sample =  $gAl_2O_3$ .



Figure 2.12 Bimodal distribution (10IIB02 + Snowtex 20L).

### 2.4.4.2 Effect of Electrostatic Field

Figure 2.13 shows the effect of electrostatic field on total removal of particle of two different sizes. Results indicate that the removal rate is fast during the first 3 minutes (data not shown). The final removal efficiency for the 10IIB02 + Snowtex 20L system was 7, 34, 48, 69, 78, and 80%, respectively, at the electrostatic field of 0, 32.3, 64.5, 96.8, 124.5, and 126.5 V/cm. As expected, high electrostatic fields will enhance the particle removal efficiency.

## 2.4.4.3 Particle Size Distribution of in the Filtrate

The particle size distribution can be expressed as function measurable parameters such as the mean, standard deviation and peak value. The most common particle size distribution is called the log-normal distribution which is based on the Gaussian distribution. Figure 2.14 (a) shows the effect of the electrostatic field on the particle size distribution of filtrates. Increasing the electrostatic field strength enhance the removal of fine particles. Increase in field strength decreased the spread (i.e. standard deviation) of fine mode (i.e. Snowtex 20L) from 0.22 to 0.18 while the mean size remained constant at 76  $\pm$  20 nm. The area under the two totally distinct curves gives the proportions of two constituents. Figure 2.14(b) shows the proportion changes as a function of electrostatic field. From the Figure 2.14(b), the proportion of larger particle size (i.e. naturally occurring particle) decreased from 42 to 15% and the proportion of smaller particle (i.e. Snowtex 20L) increased from 58 to 85% as the electrostatic field strength increased from 0 to 96.8 V/cm. Based on the results, it is clear that we can successfully separate particles of different size using the CFEF module. In this study, we used both 0.45 and 0.2  $\mu$ m pore size filters to separate the above particles. During filtration experiments the filter easily held up the fine particles, forming filter cake and rendered the filtration operation difficult.

## 2.5 Conclusion

The prototype CFEF unit works effectively without clogging problem. The final pressure at the inlet and the outlet streams always remained identical to each other. Therefore, it is not necessary to backwash the CFEF unit under the experimental conditions of this study. Naturally



Figure 2.13 Effect of electrostatic field on removal of naturally occurring particle and colloidal silica. Experimental condition: pH = 8.2; Sample: 10IIB02 + Snowtex 20L

occurring particles collected from water samples are negatively charged under the pH condition of the groundwater. The pH<sub>zpc</sub> of the naturally occurring particles was approximately  $1.5 \pm 0.5$ . The surface charge of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was positive under acidic condition since the pH<sub>zpc</sub> of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 9.2. All particle samples appeared to be monodispered. The average particle size of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and naturally occurring particles were in the range of 300 to 727 nm, respectively. For  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, in the concentration range between 50 and 200 mg/L, there was no distinct difference in solid removal efficiency. An optimal filtration rate was observed for the separation of colloidal particles. At filtration rate greater or less than 0.46 L/min, the removal efficiency of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> decreased as the filtration increased or decreased. The results show that optimum filtration rate of the cross-flow electro-filtration unit was 0.3 L/min under the experimental conditions of 100 mg/L  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and an electrostatic field of 96.8 V/cm. The removal of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and naturally colloids was 0.3 L/min under the present experimental conditions: concentration of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was



Figure 2.14 Distribution of particle size as affected by electrostatic field. Experimental condition: pH = 8.2; Sample: 10IIB02 + Snowtex 20L.

100 mg/L  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the electrostatic field was 96.8 V/cm. The removal of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and naturally colloids was faster during the first 1 to 4 minutes. The removal efficiency increased with increase in electrostatic field or decrease in pH. The final removal efficiency of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at an electrostatic field of 96.8 V/cm was 80% at an  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> concentration of 100 mg/L, pH of 5.6, and filtration rate of 0.3 L/min. The final removal efficiency of naturally occurring colloid was 95% at an electrostatic field of 156.5 V/cm, pH of 6.6, and filtration rate of 0.3 L/min for well water samples collected by the bailing technique.

Naturally occurring particles collected from groundwater samples and model colloidal silica (SiO<sub>2</sub>) particles were mixed to prepare a suspension of bimodal particle size distribution. Results indicated that the removal rate was fast during the first 3 minutes. As expected, high electrostatic fields enhanced the particle removal efficiency. According to the results, the proportion of larger particle size (i.e. naturally occurring particles) decreased as the electrostatic field strength increased. On the other hand, the proportion of smaller particles (i.e. colloidal silica) increased as the electrostatic field of different strength increased. Based on the results, we can successfully separate particles of different size using the CFEF module. It is possible to separate the naturally occurring particles by adjusting applied field strength of the CFEF unit.

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#### **CHAPTER 3**

# NANO-SIZED COLLOIDAL PARTICLES TRANSPORT IN CROSS-FLOW ELECTRO-FILTRATION PROCESS: THEORETICAL ASPECTS

## 3.1 Abstract

Cross-flow filtration takes advantage of minimizing exposure time between the filter medium and the water to be processed. However, in dealing with nano-sized colloidal particles, there is ultimate particle deposition onto the membrane surface. Further improvement of the cross-flow filtration can be achieved by applying an electrostatic field across the system. Based on the characteristics of nano-sized particles, we have developed an innovative solid-liquid separation technique, cross-flow electro-filtration process (CFEF), which can be applied to water treatment and site investigation. Many researchers have attempted to describe quantitatively the cross-flow filtration process using the film theory and the resistance-in-series model. However, the above models did not describe the transportation of charged particles in CFEF. The trajectories of nano-sized colloidal particles in a filter chamber are of great importance in the design and operation of crossflow electrofiltration system. The objective of this research was to develop a mathematical model to predict the transport of nano-sized particles in a CFEF unit. Model colloids, i.e.,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and naturally occurring colloidal particles were used to test the particle separation efficiency of the CFEF module. A sensitivity analysis of the transport model was conducted to assess the effect of pertinent parameters, such as particle size, surface charge, and applied electric field strength, on model behavior. The model results match well with those obtained experimentally. Based on model and experimental results, it is possible to separate the naturally occurring particles by manipulating the system pH (or surface charge) and/or applied electrostatic field.

## 3.2 Introduction

Separation of nano-sized particles from liquid media by conventional techniques is difficult because of small size. Most conventional separation processes involve either pressure or gravity as driving force as in dead-end filtration. Improvement of the dead-end filtration is possible by modifying the flow paten during filtration, e.g., cross flow. The cross-flow filtration takes advantage of the minimizing the exposure time between the filter medium and the water to be treated. The cross-flow filtration has the intrinsic merit of minimizing the direct solid deposition onto filter membranes. However, cross-flow filtration can only extend the backwash frequency. In dealing with nano-sized particles, there is eventual particle deposition onto the membrane surface. Further improvement of the cross-flow filtration is attained by applying an electric field to the system. If the field is of sufficient strength and proper polarity, charged particles will migrate away from the filter medium surface by electrophoresis and be collected on the surface of a collector electrode. In theory, the behavior of a cross-flow electro-filtration (CFEF) toward charged particles should approximate to that of an ideal filter; nearly complete separation of particles of all sizes without pressure drop is possible. As far as electrophoretic separation is concerned, it is immaterial whether the particles in question are of the size of an ion or a grain of sand, as long as it has sufficient charge, they will be separated freely. Since the particles do not come in direct contact with the filter media, there will be no increase in pressure drop during filtration; hence, cross-flow electro-filtration should be characterized by extremely long service intervals. Based on the characteristics of nano-sized colloidal particles, we have developed an innovative solid-liquid separation module, CFEF reactor, which will be applicable to water treatment or site investigation. The technique is capable of separating naturally occurring colloids into several size fractions while reducing the membrane fouling. The theoretical treatment of cross-flow membrane filtration is a subject of considerable complexity. A lot of models have been developed to describe the processes of the cross-flow filtration, but only a few are capable of describing the processes and explaining the difference between experimental and observed results (Huotari et al. 1999; Ripperger and Altmann 2001). The cross-flow electrofiltration may be treated theoretically as a superimposition of cross-flow filtration with an electric field. Many researchers have attempted to describe the crossflow electrofitration process using the film theory and the resistance-in-series model (Henry et al. 1977; Radovich and Chao

1982; Yukawa et al. 1983; Radovich et al. 1985; Rios et al. 1988; Bowen and Sabuni 1992; Bowen 1993; Lentsch et al. 1993; Bowen and Ahmad 1997). The factors, which influence the cross-flow electro-filtration flux, are essentially the same as those of normal cross-flow filtration. Nonetheless in crossflow electrofiltraiton there presents an external electric field which will bring about electrical effects. The aforementioned models did not describe the transportation of charged particles in cross-flow electro-filtration. There is a lack of comprehensive model on crossflow electrofiltraiton. An attempt was made to quantitatively interpret the experimental data and present a mathematical model for the observed transient behavior.

The objective of this research was to develop a mathematical model, which describes the concentration distribution and trajectories of charged particles or colloids in the cross-flow electro-filtration system.

## **3.3** Cross-Flow Electro-Filtration Module

Figure 2.1 shows the experimental apparatus and the processes flow scheme used in all laboratory experiments. As indicated in Figure 2.1 the main filter unit consisted of an external tube (insulated), an inner electrically charged cathodic filter membrane, and a co-centric anodic rod. The external tube had a diameter of 8.9 cm, the inner filter had a diameter of 3.0 cm and the co-centric electrode was a 0.5-cm stainless wire. The total module was 22.5 cm long and had a total filtration surface area of 212 cm<sup>2</sup>. The cathode and the anode were connected to an a.c. power supply. According to the charge characteristics of the particles, we can alter the polarity of the collector electrode. The pore size of filter member was greater than 10 μm. The CFEF filter unit was fed from a Milipore<sup>TM</sup> cross flow module, model ProFlux M12. A pressure sensor was installed at the inlet and the outlet of both the filtration rate and flow direction and continually record the pressure of the inlet and the outlet streams.

## 3.4 Model Development

Several factors, such as the trajectories of charged particles or colloids, can influence the flux in electro-filtration in a different way from normal crossflow filtration. The electrical effects include electrophoresis and electroosmosis. Electrophoresis is the movement of charged particles or colloids relative to a liquid, and electroosmosis is the movement of a liquid relative to a stationary charged surface such as a membrane or a filter cake/gel. Other important electrical effects are electrochemical reactions at the electrodes and Joule heating (Jagannadh and Muralidhara 1996). There is little available information on the effects of electrokinetic phenomena on membranes (Huotari et al. 1999). As noted earlier, colloid transport in cross-flow electro-filtration process can be affected only by electrophosphoresis.

Figure 3.1 illustrates the geometry of the tubular cross-flow electro-filtration. In cylindrical coordinates with the origin at the center of the cross section, "**x**" is taken in the direction of the flow and "**r**" is the radial direction. The annular region is bounded by the two concentric tubes of radii  $\mathbf{r}_i$  and  $\mathbf{r}_o$ ;  $v_x$  is the axial velocity at the inlet of the filter tube, and  $v_r$  is the filtrate velocity at the filter wall.

To describe the behavior of the trajectories of charged particles or colloids in a hydrodynamic and electrostatic field, the following assumptions were made:

- 1. For nano-size particles, the main driving force is electrostatic force;
- 2. The particles are removed as they migrate into the capture zone;
- 3. A steady state operation is attained;
- 4. Laminar flow domain is the effective capture zone due to low Reynolds number;
- 5. There is fully developed velocity at the porous wall;
- 6. Uniform withdrawal velocity is present at the porous wall;
- 7. There is constant physical and transport properties.



Figure 3.1 Collection section of a CFEF.

## 3.4.1 The Electric Field of CFEF Module

The major forces that act on the particles in the CFEF unit are gravity, viscous resistance, and electrostatic attraction. The gravity is proportional to the volume of particles of constant density ( $\propto d^3$ ). Thus the ratio of gravity to resisting viscous force is proportional to ( $d^3/d$ ) or  $\propto d^2$ . As the particle diameter decreases, this ratio falls rapidly. For electrostatic force, the resisting force is still the Stokes viscous drag force, but the electrostatic force is proportional to the square of particle diameter, i.e.,  $d^2$ . Thus the ratio of electrostatic force to resisting force is proportional to ( $d^2/d$ ) or  $\propto d$ . Accordingly it is harder for the CFEF unit to collect small particles than large ones. That is the degree of difficulty is proportional to 1/d rather than  $1/d^2$  as in the case of large particles when gravity will be the driving force. For small particles, the main driving force would be electrostatic force. When the particles are sufficiently charged, an electric field is applied to the flow region, exerting an attractive force to the particles and forces them to migrate toward the oppositely charged electrode at right angles to the flow direction.

Referring to Figure 2.1, the raw water enters from the bottom and flows upward through the cylindrical collector portion of the CFEF unit. As the flow moves upward, the electrostatic force directs the particles toward the collector electrode. The clean water passes through the filter medium and emerges from the top of the unit. Figure 3.1 shows a cross section of the CFEF with a boundary layer in which particle capture takes place.

When a charged particles with a solid charge,  $q_{p}$ , are located in the region where an electric field of strength, E, is present, a force,  $F_q$ , will exert on the particles (Figure 3.1). The magnitude of this force is given by the following expression:

$$F_{e} = q_{p}E \tag{3.1}$$

Next, let us consider a single particle in a laminar flow. Under such circumstance, the drag force can be obtained by the expression:

$$\mathbf{F}_{\mathrm{d}} = 3\,\boldsymbol{p}\boldsymbol{m}\mathbf{d}\boldsymbol{v}_{\mathrm{t}} \tag{3.2}$$

Where  $\mu$  is the viscosity of the fluid, d is the diameter of particle, and v<sub>t</sub> is the velocity of the particle.

For small particles, the terminal velocity will soon be approached under the action of these two forces. When an equilibrium state is reached, the terminal velocity becomes:

$$v_{t} = \frac{F_{e}}{3pmd_{p}} = \frac{q_{p}E}{3pmd_{p}}$$
(3.3)

In the CFEF system, the distance that a particle travels relative to fixed coordinate is the same distance as it travels relative to the flow ( $\Delta r$  in both cases). If the particle is at its terminal velocity,  $v_t$ , relative to the surrounding flow, where flow is moving at an opposite direction with velocity of  $v_r = Q_f/(\Delta x \Delta r)$ , then the velocity of the particle relative to the fixed coordinate of the CFEF unit will be:

$$v_{\rm p} = v_{\rm t} - v_{\rm r} = \frac{q_{\rm p}E}{3pmd_{\rm p}} - v_{\rm r}$$
 (3.4)

Referring to Figure 3.1, a particle, which enters the capture zone adjacent to the wall, will migrate at a distance of "dr" toward the wall while it also travels a distance of "dx" in the axial direction. Since the time required for traveling these two distances is identical, one has:

$$dr = v_{p}dt = v_{p}\frac{dx}{v_{x}}$$
(3.5)

It is assumed that the turbulent flow will distribute the particles uniformly across the entire reactor and the flow is totally mixed in the r-direction but not in the x-direction. Furthermore, it is assumed that the field strength at the collector electrode, E, varies along the length of the collection section. The fraction of particles captured is equal to the ratio of the area within the capture zone to the total cross-sectional area, that is:

$$-\frac{\mathrm{dN}}{\mathrm{N}} = \frac{\mathrm{pdr}}{\mathrm{A}} = \frac{\mathrm{p}}{\mathrm{A}} \frac{v_{\mathrm{p}}}{v_{x}} \mathrm{dx}$$
(3.6)

where p is the perimeter of the collector electrode and A is the total cross-sectional area.

Upon integration of equation (3.6), and under the following boundary condition, i.e.,  $N = N_i$  at x = 0 and allow  $v_t$  to vary with x, one has:

$$N_{x} = N_{i} exp\left(-\frac{p}{Av_{x}}\int_{0}^{x}v_{p}dx\right)$$
(3.7)

The theoretical removal efficiency,  $\eta$ , then becomes:

$$\boldsymbol{h} = \frac{N_i - N_x}{N_0} = 1 - \exp\left(-\frac{p}{Av_x} \int_0^L v_p dx\right)$$
(3.8)

By substituting the  $v_p$  term in equation (3.4) to equation (3.8), one has:

$$\boldsymbol{h} = 1 - \exp\left(-\frac{p}{Av_x}\int_0^L \left(\frac{q_p E}{3\boldsymbol{p}\boldsymbol{m}\boldsymbol{d}_p} - v_r\right) dx\right) = 1 - \exp\left(-\frac{p}{Av_x} \left(\frac{q_p}{3\boldsymbol{p}\boldsymbol{m}\boldsymbol{d}_p}\int_0^L E dx - v_r L\right)\right) \quad (3.9)$$

Noting that  $Av_x = Q_c$ , the flow rate of the concentrate stream, and that the product "pL" is equal to the collection surface area,  $A_c$ , equation (3.9) may be re-written as:

$$\boldsymbol{h} = 1 - \exp\left(-\frac{q_{p}A_{c}}{3\boldsymbol{p}\boldsymbol{m}d_{p}Q_{c}}\frac{1}{L}\int_{0}^{L}Edx + \frac{A_{c}v_{r}}{Q_{c}}\right)$$
(3.10)

Next, by defining the mean electric field strength at the collector electrode,  $E_m$ , as:

$$E_{\rm m} = \frac{1}{L} \int_0^L E dx \tag{3.11}$$

equation (3.10) becomes:

$$\boldsymbol{h} = 1 - \exp\left(-\frac{q_{p}A_{c}}{3\boldsymbol{p}\boldsymbol{m}}d_{p}Q_{c}}E_{m} + \frac{A_{c}V_{r}}{Q_{c}}\right)$$
(3.12)

Knowing  $V_r = Q_f / (\Delta x \Delta r) = Q_f / A_f$  (where  $A_f$  is the filtration surface area and  $Q_f$  is the flow rate in the filtrate stream.) and  $q_p$  equal to  $\pi d^2 \sigma_o$  (where  $\sigma_o$  is the surface charge of the particle), equation (3.12) may be rewritten as:

$$\boldsymbol{h} = 1 - \exp\left(-\frac{\boldsymbol{s}_{o} d_{p} A_{c}}{3\boldsymbol{m} Q_{c}} E_{m} + \frac{Q_{f} A_{c}}{Q_{c} A_{f}}\right)$$
(3.13)

Let  $Q_f/Q_c$  be equal to  $\phi$ , and the ratio of the area within the capture zone to the filtration zone be:

$$\frac{A_{c}}{A_{f}} = \frac{2prL}{2pRL} = \frac{r}{R}$$
(3.14)

where r is the radius of capture zone and R is the radius of filtration area, equation (3.13) then becomes:

$$\boldsymbol{h} = 1 - \exp\left(-\frac{\boldsymbol{s}_{o}d_{p}A_{c}}{3\boldsymbol{m}Q_{c}}E_{m} + \boldsymbol{f}\frac{\mathbf{r}}{R}\right)$$
(3.15)

Based on equation (3.15), the removal efficiency will increase with surface charge density  $(\sigma_0)$ , particle diameter and electrostatic field (E) applied. The diameter and the surface charge density of particles or colloids can be obtained by size and zeta potential measurements respectively. The remaining question is how to determine the electrostatic field strength in the CFEF process. The field strength is ? V/? x in a parallel-plate electrode, but it will be more

complex in the CFEF which is in two co-centric plats. In the next section we will discuss the characteristics of electric field in a CFEF module.

#### 3.4.2 Removal Efficiency for Charged Particle

First, let us consider the electric field between two concentric cylinders in between a fluid containing charged particles and ions is passing through. There is no electric current flows through the fluid. Strictly speaking, if a voltage difference exists between the electrodes, charged particles will migrate toward one of the electrode, thus inducing at least a localized current. If the particles retain their charge when they reach the collecting electrode, and if all ions present in the flow attach themselves to particles before reaching the collecting electrode, then no current will flow into the collecting electrode. We refer to this situation as involving no current flow. Figure 3.2 shows the geometry of the two concentric cylinders between which the fluid flows. We shall let  $q_v$  be the charge density, or total charge that exists in the fluid per unit volume. To analyze the electric field within the fluid, we return to the Gauss' law (Figure 3.3):

$$\oint E \bullet dA = \frac{q}{e} \tag{3.16}$$

where  $\varepsilon$  is the dielectric constant.



Figure 3.2 Electric field between two concentric cylinders.

It should be noted that when SI units are used,  $\varepsilon = \varepsilon_r \varepsilon_0$ , where  $\varepsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{J-m}$  and  $\varepsilon_r$  is the dielectric constant of the medium. For water at 298°K,  $\varepsilon_r = 78.54$ . Thus, in equation (3.16)  $\varepsilon = (78.54)(8.85 \times 10^{-12} \text{ C}^2/\text{Jm})$ . This equation states that the integral of the product of field strength normal to a surface times the surface area is proportional to the charge contained in the volume enclosed by that surface.

Take the volume as that of a cylindrical electrode whose dimension in the r direction is dr, as shown in Figure 3.3. The electric field E is distributed uniformly over the face A; the integral of the dot product  $E \cdot dA$  on the face to the left is -E(r)A and on the face to the right is E(r+dr)A. Over the other faces the dot product is zero since the area and the field vector are at right angles. Equation (3.16) may then be written as:

$$rE(r+dr)A - rE(r)A = r\frac{q}{e} = r\frac{q_vAdr}{e}$$
(3.17)

Expanding E(r+dr) in a Taylor series

$$E(r+dr) = \sum_{n=0}^{\infty} \frac{E^{(n)}}{n!} (dr)^n$$
(3.18)

$$E(r+dr) = E(r) + \frac{E'(r)}{1!}dr + \frac{E''(r)}{2!}(dr)^2 + \bullet \bullet \bullet$$



Figure 3.3 The Gauss' s law.

Neglecting the higher-order terms, further simplification gives

$$\frac{d}{dr}(rE) = r\frac{q_v}{e} \tag{3.19}$$

Integration of equation (3.19) yields

$$E = \frac{q_{\nu}r}{2\mathbf{e}} + \frac{C_1}{r} \tag{3.20}$$

The field strength is related to voltage by the following expression:

$$E = -\frac{d\tilde{V}}{dr} \tag{3.21}$$

Using equation (3.21) for the field strength in terms of the gradient of voltage gives

$$\frac{d\tilde{V}}{dr} = -\frac{q_v}{2\mathbf{e}}r - \frac{C_1}{r}$$
(3.22)

which solution is

$$\tilde{V}(r) = -\frac{q_v r^2}{4e} - C_1 \ln r + C_2$$
(3.23)

With the following boundary conditions, i.e.,  $V = V_i$  as  $r = r_i$  and V = 0 as  $r = r_o$ , one can solve for the constants  $C_1$  and  $C_2$ . When these constants are substituted into equation (3.23), the following equation arrives:

$$\tilde{V}(r) = \frac{q_{\nu}}{4e} (r_o^2 - r^2) + \left[ \tilde{V}_i - \frac{q_{\nu}}{4e} (r_o^2 - r_i^2) \right] \frac{\ln(r_o/r)}{\ln(r_o/r_i)}$$
(3.24)

From equations (3.21) and (3.24) one has the field strength at location r, i.e., E(r):

$$E(r) = \frac{q_v r}{2\mathbf{e}} + \frac{\tilde{V}_i - q_v (r_o^2 - r_i^2)/4\mathbf{e}}{\ln(r_o/r_i)} \frac{1}{r}$$
(3.25)

The field strength at the surface of the external cylinder is:

$$E_{o} = \frac{q_{v}r_{o}}{2\boldsymbol{e}} + \frac{\tilde{V}_{0} - q_{v}(r_{o}^{2} - r_{i}^{2})/4\boldsymbol{e}}{\ln(r_{o}/r_{i})} \frac{1}{r_{o}}$$
(3.26)

The field strength at the surface of the inner cylinder is:

$$E_{i} = \frac{q_{v}r_{i}}{2\boldsymbol{e}} + \frac{\tilde{V}_{i} - q_{v}(r_{o}^{2} - r_{i}^{2})/4\boldsymbol{e}}{\ln(r_{o}/r_{i})} \frac{1}{r_{0}}$$
(3.27)

In the CFEF module, the volumetric charge density in the cylinder decreases as particles are being collected but the surface charge on each particle remains unchanged. Therefore, we need to take this fact into account during derivation. The magnitude of the field strength will change depending on the location of the particles. For the sake of simplicity, the average field strength is used. The mean field strength can be determined from the following equation:

$$E_{m} = \frac{\int_{r_{i}}^{r_{o}} E(r) 2\mathbf{p} \, r dr}{\int_{r_{i}}^{r_{o}} 2\mathbf{p} \, r dr}$$
(3.28)

Substituting equation (3.25) to equation (3.28) leads to the following expression:

$$E_{m} = \frac{\int_{r_{i}}^{r_{o}} \left\{ \frac{q_{v}r}{2\mathbf{e}} + \frac{\tilde{V}_{i} - q_{v}(r_{o}^{2} - r_{i}^{2})/4\mathbf{e}}{\ln(r_{o}/r_{i})} \frac{1}{r} \right\} 2\mathbf{p} r dr}{\int_{r_{i}}^{r_{o}} 2\mathbf{p} r dr}$$

$$E_{m} = \frac{2\mathbf{p} \int_{r_{i}}^{r_{o}} \left\{ \frac{q_{v}r}{2\mathbf{e}} + \frac{\tilde{V}_{i} - q_{v}(r_{o}^{2} - r_{i}^{2})/4\mathbf{e}}{\ln r_{o}/r_{i}} \frac{1}{r} \right\} r dr}{2\mathbf{p} \int_{r_{i}}^{r_{o}} r dr}$$

$$E_{m} = \frac{\int_{r_{i}}^{r_{o}} \left\{ \frac{q_{v}r^{2}}{2\mathbf{e}} + \frac{\tilde{V}_{i} - q_{v}(r_{o}^{2} - r_{i}^{2})/4\mathbf{e}}{\ln(r_{o}/r_{i})} \right\} dr}{\int_{r_{i}}^{r_{o}} r dr}$$

$$E_{m} = \frac{\frac{q_{v}r^{3}}{6\mathbf{e}} + \frac{\tilde{V}_{i} - q_{v}(r_{o}^{2} - r_{i}^{2})/4\mathbf{e}}{\ln(r_{o}/r_{i})} r \Big|_{r_{i}}^{r_{o}}}{\frac{1}{2}r^{2}\Big|_{r_{i}}^{r_{o}}}$$

$$E_{m} = \frac{\frac{q_{v}(r_{o}^{3} - r_{i}^{3})}{6\mathbf{e}} + \frac{\tilde{V}_{i} - q_{v}(r_{o}^{2} - r_{i}^{2})/4\mathbf{e}}{\ln(r_{o}/r_{i})} (r_{o} - r_{i})}{\frac{1}{2}(r_{o}^{2} - r_{i}^{2})}$$

$$E_{m} = \frac{(r_{o} - r_{i})\left\{\frac{q_{v}\left(r_{o}^{2} + r_{o}r_{i} + r_{i}^{2}\right)}{6e} + \frac{\tilde{V}_{i} - q_{v}\left(r_{o}^{2} - r_{i}^{2}\right)/4e}{\ln(r_{o}/r_{i})}\right\}}{\frac{1}{2}(r_{0} + r_{i})\left(r_{0} - r_{i}\right)}$$

$$E_{m} = \frac{\left\{\frac{q_{v}\left(r_{o}^{2} + r_{o}r_{i} + r_{i}^{2}\right)}{6e} + \frac{\tilde{V}_{i} - q_{v}\left(r_{o}^{2} - r_{i}^{2}\right)/4e}{\ln(r_{o}/r_{i})}\right\}}{\frac{1}{2}(r_{o} + r_{i})}$$

$$E_{m} = \frac{q_{v}\left(r_{o}^{2} + r_{o}r_{i} + r_{i}^{2}\right)}{3e(r_{o} + r_{i})} + \frac{2\left[\tilde{V}_{i} - q_{v}\left(r_{o}^{2} - r_{i}^{2}\right)/4e\right]}{(r_{o} + r_{i})\ln(r_{o}/r_{i})}$$

$$E_{m} = \frac{q_{v}}{e(r_{o} + r_{i})}\left[\frac{\left(r_{o}^{2} + r_{o}r_{i} + r_{i}^{2}\right)}{3} - \frac{\left(r_{o}^{2} - r_{i}^{2}\right)}{2\ln(r_{o}/r_{i})}\right] + \frac{2\tilde{V}_{i}}{(r_{o} + r_{i})\ln(r_{o}/r_{i})}$$

$$(3.29)$$

Figure 3.4 shows the arrangement of CFEF unit. The particle concentration, C, varies with distance along the cylinder as particles are being collected, which is caused by the applied field, E. Since E depends on the particles concentration as shown in equation (3.29), it will be best to derive the equation for collection efficiency (or removal efficiency) for this situation instead of using equation (3.6). From the derivation which leads to equation (3.6), the rate of decrease of particles crossing a given section at position x is given by



Figure 3.4 Analysis of CFEF.

Noting that  $dr = v_p dx/v_x$ ,  $p \approx 2\pi r_i$ ,  $Av_x = Q_c$  and  $v_p = v_t - v_r = (q_p E/3\pi\mu d_p - v_r)$ , equation (3.6) may be written as

$$-\frac{dN}{N} = \frac{p}{A} \frac{v_p dx}{v_x}$$
$$-\frac{dN}{N} = \frac{p}{A} \left( \frac{q_p E}{3pmd_p} - v_r \right) \frac{dx}{v_x}$$
$$-\frac{dN}{N} = \frac{2p r_i}{Q_c} \left( \frac{q_p E}{3pmd_p} - v_r \right) dx$$
(3.30)

The rate at which particles cross a given section, N, is related to the particle concentration by the following expression:

$$N = CQ_c \tag{3.31}$$

and noting that the charge density is related to the particle charge and particle concentration, C, as:

$$\tilde{q}_{vx} = q_p \tilde{C}_x \quad \tilde{q}_{vi} = q_p \tilde{C}_i \tag{3.32}$$

Substituting equations (3.31) and (3.32) into equation (3.30) leads to the following equation:

$$-\frac{dN}{N} = -\frac{dC}{C} = \frac{2\mathbf{p}r_i}{Q_c} \left(\frac{q_p E}{3\mathbf{pm}d_p} - v_r\right) dx$$
(3.33)

Substituting equations (3.29) and (3.32) into equation (3.33) leads to the following expression:

$$-\frac{dC}{C} = \frac{2\mathbf{p}r_i}{Q_c} \left\{ \frac{q_p}{3\mathbf{pmd}_p} \left[ \frac{q_v}{\mathbf{e}(r_o + r_i)} \left( \frac{\left(r_o^2 + r_o r_i + r_i^2\right)}{3} - \frac{\left(r_o^2 - r_i^2\right)}{2\ln(r_o/r_i)} \right) + \frac{2\tilde{V_i}}{(r_o + r_i)\ln(r_o/r_i)} \right] - v_r \right\} dx$$
$$-\frac{dC}{C} = \frac{2\mathbf{p}r_i}{Q_c} \left\{ \frac{q_p}{3\mathbf{pmd}_p} \left[ \frac{q_pC}{\mathbf{e}(r_o + r_i)} \left( \frac{\left(r_o^2 + r_o r_i + r_i^2\right)}{3} - \frac{\left(r_o^2 - r_i^2\right)}{2\ln(r_o/r_i)} \right) + \frac{2\tilde{V_i}}{(r_o + r_i)\ln(r_o/r_i)} \right] - v_r \right\} dx$$

$$-\frac{dC}{C} = \left\{ \frac{2\mathbf{p} r_i q_p}{3\mathbf{pm} Q_c d_p} \left[ \frac{q_p C}{\mathbf{e}(r_o + r_i)} \left( \frac{\left(r_o^2 + r_o r_i + r_i^2\right)}{3} - \frac{\left(r_o^2 - r_i^2\right)}{2\ln(r_o/r_i)} \right) + \frac{2\tilde{V}_i}{(r_o + r_i)\ln(r_o/r_i)} \right] - \frac{2\mathbf{p} r_i}{Q_c} v_r \right\} dx$$
(3.34)

To simplify the above equations, let us define the following terms:

$$a_1 = \frac{2r_i q_p}{3\mathbf{m} d_p Q_c} \tag{3.35}$$

$$a_{2} = \frac{q_{p}}{\boldsymbol{e}(r_{o} + r_{i})} \left[ \frac{\left(r_{o}^{2} + r_{o}r_{i} + r_{i}^{2}\right)}{3} - \frac{\left(r_{o}^{2} - r_{i}^{2}\right)}{2\ln(r_{o}/r_{i})} \right]$$
(3.36)

$$a_{3} = \frac{2\tilde{V}_{i}}{(r_{o} + r_{i})\ln(r_{o}/r_{i})}$$
(3.37)

$$a_4 = \frac{2\mathbf{p}\,r_i}{Q_c} v_r \tag{3.38}$$

and

Equation (3.34) then becomes:

$$-\frac{dC}{C} = (a_1(a_2C + a_3) - a_4)dx$$
  
$$-\frac{dC}{C} = (a_1a_2C + a_1a_3 - a_4)dx$$
  
$$-\frac{dC}{C} = (a_1a_2C + (a_1a_3 - a_4))dx$$
  
$$-\frac{dC}{C(a_1a_2C + (a_1a_3 - a_4))} = dx$$
(3.39)

This equation may be readily integrated from  $\tilde{C}_i$  at x = 0 to  $\tilde{C}_L$  at x = L to obtain the following equation:

$$\frac{1}{(a_1a_3 - a_4)} \ln \frac{a_1a_2C + (a_1a_3 - a_4)}{C} \Big|_{\tilde{C}_i}^{\tilde{C}_L} = x \Big|_0^L$$
$$\frac{1}{(a_1a_3 - a_4)} \left\{ \ln \frac{a_1a_2\tilde{C}_L + (a_1a_3 - a_4)}{\tilde{C}_L} - \ln \frac{a_1a_2\tilde{C}_i + (a_1a_3 - a_4)}{\tilde{C}_i} \right\} = L$$

$$\frac{1}{(a_{1}a_{3}-a_{4})}\ln\left[\frac{a_{1}a_{2}\tilde{C}_{L}+(a_{1}a_{3}-a_{4})}{a_{1}a_{2}\tilde{C}_{i}+(a_{1}a_{3}-a_{4})}\times\frac{\tilde{C}_{i}}{\tilde{C}_{L}}\right] = L$$

$$\frac{1}{(a_{1}a_{3}-a_{4})}\ln\left[\frac{a_{1}a_{2}\tilde{C}_{i}+(a_{1}a_{3}-a_{4})\frac{\tilde{C}_{i}}{\tilde{C}_{L}}}{a_{1}a_{2}\tilde{C}_{i}+(a_{1}a_{3}-a_{4})}\right] = L$$
(3.40)

Noting that  $\tilde{C}_L = (1-\eta)\tilde{C}_i$ , Equation (3.40) may be written as

$$\frac{1}{(a_1a_3 - a_4)} \ln \left[ \frac{a_1a_2\tilde{C}_i + (a_1a_3 - a_4)(\frac{1}{1 - h})}{a_1a_2\tilde{C}_i + (a_1a_3 - a_4)} \right] = L$$
(3.41)

By rearranging equation (3.41), one has:

$$\ln\left[\frac{a_{1}a_{2}\tilde{C}_{i} + (a_{1}a_{3} - a_{4})(\frac{1}{1-h})}{a_{1}a_{2}\tilde{C}_{i} + (a_{1}a_{3} - a_{4})}\right] = (a_{1}a_{3} - a_{4})L$$

$$\frac{a_1 a_2 \tilde{C}_i + (a_1 a_3 - a_4)(\frac{1}{1 - h})}{a_1 a_2 \tilde{C}_i + (a_1 a_3 - a_4)} = \exp\left[(a_1 a_3 - a_4)L\right]$$

$$a_1 a_2 \tilde{C}_i + (a_1 a_3 - a_4) (\frac{1}{1 - h}) = \left[ a_1 a_2 \tilde{C}_i + (a_1 a_3 - a_4) \right] \exp\left[ (a_1 a_3 - a_4) L \right]$$

$$(a_1a_3 - a_4)(\frac{1}{1 - \boldsymbol{h}}) = \left[a_1a_2\tilde{C}_i + (a_1a_3 - a_4)\right] \exp\left[(a_1a_3 - a_4)L\right] - a_1a_2\tilde{C}_i$$

$$\left(\frac{1}{1-\boldsymbol{h}}\right) = \frac{\left[a_1a_2\tilde{C}_i + (a_1a_3 - a_4)\right]\exp\left[(a_1a_3 - a_4)L\right] - a_1a_2\tilde{C}_i}{(a_1a_3 - a_4)}$$

$$1 - \mathbf{h} = \frac{(a_{1}a_{3} - a_{4})}{\left\{ \left[ a_{1}a_{2}\tilde{C}_{i} + (a_{1}a_{3} - a_{4}) \right] \exp[(a_{1}a_{3} - a_{4})L] \right\} - a_{1}a_{2}\tilde{C}_{i}}$$
$$\mathbf{h} = 1 - \frac{(a_{1}a_{3} - a_{4})}{\left\{ \left[ a_{1}a_{2}\tilde{C}_{i} + (a_{1}a_{3} - a_{4}) \right] \exp[(a_{1}a_{3} - a_{4})L] \right\} - a_{1}a_{2}\tilde{C}_{i}}$$
(3.42)

#### 3.5 Material and Experiment

Experiments were conducted to characterize the performance of the CFEF module under various applied electrostatic field. The initial pH values were measured while the suspension was being stirred. To ensure a constant influent concentration, test suspensions were stirred for about two hours before the start of any experiment. The electric field strength applied was from 0 to 152 V/cm. In this research, we select model colloid particles,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, and one naturally colloid particle sample collected from a groundwater. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> were obtained from the Degussa Company (Darmstadt, Germany) and the Nissan Chemical Industries, Ltd. (Chiba, Japan), respectively. The naturally occurring colloids were collected from the well water sample with low-flow-purging, high-flow-purging, and bailer techniques at the Denzer-Schaefer site, Toms River, NJ. The turbidity of the filtrate was measured against a calibration curve using dilute water sample solutions. A linear relationship exits between turbidity and the solid concentration of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and naturally occurring colloidal particle was observed with a linear correlation coefficient of 0.99. So we can use turbidity as a means to monitor the solid concentration. The characteristics of CFEF system and the details of the experimental setup and procedures are given in Chapter 2.

## 3.6 Results and Discussion

#### 3.6.1 Particle and Characterization

A surrogate colloidal particle,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and naturally occurring colloids collected from well water in the state of New Jersey were studied. The results show that all particles appear to be monodispersed. The average particle size of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> was 209 and 76 nm, respectively. The average diameter of particles in the well water was in the range of 297 to 1007 nm. The pH<sub>zpc</sub> for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was approximately 9.2. and the pH<sub>zpc</sub> for SiO<sub>2</sub> and naturally occurring colloid was less than 2. This implies that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is positively charged and SiO<sub>2</sub> and naturally occurring colloids are negatively charged in the pH range studied, i.e. 4 to 9. Table 3.1 summarizes the type and properties of model colloids and naturally occurring colloidal particles collected from groundwater for use in the experiments.

## 3.6.2 Model Results and Sensitivity Analysis

The proposed colloid transport model was applied to simulate the migration of colloids through the CFEF module. The module parameters are listed in Table 3.2. The influent solution of colloids was continuously fed at a constant flow rate. All simulations were conducted under constant water flow velocity condition. Since the Reynolds number is very low, i.e. less than 0.1, the Laminar flow domain is applicable in the CFEF module.

To investigate the effect of various parameters on model results, we conducted a sensitivity analysis. Critical parameters such as particle size, surface charge of particle, and applied electrostatic field strength were selected to analyze the model behavior. Other parameters were left unchanged unless otherwise specified. The ranges of particle size and surface charge depend on the characteristics of colloids. However, the range of parameters studied should cover the values for most naturally occurring colloidal particles encountered. Thus Table 3.1 includes values within these ranges. Results are presented as removal efficiency expressed as percentages of filtrate concentration to influent concentration. The values of Reynolds number were calculated and less than 0.1, which indicates that Laminar flow domain in effective in the CFEF unit.

Figure 3.5 illustrates the removal efficiency of colloidal particles as a function of applied electrostatic field and the model sensitivity to various particle sizes. In all cases the removal efficiency increases as applied electrostatic field strength increases. For example, increase the applied electrostatic field strength by 300%, e.g., from 50 to 150 V/cm increases the removal efficiency by approximately 300% at a particle size of 100 nm. A seen in Figure 3.5, under conditions examined, the variation in removal efficiency is quite sensitive to changes in particle size. An order of magnitude change in particle size from 100 to 1000 nm under 50 V/cm of applied electrostatic field shows an increase of removal efficiency up to 400%.

Particle type	Mean size (nm)	pH <sub>zpc</sub>
γ-Al <sub>2</sub> O <sub>3</sub>	209	9.2
Naturally occurring colloids	297 ~ 1007	< 2
Snowtex 20L	76	< 2

 Table 3.1
 The physical-chemical characteristics of colloidal particles

 Table 3.2
 Parameters used in the model calculation

Parameter	Value	
r <sub>o</sub>	0.032 m	
$r_{i}$	0.015 m	
L	0.225 m	
μ	0.001 kg/m sec	
ε	6.95 x 10 <sup>-10</sup>	

Figure 3.6 presents the removal efficiency of colloidal particles as a function of particle size in the presence of an electrical field strength less than 96.8 V/cm and the sensitivity of the model to various surface charges. In all cases the removal efficiency increases as particle size increases under constant surface charge. An increase in particle size from 100 to 1000 nm produces as much as 340% increase in removal efficiency at a surface charge of  $10^{-3}$  C/m<sup>2</sup>. This sensitivity is similar to that of particle size (Figure 3.5).

## 3.6.3 Model Validation

The proposed model has been applied to simulate the transport of model colloids, e.g.,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and naturally occurring particles collected from well water using different groundwater sampling methods. First, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was tested. In this particular experiment, a colloidal



Figure 3.5 Predicting the removal efficiency of colloidal particles as a function of applied electrostatic field. The surface charge of colloidal particles is 18 C/m<sup>2</sup>.



Figure 3.6 Predicting the removal efficiency of colloidal particles as a function of particle size. The applied electrostatic field strength is 96.8 V/cm.

suspension was prepared with a known concentration of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles. The dispersion was stirred in the feed tank and recirculated for sufficient time to product a homogenous mixture while allowing the particles to adsorb onto the surfaces in the rig. The suspension pH was then altered to the required value using NaOH (0.1 M) or HCl (0.1 M). Laboratory experiments were run under the following conditions: (1) filtration rate, (2) pH, and (3) electrostatic field applied. The filtration rate was from 0.3 to 0.78 L/min. The pH values were in the range of 4 to 8. The electrostatic field strength was from 0 to 156.5 V/m.

Each experiment was run until both the turbidity of the filtrate and the concentrate streams (i.e. total solid concentration) reached a "steady state". Since a true steady state was not always reached, for the propose of simplicity it was taken to be when the turbidity changed by less than 2 %. For each case the model parameters were determined directly from the experimental results. The effects of the process variables, i.e. electrostatic field strength, filtrate flow rate, and pH, have been examined in some details previously (Chapter 2). Table 3.3 summarizes the model parameters used for colloidal transport simulation under various experimental conditions.

The following figures show results of a fitted experimental data with theoretical predictions. The solid and dash lines represent data from model calculation using particle size distribution and mean particle size, respectively. The experiments were begun by adjusting the pumping speed while keeping the pH at 5.6, before applying an electrostatic field, which was set at 96.8 V/cm to the electrodes. Figure 3.7 shows the effect of filtration rate on the performance of the CFEF unit. The model-generated curve for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> matches experimental data well. At a pH of 5.6 and applied electrostatic field of 96.8 V/cm, the removal efficiency, almost doubles when the flow rate decreases from 0.78 to 0.3 L/min. This indicates that as expected, high filtration rate will decrease the particle removal efficiency. According to equation (3.42) (or Figure 3.6), high surface charge will result in high particle removal efficiency. The effect of surface charge was investigated by altering the suspension pH. Figure 3.8 shows the effect of pH on the performance of the CFEF system. Based on the results, the particle removal efficiency increases

Particle	Variation	Field Strength (V/cm)	Filtrate flow rate (L/min)	Concentrate flow rate (L/min)	pН
γ-Al <sub>2</sub> O <sub>3</sub>	Field strength	0 ~ 96.8	0.30	0.40	5.6
γ-Al <sub>2</sub> O <sub>3</sub>	рН	96.8	0.30	0.40	4 ~ 8
γ-Al <sub>2</sub> O <sub>3</sub>	Velocity	96.8	0.3 ~ 0.78	0.35 ~ 0.95	5.6
10IL01	Field strength	0 ~ 200	0.30	0.39	6.5
5SIIL02	Field strength	0 ~ 156.8	0.37	0.37	6.6
$10IIB02 + SiO_2$	Field strength	0 ~ 126.5	0.28	0.54	8.2

Table 3.3The summary of model parameters used for colloid transport simulation under<br/>various experimental conditions.



Figure 3.7 Predicting the removal of **g**Al<sub>2</sub>O<sub>3</sub> as a function of filtrate flow rate.


Figure 3.8 Predicting the removal of **g**Al<sub>2</sub>O<sub>3</sub> as a function of pH.

with decreasing pH. Because the  $pH_{zpc}$  of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 9.2; pH value less than  $pH_{zpc}$  indicates that the particles are positively charged.

The larger the difference between pH and  $pH_{zpc}$ , the greater is the surface charge. Figure 3.8 shows that there is a good agreement between the calculated values with the experimental data.

The extent of improvement in removal efficiency is also dependent primarily on the magnitude of the imposed field gradient. Removal efficiency enhancements are possible when using steeper field gradients. The field gradient is dependent on the applied voltage and the inter-electrode distance. Figure 3.9 shows the influence of applied electrostatic field on the filtrate removal efficiency during cros-sflow electro-filtration of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> suspension and well waters. Results show that the equilibrium turbidity decreases by a factor of 1.8, 3, and 5 times on the application of electric field gradient of 32.3, 64.5 and 96.8 V/cm, respectively. Model

calculations of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system were in excellent agreement with measurements. The naturally occurring colloidal particles were also used to validate the model. Because naturally occurring colloids are negatively charged in the pH range studied, i.e. 4 to 9, the collector electrode was made cathodic. In this experiment the colloid suspension was made up to a known concentration with distilled water and the resultant mixture was stirred in the feed tank for two hours to ensure a constant influent concentration. Figure 3.9 shows the calculated particle removal efficiency (by Equation (3.42). Results compare favorably with the experimental data. It can been seen that the relationship between removal efficiency and electric field, e.g., turbidity = f(E), is not linear for all there filtration experiments studied. An increase in E from 0 to 157 V/cm enhances substantially the average removal efficiency. At higher electrostatic field strength (E > 65 V/cm), the particle removal efficiency decreased. The calculated values were in good agreement with those obtained experimentally.



Figure 3.9 Predicting the removal of **g**Al<sub>2</sub>O<sub>3</sub> and naturally occurring colloidal particles as a function of applied electrostatic field.

Any deviation between experimental and predicted data can be attributed to uncertainly in the mean electrostatic field and particle size distribution. Several researchers have reported that the electrostatic field strength may not be calculated from the overall applied voltage, since the drop in voltage at electrode-filter-solution interface (over potential) is unknown (Bowen and Sabuni 1992; Bowen and Ahmad 1997; Huotari et al. 1999). While any deviations caused by the particle size distribution should have been covered by the mobility spectrum, the ideal flow conditions based on this estimation are not completely achieved in the filtration because of the use of space nettings. The assumption of a homogeneous electric field may also be to simple. In the following section, the effect of particle size distribution on the prediction of removal efficiency will be discussed.

The mean particle size was used in calculation model and the results are shown in the Figures 3.7 and 3.8 (in dash lines). An improvement would be using the particle size distribution instead of the mean diameter. The equation (3.42) can be rewritten as:

$$\boldsymbol{h} = \sum_{1}^{n} \boldsymbol{h}_{i} f_{i} \tag{3.43}$$

where  $\eta_i$  is the removal rate of particle size of the ith order and  $f_i$  is the fraction of particle size of the ith order in the class.

Figures 3.7 and 3.8 also show the results of model calculation based on equation (3.43) (solid lines). Results clearly indicate that data calculated from particle distribution is better than those from mean particle size.

#### **3.6.4** Separation Various Particle Size Using CFEF Model

Because the range of the particle size distribution of naturally occurring particles collected from groundwater samples is very narrow. We cannot observe a significant separation effect of particle size using the CFEF technique. Therefore, the naturally occurring particles collected from groundwater samples and model silica (SiO<sub>2</sub>) were used to prepare a bimodal particle size distribution. Under the prevailing pH conditions of most groundwater, the surface charge of colloidal silica and naturally occurring colloidal particles are negative. The mean particle sizes of colloidal silica and naturally occurring colloidal particles are 76 and 441 nm, respectively. The colloidal silica and naturally occurring colloidal particles were prepared at different concentration to determine the best proportion for bimodal distribution (Figure 3.10(a) solid line). Figure 3.10(a) shows the effect of the electrostatic field on the size distribution of particles in the filtrate stream. It is desirable to use parameters such as the mean diameter, standard deviation and peak value (most probable value), to describe the particle size distribution. The most common particle size distribution function is the log-normal distribution which is based on the Gaussian distribution. Figure 3.10(a) shows the effect of the electrostatic field on the particle size distribution of particles in the filtrate. Increasing the electrostatic field strength causes the coarse particles (i.e. naturally occurring colloidal particles) to be separated more rapidly. The differences are subtle: the main effect of increasing field strength is to decrease the spread (i.e. standard deviation) of the fine particle group (i.e. Snowtex 20L) from 0.23 to 0.18 while the mean size remains constant at 76  $\pm$  20 nm at electrostatic field strength of 0 and 96.8 V/cm. The area under the two quite distinct curves gives the proportions of two constituents.

The insert of Figure 3.10 shows the proportion changes as function of electrostatic field. According to the insert of Figure 3.10, the proportion of larger particle size (i.e. naturally occurring particle) decreases from 42 to 15% and the proportion of smaller particle (i.e. Snowtex 20L) increases58 to 85% as the electrostatic field of different strength increases from 0 to 96.8 V/cm. Figure 3.10(b) shows the model prediction using equation (3.42). As seen in Figure 3.10(b), the fraction of larger particle size decrease with increasing the electrostatic field strength. The proportion of smaller particle size increases simultaneously. The general pattern of distribution is similar to the experimental data. The insert of Figure 3.10 shows the relationship between experimental and model-calculated data. Good agreement (with a correlation coefficient, r, > 0.997) was found between the experimental and the calculated proportion. It indicates the data calculated by model lie close to the experimental data. Therefore the mode-generated curve matches with experimental data well as shown in Figure 3.10.

### 3.7 Conclusion

A mathematical model describing the nano-sized colloidal particle transport in the cross-flow electro-filtration system was developed. Experimental data were used to validate the model. Results indicate that the model can describe the colloid transport successfully in the cross-flow electro-filtration system. The results of sensitivity analysis reveal that the presence of the electrostatic field remarkably increases the removal rate of colloidal particles.



Figure 3.10 Predicting the distribution of particle size as a function of applied electrostatic field. (a) experimental data; (b) model prediction.

3.8	List of Symbol
A:	Area, $m^2$ .
C:	Number of particles per unit volume, m <sup>-3</sup> .
$ ilde{C}_i$ :	Initial number of particles per unit volume at $x = 0$ , m <sup>-3</sup> .
$\tilde{C}_L$ :	Final number of particles per unit volume at $x = L$ , m <sup>3</sup> .
$\tilde{C}_x$ :	Number of particles per unit volume at x position, $m^{-3}$ .
d <sub>p</sub> :	Particle diameter, m.
E:	Electric field strength, V/m.
E <sub>m</sub> :	Mean electric field strength, V/m.
f:	Fraction.
L:	Length, m.
N:	Total number of particles.
p:	Perimeter, m.
Q:	Volumetric flow rate, m <sup>3</sup> /s.
$Q_c$ :	Volumetric flow rate of concentrate, m <sup>3</sup> /s.
Q <sub>f</sub> :	Volumetric flow rate of filtrate, $m^3/s$ .
q:	Charge, C.
$\widetilde{q}_{\scriptscriptstyle vi}$ :	Charge density, $C/m^3$ .
$\widetilde{q}_{\scriptscriptstyle vL}$ :	Initial charge density at $x = 0$ , C/m <sup>3</sup> .
$\widetilde{q}_{\scriptscriptstyle vx}$ :	Final charge density at $x = L$ , C/m <sup>3</sup> .
$q_{vx}$ :	Charge density at x position, $C/m^3$ .
r:	Radius, m.
r <sub>I</sub> :	Inner radius, m.
r <sub>o</sub> :	Otter radius, m.
$\widetilde{V}$ :	Voltage, V.
v <sub>p</sub> :	Particle velocity, m/s.
v <sub>r</sub> :	Velocity at x direction, m/s.
v <sub>t</sub> :	Terrminal velocity, m/s.
V <sub>x:</sub>	Velocity at x direction, m/s.
x:	Distance from bottom of CFEF to control surface, m.
η:	Removal efficiency.
ε:	Dielectric constant, $C^2/J \cdot m$ .
$\epsilon_0$ :	Permittivity constant, $8.85 \times 10^{-12} \text{ C}^2/\text{J} \cdot \text{m}$ .
$\epsilon_r$ :	Dielectric constant of medium.
μ:	Dynamic viscosity, kg/m·s.
к:	Conductivity, mho.
ρ:	Density, $kg/m^3$ .

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#### **CHAPTER 4**

# COMPARISON OF SAMPLING TECHNIQUES FOR MONITORING NATURALLY OCCURRING COLLOIDAL PARTICLES IN GROUNDWATER

#### 4.1 Abstract

Low-flow-purging, bailing and high-flow-purging sampling methods were used to sample well water which contains naturally occurring colloids. The water samples were filtered using the CFEF unit at various field strengths (which controls particle size) and pH (which controls surface charge). Results indicate that water-sampling methods appear to strongly affect the particle size distribution, total solid content and total lead concentration. Apparently the disturbance caused by bailer and high-flow-purging technique brings about high total solid concentration in the water samples. Results also show that lead in the well water almost all associated with the colloids. From the total solid content and lead concentration of water samples data, the larger the concentration of total solid the greater is the lead concentration in the water samples. The CFEF module consists of an external tube, an inner charged cathodic filter membrane (circular shape), and a co-centric anodic rod. The cathode/filter and the anode collector are connected to a d.c. power supply that provides the electric field. By adjusting the applied field it is possible to differentiate the colloidal particles into various size and surface charge fractions. The concentrations of lead in particles of different size and surface charge are different. Generally, the concentration of lead species increases with increasing field strength, that is, the smaller the particles the greater the metal concentration content regardless of sampling method. While the difference in lead concentration in particles of different charge is not as significant as that of particle size, there is clear indication that the lead concentration is affected by the pH under which the particles are separated. The CFEF process can be an important technique for the speciation of various chemicals in natural water such as groundwater. Moreover, CFEF is able to separate naturally colloidal particles without operational difficulties such as clogging.

#### 4.2 Introduction

Numerous studies have demonstrated that the presence of colloidal material in groundwater may facilitate the transport of organic and inorganic contaminants (Sheppard et al. 1979; Means and Wijayaratne 1982; Takayanagi and Wong 1983; Chiou et al. 1986). Groundwater monitoring collects necessary data for environmental site investigation. Conventional groundwater sampling procedures stress speedy pumping and rely on filtration to compensate for turbidity. The validity of the resulting samples to present actual groundwater constituents is therefore questionable (Kearl et al. 1992). It is generally accepted that the water in the well casing may not be representative of the formation water, so it needs to be purged prior to collecting the water samples. This can lead to excessive drawdown, accelerated groundwater flow, aeration of water, stirring up of sediments, and abrasion of the well casing. Following the purge, the water is generally filtered, especially for metal analysis, then analyzed for dissolved constituents such as lead. Examination of a wide variety of standard methods compendia dealing with water samples as well as regulatory requirements indicates that the current and almost universally accepted definition of a dissolved constituent is an operational one – only substances which pass a 0.45-µm membrane filter are considered to be dissolved (U.S. Environmental Protection Agency 1983; APHA et al. 1989; ASTM 1995). This will include colloidal material between 0.01- 0.45  $\mu$ m and exclude the 0.45 to 10- $\mu$ m portion of colloids in the determination of dissolved metal. As the reported ambient levels of dissolved trace elements have declined from the tens of parts per million (ppb,  $\mu g/L$ ) into the signal digit ppb range, the inclusion/exclusion of varying amounts of colloids and their affect on dissolved (or filtered) heavy metal concentrations has become more significant (Horowitz et al. 1996). Many researchers have indicated the dissolved heavy metal concentrations quantified by analyzing filtrates generated by processing whole water sample through similar pore-sized filters may not be equal or comparable (Horowitz et al. 1992; Karlsson et al. 1994; Horowitz et al. 1996). Horowitz et al. studied the problems associated with using filtration to define dissolved trace element concentrations in natural water samples (Horowitz et al. 1996). Based on their results, field and laboratory experiments indicate that dissolved concentrations generated by analyzing filtrates using the same pore-sized filters are not reproducible for a number of chemical constituents. The results also imply that chemical trends may be artificially induced by how samples are collected and processed and may not, in fact, represent actual changes in the ambient levels of trace elements. Detailed sampling and processing guidelines probably will not eliminate the problems associated with these artifacts because of randomly changing environmental factors. Low-flow-purging sampling was developed to allow the collection of samples while causing as little disturbance in the well and the surrounding formation as possible. Although low-flow-purging technique can minimize the introduction of particulate into groundwater samples, it is also slow and expensive. Furthermore, these analytical samples collected by low-flow-purging sampling technique need to be filtered to compensate for the excess turbidity. But samples collected for the determination of the colloids and low-solubility contaminants must not be filtered because some colloids are removed during filtration (Backhus et al. 1993). For site investigations or monitoring programs to be useful, metal concentrations need to be representative of concentrations in the aquifer, reproducible to the degree that concentrations in the aquifer are uniform, and precise enough to allow identification of temporal or spatial variation. As mentioned above, in order to accurately assess the concentration of specific contaminants, it is necessary to develop an effective solid separation method.

The objectives of this study were 1) to compare the effect of particle size on lead concentration in groundwater using low-flow-purging, bailer, and high-flow-purging methods, 2) to improve groundwater sampling methods using cross-flow electro-filtration (CFEF) process, and 3) to assess the effect of surface charge and particle size on the distribution of heavy metal, exemplified by lead, in New Jersey well waters.

### 4.3 Material and Experiment

### 4.3.1 Sampling Sites

The well water samples were taken from both #10 and #5S wells at the Denzer-Schaefer site, Toms River, NJ. Low-flow-purging, bailer, and high-flow-purging techniques were used. The flow rate of low-flow-purge and high-flow-purging were 0.1 and 5 L/min, respectively. At the well #10, the depth to static water was approximately 7.6 m. The final drawdown water level of low-flow-purging, bailer, and high-flow-purging were approximately 7.6, 9.4, and 8.8 m, respectively. At well #5S, the depth to static water was approximately 7.3 m. The final drawdown water level of low-flow-purging, bailer, and high-flow-purging, bailer, and high-flow-purging were approximately 7.3 m. The final drawdown water level of low-flow-purging, bailer, and high-flow-purging, bailer, and high-flow-purging were approximately 7.3 m. The final drawdown water level of low-flow-purging, bailer, and high-flow-purging, bailer, and high-flow-purging were approximately 7.3 m.

### 4.3.2 Sampling Materials and Devices

A Grundfos Redi-Flo2<sup>®</sup> electric submersible pump was used to sample the wells using lowflow-purging and high-flow-purging techniques. The pump was set with the pump intake at  $\sim$  0.6 m above the bottom of the wells and 0.6 m below the top of the wells over the 3-m long screens, and 0.6 m below the top of the screen in the 1.2-m long screen. A PE bailer with 1-L capacity was used to sample the same wells. The CFEF module consisted of an external tube, an inner charged cathodic filter membrane (circular shape), and a co-centric anodic rod. The cathode/filter and the anode collector were connected to a d.c. power supply that provided the electric field. The characterization of CFEF module were described in Chapter 2.

# 4.3.3 Sampling Procedures

To assure that any observed changes in water quality were brought about by the use of lowflow-purging sampling, two wells were resampled using the other traditional methods immediately after it had been sampled by low-flow-purging method. All traditional low-flowpurging, bailed and a high-flow-purging sample were collected and analyzed for unfiltered metals and filtered metals in the laboratory. All samples collected



Figure 4.1 Groundwater sampling process.

were directly pumped to the CFEF module. Figure 4.1 show the groundwater sampling scheme and process details.

All wells were test pumped and stabilized prior to the first monitoring event. This allowed practice runs with the low-flow-purging sampling method and equipment, and for establishing the initial well-specific pumping rates. The low-flow-purging sampling method was refined after each of the events, although care was taken not to change anything so drastically as to bring into question the comparability of one event's results to the next. A target of 0.5 ft or less of drawdown was chosen based on the low production rates of the well, and the high background gradient and pumping rates were modified bases on observed drawdown. Flow rates were measured with graduated cylinders, and purged water volumes were regulated from a control

unit. The wells were purged, and the samples were collected at various pumping rates. Drawdown was monitored continuously during purging and sampling.

The six stabilization parameters monitored in the field included redox potential, pH, temperature, specific conductance, dissolved oxygen, and turbidity. Stabilization parameters monitored were measured on-site at a frequency of approximately six runs per well volume. Samples for measuring field stabilization parameters were collected in laboratory-grade glassware. Stabilization measurements were performed and recorded after a sufficient volume of groundwater (approximately 300 mL) was collected from pumping. The preferred method of measuring the field parameters is a flow-through cell. However, at the time, there was no commercially available instrument that permitted measuring all the parameters selected for this work. In addition, most available cells were designed for much higher flow rates. At this project, pump discharge was collected in a 100-L tank that could accommodate all the probes. The low-flow-purging and high-flow-purging sampling procedure was generally followed when using the Grundfos Redi-Flo2<sup>®</sup> electric submersible pump to collect samples. Water levels were measured and recorded prior to purging and were monitored continuously during purging to evaluate drawdown in the wells; flow rates were adjusted from 0.1 to 0.5 L/min to minimize drawdown to < 0.1 m. Dissolved oxygen, pH, temperature, specific conductance, turbidity were measured about every 2-5 minute. All instruments were precalibrated daily according to manufacturer's recommendations. Stability of water quality parameters (WQP's) was defined as three successive readings within  $\pm$  10% for dissolved oxygen (DO) and turbidity,  $\pm$  3% for specific conductance, and  $\pm 0.1$  for pH. Temperature was recorded but not used for stabilization assessment. Samples were collected after turbidity equilibrated during purging.

When the bailer was used, three well volumes (volume of water standing in the casing and screened interval) were used as standard purge volume criterion. The same WQP's were measured, but only after each well volume was collected, and these values were not used for evaluation of well purging sufficiency. These samples had substantially greater turbidity than those collected using low-flow-purge and sampling techniques.

### 4.3.4 Chemical Analysis

#### 4.3.4.1 Particle Size

Particles are ubiquitous in natural waters and in water and wastewater treatment streams. Particle size distribution analysis can help to determine the makeup of natural waters, treatment plant influent, process water, and finished water. Similarly, it can aid in designing treatment processes, making decisions about changes in operations, and/or determining processes efficiency. Methods for measuring particle size distribution generally involve electronic devices because manual methods are likely to be too slow for routine analysis. However, when particle size analysis is to include size distribution of large (> 500  $\mu$ m) aggregates, direct microscopic counting and sizing can be used. Three such types of instrument are available: electrical sensing zone, light-blockage, and light-scattering instruments.

Light scattering arises from the interaction of light with matter. When light interacts with an isolated molecule, the oscillating electromagnetic wave induces a dipole in the molecule that oscillates with the same frequency as the incident light. Characteristic of an oscillating dipole is 'acceleration of charge.' When a charge is accelerated, energy is emitted in all directions within a plane perpendicular to the line of acceleration. It is the energy emitted from the oscillating dipole, induced by the interaction of the incident light with the molecule, which is referred to as scattered light. The frequency of the scattered light is equivalent to the oscillation frequency in the induced dipole, which is equivalent to the frequency of the incident light. Hence the frequency of the scattered light is the same as that of the incident beam. For particles much smaller than the wavelength of the incident light, the assumption that the particle interacts with only a single photon is valid. As the particle increases in size, the likelihood of multiple photons striking the same particle also increases. Multiple photons interacting with the same isolated particle will induce multiple dipoles. The scattering intensity monitored at a fixed position detector will be the sum of the intensities generated from each of these dipoles. As a consequence of constructive and destructive interference then, the scattering intensity from a

large isolated molecule is dependent upon the location of the detector, i.e. the scattering angle. In dynamic light scattering, it is the time dependent fluctuation in the scattering intensity that is used. These fluctuations arise because the solution particles are not fixed in space, but move randomly about due to Brownian motion. The scattering intensity measured at the detector is the sum of the scattering from all the particles. As the particles move, the phase of the light scattered from each particle varies, leading to constructive and destructive interference and fluctuations in the sum of the intensities measured at the detector. Consider for example, two snapshots of a system of particles taken across a very short time interval. If the time interval is short enough, the waveforms measured at the detector are going to be very similar, since the particles have had insufficient time to diffuse a great distance. The mathematical technique used to determine the frequency spectrum of this signal is autocorrelation, and this is the technique used in dynamic light scattering to measure the particle translational diffusion coefficient.

In general terms, the similarity between the signal waveform and a slightly time-delayed copy of itself is determined by multiplying the two waveforms together, element by element, and summing the results. In other words, the autocorrelation function of the signal from the scattered intensity is the convolution of the intensity as a function of time with itself. In more abstract terms, if the detected intensity is described as a function I(t), then the autocorrelation function of this signal is given by the following expression, where t is the shift time.

$$G(t) = \int_{0}^{\infty} I(t) I(t+t) dt$$
(4.1)

The above function is also called the intensity correlation function, and it is used to describe the correlation between the scattering intensities measured at t = 0 and some later time ( $t_n = t_0 + \tau$ ). The correlation in particle position at small shift times is contained within the measured intensity correlation function, an example of which is shown below. In the absence of any applied forces, the particle position is dictated by the degree of Brownian motion. As such, the measured intensity correlation curve is an indirect measure of the particle's diffusion coefficient. The discrete autocorrelation function is generated in real time for a digitized input signal. At the end of this process, the correlation coefficients of the discrete autocorrelation function are found in the elements of the accumulation register. The time coordinates are given by the delay times of the elements of the shift register used to generate the function. The autocorrelation coefficients are exported by the DynaPro<sup>TM</sup> as a series of integers. These integers are then normalized by dividing them by the expected steady photon background count which is the total number of photons counted during the sampling period times the mean number of photons acquired in each channel. For typical diffusion processes the intensity autocorrelation function has the form of 1 plus an exponential decay function.

$$G(t) = 1 + \exp(-\Gamma t) \tag{4.2}$$

The decay constant ( $\Gamma$ ) is representative of the diffusional properties of the particle under examination as shown below, where D is the translational diffusion coefficient, q is the scattering vector,  $\tilde{n}$  is the solvent refractive index,  $\lambda_o$  is the vacuum wavelength of the incident light, and  $\theta$ is the scattering angle.

$$G = 2Dq^{2} = 2D\left[\frac{4p \tilde{n}}{?_{o}} \sin\left(\frac{?}{2}\right)\right]^{2}$$
(4.3)

Hence, evaluation of  $\Gamma$  leads to the particle diffusion coefficient, which in turn is used to calculate the hydrodynamic radius (R<sub>H</sub>) via the Stokes Einstein equation given below, where k is the Boltzmann constant, T is the temperature, and  $\eta$  is the solvent viscosity.

$$R_{\rm H} = \frac{kT}{6phD}$$
(4.4)

The average particle size was determined by a dynamic light scattering size analyzer using the ZETASIZER 3000HSA particle measurement (Malvern Instrument Ltd., Malvern, Worcs, United Kingdom) in this research.

# 4.3.4.2 The Electrophoretic Mobility of Particles

The electrophoretic mobility of particles in the well water samples was determined by the ZETASIZER 3000HSA zeta potential meter (Malvern Instrument Ltd., Malvern, Worcs, U. K.). Zeta potentials were measured in different ionic strengths  $(10^{-3}, 10^{-2}, 10^{-1} \text{ M NaClO}_4)$  as a function of pH. The initial pH was measured while the suspension was being stirred. Then the pH was adjusted to the range from 2.0 to 10.0 by NaOH (o.1 M) and HClO<sub>4</sub> (0.1 M). About 20 mL of the sample was injected into the electrophoresis chamber.

### 4.3.4.3 The Total Solid Content

Analytical procedures for total solid content followed (2540.B) the Standards Methods for the Examination of Water and Wastewater (1995). A well-mixed sample was evaporated in a weighed dish and dried to constant weight in an oven at  $104 \pm 1$  °C. The increase in weight over that of the empty dish represents the total solid. Briefly the following describe the procedures.

- 1. Heat clean dishes to  $104 \pm 1$  °C for 1 h;
- 2. Store and cool dish in desecrator until needed. Weigh immediately before use (A);
- 3. Choose a sample volume that will yield a residue between 10 to 200 mg. Pipette a a given amount of well-mixed water sample to a pre-weighed dish and evaporate it to dryness in a drying oven. Stir sample with a magnetic stirrer during transfer;
- 4. Dry evaporated sample for at least 1 h in an oven at  $104 \pm 1$  °C;
- 5. Cool dishes in desiccators to room temperature, and weigh (B). Repeat cycle of drying, cooling, desiccating, and weighing until a constant weigh is obtained, or until weigh change is less than 4% of previous weight or 0.5 mg, whichever is less;
- 6. Calculate the total solid; mg total solids/L = (A-B)\*1000/(sample volume, mL). A = weight of dried residue (mg) + empty dish (mg), and B = weight of empty dish (mg).

#### 4.4 **Results and Discussion**

### 4.4.1 The Characteristics of Groundwater

### 4.4.1.1 Turbidity

Suspended particles were minimized in the samples collected by low-flow-purging sampling method and continuous monitoring of turbidity until it reached a stable level. The stable aquifer condition was assumed when three successive readings 10 min apart yielded turbidity values within  $\pm$  3%. Stabilization of turbidity varied from well to well and was independent of the number of casing volumes purged, but pumping time always exceeded the length of time necessary for the other field parameters (i.e. D.O., pH, specific conductance, and temperature) to reach aquifer stability. The initially high, but steadily decreasing, turbidity levels observed during well purging may be caused by (1) removal of well construction-related particles, (2) purging of particles formed or collected within the well casing, or (3) shearing of particles attracted to aquifer material near the well(Backhus et al. 1993). This results of the longer purge time, which indicated that the amount of naturally occurring colloidal particles in water in a well decreases to a stable minimal amount several hours after the introduction of a pump, are consistent with the conclusion of other research (Kearl et al. 1992; Backhus et al. 1993; Gibs et al. 2000; Ivahnenko et al. 2001). Turbidity stabilized 2 to 4 hour after initiation of pumping. Typically, stabilization occurred after 4-6 casing volumes of water were removed from well. This result may indicate that a minimum of 2 hour of purging is required until the particulates that were artificially mobilized by the surging action of the pump entering the well and by the increase in the velocity of ground-water flow caused by the pumping are removed, and particulate concentration, as determined by turbidity measurement, is stabilized.

### 4.4.1.2 Particle Size

The results show that the particles appear to be monodispersed in the well #10 and #5S. The average particle diameter of particles in the water sample from well #10 was in the range of 297

to 495 nm. The average diameter of particles in well water sample in well #5S was in the range of 522 to 1,007 nm. The above results shows that the size of particles in water samples in well #5 was larger than that from well #10. Another observation was that the particle size of water samples in well #10 and #5S by bailing and high-flow-purging sampling method were larger than those from well #10 and #5S by low-flow-purging method. In well #5S, the particle size of water sample collected by low-flow-purging sampling, high-flow-purging sample, and bailing sampling method were  $522 \pm 16$ ,  $817 \pm 77$ , and  $1007 \pm 72$  nm, respectively (Figure 4.2). Results also indicate that water-sampling methods appeared to strongly effect the particle size distribution. It has been reported that sampling method significantly influences the size of colloids collected from well waters. Backhus et al. (1993) studied the sampling of colloids in groundwater (Backhus et al. 1993). Samples collected by bailing were compared with those collected by low-flow-purging sampling method (less than 200 mL/min) from the same wells at the New Jersey site studied. Bailed samples were obtained after the removal of three and eight well volumes and pumped samples were obtained on the following day. The bailed samples contained particles in the range of 1-100 µm, whereas the low-flow-purging samples contained mainly particles less than 5 µm in diameter.

### 4.4.1.3 The Electrophoretic Mobility of Particle

In the well #10 water samples, the zeta potential of particle was around -12 mV at pH 2. In the well #5S water samples, the zeta potential of particle was similar to well #10 water samples. Results showed that the  $pH_{zpc}$  of all water samples collected by low-flow-purging, high-flow-purging, and bailing sampling method was approximately 1 and that the colloidal particles were negatively charged at the pH values greater than 2. The results also indicate that water-sampling methods has no effect on the  $pH_{zpc}$  and surface charge of colloidal particles as expected.



Figure 4.2 Distribution of colloidal particle size as affected of groundwater sampling methods. Well: #58. LFP: low-flow-purging; HFP: high-flow-purging.

### 4.4.2 The Total Solid Content

Figure 4.3 shows the concentration of total solid in the #5S water samples by bailer, low-flow-purging and high-flow-purging technique. In the well #10 water samples, the total solid content was in the range of 0.94 to 1.74 g/L. The total solid concentration was in the range of 2.94 to 12.22 g/L for well water #5S. The results show that the total solid concentration of water samples in well #5S was greater than those in the well #10. Results indicate that the total solid concentrations of well #5S are  $2.94 \pm 0.01$ ,  $11.98 \pm 0.02$  and  $12.22 \pm 0.03$  g/L, respectively, for water samples obtained by low-flow-purging, high-flow-purging and bailing methods. The total solid content of water samples in well #5S collected by low-flow-purging sampling method was less than those by high-flow-purging sampling and bailing method. For the well #10, the results of water samples were similar to well #5S: the total solid content of water samples collected by low-flow-purging sampling was less than bailing sampling technique. Apparently the disturbance caused by bailer and high-flow-purging technique brought about high total solid concentration in the water samples. This result is similar to that reported by Backhus et al. (1993), who studied the sampling colloids and colloid-associated contaminants in groundwater

(Backhus et al. 1993). Their results showed that bailed samples from a coal tar-contaminated site contained 10-100 times greater colloid concentrations and up to 750 times greater polycyclic aromatic hydrocarbon concentrations than were detected in low-flow-purging samples.



Figure 4.3 Distribution of total solid content as affected by groundwater sampling methods. Well: #5S. LFP: low-flow-purging; HFP: high-flow purging.

### 4.4.3 The Total and Soluble Lead

Figure 4.4 gives the typical total lead and soluble lead in well waters. The range of the average total lead concentration was 164, 377 and 401  $\mu$ g/L, respectively, in water sample collected by low-flow-purging, high-flow-purging and bailing sampling method in well #5S. The range of the soluble lead concentration in well #5S was 4, 3 and 4  $\mu$ g/L for the low-flow-purging, high-flow-purging and the bailer technique. For well #10, the total lead concentration of water collected by low-flow-purging and bailing sampling method was 11 and 28  $\mu$ g/L, respectively. The soluble lead concentration in well #10 was 1  $\mu$ g/L for both water sampling techniques. Based on above results, the lead concentration of well #5S water samples was greater than those in well #10. Results show that the lead almost all associated with the colloid.

Another observation is that the total lead concentrations in water samples collected by bailing and high-flow-purging sampling method were generally greater than those water samples collected by low-flow-purging sampling method. According results of total solid content and lead concentration, it is clear that the greater total solid content, the higher are the lead concentration in the water samples.



Figure 4.4 Distribution of lead concentration as affected by groundwater sampling methods. Well: #5S; LFP: low-flow-purging; HFP: high-flow-purging.

Figure 4.5 shows the total lead concentration of water samples taken by high-flow-purging method followed by particle separation using the ECFC module. As expected, the total lead concentration decreases with the applied electrical field strength increases. This is due to the fact that as the field strength increases, more fine particles are removed from the water sample. As a result, the total lead concentration in the filtrate decreases. Figure 4.5 also presents total lead concentration of the well water as determined by slow flow purging technique that is currently the standard method for water sampling. The result clearly shows that by applying a field strength of 62.5 V/cm, it is possible to obtain groundwater samples with total lead concentration equivalent to those obtained by low flow purging technique. Note that the sampling time of low

flow purging is about 50 times (e.g., 5 mL/min versus 0.1 mL/min) slower than the high flow purging. Obviously the use of CFEF technique for groundwater sampling will mean great savings in time and cost. As indicated in Figure 4.6, it is seen that the average diameter of particles collected by the CFEF module was about 490 nm or 0.49  $\mu$ m which is close to the pore size of the filter used to prepare the water samples for total lead analysis, e.g., 0.45  $\mu$ m. In other words, the CEFE module is able to process water samples at fast rate with a total lead concentration that is close to water samples prepared by slow-purging technique. The particle size at the critical field strength of 62.5 V/m or 490 nm versus 450 nm of current pore size used in water monitoring can well be a coincident event. It is expected that this critical particle size and its corresponding critical field strength would be different for different groundwater systems. Data used to plot Figure 4.5 are listed in Table A14.



Figure 4.5 Distribution of lead concentration as affected by groundwater sampling methods. Well: #5S; LFP: low-flow-purging; CFEF: Cross-Flow Electro-Filtration Process.

### 4.4.4 Operation and Performance of CFEF Module

Since the solid concentration of the water sample exceeds the detection limit of 1,000 NTU (neupholometic turbidity units) and the total volume of each water sample available was about 20 liters, the water samples were diluted with distilled water. Experiments were conducted to evaluate the performance of the cross-flow electro-filtration unit. The following operational conditions were tested: (1) clogging, (2) flux production, (3) quality of flux, and (4) backwash frequency. Results show that there is no filter clogging after 2 hours of operation. Therefore, it is not necessary to backwash the filter. Results clearly demonstrate that the naturally occurring particles can be separated according to particle size and surface charge. Furthermore, it is expected that pH and applied field control the particle size and surface charge of naturally occurring particulates. Laboratory experiments were run under the following conditions: initial filtration rate was kept constant at 1.1 cm<sup>3</sup>/cm<sup>2</sup>-min and electrostatic field strength applied was between 32.3 V/cm and 156 V/cm.

### 4.4.4.1 The Particle Size Distribution of Filtrate and Concentrate

The average particle size of particles in the filtrate of water samples collected by the lowflow-purging, bailing and high-flow-purging from well #10 and #5S was less than those in the raw and concentrate streams. Figure 4.6 shows the effect of electrostatic field on the particle size distribution of particles in the filtrate and concentrate streams. The mean particle size of particles in the filtrate decreased as the applied electrostatic field increased.

### 4.4.4.2 The Total and Soluble Lead Concentration of Filtrate and Concentrate

Figure 4.7 shows the effect of electrostatic field on lead concentration. For well #5S water samples collected by the low-flow-purging sampling method, the soluble lead concentration of the filtrate and the concentrate streams were between < 0.5 and 4 µg/L at the electrostatic field of 32, 64, 97, 129, and 157 V/cm. The total lead concentration in the filtrate was less than 0.5 µg/L, under all levels of electrostatic field strength. The total lead concentration of the



Figure 4.6 Distribution of particle size as affected by electrostatic field. Well: #5S.



Figure 4.7 Distribution of lead concentration as affected by electrostatic field. Sample: #5S. SF: soluble concentration of filtrate; TF: total concentration of filtrate; SC: soluble concentration of concentrate; TC: total concentration of concentrate. D.L.: detection limit.

concentrate stream was 24, 42, 55, 72, and 78  $\mu$ g/L, respectively, at electrostatic field of 32, 64, 97, 129, and 157 V/cm. Results show that the total lead concentration increased as the applied electrostatic field increased. Results suggest that the high lead concentration can be attributed to high particle loading and high degree collection of fine particles in the concentrate stream.

### 4.5 Conclusion

Results show that the mean particle size, total solid content, and total lead concentrations of well #5S and #10 collected by the low-flow-purging sampling method were less than those by bailing and high-flow-purging sampling method. Apparently the disturbance caused by bailing and high-flow-purging techniques brings about high total lead concentrations in the well water samples. This can be preliminarily attributed to the high total solid content in the well waters collected by bailing and high-flow-purging techniques. Results demonstrate that the concentration of lead species increased with increase in field strength, that is, the smaller the particles the greater was the lead concentration regardless of sampling method, especially in the concentrate stream. While the effect of particle charge on lead concentration was not as significant as that of particle size, there is clear indication that the lead concentration was affected by the pH under which the particles were separated. The CFEF process can be an important technique for the speciation of various chemicals in natural water such as groundwater. CFEF is able to separate naturally colloidal particles without operational difficulties such as clogging of filter.

It is possible to sample groundwater at high-flow and separate the aquatic particulates using the CFEF technique. Once the critical particle size is selected, e.g., about 490 nm in this case, it is possible to determine the critical electrical field strength. By quickly sampling the well water using high-flow-pumping, the water sample is then filtered through the CFEF at the critical field strength, one can readily decide the cut-off particles size for the determination of total lead concentration. Since most naturally occurring particles are negatively charged, with a pH<sub>zpc</sub> near

1, it is not necessary to adjust the pH value of the water sample of interest before filtration by the CFEF. Preliminary data appear promising to suggest that the CFEF module can replace current low-flow purging technique for water sampling for purpose of site investigation.

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#### **CHAPTER 5**

# SPECIATION OF LEAD IN GROUNDWATER USING CROSS-FLOW ELECTRO-FILTRATION TECHNIQUE

### 5.1 Abstract

Naturally occurring colloidal particles were collected from two New Jersey wells using three different sampling techniques, i.e. low-flow-purging, bailing, and high-flow-purging methods. The particles in the well water were separated into different size fractions using cross-flow electro-filtration process (CFEF). Particles of various size fractions were subjected to a sequential chemical phase extraction procedure to differentiate the exchangeable, carbonate, Fe/Mn oxide, organic and residual phases. Results show that lead concentrations increase with increasing electrostatic field. For well water #10 and #5S samples, the highest concentrations of lead were found in the smallest size fraction. The major lead-laden phases were organic matter and residual phases, but the relative importance of each phase varied for individual sampling method and grain sizes. The percentage of lead associated with various fractions followed the order: residual > (or  $\approx$ ) organic matter > Fe-Mn oxide  $\approx$  carbonate > exchangeable. The extraction data show increase in potential bioavailability of lead with decrease in grain size. The concentration of fine particles is crucial to overall lead speciation. The trend in colloids associated lead is significant in the terms of assessing the bioavailability of heavy metals in the groundwater system. It also provides valuable insight into the fate of pollutants in the environment. The distribution of lead among the various size fractions and chemical phases were determined and analyzed in order to define relationships necessary to assess the overall bioavailability of lead. Results clearly indicate that the CFEF is able to separate the colloidal particles according to their size and surface charge. Most importantly, the distribution of lead in particles of different size is different. Generally, the concentration of lead species increased with increases in field strength. That is, the smaller the particles the greater was the metal content in solid of all size fractions. The CFEF process can be an important technique for the speciation of chemical species in natural water such as groundwater. Moreover, CFEF is able to separate naturally colloidal particles with great ease; clogging, the most common operational problem in filtration is almost totally eliminated.

### 5.2 Introduction

Contamination of heavy metals in the environment is a major concern because of their toxicity and threat to human life and the environment (Purves 1985). It is important to predict the mobility and bioavailability of metals in environmental systems, since these processes determine the transport and the fate of heavy metals in hydrobiological systems, e.g., surface waters and groundwater. Most studies dealing with metals in environmental systems are concerned with total metal concentrations. Relatively few attempts have been made to evaluate the speciation of particulate metals, i.e. partitioning among the various forms in which they might exist. It has been reported that heavy metals in plants are determined not only by their concentrations in soils, but also by the physiochemical properties of soils (Xian 1989). Therefore, use of the total metal concentration as a criterion to assess the potential effects of heavy metals in soils or groundwater implies that all forms of metals have an equal impact on the environment; such assumption is clearly unrealistic (Tessier et al. 1979). It is, in fact, the physicochemical forms of the heavy metals that determine their bioavailability and remobilization.

Metals in solid matter may be present in several different geochemical phases that act as reservoirs or sinks of heavy metals in the environment (Kramer and Allen 1988; Li et al. 1995). These phases include the following broad categories: specifically adsorbed; carbonate; Fe- and Mn-oxides; organic matter; and mineral lattice (Tessier et al. 1979; Salomons and Forstner 1980; Beckett 1989). Recently, analytical determination of the distribution of metals among these phases has been made by direct and indirect methods. Direct methods for the determination of soil state metal speciation that require specialized equipment, are generally of insufficient sensitivity in environmental trace analysis (e.g. NMR spectroscopy) or require very specialized

equipment (e.g. EXAFS) (Glidewell and Goodman 1995). The other approach to the analytical determination of the distribution of metals among various physicochemical phases has been made by phase-selective chemical extractions involving single (Lindsay and Norvell 1978; Leschber et al. 1985; Beckett 1989) or multiple extracting reagents (Tessier et al. 1979; Slavek and Pickering 1986; Ure et al. 1993; Ramos et al. 1994; Ma and Uren 1998). Multistep sequential extraction schemes provide a more complete picture for predicting the heavy metal distribution, mobility, and bioavailability in environmental solid matrixes. Generally three to nine extractants are used in a sequence in which the earlier ones are the least aggressive and the most specific, and subsequent extractants are progressively more destructive and less specific, except that late in the sequence there may remain only or two groups of compounds that they can dissolve (Beckett 1989; Elliott et al. 1990).

Although the selective sequential extraction methods is useful for obtaining information on heavy metals distributions, a number of investigators have highlighted pitfalls in the use of sequential extraction (Nirel and Morel 1990). Three major experimental problems with sequential procedures have been recognized (1) the limited selectivity of extractants, (2) the redistribution of metals during the extraction process, and (3) the deficiency of reagent dose if metal content is too high (Tessier et al. 1979; Tipping et al. 1985; Kheboian and Bauer 1987; Dudka and Chlopecka 1990; Nirel and Morel 1990). Howard and Vandenbrink (1999) evaluate the utility of sequential extraction process for counteracting resorption during sequential extraction analysis using sediments with a wider range in composition. The results of this study indicate that significant resorption may occur during sequential extraction analysis, thereby reducing the accuracy of the method. However, this problem may be important only at very high levels of contamination. Notwithstanding, these limitations mean that sequential extraction can not be used to determine specific geochemical associations, but the approach is still of value for characterizing solid-phase associated metals in environmental solid matrixes (Li et al. 1995).

Most naturally occurring colloidal particles are negatively charged and negatively charged colloids are expected to be more mobile than positively charged ones. Numerous studies have demonstrated that the presence of colloidal particles in groundwater may facilitate the transport of organic and inorganic contaminants (Sheppard et al. 1979; Means and Wijayaratne 1982; Takayanagi and Wong 1983; Chiou et al. 1986; Beckett et al. 1988). It is an established fact that colloidal matter has a high affinity for heavy metals (McCarthy and Zachara 1989; Gounaris et al. 1993; Chorapcioglu and Choi 1996). Sheppard et al. (1980) reported that lead was 4 orders of magnitude more mobile than what is predicted in soils. They attributed this enhanced mobility to associations of lead with mobile humic acids and colloids. The presence of colloidal-bound heavy metals in groundwater affects the total concentrations as well as their behavior in the aquifer. The bioavailability and toxicity of colloid-associated metals are influenced by their speciation and transport dynamics which are linked to the textural composition and grain size of the naturally occurring colloidal particles. Grain size influences the surface area of naturally occurring colloidal particles, as well as the degree of chemical partitioning onto the colloid. Therefore, there is a need for more comprehensive characterization of metals in naturally occurring colloidal particles in well water, because the concentration levels vary with the water quality and the nature and source of chemical additives. Yet a review of the literature yields very limited information regarding the total concentrations of toxic metals in groundwater; nearly all of these studies deal with naturally occurring colloidal particles in the bulk unfractionated form. Very few field observations have been made on the speciation of heavy metals in groundwater (Jensen et al. 1999).

In this chapter we, for the first time, used the cross-flow electro-filtration separation technique to study the speciation of lead in groundwater. This method allows fractionation of particles into various size fractions, which was traditionally ignored or poorly characterized due to the aforementioned difficulties and only now it is widely recognized as an important component in understanding the role of naturally occurring colloidal particles in natural water. The specific goal of this study was to evaluate the content and the chemical fraction of lead in naturally occurring colloidal particles collected from well water using different water sampling methods. A five-step chemical fraction was used to characterize the partitioning of heavy metals

in naturally occurring colloidal particles. This approach was used, not only for bulk samples but also for different size fractions so that the detailed relationships and changes among chemical forms, particle sizes and well water sampling methods, and the processes affecting them, can be more precisely defined and better understood.

### 5.3 Methods and Material

### 5.3.1 Sample Collection

The well water samples were taken from both #10 and #5S wells at the Denzer-Schaefer site, Toms River, NJ. Low-flow-purging, bailer, and high-flow-purging techniques were used to sample the well water as to obtain naturally occurring colloid particles. The flow rate of lowflow-purging and high-flow-purging were 0.1 and 5 L/min, respectively. Then, the water samples were filtered using the cross-flow electro-filtration (CFEF) unit to separate naturally occurring colloidal particles into various size fractions by controlling the field strength and pH. All samples and solutions were stored at 4°C prior to experiments and chemical analysis.

# 5.3.2 Separation of Particle

When the size of naturally occurring particles becomes small, the surface area to volume ratio increases and it becomes an important factor in solid-liquid separation. Further improvement of naturally occurring colloidal particles separation efficiency can be made by the application of an electrostatic field. In the presence of an electrostatic field, the particles are collected on the surface of the electrode. Based on this principle, the CFEF technique was successfully developed. Lin and Huang have shown that the CFEF is able to separate the colloidal particles according to their size and surface charge by adjusting applied field strength of the CFEF unit and the pH of the water (Lin and Huang 2003). The CFEF module consists of an external tube, an inner charged cathodic filter membrane (circular shape), and a co-centric anodic rod. The cathode/filter and the anode collector are connected to a d.c. power supply that provides the electric field. The characterization of CFEF module is described in chapter 2.

### **5.3.3** Sequential Extraction Procedure

The solids collected from the filtrate and the concentrated streams were further separated by centrifugation at relative centrifugation force (RCF) 10,621g (or 10,000 rpm) for 60 minutes then dried at 105° C in a drying oven. The samples were stored in a desiccator. The sequential methodology was employed (modified from Tessier et al., 1979) to partition the particulates into various size fractions. We can make comparative observations of the relative distribution of lead among various grain-size fractions. The five metal fractions are considered operationally defined according to the following method of extraction.

#### The exchangeable or adsorbed metals:

The metals are loosely bound to the substrate and would change in concentration with changes in ionic composition of the overlying water. This fraction is obtained using magnesium chloride solution at pH 7.0 (1 M MgCl<sub>2</sub>, pH 7.0).

### The metals bound to carbonates:

Changes in environmental pH would affect the binding of metals to carbonates. It is extracted with sodium acetate at pH 5.0 (1 M NaOAc adjusted to pH 5 with 0.5 M HOAc).

### The metal co-precipitated with Fe and Mn oxides as coatings on particles:

These are extracted using hydroxylamine hydrogen chloride (0.04 M  $NH_2OH \cdot HCl$  in 25 % (v/v) HOAc).

#### The metals associated with organic matter:

Metals can either be incorporated into the tissues of living organisms, deposited as detritus, or can be found as a coating on grains. Metals associated with organic matter would be released into the environment under oxidizing conditions. The organic fraction was extracted using nitric acid, hydrogen peroxide and ammonium acetate (0.02 M HNO<sub>3</sub>, 30%  $H_2O_2$ , 3.2 M NH<sub>4</sub>OAc).

### The metals in the residual fraction:

The residual fraction of heavy metals is that trapped in the crystal lattices of primary and secondary minerals and only released to the environment upon complete destruction of the crystal in which they are found. The residual fraction was extracted using a mixture of concentrated hydrofluoric and perchloric acids (HF-HClO<sub>4</sub>).

The selective extraction was conducted in centrifuge tubes (Teflon, 50 mL) to minimize Between each successive extraction, solids were separated by losses of solid material. centrifugation (Labnet, model Z383K), at (RCF) 10,621 g (or 10,000 rpm) for 60 minutes. The supernatant was removed with a pipette and analyzed for heavy metals; whereas the residue was washed with 8-mL of deionized water. After centrifugation for 60 minutes, this second supernatant was discarded. The volume of rinse water used was kept to minimum as to avoid excessive solubilization of solid material, particularly organic matter. For residual trace metal analysis, the solid was digested with 5:1 mixture of hydrofluoric and perchloric acids. The sample was first digested in a PTFE beaker with a solution of concentrated  $HClO_4$  (2 mL) and HF (10 mL) to near dryness; subsequently a second addition of HClO<sub>4</sub> (1 mL) and HF (10 mL) was made and again the mixture was evaporated to near dryness. Finally, HClO<sub>4</sub> (1 mL) alone was added and the sample was evaporated until white fumes appeared. The residue was dissolved in 12 N HCl (5 mL) and diluted to 25 mL. Table 5.1 shows the detailed procedures of the Tessier method for the sequential extraction of lead.

The lead concentrations of the solutions were determined by atomic absorption spectrometry in an electrothermal atomization mode using Aanalyst-800 (?berlingen, Germany) in THGA graphite furnace. Standard solutions were prepared from 1 g/L of lead standard solution (Fisher Scientific) and freshly diluted before use. Lead was measured at 283.3 nm (0.05 mg NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> + 0.003 mg Mg(NO<sub>3</sub>)<sub>2</sub>). The concentration of lead was measured with RSD < 5% from solutions. The limit of detection for lead was found to be 0.1 µg/L. Before analysis, allow the lamp to warm up for a minimum of 15 minutes. During this period, align the position of autosampler. Multilevel standards were prepared for each extraction step in the same matrix as

Step	Form	Abbr	Extraction Agents	Time	Temperature
1	Exchangeable	EXC	8-mL of 1 M MgCl <sub>2</sub> , pH 7.0	Shaking 1.0 h	25°C
2	Carbonate	CAB	8-mL of 1 M NaOAc – 0.5 M HOAc, pH 5.0	Soaking 5 h and shaking 3 h	25°C
3	Fe and Mn oxides	FMO	20-mL of 0.04M NH <sub>2</sub> OH•HCl, 25% HOAC at $96\pm3^{\circ}$	Soaking 15 h and shaking 2 h in daylight	96°C
4	Organic matter	ORM	3-mL 0.02 M HNO <sub>3</sub> , 5-mL 30% $H_2O_2$ , pH 2, mixture was heated at 85±2 ° C for 2 h.	2 h	- 85°C
			A second 3-mL aliquot of 30% $H_2O_2$ (pH 2 with HNO <sub>3</sub> ) was added and heated at 85±2 ° C for 3 h.	3 h	
			After cooling, $5 \text{-mL} 3.2 \text{ M NH}_4\text{OAc}$ in 20% (v/v) HNO <sub>3</sub> was added and diluted to 20-mL and shaking 30 min.	0.5 h	25°C
5	Residual forms	RES	The residue was digested with HF- HClO <sub>4</sub> mixture.	-	-

 Table 5.1
 The Tessier sequential extraction procedures for lead speciation.

1. The selective extractions were conducted in centrifuge tubes (Teflon, 50 mL) to minimize losses of solid material.

2. Between each successive extraction, separation was effected by centrifuging at RCF 10,621 g (10,000 rpm) for 30 min.

- 3. The supernatant was removed with pipette and analyzed for trace metals; whereas the residue was washed with 8-mL of deionized water, after centrifugation for 30 min; this second supernatant was discarded.
- 4. The volume of rinse water used was kept to a minimum to avoid excessive solubilization of solid material, particularly organic matter.
- 5. For total or residual trace metal analysis, the solid was digested with a 5:1 mixture of hydrofluoric and perchloric acids. The sediment was first digested in a PTFE beaker with a solution of concentrated HClO<sub>4</sub> (2-mL) and HF (10-mL) to near dryness; subsequently a second addition of HClO<sub>4</sub> (1-mL) and HF (10-mL) was made and again the mixture was evaporated to near dryness. Finally, HClO<sub>4</sub> (1-mL) alone was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 5-mL 12 N HCl and diluted to 25-mL.

the extracting reagents to minimize matrix effects. Blanks were used for background correction and other sources of error. Data from the blanks were generally either below the detection limit and /or were sufficiently low relative to the measured concentrations as to be insignificant. At least one duplicate and one spike sample were run for every 10 samples to verify precision of the method. The spike recovery and precision were found to be within 100  $\pm$  10%. A calibration
curve was constructed by plotting the concentration of standards against absorbance. Standards were run each time a series of samples was run. A standard was run for approximately every 10 sample runs. Deionized water used in preparing stock solution and each leaching step was obtained from CORNING MEGA-PURE system MP-290 (New York, USA). All glassware, polypropylene, or Teflon containers, including sample bottles, flasks and pipettes, should be washed in the following sequence: detergent, distilled water, soaked for 24 h in 10% v/v hydrochloric acid, distilled water. All acids used in the digestion and sequential extraction procedures were of trace metal grade and all other reagents used were of analytical grade or better.

## 5.4 Results and Discussion

### 5.4.1 Geochemical Composition of Naturally Occurring Colloidal Particles

The sequential extraction scheme followed in this work does not provide a direct characterization of heavy metal speciation, but rather an indication of the chemical reactivity of heavy metal in question. The extraction procedure gives information about its distribution in different fractions and therefore, about the most important source of potentially available heavy metal, as well as the differences in mobility and bioavailability for heavy metal in naturally occurring colloidal particles collected by various groundwater sampling techniques. The basic properties of the naturally occurring colloidal particles collected from the well water have been described in chapter 4. The five-step protocol proposed by Tessier et al. (1979), slightly modified, was followed. Table 5.2 shows the concentrations of lead in various geochemical fractions of the naturally occurring colloidal particles collected from well waters. Figures 5.1 - 5.3 summarize the speciation patterns of lead. Metal speciation in the exchange, bound to carbonates, bound to reducible metal oxides (i.e. Fe- and Mn-oxides), bound to organic matter,

Well	Method	Sample	-	Field		a . ph	- roh	opth	550	m th
	а	ID	Date	Strength	EXC	CAB	FMO <sup>®</sup>	ORM	RES	Total
				V/cm			0.40			
	I FP			0.0	0.00	0.00	0.49	0.73	6.51	7.72
		5SIIIL01		32.3	0.00	0.24	1.41	1.41	7.44	10.05
			05/31/02	64.5	0.00	0.28	1.51	1.38	6.46	9.61
				96.8	0.00	0.21	1.15	1.19	5.98	8.53
				119.7	0.00	0.22	1.08	1.12	5.49	7.92
				123.9	0.00	0.24	0.96	1.01	10.97	12.90
			04/04/01	0.0	0.00	0.00	0.09	1.20	1.98	3.27
				32.3	0.00	0.15	0.71	1.40	2.30	4.56
55		55111 02		64.5	0.00	0.33	0.64	3.76	3.16	7.89
50		55111.02		96.8	0.00	1.18	1.00	4.73	2.51	9.42
				129.0	0.00	2.31	1.54	4.88	3.17	11.90
				156.8	0.00	1.83	3.13	5.71	5.25	15.92
	В			0.0	0.01	0.00	0.97	0.89	2.22	4.09
		5SIIIB02	05/31/02	32.3	0.01	0.40	2.01	1.29	2.35	6.06
				64.5	0.01	0.20	1.24	1.03	3.53	6.00
				96.8	0.00	0.15	1.05	1.03	8.69	10.91
				129.0	0.00	0.14	0.89	0.94	7.04	9.01
				138.7	0.00	0.14	0.76	0.85	7.70	9.45
		5SIIB03	04/04/01	0.0	0.00	0.00	0.10	0.90	1.70	2.70
				32.3	0.00	0.15	0.12	1.20	2.15	3.62
	р			64.5	0.00	0.16	0.66	2.30	2.30	5.42
	D			96.8	0.00	0.30	0.70	4.60	2.70	8.30
				129.0	0.10	0.50	0.80	4.90	2.90	9.20
5S				156.8	0.20	0.60	1.10	5.60	5.25	12.75
				0.0	0.01	0.00	1.08	0.83	7.38	9.29
				32.3	0.01	0.20	1.05	1.05	9.81	12.10
	HFP	5SIIIH02	05/31/02	64.5	0.01	0.14	0.88	0.97	6.86	8.86
				96.8	0.01	0.13	0.70	0.78	8.81	10.42
				117.7	0.00	0.11	0.69	0.81	11.60	13.21
	LED	10IIL01		0.0	0.00	0.00	1.19	0.27	8.50	9.96
10	LFP	10IIL02	04/04/01	0.0	0.00	0.00	0.98	0.32	8.83	10.13
10	D	10IIB01	04/04/01	0.0	0.00	0.00	0.38	0.10	7.82	8.30
	Б	10IIB02		0.0	0.00	0.00	0.19	0.28	6.65	7.12

## Table 5.2Summary of the concentration of sequentially extracted lead as affected by<br/>sampling methods and electrostatic field strength.

a: B: Bailer; LFP: Low-Flow-Purging; HFP: High-Flow-Purging;

b: unit: Pb-µg/particle-g

and residual metal phase were determined and their sums were normalized to 100% in Figures 5.4 - 5.6.

The distribution of lead into different fractions (Pb speciation) shown in Figures 5.1 - 5.3, is almost identical among different well water samples. For well water #5S (Figures 5.5 and 5.6), the percentage of lead associated with various fractions followed the order: residual ( $61 \sim 87\%$ ) > organic matter ( $8 \sim 37\%$ ) > Fe-Mn oxide ( $3 \sim 15\%$ ). For well water #10 (Figure 5.4), the percentage of lead associated with various fractions followed the order: residual ( $85 \sim 94\%$ ) > Fe-Mn oxide ( $3 \sim 12\%$ ) > organic matter ( $1 \sim 4\%$ ) > exchangeable and carbonate form (< 1%). Two features of the data in Figures 5.1-5.3 are obvious. A small percentage of the total lead in these naturally occurring particles was in the easily mobile, exchangeable or bound to carbonate fraction. At other extreme, 80% or more of the lead were found in the residual or organic form. This is consistent with those reported by other investigators (Barona and Romero 1996; Carapeto and Purchase 2000). The exchangeable fraction represents the fraction of adsorbed metals that are easily affected by changes in ionic composition of water (Carapeto and Purchase 2000). Metals associated with carbonate are usually in the form of carbonate precipates or coprecipitates.

The sum of these first two fractions (exchangeable and bound to carbonate) has been used to reflect maximum availability of metals in contaminated soils (Gibson and Farmer 1986). Xian (1989) found that the sum of exchangeable and carbonate-bound forms was strongly correlated with lead uptake by cabbage plants. The sum of lead in the exchangeable and carbonate fractions in our study was less than 1%, which indicates that the lead in naturally occurring colloidal particles may not be highly available to plants. The exchangeable and carbonate fractions had very small amount of lead suggesting that the solubility and mobility of the metal



Figure 5.1 Distribution of lead species in particluate collected from well #10 water sample. EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms.



Figure 5.2 Distribution of lead species in particulate collected from well #5S water sample (5SIIL02 and 5SIIB03). EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms.



Figure 5.3 Distribution of lead species in particulate collected from well #5S water sample (5SIIIL01, 5SIIIB02, and 5SIIIH02). EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms



Figure 5.4 Effect of sampling method on the proportions of lead species in particulate collected from well #10 sample in sequential extraction fractions. Low-Flow-Purging method: 10IIL01, 10IIL02; Bailer: 10IIB01, 10IIB02. EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms.



Figure 5.5 Effect of sampling method on the proportions of lead species in particulate collected from well #5S sample in sequential extraction fractions. Low-Flow-Purging method: 5SIIL02; Bailer: 5SIIB03. EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms.



Figure 5.6 Effect of sampling method on the proportions of lead species in particulate collected from well #5S sample in sequential extraction fractions. Low-Flow-Purging method: 5SIIIL01; Bailer: 5SIIIB02; High-Flow-Purging: 5SIIIH02. EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms.

was low in the soils (Xian 1989). The proportion of exchangeable and carbonate-bound lead in the soil samples reported by Barona and Romero and Carpeto and Purchase were similar to that of the present study (Barona and Romero 1996; Carapeto and Purchase 2000). Heavy metals in the other chemical forms, such as Fe-Mn oxides, organic matter and residual have very low solubility and high stability for biologic uptake. Some authors also found that lead in soils is immobile and stated that the relative retention of lead in soils is rather high even though heavy metals are not permanently bound into soil, even after long deposition times (Schalscha et al. 1982; King 1988; Berthelsen et al. 1994). Metals associated with Fe-/Mn-oxide and organic matter would be released into the environment under redox conditions (Tessier et al. 1979; Charlesworth and Lees 1999). The range of organic fractions of total lead in the naturally occurring colloidal particles was comparable to those reported by other studies. Carapeto and Purchase (2000) conducted sequential digestion of sediment samples from a constructed wetland and reported that high proportion (53 - 72%) of lead associated with the fraction bound to the organic matter (Carapeto and Purchase 2000). Cabral and Lefebvre (1998) studied two silty soils having low clay content and CEC and found a low proportion (0.6 - 2.5%) of lead associated with the fraction bound to the organic matter (Cabral and Lefebvre 1998). This discrepancy may be attributed to the organic matter content. The lowest organic content value found in Carapeto and Purchase study was 8.4%, which was four folds above the highest value reported by Cabral and Lefebvre (2.3%). Lead was mostly concentrated in the residual fraction in this study, although it was also present in the other fractions (Figure 5.2). The greater percentage of lead in the residual fraction probably reflects the greater tendency for lead to become unavailable once it was in soils. The large percentage of metals bound to residual fraction in this study is hence less bioavailable than those bound to exchangeable and carbonate fractions. This result is similar to those reported by Rate et al. (2000), who studied the distribution of lead in near-shore sediments of river estuary. They found that the lead was almost concentrated on the residual fraction (Rate et al. 2000). Lead is not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature. Because the residual phase represents the remaining metal in the mineral structure of the naturally occurring colloidal particles.

#### 5.4.2 The Effect of Sampling Method

Naturally occurring colloidal particles used in this study were collected with different groundwater sampling methods (i.e. low-flow-purging, bailing, and high-flow purging technique). The order of the degree of lead association with various chemical fractions was the same for three sampling methods in the same well. In general, the association of lead in these naturally occurring colloidal particles was in the decreasing order of: residual > organic matter > Fe-Mn oxides > carbonates  $\approx$  exchangeable (Figures 5.1-5.3). The results indicate that water-sampling methods appear to have insignificant effect on the distribution of lead in naturally occurring colloidal particles. The concentrations of lead forms in each sampling method show that the naturally occurring colloidal particles are characterized by a dominance of the residual forms (61 – 94%), but that their proportions are little changed in the different sampling method. The lead concentration of residual form in well water samples collected by bailing sampling method. Although a large percentage of the total lead was in the residual fractions of these samples, the amount of lead present in the nonresidual fractions (i.e. Fe/Mn oxide and organic form) was also appreciable from the standpoint of potential lead mobility and bioavailability.

It is observed that water-sampling methods appear to impose significant effect on the total lead concentration (Figure 4.4) in naturally occurring colloidal particles. The total lead concentration in well water samples collected by bailing and high-flow-purging sampling method were generally greater than those in water samples collected by low-flow-purging sampling method. This can be preliminary attributed to the high total solid content in the water samples. An attempt was made to correlate the effect of total lead content in naturally occurring colloidal particles on the distribution of lead in the various chemical fractions. It was found that the distribution was independent of the total amount of lead present in the naturally occurring colloidal particles.

## 5.4.3 The Effect of Particle Size

There is considerable evidence that partitioning between solid and aqueous phase has a major effect on the occurrence, transport, fate and biological effects of natural and anthropogenic chemicals in aquatic system. A number of studies are now available that show the importance of colloid-associated transport of contaminants such as trace metals, organic compounds and nutrients in natural waters, soils and groundwater (Means and Wijayaratne 1982; McCarthy and Zachara 1989; Orlandini et al. 1990; Horowitz et al. 1996; Ran et al. 2000). Colloids are capable of sorbing large concentrations of trace elements. They fall on the continuum between suspended particles and dissolved constituents; as such, there is much controversy as to when a solid-phase material changes from being a suspended particles to a colloid and when a colloid changes to a dissolved form (Karlsson et al. 1994; Horowitz et al. 1996). Unfortunately, many of these studies have used a two phase (membrane filtration) separation method to separate the "particulates" (i.e.  $> 0.45 \mu m$  in size) and "dissolved" fractions, and by including the colloidal particles in the dissolved fraction, one should have neglected the role of colloids in any transfer This simple two-phase separation can hide the complexity of the interactions processes. occurring and may even provide incorrect information on the speciation and bioavailability of a particular contaminant (Hart et al. 1993; Ran et al. 2000). Furthermore, the data from samples processed through any 0.45-µm membrane filter are questionable and not comparable (Horowitz et al. 1996).

In order to determine the metal speciation in groundwater, it is necessary to separate the naturally occurring colloidal particles into various size fractions then analyze the metal content in each individual fraction separately. The cross-flow electro-filtration separation technique (CFEF) was developed for this purpose. Since most naturally occurring colloidal particles are negatively charged, they can migrate to the collection (i.e. anode) electrode when an electrostatic field is applied. By applying an electrostatic field greater than the critical value, the particles whose size is smaller and whose surface charge is greater than the corresponding critical field value will be collected onto the surface of the collection electrode and appeared in the

concentrated stream of the CFEF module. Furthermore, it is expected that applied field control the particle size and surface charge of naturally occurring particulate. High electrostatic field will enhance the removal efficiency of smaller particles. The detail of experimental process and condition are described in the Chapters 2 and 3.

Table 5.2 shows the total metal concentrations by various sampling methods and grain size fractions. The highest lead concentration was present in the finest fraction (the highest electrostatic field). The data show a significant increase in lead with decreasing grain size for well #5S samples collected by low flow purging, bailing, and high flow purging methods. This relationship has been observed by numerous studies examining fluvial sediments impacted by industrial activities (Brook and Moore 1988; Martincic et al. 1990; Vaithiyanathan et al. 1993; Stone and Droppo 1996).

The lead species, such as exchangeable metals, metals bound to carbonates, metals bound to Fe/Mn oxides, metals bound to organic matter and residual metals in the various electrostatic field (i.e. different size) fractions are presented in Figures 5.7-5.13. For samples 5SIIL02 and 5SIIB03, the percentage of lead associated with various fractions followed the order: organic matter  $(31\%-55\%) \approx$  residual (27%-59%) > Fe-Mn oxide  $(3\%-20\%) \approx$  carbonate (3%-19%). Exchangeable metal ions and carbonate form are a measure of trace metals which are released most readily into the environment. In relation to the total lead content, exchangeable lead is a minor component (generally less than 2%) and varies slightly with electrostatic field (i.e. grain size) for all samples. For the samples 5SIIL02 and 5SIIB03, the largest concentration of exchangeable lead was associated with the largest grain size fraction (E = 156.8 V/m) of sample 5SIIB03. For some metals, co-precipitation with carbonates is an important removal mechanism, especially when hydrous iron oxide and organic coatings are less abundant in the particles (Forstner 1981). The results show that the lead concentrations in the carbonate form increased with increase in electrostatic field. The largest lead concentration in the carbonate form was associated with the highest electrostatic field. The hydrous oxides of Fe and Mn on the particulate surfaces, particularly the redox-sensitive iron and manganese hydroxides under



Figure 5.7 Distribution of lead species in particulate collected from well water sample as affected by electrostatic field. Experimental conditions: (a) 5SIIL02: pH = 6.7; initial turbidity = 939 NTU; Low-Flow-Purging; (b) 5SIIB03: pH = 6.6, initial turbidity = 748 NTU, Bailing. EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms.



Figure 5.8 Effect of electrostatic field on the proportions of lead species in particulate collected from well #5S in sequential extraction fractions. Experimental condition: pH = 6.7, initial turbidity = 939 NTU, sampling method: Low-Flow-Purging. Sample: 5SIIL02. EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms.



Figure 5.9 Effect of electrostatic field on the proportions of lead species in particulate collected from well #5S in sequential extraction fractions. Experimental condition: pH = 6.6, initial turbidity = 748 NTU, sampling method: Bailing. Sample: 5SIIB03. EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms.



Figure 5.10 Distribution of lead species in particulate collected from well water sample as affected by electrostatic field. (a) 5SIIIL01: experimental condition: pH = 6.8, initial turbidity = 680 NTU, sampling method: Low-Flow-Purging; (b) 5SIIIB02: experimental condition: pH = 6.8, initial turbidity = 750 NTU, sampling method: Bailing; (c) 5SIIIH02: experimental condition: pH = 7.1, initial turbidity = 720 NTU, sampling method: High-Flow-Purging. EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms.



Figure 5.11 Effect of electrostatic field on the proportions of lead species in particulate collected from well #5S in sequential extraction fractions. Experimental condition: pH = 6.8, initial turbidity = 680 NTU, sampling method: Low-Flow-Purging. Sample: 5SIIIL01. EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms.



Figure 5.12 Effect of electrostatic field on the proportions of lead species in particulate collected from well #5S in sequential extraction fractions. Experimental condition: pH = 6.8, initial turbidity = 750 NTU, sampling method: Bailing. Sample: 5SIIIB02. EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms.



Figure 5.13 Effect of electrostatic field on the proportions of lead species in particulate collected from well #5S in sequential extraction fractions. Experimental condition: pH = 7.1, initial turbidity = 720 NTU, sampling method: High-Flow-Purging. Sample: 5SIIIH02. EXC: exchangeable; CAB: carbonate; FMO: Fe/Mn oxides; ORM: organic matter; RES: residual forms.

oxidizing conditions, are significant for concentrating metals in aquatic systems (Horowitz et al. 1988). The significance of the Fe/Mn oxide phase for concentrating lead was a function of grain size (Figure 5.7). The concentrations of lead forms in each size fraction also show that the naturally occurring colloidal particles are characterized by a dominance of the organic and residual forms, but that their proportions are dramatically changed in the different sizes. Organic matter in naturally occurring colloidal particles consists of a complex mixture of plant and animal detritus, in varying degrees of decomposition which also occurs as coatings on the other substrates (Davis 1984). Organic substances exhibit a high degree of selectivity for divalent ions and in aquatic systems, the order of binding strength for lead ions onto organic matter of the finest size fraction was greater than that binding onto the largest size fraction in samples 5SIIL02 and 5SIIB03. Based on results reported by other researchers, the higher lead concentration can be attributed to the higher organic content in the smaller size fraction (Cabral and Lefebvre 1998; Carapeto and Purchase 2000). Based on the results of samples 5SIIL02 and 5SIIB03, the lead concentration of various chemical forms is dependent on the particle size. The lead concentrations in the carbonate, Fe-Mn oxide, and organic matter fractions increase with increasing electrostatic field strength.

The results for the samples 5SIIIL01, 5SIIIB02, and 5SIIIH02, given in Figures 5.10-5.13, illustrate that lead in the residual form was the overwhelmingly dominant chemical phases in each size fraction while carbonate and exchangeable contributions were insignificant. A summation over all naturally occurring colloidal particles collected by samples 5SIIIL01, 5SIIIB02, and 5SIIIH02 show that more than 97% of lead were associated with either the residual (39-88%), the organic (6-21%) or the Fe/Mn oxide (5-32%) phases in each size fraction.

In relation to the total lead content, exchangeable and carbonate lead was a minor component (generally less than 3%) and varied slightly with the grain size for all samples. For the samples 5SIIL02 and 5SIIB03, the lead concentrations in the Fe/Mn oxide and organic form increased with increase in the electrostatic field. This trend, however, was not apparent for samples 5SIIIL01, 5SIIIB02, and 5SIIIH02. The results also show that the naturally occurring colloidal

particles were characterized by a dominance of the residual form, but that their proportions were changed in the different size fractions (Figure 5.10). This trend was same as the samples 5SIIL02 and 5SIIB03. Lead concentrations in the residual form generally increased with decrease in the grain size.

The percentage metal in the different size fractions of the naturally occurring colloidal particles collected from well water samples demonstrates clearly that most of the lead was associated with the fine fraction. Smaller particles with higher pollutant concentrations will remain suspended in the aquatic system for longer periods of time, thus permitting pollutants associated with fine-grained particles to be transported further into receiving waters and allowing more time for the pollutants to exchange with the aquatic system and aquatic biota (McCarthy and Zachara 1989; Grolimund et al. 1996).

#### 5.5 Conclusion

The distribution of lead into different fractions (Pb speciation) is very similar among all water samples obtained by three different well water sampling techniques. A small percentage of the total lead in these naturally occurring colloidal particles was in the easily mobile, exchangeable or bound to carbonate fraction. At other extreme, 80% or more of the lead were found in the residual or the organic form. The percentage of lead associated with various fractions followed the order: residual > (or  $\approx$ ) organic matter > Fe-Mn oxide  $\approx$  carbonate > exchangeable. The results show that concentration of lead in the organic and residual phase were strongly influenced by the size of the particles at any given well water samples. Based on the results, the lead concentrations in various chemical forms were dependent on the particle size. The lead concentrations in the carbonate, the Fe-Mn oxide, and the organic matter fractions increased with increase in electrostatic field strength. The lead studied in this project can be classified as being only potentially available to the ecosystem, though they may become available through various environmental changes.

Results clearly indicate that the CFEF is able to separate the colloidal particles according to their size and surface charge. Most importantly, the distribution of lead in particles of different size fractions was different. Generally, the concentration of lead species increased with increase in field strength. That is, the smaller the particles the greater were the metal concentration in all fractions. The CFEF process can be an important technique for the speciation of various chemical species in natural water including groundwater. Moreover, CFEF is able to separate naturally colloidal particles with great ease; clogging, the most common operational problem is eliminated.

## 5.6 References

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#### **CHAPTER 6**

## SUMMARY AND RECOMMENDATION FOR RUTURE RESEARCH

## 6.1 Summary

In Chapter 2 the performance of a cross-flow electro-filtration (CFEF) devise and the major factors controlling the operation of the CFEF unit using model colloid particle,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, and naturally occurring particles from well waters were investigated. CFEF unit consists of an external tube (insulated), an inner electrically charged cathodic filter membrane, and a cocentric anodic rod. The external tube had a diameter of 8.9 cm, the inner filter had a diameter of 3.0 cm and the co-centric rod was a 0.5-cm stainless wire. The total module was 22.5 cm long and had a total filtration surface area of 212 cm<sup>2</sup>. The cathode and the anode were connected to an a. c. power supply. A stabilized power supply with a maximum out of 600 voltages d.c. at 1 amps was used to provide an electric field across the membrane. To prevent and reduce membrane fouling by gas bubbles and gas generation at the electrodes by electrolysis and heat generation, the current was limited below than 1 amp. And one electrode downstream of the membrane support was added, so that bubbles were carried away with the filtrate flow. The other electrode could not be placed closer than about 3 mm from the membrane surface, and gas evolved from this electrode was flushed out of the filter by the concentrate stream.

Model colloidal particles,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, and naturally occurring colloidal particles collected from well waters were used to study the performance of the CFEF. Naturally occurring particles collected from well waters and SiO<sub>2</sub> were negatively charged under the pH condition of the groundwater. The pH<sub>zpc</sub> was approximately 1 to 2. The surface charge of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was positive under acidic condition. The pH<sub>zpc</sub> of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 9.2. All particle samples appear to be monodispered. The results show that the prototype CFEF unit works effectively without clogging problem. Therefore, it is not necessary to backwash the CFEF unit under the experimental conditions of this study. An optimal filtration rate was observed for the separation of colloidal particles. Results also show that there was no distinct difference in solid removal efficiency in this study. The removal of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and naturally occurring colloids was faster during the first 1 to 4 minutes. The removal efficiency increased with increase in electrostatic field. Naturally occurring particles collected from groundwater samples and model colloidal silica (SiO<sub>2</sub>) were mixed to prepare a solution of bimodal particle size distribution. As expected, high electrostatic fields will enhance the particle removal efficiency. From the results, the portion of larger particle size (i.e. naturally occurring particle) decreased as the electrostatic field strength increased. On the other hand, the portion of smaller particle (i.e. colloidal silica) increased as the electrostatic field of different strength increased. Base on the results, we can successfully separate particles of different size using the CFEF module.

A mathematical model which describes the concentration distribution and trajectories of charged particles or colloids in the cross-flow electro-filtration system is presented in Chapter 3. To investigate the effect of various parameters on model results, a sensitivity analysis was conducted. Critical parameters such as particle size, surface charge of particle, and applied electrostatic field strength were selected to analyze the model behavior. In all cases the removal efficiency increased as applied electrostatic field strength, surface charge, and particle size increased. Experimental data were used to validate the model. Results indicate that the model can describe the colloid transport successfully in cross-flow electro-filtration system.

Chapter 4 gives a comparison of sampling techniques for monitoring naturally occurring colloidal particles in groundwater. Results showed that the mean particle size, total solid content, and total lead concentration of well water collected by low-flow-purging sampling method were less than those collected by bailing and high-flow-purging sampling method. Apparently the disturbance caused by bailing and high-flow-purging techniques bring about high total lead concentration in the well water samples. Results show that the concentration of lead species increased with increase in field strength, hence, the smaller the particles the greater was the metal concentration regardless of sampling method. While the difference in lead concentration in particles of different charge was not as significant as that of particle size, there is clear indication that the lead concentration was affected by the pH under which the particles were

being separated. Results also show that it is possible to replace the current low-flow purging technique for groundwater sampling with the CFEF method. In this study, the total lead concentration obtained with CFEF method, operated at a field strength of 69.2 V/m and high-flow, was identical to that by low-flow purging technique. Incidentally the particle size separated at this field strength was 490 nm which was close to the pore size of conventional filtration media of 450 nm. Further investigation is necessary to further verify this relationship.

In Chapter 5 the speciation of lead in groundwater using CFEF technique was investigated. The distribution of lead into different fractions (Pb speciation) was very similar among the three different well water-sampling methods. A small percentage of the total lead in these naturally occurring colloidal particles was in the easily mobile, exchangeable or bound to carbonate fraction. At the other extreme, 80% or more of the lead were found in the residual or organic form. The results show that concentration of lead in the organic and residual phase are strongly influenced by the size of the particles at any given well water samples. Based on the results, the lead concentration of various chemical forms is dependent on the particle size.

Results clearly indicate that the CFEF is able to separate the colloidal particles according to their size and surface charge. Most importantly, the distribution of lead in particles of different size is different. Generally, the concentration of lead species increases with increasing field strength. That is, the smaller the particles the greater the metal concentration content at all fractions. The CFEF process can be an important technique for the speciation of various chemical species in natural water including groundwater. Moreover, CFEF is able to separate naturally colloidal particles with great ease; clogging, the most common operational problem is eliminated.

#### 6.2 Future Research

The research presented in this dissertation provides insight into the performance and the separation mechanism of CFEF module, and lead speciation in groundwater system. The information is only a small part of the whole picture. A number of researches can be conducted in the future.

1 Improvement of the CFEF module

The configuration of CFEF is to insert the electrodes into the solution. This construction has two major disadvantages. The first is that the electrolysis products enter the filtration and may alter the product or change the suspension, e.g. its pH value. The second disadvantage is that CFEF can not work in high conductivity solutions. The described disadvantages may be avoided by an additional rinsing cycle that removes the electrolysis products and increases the resistance between electrodes. The filtration and rinsing cycles have to be separated which could be done by ion exchange membranes.

2 Application of CFEF module

CFEF can separate naturally occurring colloidal particles of different size in groundwater system. We also can use this technique to separate and treat nano-sized colloidal particles collected from the industrial waste water (for example, Chemical-mechanical polishing (CMP) wastewater).

3 The relationship of metal speciation and colloidal particle in fresh water and marine systems

One of most important questions about metal behavior in the environment that deserves further research is the relationship between metal speciation and colloids in the environment. As far as metal speciation is concerned, there have been abundant investigations on the distribution of metals in surface water, e.g. river and lakes, and marine system. A few researchers have been begun to investigate metal uptake by aquatic particles in the nano-sized group. But the majority of the studies still adhere to the conventional 0.45 um-filter technique. As discussed in Chapter 4, the results of conventional filtration are questionable and not comparable. However, the lake of effective separation techniques for the nano-sized naturally occurring colloidal particles has greatly hampered scientific progress in this needed area. Therefore, there is great need to investigate the distribution of metal ions by nano-sized occurring colloidal particles using CFEF technique.

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APPENDIX A: SUPPLEMENTARY MATERIAL

Well Name	Method <sup>a</sup>	Date	Size (L)	No. (#)	Field ID <sup>b</sup>	Laboratory ID	Weather			
10	В	01/10/01	40	1	10-UD-004-01	10IB01	Snowy			
	LFP	01/10/01	20	1	LFP-10-UD-009-01	10IL01	Snowy			
	В	01/15/02	1	1	10-UD-026-01	10IIB01				
		01/15/02	20	2	10-UD-026-02	10IIB02	Suppy			
	I FD	01/15/02	1	1	LFP-10-UD-025-01	10IIL01	Sullity			
	LIT	01/15/02	20	2	LFP-10-UD-025-02	10IIL02				
	В	01/10/01	20	1	5S-UD-005-01	5SIB01	Snowy			
				1	LFP-5S-UD-012-01	5SIL01				
			1	2	LFP-5S-UD-012-02	5SIL02				
		01/10/01		3	LFP-5S-UD-012-03	5SIL03	Snowy			
	LFP			4	LFP-5S-UD-012-04	5SIL04				
				5	LFP-5S-UD-012-05	5SIL05				
				6	LFP-5S-UD-012-06	5SIL06				
				7	LFP-5S-UD-012-07	5SIL07				
				8	LFP-5S-UD-012-08	5SIL08				
				9	LFP-5S-UD-012-09	5SIL09				
				10	LFP-5S-UD-012-10	5SIL10				
5S	LFP	04/04/01	5	1	LFP-5S-UD-019-01	5SIIL01	Sunny			
	LFP	04/04/01	20	2	LFP-5S-UD-019-02	5SIIL02	Suppy			
				3	LFP-5S-UD-019-03	5SIIL03	Sunny			
	D	04/04/01	20	1	5S-UD-021-01	5SIIB01	Sunny			
	D			2	5S-UD-021-02	5SIIB02				
	В	04/04/01	5	3	5S-UD-021-03	5SIIB03	Sunny			
	I ED	05/31/02	20	1	5S-UD-027-01	5SIIIL01	Sunny			
	LFF			2	5S-UD-027-02	5SIIIL02				
	LFP	05/31/02	10	3	5S-UD-027-03	5SIIIL03	Sunny			
	В	05/31/02	20	1	5S-UD-028-01	5SIIIB01 Sume				
				2	5S-UD-028-02	5SIIIB02	Sumry			
	В	05/31/02	10	3	5S-UD-028-03	5SIIIB03	Sunny			

Table A1.List of field samples

a: B: Bailer; LFP: Low flow purge; HFP: High flow purge

b: Well-analysis location-sample number; Well Name-Lab Name-Sample Series- Sample Number

Well Size Laboratory Field ID<sup>b</sup> Weather Method<sup>a</sup> Date No. (#) Name (L) ID 5S-UD-029-01 **5SIIIH01** 1 HFP 05/31/02 20 Sunny 2 5S-UD-029-02 5SIIIH02 5S HFP 05/31/02 10 3 5S-UD-029-03 5SIIIH03 Sunny HFP 5S-UD-029-04 5SIIIH04 05/31/02 8 4 Sunny MW3-UD-022-01 MW3IB01 1 В 04/04/01 20 Sunny 2 MW3-UD-022-02 MW3IB02 3 MW3IB03 В 04/04/01 8 MW3-UD-022-03 Sunny MW3 LFP 04/04/01 LPF-MW3-UD-024-01 MW3IL01 8 1 Sunny 2 LPF-MW3-UD-024-02 MW3IL02 LFP 04/04/01 20 Sunny 3 LPF-MW3-UD-024-03 MW3IL03

 Table A1.
 List of field samples (continued)

a: B: Bailer; LFP: Low flow purge; HFP: High flow purge

b: Well-analysis location-sample number; Well Name-Lab Name-Sample Series- Sample Number

<b></b>		Experimental	Turbidit	y (NTU)	Demoval		
Sample	Variation	Filtration Rate (L/min)	Electrostatic Field (V/cm)	pН	Initial	Final	(%)
		0.77	00.0	5.6	29	28.3	3
		0.77	00.0	5.6	29	28.6	3
		0.77	00.0	5.6	29	28.5	3
		0.77	12.9	5.6	29	25.2	13
		0.77	12.9	5.6	29	25.4	13
		0.77	12.9	5.6	29	25.1	13
		0.77	16.1	5.6	29	24.1	18
		0.77	16.1	5.6	29	24.5	18
		0.77	16.1	5.6	29	24.3	18
		0.46	16.1	5.6	31	24.6	23
	Electrostatic Field	0.77	16.1	5.6	31	24.3	23
		0.77	16.1	5.6	31	24.4	23
		0.46	32.3	5.6	29	15.1	46
		0.46	32.3	5.6	29	15.4	46
		0.46	32.3	5.6	29	15.3	46
		0.46	48.4	5.6	29	12.5	60
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>		0.46	48.4	5.6	29	12.6	60
		0.46	48.4	5.6	29	12.4	60
		0.46	64.5	5.6	29	9.1	68
		0.46	64.8	5.6	29	9.3	68
		0.46	64.8	5.6	29	9.3	68
		0.46	80.6	5.6	29	8.4	72
		0.46	80.6	5.6	29	8.4	72
		0.46	80.6	5.6	29	8.4	72
		0.46	96.8	5.6	29	6.0	80
		0.27	96.8	5.6	29	7.0	75
		0.46	96.8	5.6	29	6.0	80
	Filtration	0.77	96.8	5.6	29	10.0	64
	Rate	1.08	96.8	5.6	29	14.0	53
		1.39	96.8	5.6	29	16.0	45
		1.70	96.8	5.6	29	16.0	46
	nН	0.46	96.8	4.0	30	5.0	84
	PII	0.46	96.8	5.0	30	8.0	72

# Table A2.The summary of performance of the cross-flow electro-filtration module under<br/>various experimental conditions with water samples

		Experimental (	Turbidit	y (NTU)	Domoval			
Sample	Variation	Filtration Rate (L/min)	Electrostatic Field (V/cm)	pН	Initial	Final	(%)	
γ-Al <sub>2</sub> O <sub>3</sub>	рН	0.46	96.8	6.0	30	11	64	
		0.46	96.8	7.0	30	16	45	
		0.46	96.8	8.0	30	16	46	
		0.46	00.0	6.2	35	35	2	
		0.46	32.3	6.2	35	28	20	
	Electrostatio	0.46	64.5	6.2	35	19	45	
	Field	0.46	96.8	6.2	35	10	71	
Snowtex	Ticiu	0.46	129.0	6.2	35	2	94	
20L		0.46	161.3	6.2	35	2	95	
		0.46	174.2	6.2	35	2	96	
	рН	0.46	96.8	9.0	35	11	69	
		0.46	96.8	7.0	35	4	88	
		0.46	96.8	6.2	35	10	71	
	Electrostatic Field	0.46	00.0	5.0	58	56	3	
Snowtay		0.46	32.3	5.0	58	46	21	
7I		0.46	64.5	5.0	58	23	60	
		0.46	96.8	5.0	58	18	70	
		0.46	129.0	5.0	58	4	93	
	Electrostatic Field pH	0.46	161.3	5.0	58	2	97	
Spowtov		0.46	187.7	5.0	58	1	98	
7I		0.46	96.8	9.0	58	24	58	
		0.46	96.8	7.0	58	29	50	
		0.46	96.8	5.0	58	18	70	
		0.46	00.0	6.5	223	213	4	
		0.46	32.3	6.5	223	127	43	
		0.46	64.5	6.5	223	68	69	
		0.46	96.8	6.5	223	45	80	
10IB01	Electrostatic	0.46	129.1	6.5	223	38	83	
101001	Field	0.46	161.3	6.5	223	35	84	
		0.46	00.0	6.5	799	717	10	
		0.46	32.3	6.5	799	344	57	
		0.46	48.4	6.5	799	272	66	
		0.46	62.6	6.5	799	196	75	

 Table A2.
 The summary of performance of the cross-flow electro-filtration module under various experimental conditions with water samples (continued)

		Experimental	Condition		Turbidit	y (NTU)	Demoval	
Sample	Variation	Filtration Rate (L/min)	Electrostatic Field (V/cm)	pН	Initial	Final	(%)	
		0.46	32.3	5.0	799	248	69	
		0.46	48.4	7.0	799	239	70	
		0.46	48.4	9.0	799	212	73	
		0.46	00.0	6.5	548	521	5	
10IB01	Electrostatic	0.46	32.3	6.5	548	278	49	
101001	Field	0.46	48.4	6.5	548	164	70	
		0.46	64.5	6.5	548	136	75	
		0.46	32.3	5.0	548	202	63	
		0.46	48.4	7.0	548	144	74	
		0.46	48.4	9.0	548	149	73	
	Electrostatic Field	0.46	00.0	6.8	207	195	6	
		0.46	32.3	6.8	207	142	31	
		0.46	64.5	6.8	207	94	54	
		0.46	71.3	6.8	207	74	64	
10IIB02		0.46	00.0	6.8	98	4	4	
		0.46	32.3	6.8	98	65	35	
		0.46	64.5	6.8	98	48	52	
		0.46	96.8	6.8	98	33	66	
		0.46	112.6	6.8	98	26	74	
10111-02	Electrostatic Field	0.46	00.0	7.1	31	31	2	
10111102		0.46	60.3	7.1	31	11	64	
		0.46	00.0	6.6	748	694	7	
		0.46	32.3	6.6	748	456	39	
		0.46	64.5	6.6	748	283	62	
	Electrostatic	0.46	96.8	6.6	748	131	82	
5SIIB03	Field	0.46	129.0	6.6	748	51	93	
	гіеїа	0.46	156.5	6.6	748	39	95	
		0.46	96.8	5.0	748	45	94	
		0.46	96.8	7.0	748	56	93	
		0.46	96.8	9.0	748	120	84	
	Electrostatio	0.46	00.0	6.7	939	850	9	
5SIIL02	Field	0.46	32.3	6.7	939	331	65	
		0.46	64.5	6.7	939	125	87	

Table A2.The summary of performance of the cross-flow electro-filtration module under<br/>various experimental conditions with water samples (continued)

	Variation	Experimental C	Turbidity	v (NTU)	Domosio1		
Sample		Filtration Rate (L/min)	Electrostatic Field (V/cm)	pН	Initial	Final	(%)
		0.46	96.8	6.7	939	84	91
	Electrostatic	0.46	129.0	6.7	939	79	92
5SIII 02		0.46	156.8	6.7	939	55	94
JSHL02	Field	0.46	96.8	4.5	939	50	95
		0.46	96.8	6.5	939	78	92
		0.46	96.8	9.0	939	95	90
		0.46	00.0	6.8	680	632	7
		0.46	32.3	6.8	680	411	40
		0.46	64.5	6.8	680	311	54
		0.46	96.8	6.8	680	213	69
	Electrostatic Field	0.46	119.7	6.8	680	149	78
<b>5</b> 51111 01		0.46	123.9	6.8	680	169	75
JSHILUI		0.46	00.0	6.6	422	391	7
		0.46	32.3	6.6	422	267	37
		0.46	64.5	6.6	422	207	51
		0.46	96.8	6.6	422	141	67
		0.46	129.0	6.6	422	75	82
		0.46	137.1	6.6	422	69	84
	Electrostatic	0.46	00.0	6.8	750	703	6
		0.46	32.3	6.8	750	495	34
		0.46	64.5	6.8	750	389	48
		0.46	96.8	6.8	750	272	64
		0.46	129.0	6.8	750	154	80
5 SHIDO2		0.46	138.7	6.8	750	139	82
55HID02	Field	0.46	00.0	6.6	390	351	10
		0.46	32.3	6.6	390	274	30
		0.46	64.5	6.6	390	204	48
		0.46	96.8	6.6	390	142	64
		0.46	129.0	6.6	390	78	80
		0.46	152.9	6.6	390	50	87
	Electrostatic	0.46	00.0	7.1	720	693	4
5SIIIH02	Field	0.46	32.3	7.1	720	506	30
		0.46	64.5	7.1	720	380	47

## Table A2.The summary of performance of the cross-flow electro-filtration module under<br/>various experimental conditions with water samples (continued)
	Variation	Experimental C	ondition		Turbidity (NTU)		Removal
Sample		Filtration Rate (L/min)	Electrostatic Field (V/cm)	pН	Initial	Final	(%)
		0.46	96.8	7.1	720	291	60
		0.46	117.7	7.1	720	219	70
		0.46	00.0	6.8	285	269	6
5SIIIH02	Electrostatic	0.46	32.3	6.8	285	181	37
55111102	Field	0.46	64.5	6.8	285	126	56
		0.46	96.8	6.8	285	112	61
		0.46	129.0	6.8	285	72	75
		0.46	142.6	6.8	285	57	80
		0.46	00.0	7.9	582	514	12
MW2ID		0.46	17.1	7.9	582	312	46
01	Field	0.46	10.3	5.0	582	322	45
01		0.46	13.2	7.0	582	303	48
		0.46	14.8	9.0	582	287	51
		0.46	00.0	8.2	72	67	7
10IIB02		0.46	32.3	8.2	72	48	34
+	Electrostatic	0.46	64.5	8.2	72	37	48
Snowtex	Field	0.46	96.8	8.2	72	23	69
20L		0.46	124.5	8.2	72	16	78
		0.46	126.5	8.2	72	14	80

## Table A2.The summary of performance of the cross-flow electro-filtration module under<br/>various experimental conditions with water samples (continued)

Samula	Electrostatic	Initial Total	Solid	Removal	Error	
Sample	Field (V/cm)	Concentration (g/L)		(%)	(%)	
	00.0	0.6798		7.1	0.60	
	00.0	0.4264		7.3	0.09	
	22.2	0.6798		39.6	1.00	
	32.3	0.4264		36.7	1.90	
	64.5	0.6798		54.3	1.62	
551111 01		0.4264		50.9	1.02	
JSHILUI	06.9	0.6798		68.7	0.79	
	90.0	0.4264		66.6	0.78	
	119.7	0.6798		78.1	-	
	123.9	0.6798		75.1	-	
	129.0	0.4264		82.3	-	
	137.1	0.4264		83.6	-	
	00.0	0.5188		6.3	11.25	
	00.0	0.2717	.2717 10.0			
	37.3	0.5188		34.0	3 38	
	52.5	0.2717		29.7	5.56	
	64.5	0.5188		48.1	0.21	
5SIIIP02	04.3	0.2717		47.7	0.21	
JSHID02	06.8	0.5188		63.7	0.04	
	70.0	0.2717	63.6	0.04		
	120.0	0.5188		79.5	0.19	
	127.0	0.2717		80.1		
	138.7	0.5188		81.5	-	
	152.9	0.2717		87.1	-	
	00.0	0.4447		3.8	12.38	
	00.0	0.1818		6.3	12.38	
	32.3	0.4447		29.7	5 14	
	52.5	0.1818		36.5	5.14	
	64.5	0.4447		47.2	4 17	
5SIIIH02	04.5	0.1818		55.8	4.17	
	06.8	0.4447		59.6	0.46	
	70.0	0.1818		60.7	0.46	
	117.7	0.4447		69.6	-	
	129.0	0.1818		74.8	-	
	142.6	0.1818		80.1	-	

Figure A3. The effect of total solid concentration under various electrostatic field strength

	Exper. Condition	n		Filtrate		Concentrate	
Sample	Electrostatic	Voltage	лЦ	Soluble	Total	Soluble	Total
	Field (V/cm)	Voltage	pm	(µg/L)	(µg/L)	(µg/L)	$(\mu g/L)$
	32.3	100	6.5	< 1	3	< 1	91
1011-01	48.4	150	6.5	< 1	< 1	< 1	77
	64.5	200	6.5	< 1	< 1	< 1	-
TOILOT	32.3	100	5.0	< 1	< 1	< 1	75
	48.4	150	7.0	< 1	< 1	< 1	118
	48.4	150	9.0	< 1	< 1	< 1	80
	00.0	00	7.1	< 1	5	< 1	3
10IIL02	32.3	100	7.1	1	6	2	13
	60.3	187	7.1	1	6	1	12
	00.0	00	6.8	< 1	< 1	< 1	2
	32.3	100	6.8	< 1	< 1	< 1	6
	64.5	200	6.8	< 1	< 1	< 1	5
	71.3	221	6.8	< 1	< 1	< 1	6
10IIB02	00.0	00	6.8	< 1	< 1	< 1	2
	32.3	100	6.8	< 1	< 1	< 1	4
	64.5	200	6.8	< 1	< 1	< 1	5
	96.8	300	6.8	< 1	< 1	< 1	6
	112.6	349	6.8	< 1	< 1	< 1	6
	32.3	100	6.6	< 1	8	-	-
	64.5	200	6.6	< 1	3	-	-
	96.8	300	6.6	< 1	< 1	-	-
5SIIB03	129.0	400	6.6	< 1	< 1	-	-
5511005	156.5	485	6.6	< 1	< 1	< 1	18
	96.8	300	5.0	< 1	< 1	< 1	12
	96.8	300	7.0	< 1	< 1	< 1	9
	96.8	300	9.0	< 1	< 1	< 1	10
	32.3	100	6.7	< 1	4	< 1	24
	64.5	200	6.7	< 1	< 1	< 1	42
	96.8	300	6.7	< 1	< 1	< 1	55
55111 02	129.0	400	6.7	< 1	< 1	< 1	72
5511202	156.8	486	6.7	< 1	< 1	< 1	78
	96.8	300	4.5	< 1	< 1	2	73
	96.8	300	6.5	< 1	< 1	< 1	70
	96.8	300	9.0	< 1	< 1	< 1	98

Table A4.The concentration of total and soluble lead in the filtrate and concentrate of<br/>CFEF operation

	Exper. Conditio	n		Filtrate		Concentrate	
Sample	Electrostatic	Voltage	лH	Soluble	Total	Soluble	Total
	Field (V/cm)	Voltage	pm	(µg/L)	(µg/L)	(µg/L)	(µg/L)
	00.0	00	6.8	1	20	2	20
	32.3	100	6.8	1	17	2	23
<b>5SIIII</b> 01	64.5	200	6.8	1	13	2	26
55111201	96.8	300	6.8	1	10	1	34
	119.7	371	6.8	1	8	2	28
	123.9	384	6.8	1	9	2	29
	00.0	0	6.8	1	27	1	18
	32.3	100	6.8	1	13	1	26
55111002	64.5	200	6.8	1	12	1	25
JSIIID02	96.8	300	6.8	1	9	1	32
	129.0	400	6.8	1	7	1	28
	138.7	430	6.8	1	5	1	27
	00.0	0	7.1	1	23	2	23
	32.3	100	7.1	1	18	1	29
5SIIIH02	64.5	200	7.1	2	16	2	30
	96.8	300	7.1	1	13	2	32
	117.7	365	7.1	2	13	2	34
	17.1	53	7.9	< 1	< 1	< 1	< 1
	10.3	32	5.0	< 1	< 1	< 1	< 1
	13.2	41	7.0	< 1	< 1	< 1	< 1
	14.8	46	9.0	< 1	< 1	< 1	< 1

## Table A4.The concentration of total and soluble lead in the filtrate and concentrate of<br/>CFEF operation (continued)

						unit: pb-µg/s	soil-g
Field strength	E = 00 V/cm (V = 00)	E = 32.3 V/cm (V = 100)	E = 48.4 V/cm (V = 150)	E = 48.4 V/cm (V = 150)	E = 32.3 V/cm (V = 100)	E = 48.4 V/cm (V = 150)	E = 64.5 V/cm (V = 200)
pН	6.50	5.00	7.00	9.00	6.50	6.50	6.50
Exchangeable	0.00	1.94	2.33	0.15	0.17	0.15	0.65
Carbonate	0.00	0.00	0.00	1.44	1.79	1.10	1.46
Fe-Mn oxide	1.73	3.50	8.32	4.79	0.50	0.41	0.62
Organic matter	5.07	8.35	11.45	7.86	6.69	5.95	6.45
Residual form	9.28	9.48	9.61	6.77	7.78	9.43	8.13
Total	16.08	23.28	31.71	21.01	16.94	17.05	17.31

 Table A5.
 Concentration of sequentially extracted and total lead as affected by electrostatic field strength in particles of well water sample 10IB01

Experimental conditions: initial total solid concentration = 0.62 g/L; pH = 6.5; sample: 10IB01

						unit: pb-µg/so	oil-g
Field strength	E = 00 V/cm (V = 00)	E = 32.3 V/cm (V = 100)	E = 48.4 V/cm (V = 150)	E = 48.4 V/cm (V = 150)	E = 32.3 V/cm (V = 100)	E = 48.4 V/cm (V = 150)	E = 64.5 V/cm (V = 200)
pН	6.5	5.0	7.0	9.0	6.5	6.5	6.5
Exchangeable	0.00	0.00	0.81	0.00	0.00	0.00	0.00
Carbonate	0.00	2.05	24.62	2.53	1.99	1.23	2.91
Fe-Mn oxide	2.29	1.44	5.15	0.99	6.33	2.61	3.62
Organic matter	1.78	8.77	26.99	4.08	3.55	3.00	4.48
Residual form	1.04	2.26	2.13	3.55	1.18	1.29	1.62
Total	5.10	14.53	59.71	11.13	13.04	8.12	12.63

 Table A6.
 Concentration of sequentially extracted and total lead as affected by electrostatic field strength in particles of well water sample 10IL01

Experimental conditions: initial total solid concentration = 0.43 g/L; pH = 6.5; sample: 10IL01

Table A7.	Concentration of sequentially extracted and total lead as affected by electrostatic field strength in particles of well
	water sample 5SIIB03

			unit:	pb-µg/soil-g
Field Strength	E = 00 V/cm (V = 00)	E = 96.8 V/cm (V = 300)	E = 96.8 V/cm (V = 300)	E = 96.8 V/cm (V = 300)
pН	6.5	5.0	7.0	9.0
Exchangeable	0.00	0.00	0.00	0.00
Carbonate	0.00	0.00	0.00	0.00
Fe-Mn oxide	0.14	0.11	0.13	0.15
Organic matter	1.12	1.44	1.42	1.34
Residual form	3.56	2.60	2.74	4.21
Total	4.82	4.15	4.29	5.69

Experimental conditions: initial total solid concentration = 0.43 g/L; pH = 6.5; sample: 10IL0

							u	nit: pb-µg/:	soil-g
	E = 00	E = 96.8	E = 96.8	E = 96.8	E = 32.3	E = 64.5	E = 96.8	E = 129.0	E = 156.8
Field Strength	V/cm	V/cm	V/cm	V/cm	V/cm	V/cm	V/cm	V/cm	V/cm
	(V=00)	(V = 300)	(V = 300)	(V = 300)	(V = 100)	(V = 200)	(V = 300)	(V = 400)	(V = 486)
pН	6.5	4.5	6.5	9.0	6.5	6.5	6.5	6.5	6.5
Exchangeable	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbonate	0.00	0.63	1.01	1.52	0.15	0.33	1.18	2.31	1.83
Fe-Mn oxide	0.09	3.18	2.06	1.89	0.71	0.64	1.00	1.54	3.13
Organic matter	1.09	3.96	3.29	5.54	3.89	3.76	4.73	4.88	5.71
Residual form	2.41	2.49	6.09	1.11	1.00	3.16	2.51	3.17	5.25
Total	3.58	10.26	12.46	10.05	5.74	7.89	9.42	11.89	15.93

 Table A8.
 Concentration of sequentially extracted and total lead as affected by electrostatic field strength in particle of well water sample 5SIIL02

Experimental conditions: initial total solid concentration = 0.40 g/L; pH = 6.5; sample: 5SIIL02

			unit	: pb-µg/soil-g
Field strength	E = 00 V/cm (V = 00)	E = 32.3 V/cm (V = 100)	E = 64.5 V/cm (V = 200)	E = 71.3 V/cm (V = 221)
pН	6.8	6.8	6.8	6.8
Exchangeable	0.00	0.00	0.00	0.00
Carbonate	0.00	14.05	12.52	8.97
Fe-Mn oxide	1.13	3.38	2.41	2.13
Organic matter	13.30	2.44	1.92	1.99
Residual form	17.41	9.28	8.81	10.94
Total	31.84	29.14	25.65	24.04

## Table A9. Concentration of sequentially extracted and total lead as affected by electrostatic field strength in particles of well water sample 10IIB02

Experimental conditions: initial total solid concentration = 0.26 g/L; pH = 6.8; sample: 10IIB02

			unit	t: pb-µg/soil-g
Field strength	E = 32.3 V/cm (V = 100)	E = 64.5 V/cm (V = 200)	E = 96.8 V/cm (V = 300)	E = 112.6 V/cm (V = 349)
рН	6.8	6.8	6.8	6.8
Exchangeable	0.00	0.00	0.00	0.00
Carbonate	11.05	9.85	6.03	6.09
Fe-Mn oxide	12.80	9.59	4.75	4.62
Organic matter	1.84	1.25	1.35	1.28

Residual form

Total

12.87

38.55

## Table A10. Concentration of sequentially extracted and total lead as affected by electrostatic field strength in particles of well water sample 10IIB02

Experimental conditions: initial total solid concentration = 0.43 g/L; pH = 6.5; sample: 10IL0

11.26

31.96

11.87

24.00

9.33

21.32

					unit	: pb-µg/soil-g
Field strength	E = 00 V/cm (V = 00)	E = 32.3  V/cm (V = 100)	E = 64.5  V/cm (V = 200)	E = 96.8 V/cm (V = 300)	E = 119.7 V/cm (V = 371)	E = 123.9  V/cm (V = 384)
рН	6.8	6.8	6.8	6.8	6.8	6.8
Exchangeable	0.00	0.00	0.00	0.00	0.00	0.00
Carbonate	0.00	0.24	0.28	0.21	0.22	0.24
Fe-Mn oxide	0.49	1.41	1.51	1.15	1.08	0.96
Organic matter	0.73	1.41	1.38	1.19	1.12	1.01
Residual	6.51	7.44	6.46	5.98	5.49	10.69
Total	7.72	10.50	9.61	8.53	7.92	12.90

 Table A11. Concentration of sequentially extracted lead as affected by electrostatic field strength in particles of well water sample 5SIIIL01

Experimental conditions: initial total solid concentration = 0.68 g/L; pH = 6.8; sample: 5SIIIL01

					unit: pb-µg/soil-g						
Field strength	E = 00 V/cm (V = 00)	E = 32.3 V/cm (V = 100)	E = 64.5 V/cm (V = 200)	E = 96.8 V/cm (V = 300)	E = 129.0 V/cm (V = 400)	E = 138.7 V/cm (V = 430)					
pН	6.6	6.6	6.6	6.6	6.6	6.6					
Exchangeable	0.01	0.01	0.01	0.00	0.00	0.00					
Carbonate	0.00	0.40	0.20	0.15	0.14	0.14					
Fe-Mn oxide	0.97	2.01	1.24	1.05	0.89	0.76					
Organic matter	0.89	1.29	1.03	1.03	0.94	0.85					
Residual	2.22	2.35	3.53	8.69	7.04	7.70					
Total	4.09	6.06	6.00	10.91	9.01	9.45					

 Table A12. Concentration of sequentially extracted lead as affected by electrostatic field strength in particles of well water sample 5SIIIB02

Experimental conditions: initial total solid concentration = 0.52 g/L; pH = 6.8; sample: 5SIIIB02

				unit: pb-µg/soil-g						
Field strength	E = 00  V/cm	E = 32.3  V/cm	E = 64.5  V/cm	E = 96.8  V/cm	E = 117.7  V/cm					
	$(\mathbf{V}=00)$	(V = 100)	(V = 200)	(V = 300)	(V = 365)					
pН	7.1	7.1	7.1	7.1	7.1					
Exchangeable	0.01	0.01	0.01	0.01	0.00					
Carbonate	0.00	0.20	0.14	0.13	0.11					
Fe-Mn oxide	1.08	1.05	0.88	0.70	0.69					
Organic matter	0.83	1.05	0.97	0.78	0.81					
Residual	7.38	9.81	6.86	8.81	11.60					
Total	9.29	12.10	8.86	10.42	13.21					

 Table A13. Concentration of sequentially extracted lead as affected by electrostatic field strength in particles of well water sample 5SIIIH02

Experimental conditions: initial total solid concentration = 0.44 g/L; pH = 7.1; sample: 5SIIIH0

Sampling	Low flow purge					High flow purge			Bailer								
Method																	
Medium	In filtrate, after electrofiltration					In filtra	ate, afte	e, after electrofiltration In			filtrate, after electrofiltration						
Applied Field	0*	32.2	64.5	96.8	119.7	123.9	0*	32.3	64.5	96.8	117	0*	32.3	64.5	96.8	129.0	138.7
Strength (V/cm)																	
Mean particle	<522	na	na	na	na	na	<817	<53	<49	<49	na	<1007	na	na	na	na	na
size (nm) <sup>a</sup>								4	7	4							
Total solids	2.94	2.74	1.78	0.92	0.64	0.52	11.36	8.42	6.33	4.84	3.64	11.45	8.07	6.33	4.44	2.51	2.26
$(g/L)^{b}$																	
Total lead	20	17	13	10	8	9	23	18	16	13	13	27	13	12	9	7	5
$(\mu g/L)^{c}$																	

Table A14. Summary of Lead Analysis from Well 5S by Various Water Sampling Methods

\*: Without electrofiltration; a: Figure 4.2 and Figure 4.5; b: Figure 4.3 and calculated from solid removal efficiency listed in Table A3 which was obtained with dilute water; c: from Table A4