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DETERMINATION AND SEPARATION OF FLUORIDE IN NATURAL WATERS

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Bornova- İZMİR

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tarafından değerlendirilmiş olup, Yapılan Tez Savunma Sınavında aday oy birliği/ ~~oy çokluğu~~ ile başarılı bulunmuştur.

ÖZET

DOĞAL SULARDA FLORÜR TAYİNİ VE AYRILMASI

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Eser düzeydeki florür, kemiklerin ve diş minesinin oluşumu için gerekli bir mineraldir. Ancak aşırı miktarda alındığında florosis adı verilen diş ve iskelet hastalığının ortaya çıkmasına neden olmaktadır ve DNA'nın yapısı bozulmaktadır. Bu zararlı etkilerinden dolayı sularda florür iyonunun tayini büyük önem taşımaktadır.

Sularda florür iyonu için izin verilen derişim 1.0 mg/L'dir ve yetişkinler için öldürücü doz 0.20-0.35 g/kg vücut ağırlığı olarak belirlenmiştir. Sulu çözeltilerde ve sularda florür tayini için, kromatografik, spektrofotometrik, potansiyometrik yöntemler gibi bir çok yöntem geliştirilmiştir.

Bu çalışmada, çeşitli doğal ve mineral sularda bulunan florür iyonunun tayini florür seçimli elektrot (WTW F800) kullanılarak yapılmıştır. Ölçümler doğrudan ve standart katma yöntemleriyle gerçekleştirilmiştir. Florür derişimleri Shimadzu IC-Ai

model iyon kromatografi cihazı kullanarak kromatografik olarak da ölçülmüştür. Sulardan florür giderimi için sorpsiyon ve elektrodiyaliz yöntemleri kullanılmıştır.

Tokuyama TS-1-10 elektrodiyaliz cihazı kullanılarak, Balçova jeotermal suyundan florür etkin bir şekilde giderilmiştir. Deney sırasında, seyreltik ve derişik bölmelerden periyodik olarak örnekler~~i~~ alınarak iyon derişimleri analitik olarak tayin edilmiştir.

Metal yüklü zeolitlerle kesikli sorpsiyon çalışmaları gerçekleştirilmiştir. ZEO-1 ve ZEO-2 tipi zeolit örneklerine Al^{3+} ve ZrO^{2+} metal iyonları yüklenerek hazırlanan adsorbentler kullanılarak Balçova jeotermal suyundan florür giderimi için optimum zeolit miktarı belirlenmiştir. Zr-ZEO-2 tipi zeolitlerle kinetik çalışmalar da gerçekleştirilmiştir.

ANAHTAR KELİMELER: Florür, florür iyon seçimli elektrot, iyon kromatografi, su, jeotermal su, elektrodiyaliz, zeolit, metal yüklü zeolit

ABSTRACT

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Fluoride in trace quantity is an essential element for normal mineralization of bones and formation of dental enamel. However, its excessive intake may result in several health problems such as fluorosis. The toxic effects of fluoride, other than dental and skeletal fluorosis, include enzyme damages, which result in a wide range of chronic diseases such as genetic damage, mental retardation, cancer, bone pathology, and others. Because of these effects, careful control of fluoride levels is required.

The maximum acceptable concentration of fluoride in water is 1.0 mg/L and for adults the lethal dose is 0.20-0.35 g fluoride per kg body weight. Many methods such as chromatographic, spectrophotometric, potentiometric methods have been developed to determine the fluoride concentration in aqueus solutions and water.

In this study, determination of fluoride in various mineral and natural waters was investigated by using fluoride selective electrode F-ISE (WTW F800 Fluoride

Combination Electrode). Measurements were performed by using direct and standart addition methods. The fluoride analyses in water samples were also performed by means of Ion Chromatography using a Shimadzu IC-A*i* model ion chromatography equipment. Some investigations have been performed for removal of fluoride from water using sorption and electrodialysis method.

Fluoride was effectively removed from Balçova geothermal water by electrodialysis using TS-1-10 electrodialysis equipment (Tokuyama). During the tests, water samples were taken periodically from dilute and concentrate streams, and the ion concentrations were determined analytically.

Batch-mode sorption studies were performed by metal loaded zeolites. Al^{3+} and ZrO^{2+} metal ions were loaded on ZEO-1 and ZEO-2 type zeolite samples and optimum zeolite amount was determined for fluoride removal from Balçova geothermal water. Kinetic tests were performed by using Zr-ZEO-2.

KEY WORDS: Fluoride, Fluoride selective electrode, ion chromatography, water, geothermal water, electrodialysis, zeolite, metal loaded zeolite

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NOMENCLATURE

C	Concentration (mg/L)
E	Potential
I	Current
T	Time
V	Volume

Subscripts

D	Dilute
C	concentrate
0	Initial
rpm	round per minute

1. INTRODUCTION

1.1. Fluoride in Water

Water is an essential natural resource for sustaining life and environment that we have always thought to be available in abundance and free gift of nature. However, chemical composition of surface or subsurface is one of the prime factors on which the suitability of water for domestic, industrial or agricultural purpose depends. Freshwater occurs as surface water and groundwater. Due to various ecological factors either natural or anthropogenic, the groundwater is getting polluted because of deep percolation from intensively cultivated fields, disposal of hazardous wastes, liquid and solid wastes from industries, sewage disposal, surface impoundments etc. (Meenakshi, 2006).

Natural waters contain many cations like Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} etc. and many anions like SO_4^{2-}, NO_3^{-}, PO_4^{2-}, F^{-} etc. The element fluorine occurs very widely as fluoride. It is present in water, minerals, most foods and many plant and animal tissues. It enters the soil through weathering of rocks, precipitation or waste run off. Surface waters generally do not contain more than 0.3 mg/L (Campbell, 1987) of fluoride unless they are polluted from external sources. Water with high fluoride content is generally soft, has high pH and contains large amount of silica. In groundwater, the natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, temperature, the action of other chemicals and the depth of wells. It is of particular interest because of its inclusion in the list of elements believed to be essential for animal-life and also because of its toxic effects at higher concentrations. In many parts of the world there is an inverse relationship between the fluoride content of drinking water and the amount of dental caries in the population and the fluoridation of public water supplies to a level of about 1 mg/L (WHO, 1984) is now relatively common. However careful control of fluoride levels is required because high concentrations are known to cause mottling of the teeth and various bone disorders (Campbell, 1987).

There are more than 20 developed and developing nations that are endemic for fluorosis. These are Argentina, U.S.A., Morocco, Algeria, Libya, Egypt, Jordan, Turkey, Iran, Iraq, Kenya, Tanzania, S. Africa, China, Australia, New Zealand, Japan, Thailand, Canada, Saudi Arabia, Persian Gulf, Sri Lanka, Syria, India, etc. (Meenakshi, 2006).

Drinking water is the major contributor (75–90% of daily intake), other sources of fluoride poisoning are food, industrial exposure, drugs, cosmetics, etc. The fluoride content of some major food products is given in Table 1.1.

Table 1.1. Fluoride concentration in agricultural crops and other edible items (Sengupta et al., 1971)

Food products	Fluoride concentration (mg/kg)
Wheat	4.6
Rice	5.9
Pulses and legumes	5.6
Soya bean	4.0
Tomato	3.4
Cucumber	4.1
Spinach	2.0
Potato	2.8
Carrot	4.1
Mango	3.7
Apple	5.7
Almond	4.0
Coconut	4.4
Tea	60-112
Aerated drinks	0.77-1.44
Garlic	5.0
Beef	4.0-5.0
Fishes	1.0-6.5
Rock salts	200.0–250.0
Tobacco	3.2–3.8

1.2. Health Effects of Fluoride for Human Being

Fluorine being a highly electronegative element has extraordinary tendency to get attracted by positively charged ions like calcium. Hence the effect of fluoride on mineralized tissues like bone and teeth leading to developmental alternations is of clinical significance as they have highest amount of calcium and thus attract the maximum amount of fluoride that gets deposited as calcium–fluorapatite crystals. Tooth enamel is composed principally of crystalline hydroxylapatite. Under normal conditions, when fluoride is present in water supply, most of the ingested fluoride ions get incorporated into the apatite crystal lattice of calciferous tissue enamel during its formation. The hydroxyl ion gets substituted by fluoride ion since fluorapatite is more stable than hydroxylapatite. Thus, a large amount of fluoride gets bound in these tissues and only a small amount is excreted through sweat, urine and stool. The intensity of fluorosis is not merely dependent on the fluoride content in water, but also on the fluoride from other sources, physical activity and dietary habits. The various forms of fluorosis arising due to excessive intake of fluoride are briefly shown in Table 1.2

Table 1.2. Effects of fluoride in water on human health (US Public Health Service Drinking Water Standards, 1962)

Fluoride concentration (mg/L)	**Effects**
<1.0	Safe limit
1.0–3.0	Dental fluorosis (discoloration, mottling and pitting of teeth)
3.0–4.0	Stiffened and brittle bones and joints
4.0–6.0 and above	Deformities in knee and hip bones and finally paralysis making the person unable to walk or stand in straight posture, crippling fluorosis

1.2.1. Dental fluorosis

Due to excessive fluoride intake, enamel loses its lustre. In its mild form, dental fluorosis is characterized by white, opaque areas on the tooth surface and in severe form, it is manifestated as yellowish brown to black stains and severe pitting of the teeth. This discoloration may be in the form of spots or horizontal streaks. Normally, the degree of dental fluorosis depends on the amount of fluoride exposure up to the age of 8–10, as fluoride stains only the developing teeth while they are being formed in the jawbones and are still under the gums (Meenakshi, 2006).

Figure 1.1. Dental fluorosis (National Research Council, 1993)

1.2.2. Skeletal fluorosis

Skeletal fluorosis affects children as well as adults. It does not easily manifest until the disease attains an advanced stage. Fluoride mainly gets deposited in the joints of neck, knee, pelvic and shoulder bones and makes it difficult to move or walk. Early symptoms of skeletal fluorosis include sporadic pain, back stiffness, burning like sensation, pricking and tingling in the limbs, muscle weakness, chronic fatigue, abnormal calcium deposits in bones and ligaments. The advanced stage is osteoporosis in long bones and bony outgrowths may occur. Vertebrae may fuse together and eventually the victim may be crippled. It may even lead to a rare bone cancer, osteosarcoma and finally spine, major joints, muscles and nervous system get damaged (Meenakshi, 2006).

Figure 1.2. Skeletal fluorosis (www.rvi.net/~fluoride/000078.htm)

1.2.3. Other problems

Besides skeletal and dental fluorosis, excessive consumption of fluoride may lead to muscle fibre degeneration, low hemoglobin levels, deformities in RBCs, excessive thirst, headache, skin rashes, nervousness, neurological manifestations, depression, gastrointestinal problems, urinary tract malfunctioning, nausea, abdominal pain, tingling sensation in fingers and toes, reduced immunity, repeated abortions or still births, etc. It is also responsible for alterations in the functional mechanisms of liver, kidney, digestive system, respiratory system, excretory system, central nervous system and reproductive system, destruction of about 60 enzymes. The effects of fluoride in drinking water on animals are analogous to those on human beings. The continuous use of water having high fluoride concentration also adversely affects the crop growth (Meenakshi, 2006).

1.3. Chemical Analysis Methods for Fluoride in Water

Chemical analysis methods for the fluoride analysis can be classified into the three categories:

- Chromatographic analysis,
- Spectrophotometric analysis,
- Potentiometric analysis.

1.3.1. Determination of fluoride by chromatographic method

Chromatography is a separation method that relies on differences in partitioning behavior between a flowing mobile phase (eluent) and a stationary phase to separate the components in a mixture. It is a convenient technique and allows for the method to be hyphenated with various detection methods, such conductivity, spectrophotometry and ICP-MS detection (Noh, 2005).

Ion chromatography and Reversed-Phase High Performance Liquid Chromatography (RP-HPLC) are common chromatography techniques for fluoride determination.

The chromatographic technique, which utilizes a non-polar adsorbent surface and a polar eluent, has been named as Reversed-Phase HPLC (RP-HPLC). Retention is the result of the interaction of the non-polar components of the solutes and the non-polar stationary phase. Typical stationary phases are non-polar hydrocarbons, waxy liquids or bonded hydrocarbons (such as C_{18}, C_8, C_4, etc.) and the solvents are polar aqueous-organic mixtures such as water-methanol or water-acetonitrile (Oszwaldowski et al., 1998).

1.3.2. Determination of fluoride by spectrophotometric method

Spectrophotometric methods for the determination of fluoride ion are either based on metal displacement from a colored complex or the formation of a mixed-ligand complex, Zr(IV)-F-Alizarin (Standard method, 1955; Crosby et al., 1968), Zr(IV)-F-SPANDS (Bellack et al., 1958; Standard method 1975 and 1998; US EPA Method 13 A and 340.1, 1971; Devine et al., 1975; Mac Leod et al., 1973; Crosby et al., 1968), Th(IV)-F-Bromocresol orange (Khalifa et al., 1998), Eriochrome cyanine R (Crosby et al., 1968), Semi-Methylthymol Blue (SMTB), Semi-Bromocresol Orange (SBCO), Methylnaphthlo Orange (MNO), Naphthol Violet (NV) (Yuchi et al., 1995).

Zirconium-alizarin method

The zirconium-alizarin lake test is a common test for fluorides. With adding of zirconium-alizarin lake, a change in color of the lake to yellow is an indication of fluoride(s) present in the sample.

$$\underset{\text{(Red)}}{\text{Zr - alizarin lake}} + \underset{\text{(colorless)}}{6\,F^-} \rightarrow \underset{\text{(colorless)}}{ZrF_6^{2-}} + \underset{\text{(yellow)}}{\text{alizarin}} \tag{1.1}$$

This method has a serious drawback in that the color development is progressive, requiring accurate timing to achieve consistent results. The waiting period is also a source of constant annoyance. The distillation step is necessary to avoid interferences. The Alizarin complexone procedure has many advantages over the other spectrophotometric methods, and is particularly suitable for samples containing only very small amounts of fluoride (0.1-2.0 mg F^- /mL) (Tunç, 2006).

SPANDS method

Bellack et al. (1958) developed a simple and rapid SPANDS (2-(*para*sulfophenylazo)- 1,8-dihydroxynaphthalene-3,6-disulfonate) method, in place of the usual alizarin-zirconium photometric methods, which yielded an accuracy within 0.02 mg/L in the fluoride concentration range of 0-1.40 mg/L. This method is applicable to the measurement of fluoride in drinking, surface, and saline waters, domestic and industrial wastes. Compared to alizarin-zirconium methods, it saved considerable time and increased precision. It was, however, still subject to many interferences, so that the distillation step had to be applied to eliminate interferences. A distillation step severely restricts the number of samples that can be analysed in a given period, so that this distillation step is often omitted when large numbers of samples have to be analysed (Harwood, 1969). Following distillation to remove interferences, the sample is treated with the SPANDS reagent. The loss of color resulting from the reaction of fluoride with the zirconyl- SPANDS dye is a function of the fluoride concentration (National Environmental Methods, 340.1, 1974, 1978).

The SPANDS method became the reference spectrophotometric method for the fluoride analysis in water. (Bellack et al., 1958; Standard method 1975 and 1998; US EPA Method 13 A and 340.1, 1971).

1.3.3. Determination of fluoride by potentiometric method

The potentiometric technique, mainly F-ISE, is considered the simplest and most reliable for fluoride determination (Durst, 1969; Fry et al., 1970; Hall et al., 1972; Hallsworth et al., 1976; Retief et at., 1985; Kissa, 1987; Villa, 1988; Vogel et al., 1990). The F-ISE method for the fluoride determination can be applied either without pretreatment technique, namely conventional potentiometric method, (Babcock et al., 1968; Frant et al., 1968; Harwood, 1969) or with pretreatment technique, the extended method, such as co precipitation and steam distillation (Okutani et al., 1989).

Babcock et al. (1968) used the electrode without the addition of any ionic buffer for the determination of fluoride in municipal water. Their particular application was basically that of monitoring a municipal water supply for fluoride. Under such conditions, the composition of the water, and hence the total ionic strength, would remain fairly constant since the water originated form the same source. Consequently, there was no great necessity to add electrolytes to ensure constant ionic strength.

Frant et al. (1968), on the other hand, have used the electrode on samples from different sources, and so had to make use of an ionic buffer. This method was selected for routine fluoride analysis. Later tests indicated that the composition of the ion buffer should be changed in order to overcome interference from aluminium. Results obtained indicate that with the new ionic buffer, satisfactory analysis for fluoride can be obtained even in the presence of up to 5 mg Al /L.

Crosby et al. (1968) evaluated ISE method and five spectrophotometric procedures for the determination of fluoride in potable waters and other aqueous solutions, with respect to reproducibility, sensitivity, range, stability of coloured products and of reagents, specificity and effect of temperature. fluoride was determined directly, without the need for any separation step. The ISE method was shown to be less susceptible than the colorimetric methods to interference from other ions in solution.

Harwood (1969) evaluated a commercially available F-ISE for use in routine fluoride determination on water samples. Tests on samples showed that aluminium interfered seriously and an ionic buffer containing CDTA was recommended in order to control this interference, since both citrate and EDTA had only limited applicability. The fluoride analysis results were compared using both SPANDS method and ISE and the results, obtained with the F-ISE, were more trustworthy because of the inherent difficulties of the SPANDS method.

1.3.4. Other methods

1.3.4.1. Pervaporation

Pervaporation is an energy efficient combination of membrane permeation and evaporation and is considered an attractive alternative for many separation processes. The process, which requires only low temperatures and pressures, has cost and performance advantages compared with distillation for constant-boiling mixtures.

Pervaporation is particularly suitable for the dehydration of organic solvents and the removal of organics, such as methanol and acetone, from aqueous streams. In the pervaporation process the liquid (mixture) is in contact with the membrane. At the permeate side, a partial pressure is generated by means of a vacuum pump, or by means of an inert gas flow. The components of the liquid that move through the membrane are vaporized by the low pressure, removed and condensed (Noh, 2005).

Papaefstathiou et al. (1995) developed a selective method for the determination of fluoride in contaminated samples based on pervaporation of a volatile derivative and potentiometric monitoring of the anion after collection in a basic solution. fluoride was converted to volatile trimethylfluorosilane by reaction with hexamethyldisilazane, and absorbed in dilute NaOH solution. Both the continuous and stopped-flow modes were used in order to accomplish a variable efficiency of the separation process thus enlarging the determination range which was established between 5 and 100 mg/L. The precision was between 2.60 and 3.58 %. The determination of the analyte in samples from different sources, such as tap water, well water, fertilizers and ceramic industry wastewater, testified to its usefulness, giving the recovery range between 87.23 and 106.09% with RSD values between 0.72 and 4.17 %.

1.3.4.2. Extraction

Extraction is primarily used to separate analytes from a matrix thus eliminating or reducing interferences from other components. Secondly, it is used to concentrate the analyte up to a detectable concentration level.

Nishimoto et al. (2001) employed spectrophotometry after solvent extraction of fluoride into chloroform using [2, 23- diethy- 8, 17- bis (2-ethoxycarbonylethyl) - 3,7,12,13,18,22- hexamethylsapphyrin (H3 sap), sapphyrin] in the presence of 0.1 M sodium nitrate. Fluoride ion was extracted from chloroform with the positively charged sapphyrin, as ion-pair complexes of $H_5sap^{2+}·F^-·NO_3^-$, that gave a new absorption maximum wavelength at 448 nm. The results provided the determination of fluoride ion at concentrations as low as 0.01 mg/L. Metal ions like Al(III) and Fe(III) did not interfere with the determination of fluoride.

1.4. Determination of Fluoride by Ion Chromatography (IC) Method

Small et al. (1975) pioneered the IC method for separation and quantitative determination of inorganic ions. It is now a well established method for the analysis of ionic species and has been approved for compliance monitoring of common anions in US drinking water since the mid-1980s, as described in USEPA method 300.1 (1997). Many regulatory and standard organizations, such as ASTM, AOAC, ISO and US EPA, have approved methods of analysis based upon IC, most of which have been published within the last 10 years (Jackson, 2000; 2001). It is a form of liquid chromatography that uses ion-exchange resins to separate atomic or molecular ions based on an ion exchange process between the mobile phase (eluent) and the exchange groups (the analyte) covalently bound to the stationary phase on the column. As the eluent flows through the column, the components of the analyte will move down the column at different speeds according to the affinity of each analyte to the stationary phase, and therefore separate from one another. Subsequently, the detector, which can be conductivity detector, ICP-MS detector and spectrofluorimetric detector etc., measure the different anions as they emerge from the column. Compared to non-chromatography techniques, the IC method has the advantages of separation before detection, increased sensitivity, simultaneous analysis in a single run, simple sample preparation and faster analysis time, which is less than 15 minutes (Dasgupta, 1992; Romano and Krol, 1992).

1.4.1. Ion chromatography (IC) system

The main components of an IC system are a high-pressure pump, a column and an injector system as well as a detector. The flow path through a single-column Ion chromatography system is shown in Figure 1.3.

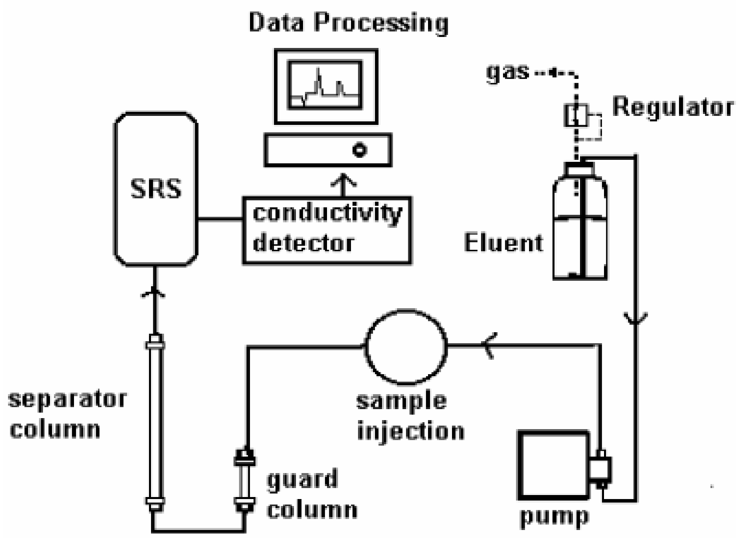

Figure 1.3. Flow scheme of ion chromatography (Noh, 2005)

The eluent is filtered and pumped through a chromatographic column, the sample is loaded and injected to the column and the effluent is monitored using a detector and recorded as peaks.

There are a number of different types of pumps that can provide the necessary pressures and flow-rates required by the modern ion chromatograph. In the early years of the LC renaissance, there were two types of pump in common use; they were the pneumatic pump, where the necessary high pressures were achieved by pneumatic amplification, and the syringe pump, which was simply a large, strongly constructed syringe with a plunger that was driven by a motor. Today the majority of modern chromatographs are fitted with reciprocating pumps fitted with either pistons or diaphragms. The pneumatic pump has a much larger flow capacity than the piston type pumps but, nowadays, is largely used for column packing and not for general analysis (Noh, 2005).

1.4.2. Sample injection (injection valve)

The injection valve has two operating positions, which are Load and Inject. In the Load position, sample is loaded into the sample loop, where it is held until injection. In the Inject position, the sample is swept to the column for analysis. Eluent flows through one of two paths, depending on the valve position (Noh, 2005).

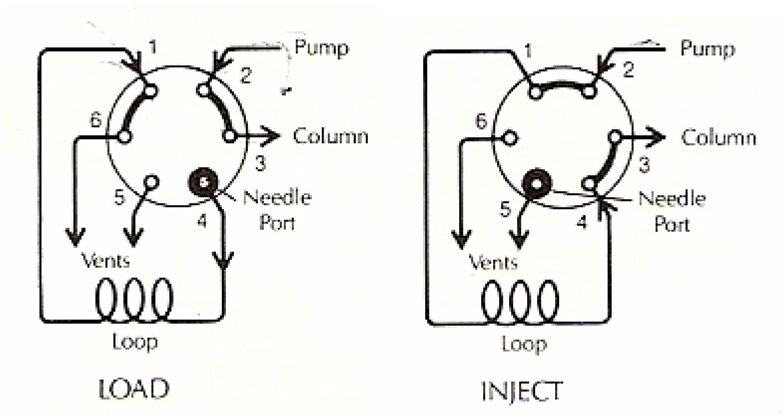

Figure 1.4. Inject positions (Manual guide of Shimadzu IC Ai)

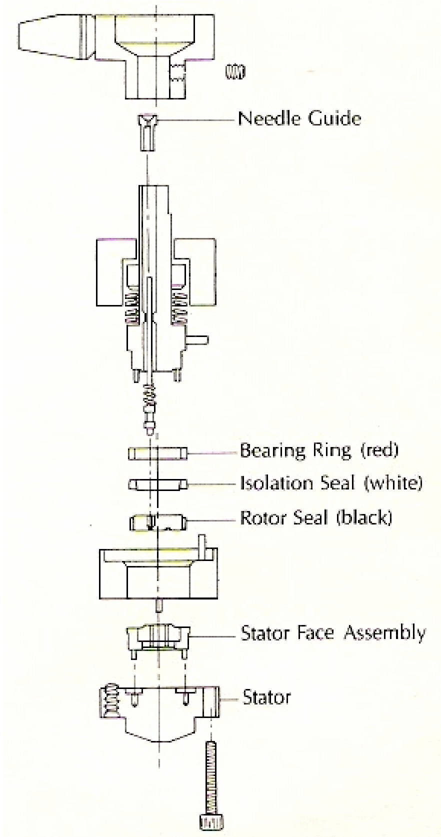

Figure 1.5. Injection valve (manual guide of Shimadzu IC Ai)

1.4.3. The separation columns

Heavy-wall glass, stainless steel and plastic are among materials that can withstand high pressures and are thus used to construct HPLC columns. They must also be able to resist the chemical action of the mobile phase. Wall irregularities will cause a well-packed column to channel near the wall or packing interface thus the tubing must have a smooth, precision bore internal diameter. Channels would cause peak broadening and a decrease in efficiency.

Column connections are made with low dead-volume fittings, which prevent stagnant pockets of eluent. Usually a short guard column, which has the same composition with analytical column and prevents poisoning of the separator column by sorbing organic contaminants and removing particulates, is placed in front of the analytical column. This serves to increase the life of the analytical column by removing particulate matter and contaminants from the solvents and has practically no influence on analytical column's chromatographic separating performance (Noh, 2005).

1.4.4. Separation mechanism in ion chromatography

Ion chromatography is a type of liquid chromatography and uses ion-exchange resins to separate ions. It base on an ion exchange process between the mobile phase (eluent) and the exchange groups (the analyte) covalently bound to the stationary phase on the column.

Basically, equilibria play the important role in ion chromatography (IC), and the separation mechanism can be described as follows (taking anion separation of S_1^- and S_2^-):

Eluent injection: $$Res - A^- + E^- \Longleftrightarrow Re\,s - E^- + A^- \tag{1.2}$$

Sample injection: $$\begin{aligned} Res - E^- + S_1^- &\Longleftrightarrow Re\,s - S_1^- + E^- \\ Res - E^- + S_2^- &\Longleftrightarrow Re\,s - S_2^- + E^- \end{aligned} \tag{1.3}$$

Elution: $$\begin{aligned} Res - S_1^- + E^- &\Longleftrightarrow Re\,s - E^- + S_1^- \\ Res - S_2^- + E^- &\Longleftrightarrow Re\,s - E^- + S_2^- \end{aligned} \tag{1.4}$$

Res： ion-change resin； E^-: eluent anion; S_1, S_2: anions of analyte 1 and 2.

Sample zones move down along the column as eluent is continuously pumped into the column, and separation is achieved because S_1^- and S_2^- anions have different affinities for the ion-exchange sites on the stationary phase (Dan Pu, 2004).

In ion chromatography, column support material is mostly polystyrene/divinylbenzene (PS/DVB) based resin (Joachim, 1986). The column material (resin) is synthesized to serve as cation exchange or anion exchange columns. The most common site on anion exchanger is the tertiary amine group $–N(CH_3)_3^+OH^-$, a strong base and the sulphonic acid group $–SO_3^-H^+$ for a cation (Noh, 2005).

1.4.5. Mobil phase- buffer

The order of elution and the separation efficiency in ion chromatography are dependent on pH. To ensure a constant pH, a buffer solution is used as the mobil phase. An important criterion for conductivity detection is that the conductivity of the buffer be kept as low as possible, to minimize the amount of zero suppression necessary (Tissuee, 2004).

1.4.6. Anion exchange resins

The exchange process of a solution, which contains an anion, AX^- on an anion exchange column, is described by the following reaction.

$$xN(CH_3)_3^+OH^-_{(solid)} + A^{X-}_{(solution)} \leftrightarrow (N(CH_3)_3^{\ +})_xA^{x-}_{(solid)} + xOH^-_{(solution)} \qquad (1.5)$$

The affinity of the resin for the anion relative to OH^- ion is $SO_4^{2-} > C_2O_4^{2-} > I^- > NO_3^- > Br^- > Cl^- > HCO^- > OH^- > F^-$. These conditions depend on various factors, such as the type of resin, size or the hydrated ion, and so on.

The structure of the anion exchange resins is illustrated in Figure 1.6.

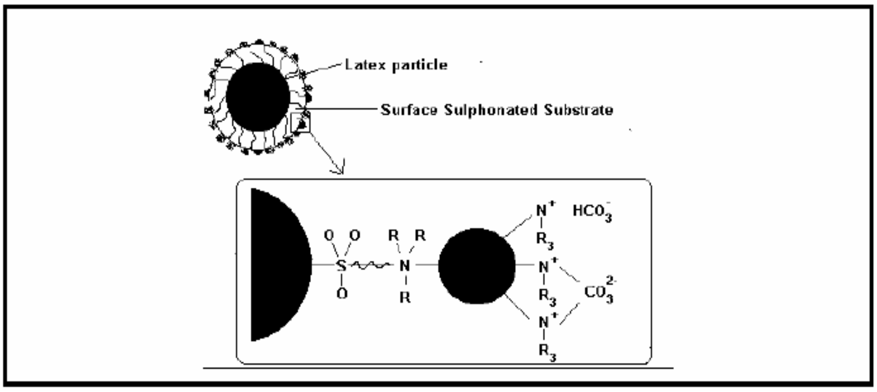

Figure 1.6. The structure of the anion exchange resins (Noh, 2005)

1.4.7. Cation exchange resins

The stationary phase of a cation exchange column is based on inert, surface sulphonated, crosslinked polystyrene (Figure 1.7).

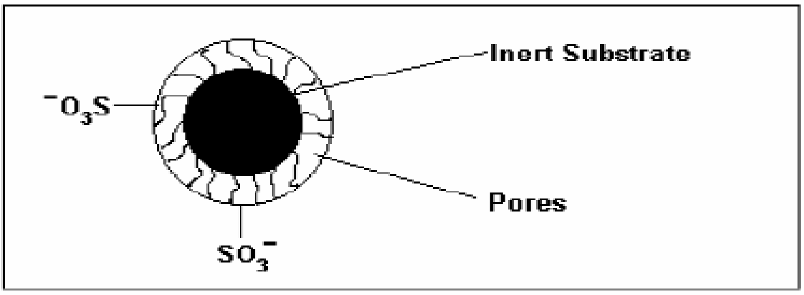

Figure 1.7. The structure of a cation exchange resin (Weiss, 1986)

The exchange process for a cation, M^{x+}, can be described by the equilibrium:

$$xRSO_3^-H^+_{(solid)} + M^{x+}_{(solution)} \leftrightarrow (RSO_3^-)_xM^{x+}_{(solid)} + xH^+_{(solution)} \qquad (1.6)$$

Since the core of a cation exchange resin is strongly hydrophobic, the diffusion into the resin of highly dissociated and hydrated species, such as Na^+, K^+, and Mg^{2+}, can be neglected. Consequently, the diffusion paths are short and high efficiencies are achieved.

1.4.8. Detectors

There are many types of detectors that can be used with IC. Some of the common detectors include Ultra-Violet (UV) detector, Fluorescence detector and Mass Spectroscopy (MS) detector.

Conductivity detectors are commonly used in ion chromatography mainly because of their excellent sensitivity and predictable response to concentration changes. Ions in solution conduct electrical current when a voltage is applied between electrodes in contact with the solution. Since the magnitude of this current is proportional to the concentration of dissolved ions, conductivity detection is useful for quantifying ionic analytes (Noh, 2005).

1.5. Determination of Fluoride by Ion Selective Electrode (ISE) Method

1.5.1 Ion Selective electrodes

The Ion Selective Electrode (ISE) is a sensor for the potentiometric determination of ionic species and one of the most frequently used devices during laboratory analysis in industry, process control, physiological measurements, and environmental monitoring. The functioning of an ISE is based on the selectivity of passage of charged species from one phase to another, leading to the creation of a potential difference. The most commonly used ISE is the pH probe. Other ions that can be measured include anions such as, F^-, Br^-, I^-, CN^-, NO_3^-, NO_2^-, the cations such as, Pb^{2+}, K^+, Ca^{2+}, Cu^{2+} and Na^+, and gases in solution such as NH_3, CO_2, N_2 and O_2.

The essential components of an ion selective measuring system include a reference electrode, a sensing electrode (or indicator electrode) and a potential measuring device (Noh, 2005).

1.5.2. Advantages of the ion selective electrode method

• It is considerably less expensive than other analytical techniques, such as Atomic Absorption Spectrophotometry (AAS) or Ion Chromatography (IC).

• It is simple to use and measurement is quick.

• It has a large range of applications and can be used over a wide concentration range.

• It is robust and durable and ideal for use in either field or laboratory environments.

• Accuracy and precision levels of ± 2% for some ions compare favourably with analytical techniques which require more complex and expensive instrumentation (Noh, 2005).

1.5.3. Fluoride ion selective electrode

The fluoride Ion-Selective Electrode for fluoride is designed for the detection of fluoride in aqueous solutions and is suitable for use in both field and laboratory applications. The fluoride electrode consists of a solid-state inorganic membrane of LaF_3 crystal, bounded into an epoxy body as shown in Figure 1.8 (Noh, 2005).

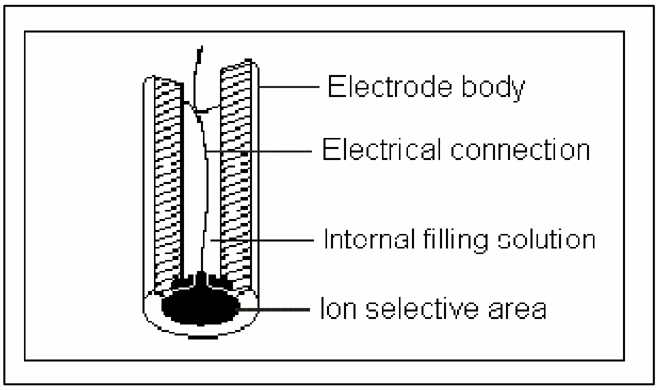

Figure 1.8. Fluoride ion selective electrode (Noh, 2005)

Within this crystal lattice, fluoride is a mobile ion whereas the lanthanum ions are in fixed lattice positions. A lattice vacancy will not accept ions other than fluoride due to differences in size, shape or charge. Therefore, the LaF_3 membrane is highly selective for conduction of fluoride ions. At the two interfaces, ionization creates a charge on the membrane surface as given by (Noh, 2005):

$$LaF_{3\,(solid)} \leftrightarrow LaF_2{}^{+}{}_{(solid)} + F^{-}{}_{(solution)} \tag{1.7}$$

When the sensor is in contact with a solution containing fluoride ion, a potential, dependent upon the level of fluoride ion in the solution, develops across the membrane. The construction of the membrane is shown in Figure 1.9.

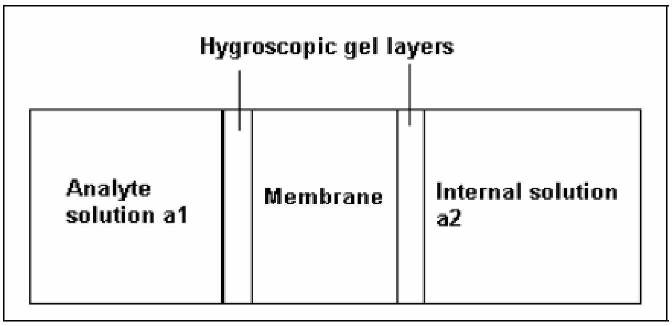

Figure 1.9. The construction of the membrane (Noh, 2005)

The Technical Specifications for the F-ISE is shown in Table 1.3.

Table 1.3. Technical Specifications for the F-ISE (Noh, 2005)

Parameter	Specification
Optimum pH	Between 5 to 6
Optimum temperature	25^{o}C
Time for stable reading after immersion	2 to 3 minutes
Potential drift (in 1000 ppm)	< 3 mV/day (8 hours)
Recommended reference electrode	Single junction AgCl or double junction lithium acetate
Electrode slope at 25^{o}C	54±5 mV/decade

The mechanism of the F-ISE

The magnitude of the charge is dependent upon the fluoride ion concentration of the solution. Thus, the side of the membrane encountering the lower fluoride ion concentration becomes positive with respect to the other surface. It is this charge difference that provides a measure of the difference in fluoride concentration of the two solutions. The membrane potential (E_m) consists of two potentials E_1 and E_2 on both sides of membrane-inner solution and membrane-outer solution interfaces. This can be written as (Skoog et al., 1998),

$$E_m = E_2 - E_1 \qquad (1.8)$$

The fluoride ion activities at each face are related to the Nernst–like relationships.

$$E_1 = j_1 - \frac{0.0592}{n} \log \frac{a_1^{'}}{a_1} \qquad (1.9)$$

$$E_2 = j_2 - \frac{0.0592}{n} \log \frac{a_2^{'}}{a_2} \tag{1.10}$$

Where, j_1 and j_2 are constants and a_1 and a_2 are activities of fluoride in the solutions on the external and internal sides of membrane respectively. The terms a_1' and a_2' are the activities of fluoride at the external and internal surfaces of the membrane. Since the two membrane surfaces are usually identical, so j_1 and j_2 as well as a_1' and a_2' are also identical. By substituting two equations and employing the equalities $j_1 = j_2$, $a_1' = a_2'$ and n=1, the membrane potential (E_m) can be rearranged like (Skoog et al., 1998),

$$E_m = E_2 - E_1 = 0.0592 \log \frac{a_2}{a_1} \tag{1.11}$$

Thus, the membrane potential E_m depends only on the fluoride ion activities of the solutions on either side of the membrane. For an ISE, the ion activity of the internal solution a_2 is a constant at temperature 25 °C, the equation can be simplified and the potential of a cell containing a lanthanum fluoride electrode is given by the equation to

$$E_m = L + 0.0592 \log a_{F^-} = L - 0.0592 \text{ pF}^- \tag{1.12}$$

where, L= 0.0592 log a_2.

The net potential is measured against a reference electrode.

$$E_{cell} = E_{ise} - E_{ref} \tag{1.13}$$

The results are usually given in mV or even directly as concentrations of the species being measured. The strength of this charge is directly proportional to the concentration of the selected ion (Skoog et al., 1998).

Total Ionic Strength Adjustment Buffer (TISAB) for F-ISE

The problems with Ion Selective Electrode measurements are the effect of interferences from other ions in solution, the effect of the ionic strength of the solution reducing the measured activity relative to the true concentration at high concentrations. TISAB (Total Ionic Strength Adjustment Buffer) is normally added to samples and standards in order to solve these problems (Front et al., 1968; Durst, 1969).

TISAB III contains CDTA (trans-1,2-cyclohexylendinitrilo) tetra acetic acid) and ammonium acetate (CH_3COONH_4) buffer at pH 5.5.

TISAB IV contains concentrated HCl (36-38%), tris(hydroxymethyl)aminomethane (for high levels of Al^{3+} interference at pH 8.5), and sodium tartrate ($Na_2C_4H_4O_6 \bullet 2H_2O$).

Low Level TISAB is used when measuring samples containing less than 0.4 mg/L F^- . It contains acetic acid, sodium chloride and NaOH (pH: 5.5).

Low Level TISAB and TISAB III are available for low-level measurement, but TISAB III is recommended in natural samples, which contain many unknown interferences. Since Low Level TISAB does not contain de-complexation agent, such as CDTA, it can not be used in natural samples.

i) Adjustment of a constant ionic strength for both standards and samples

The measured result of fluoride electrode is therefore strongly dependent on the ionic strength of the medium. TISAB ensures a constant ionic strength background, minimizing variations between samples and standards, which may otherwise influence the electrode potential. A constant ionic strength also reduces errors due to liquid junction potentials (Butler, 1969).

ii) Optimization of the pH

Of the commonly occurring ionic species (other than fluoride) the fluoride electrode responds directly only to hydroxide ions. This effect causes serious positive errors at high pH values. On the other hand under the acidic condition, below pH 5, the formation of HF and HF_2^- reduces the activity of the fluoride ions, which lead to a negative error. Use of TISAB ensures constant pH of around 5.4 is maintained eliminating the effect of pH changes (Vesely et al., 1974).

iii) De-complexation of the interference ions

Many TISAB solutions also include a masking agent to preferentially complex any potentially interfering species, e.g. di and trivalent cations such as aluminium, iron, magnesium and calcium. TISAB contains certain metal-complexing agents (masking agents) to release free fluoride ion from certain metal-F^- complexes. CDTA has found wide usage (Nicolson et al., 1981).

1.6. Removal of Fluoride from Water

Defluoridation of drinking water is the only practicable option to overcome the problem of excessive fluoride in drinking water, where alternate source is not available. During the years following the discovery of fluoride as the cause of fluorosis, extensive research has been done on various methods for removal of fluoride from water and wastewater. These methods are based on the principle of adsorption, ion-exchange, precipitation–coagulation, membrane separation process, electrolytic defluoridation, electrodialysis, etc. (Meenakshi, 2006).

1.6.1. Adsorption

Adsorption is a method used for removal of fluoride in which materials like activated carbon, activated alumina, bone char, or ion-exchange resins are used as adsorbents. Activated carbon prepared from various raw materials exhibits good capacity for removal of fluoride from drinking water (McKee et al., 1934).

The fluoride removing efficiency of activated alumina gets affected by hardness and surface loading (the ratio of total fluoride concentration to activated alumina dosage). Chloride does not affect the defluoridation capacity of activated alumina. The sorption process is highly pH dependent and is effective at pH values less than 3.0, and there is little removal at neutral pH value of 7.0. Defluoridation by activated alumina was successfully demonstrated (Boruff, 1934; Fink et al., 1936; Swope et al., 1937) and fluoride removal capacity increases directly with fluoride concentration and inversely with pH of the water (Blacket et al., 1958).

The process is highly selective but it has low adsorption capacity, poor physical integrity, requires acidification and pretreatment and its effectiveness for fluoride removal reduces after each regeneration. Mckee et al., 1934, investigated the use of powdered activated carbon for fluoride removal and achieved good results. The process is pH dependent with good results only at pH 3.0 or less. Therefore, the use of this material is expensive due to need of pH adjustment. Activated alumina technique for defluoridation is being propagated in several villages by the voluntary organizations funded by UNICEF or other agencies to provide safe drinking water (Meenakshi, 2006).

De-greased and alkali treated bones (Smith et al., 1937) and bone char (Killedar et al., 1988) are effective in the removal of fluoride from initial fluoride concentration ranging from 3.5 mg F^-/L to 10.0 mg F^-/L to less than 0.2 mg F^-/L (Srimurali et al., 1996).

The advantages of this method are process can remove fluoride up to 90% and treatment is cost-effective. Limitations are the process is highly dependent on pH and works best only in a narrow pH range (5–6), high concentration of total dissolved salts (TDS) can result in fouling of the alumina bed, presence of sulfate, phosphate or carbonate results in ionic competition, the process has low adsorption capacity, poor integrity and needs pretreatment, the regeneration is required after every 4–5 months and effectiveness of adsorbent for fluoride removal reduces after each regeneration (Meenakshi, 2006).

1.6.2. Ion exchange

Fluoride can be removed from water supplies with a strongly basic anion-exchange resin containing quarternary ammonium functional groups. The removal takes place according to the following reaction:

$$\text{Matrix-NR}_3^+\text{Cl}^- + \text{F}^- \rightarrow \text{Matrix-NR}_3^+\text{F}^- + \text{Cl}^- \qquad (1.14)$$

The fluoride ions replace the chloride ions of the resin. This process continues until all the sites on the resin are occupied. The resin is then backwashed with water that is supersaturated with dissolved sodium chloride salt. New chloride ions then replace the fluoride ions leading to recharge of the resin and starting the process again. The driving force for the replacement of chloride ions from the resin is the stronger electronegativity of the fluoride ions (Meenakshi, 2006).

This method's advantages are removes fluoride up to 90–95% and retains the taste and colour of water intact; disadvantages are, efficiency is reduced in presence of other ions like sulfate, carbonate, phosphate and alkalinity, regeneration of resin is a problem, the technique is expensive because of the cost of resin, pretreatment required to maintain the pH, regeneration and waste disposal and treated water has a very low pH and high levels of chloride.

1.6.3. Coagulation–precipitation

Lime and alum are the most commonly used coagulants. Addition of lime leads to precipitation of fluoride as insoluble calcium fluoride and raises the pH value of water upto 11–12.

$$Ca(OH)_2 + 2F^- \rightarrow CaF_2 + 2OH^- \tag{1.15}$$

As lime leaves a residue of 8.0 mg F^-/L, it is used only in conjunction with alum treatment to ensure the proper fluoride removal (Parker et al., 1975).

As a first step, precipitation occurs by lime dosing which is followed by a second step in which alum is added to cause coagulation. When alum is added to water, essentially two reactions occur. In the first reaction, alum reacts with some of the alkalinity to produce insoluble aluminium hydroxide [$Al(OH)_3$].

In the second reaction, alum reacts with fluoride ions present in the water. The best fluoride removal is accomplished at pH range of 5.5–7.5 (Potgeiter, 1990).

The Nalgonda technique of defluoridation is based on combined use of alum and lime in a two-step process and has been claimed as the most effective technique for fluoride removal. But the process removes only a smaller portion of fluoride (18–33%) in the form of precipitates and converts a greater portion of ionic fluoride (67–82%) into soluble aluminium fluoride complex ion, also, as the soluble aluminium fluoride complex is itself toxic. Due to use of aluminium sulfate as coagulant, the sulfate ion concentration increases tremendously and in few cases, it crosses the maximum permissible limit of 400 mg/L, which causes cathartic effect in human beings. The residual aluminium in excess of 0.2 mg/L in treated water causes dangerous dementia disease as well as pathophysiological, neurobehavioural, structural and biochemical changes. Due to organoleptic reasons, users do not like the taste of treated water. The process is not automatic, it requires a regular attendant for addition of chemicals and looking after treatment process (Nawalakhe et al., 1974).

1.6.4. Membrane process

In the past, the use of membrane technology for water treatment, particularly for drinking water production had been considered uneconomical in comparison with conventional means, but in the recent years the increased demand and contamination of water, rise in water quality standards and the problems associated with other methods have led to reconsideration of membrane technology for water purification. The progressive technical improvements in design and materials of the membranes have made the water treatment process economically competitive and highly reliable (Barba et al., 1997). Furthermore, membrane processes present several advantages as compared with other treatment methods as they simultaneously reject different types of ionic and molecular impurities like fluoride. Fluoride removal efficiencies upto 98 % by membrane processes have been documented by many researchers (Pervov et al., 2000).

1.6.4.1. Reverse osmosis

In the '80s, the RO membrane separation technique potentially introduced the treatment of industrial wastewaters where many successful applications were found, especially in the removal and recovery of fluoride from its effluents (Ndiaye, 2004).

RO is a physical process in which the contaminants are removed by applying pressure on the feed water to direct it through a semipermeable membrane. The process is the reverse of natural osmosis as a result of the applied pressure to the concentrated side of the membrane, which overcomes the natural osmotic pressure. RO membrane rejects ions based on size and electrical charge. The factors influencing the membrane selection are cost, recovery, rejection, raw water characteristics and pretreatment (Meenakshi, 2006).

Efficiency of the process is governed by different factors such as raw water characteristics, pressure, temperature and regular monitoring and maintenance, etc.

1.6.4.2. Electrodialysis

Electrodialysis (ED) also belongs to the group of membrane–based separation processes that competes with reverse osmosis for desalination and the removal of specific inorganic contaminants like fluoride. It is an electromembrane process which was first developed for desalting brackish water, brine production and demineralization .

1.6.4.3. Others

Another types of membranes that can remove fluoride from water are nanofiltration (NF) membranes. NF is a relatively low pressure process that removes primarily the larger dissolved solids as compared to RO. Conversely, RO operates at higher pressures with greater rejection of all dissolved solids.

Advantages of this method are the process is highly effective for fluoride removal, membranes also provide an effective barrier to suspended solids, all inorganic pollutants, organic micropollutants, pesticides and microorganisms, etc, the process permits the treatment and disinfection of water in one step, no chemicals are required and very little maintenance is needed, life of membrane is sufficiently long, so problem of regeneration or replacement is encountered less frequently, it works under wide pH range, no interference by other ions is observed and the process works in a simple, reliable automated operating regime with minimal manpower using compact modular model.

Disadvantages of the method are it removes all the ions present in water, though some minerals are essential for proper growth, remineralization is required after treatment, the process is expensive in comparison to other options, the water becomes acidic and needs pH correction, lot of water gets wasted as brine and disposal of brine is a problem (Meenakshi, 2006).

1.7. Removal of Fluoride from Water by Electrodialysis Process

1.7.1. Principle of electrodialysis

Electrodialysis (ED) is a membrane process in which ions are transported through ion permeable membranes from one solution to another under the influence of an applied electrical potential. The basic principles of electrodialysis were reviewed by Strathmann in the literature (Demircioğlu et al., 2000).

In a typical electrodialysis cell, a series of anion and cation-exchange membranes are arranged in an alternating pattern between an anode and a cathode to form individual cells. When DC power is applied between two electrodes, the cations move to the cathode and anions to the anode passing through negatively charged cation-exchange and positively charged anion-exchange membranes, respectively. Thus, ion concentrations increase in alternate compartments with a simultaneous decrease of ions in other compartments (Kabay et al., 2006).

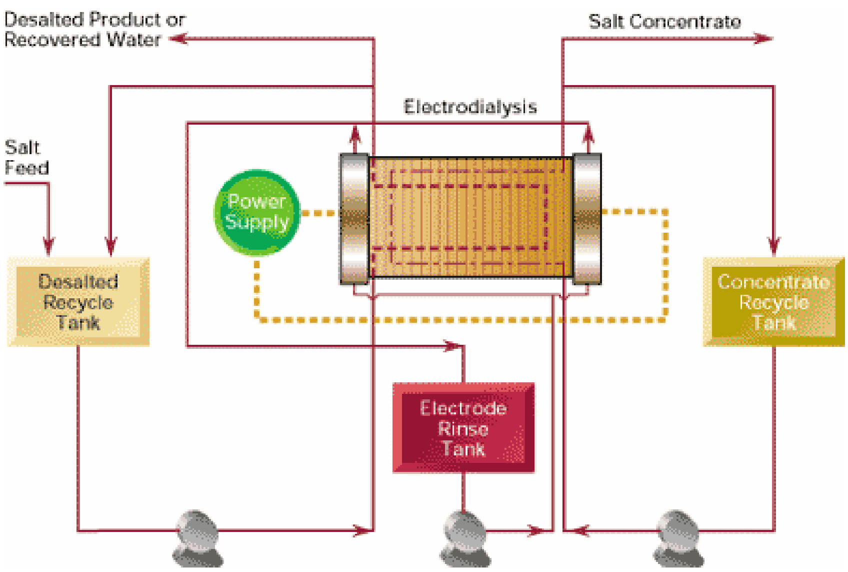

Figure 1.10. Batch-mode operation of electrodialysis system (Samatya, 2006)

As a result of the anion and cation migration, electric current flows between the cathode and anode. Only an equal number of anion and cation charge equivalents are transferred from the dilute stream (D) into the concentrate stream (C) and so the charge balance is maintained in each stream.

The E stream is the electrode stream that flows past each electrode in the stack. This stream may consist of the same composition as the feed stream (e.g., sodium chloride) or may be a separate solution containing a different species (e.g., sodium sulfate) (AWWA, 1995).

Depending on the stack configuration, anions and cations from the electrode stream may be transported into the C stream, or anions and cations from the D stream may be transported into the E stream. In each case, this transport is necessary to carry current across the stack and maintain electrically neutral stack solutions.

Using the right combination of anion exchange and cation exchange membranes we can separate the ions in the inlet solution and create a desalted flow.

This process has been widely applied to treat brackish water for potable use or to desalt and concentrate effluents for reuse (Demircioglu et al., 2002).

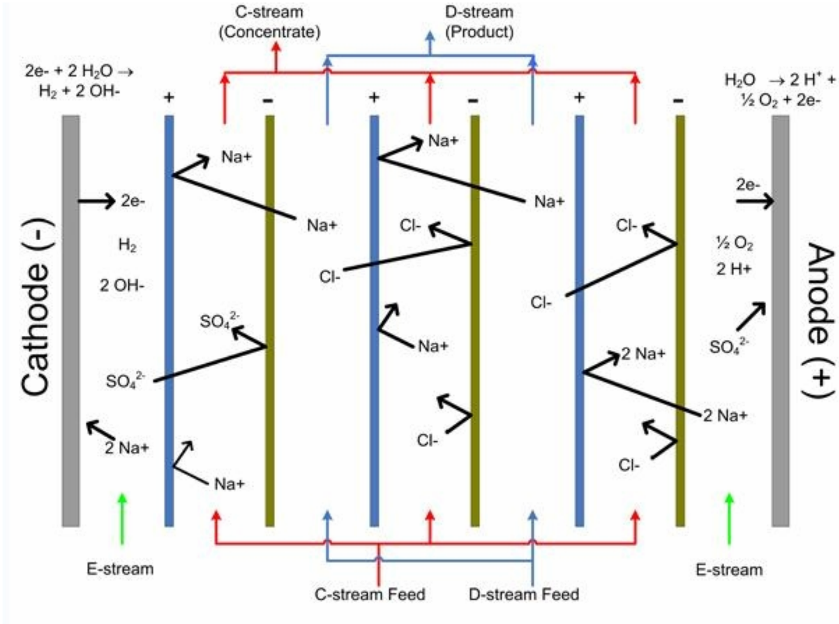

Figure 1.11. Principle of electrodialysis system (Courtesy EET Corporation, 2007)

1.7.2. Ion exchange membranes for electrodialysis

In electromembrane processes ion-permselective membranes are used in combination with electrical or chemical potential gradients for the selective transport of certain ionic components. The key elements in these processes are the ion exchange membranes. Their properties are determined by their chemical nature and the charge of the fixed ions and their density in the matrix polymer. There are three types of ion exchange membranes: cation-exchange membranes carrying negative charges, anion-exchange membranes carrying positive charges and bipolar membranes carrying positive and negative charges located on each side of the membrane.

The most desired properties of ion-exchange membranes are high permselectivity, low electrical resistance, good mechanical strength, and high chemical and thermal stability. Many of today's available membranes meet most of these requirements for applications in the chlorine-alkaline electrolysis and in electrodialysis. But for many other applications these membrane are unsatisfactory because of low selectivity, high electrical resistance and high costs (Rauthenbach et al., 1989).

1.7.2.1. Cation permeable membranes

Cation permeable membranes with high permeability and high selectivity are important for various electrochemical applications. For example, they may serve in electrodialysis modules as separators between concentrate and dilute compartments, in fuel cells, as proton conductors, and as a cation permeable layer of bipolar membranes selectively permeable for protons and water while retaining anions. The basic requirements are the same in different applications: selectivity, permeability, and stability must be sufficient (Wilhelm et al., 2001).

1.7.2.2. Anion permeable membranes

Anion exchange membranes have a similar structure with attached quarternary ammonium groups. Anion exchange membranes contain cationic groups fixed to the resin matrix. The fixed cations are in electrical equilibrium with mobil anions in the interstices of the resin. When such a membrane is immersed in an electrolyte solution, the anions in the solution can intrude into the resin matrix and replace the anions initially present, whereas the cations are prevented from entering the matrix by the repulsion of the cations fixed to the resin (Keithscott, 1995).

1.7.2.3. Bipolar membranes

Bipolar membranes are used in electrodialysis in combination with monopolar membranes to dissociate water into H^+ and OH^- ions and produce acids and bases from the corresponding salt solutions. The process has a multitude of interesting applications not only for the production of acids and bases but also for the regeneration of ion exchange resins and the pH control in chemical and biochemical reactions (Strathmann, 2004).

1.7.3. Main components of electrodialysis

1.7.3.1. <u>Electrodialysis stack</u>

The cell consists of two electrode-end blocks and the membranes stacked between them. The end blocks contain the in- and outlet adapters and the electrical connections. They are pressed together by a steel frame.

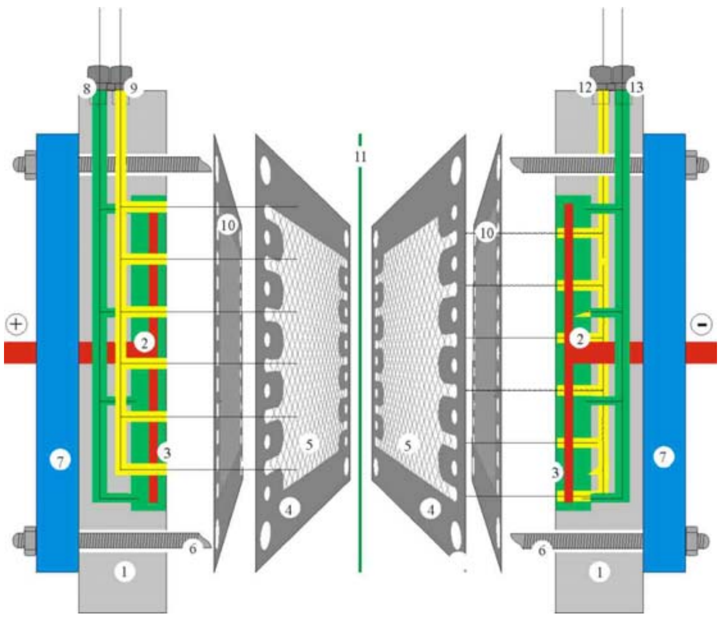

Figure 1.12. Electrodialysis stack (PCA company, 2007)

1: Polypropylene end plate
2: Electrode
3: Electrode chamber
4: spacer-sealing PVC
5: Spacer fabric
6: Screws
7: Steel frame
8: Inlet anode cell
9: Inlet concentrate cell
10: cation exchange membrane
11: AAM
12: Inlet diluate cell
13: Inlet cathode chamber

The membranes are separated by spacers consisting of a fabric in the active area filled with the electrolyte combined with a sealing around it. The spacer net prevents the membranes from touching each other. The stacked spacers form with their holes tubes, which are arranged in a way to build two different channel systems. By this way, the concentrate and dilute circuit is built.

Anode and cathode reactions

Reactions take place at each electrode.
At the cathode,

$$2e^- + 2\ H_2O \rightarrow H_{2\,(g)} + 2\ OH^- \tag{1.16}$$

while at the anode,

$$H_2O \rightarrow 2\ H^+ + \tfrac{1}{2}\ O_{2\,(g)} + 2e^- \quad \text{or} \tag{1.17}$$

$$2\ Cl^- \rightarrow Cl_{2\,(g)} + 2e^- \tag{1.18}$$

One important effect is the polarization of the ions on the membrane surface: Within the solution, all ions move in the extent of their concentration and mobility. On the membrane's surface, both mobility and concentration change dramatically. This means that there is a boundary layer of ions depletion or concentration.

An important point is ionic depletion, which has to be prevented because it leads to a high ohms resistance and to water splitting and it may burn the membranes (Mulder, 1996).

1.7.3.2. Hydraulic flow system

The primary considerations in designing the hydraulic flow system are to obtain low hydraulic pressure drops while simultaneously achieving the required high volume flow rates. The pressure drop in the electrodialysis system is on the order of 2 to 8 bars. Therefore, simple plastic centrifugal pumps are generally used for circulating the different solutions through the stack (Bungay et al., 1983).

1.7.3.3. The electric power supply

The energy requirements for electrodialysis are entirely electrical. These requirements may be categorized in two groups: AC power for pumping effluents to the membrane stack and DC power for the electrodialysis stack.

The DC power is usually supplied on-site by use of a rectifier, which converts alternating current to direct current. Constant voltage regulators are utilized to maintain stable plant operation. They are used to prevent stack damage. Stack resistance changes occur as a result of scale formation, membrane deterioration and changes in the fluid concentrations within the stack. The voltage regulator is adjusted periodically to compensate for these changes. Direct current is applied to the electrodes on the membrane stack, which energizes the ion in the feed stream causing them to migrate through the selective membranes as discussed previously (Bungay et al., 1983; Montgomery, 1983).

1.7.3.4. Process control devices

The following variables are usually measured or controlled, or both:

- DC voltage and current supplied to each electrodialysis unit
- Flow rates and pressures of the depleting and concentrating streams, and of the electrode rinse streams
- Electrolyte concentrations of the depleting and concentrating streams at the inlets and outlets to the electrodialysis stacks
- pH of the depleting stream and the electrode rinse streams
- Temperature in the feed stream (Samatya, 2006)

1.7.4. The limiting current density

The limiting current density is very difficult to estimate theoretically since the mass transfer coefficient in the laminar boundary layer at the membrane surface in the diluate solution is a function of the spacer geometry, membrane surface roughness, flow velocity, etc., and is difficult to calculate on a strictly theoretical data. Therefore, the experimentally derived relation given in Eq. (1.19) is generally used. The key parameters in this equation are the constants a and b. The experimentally derived data indicate that a and b may be considered as constant for a linear diluate flow rate between 2 and 6 cm/s.

$$i_{emp} = aC_s^d u^b \tag{1.19}$$

Here i_{emp} is the empirically determined limiting current density; a and b are constants which are determined by measuring the limiting current density at various linear flow velocities (Lee et al., 2001).

1.7.5. Effect of the spacer on current density and cell volume

The so-called shadow effect of the spacer on current density can be estimated by considering the spacer construction or determined experimentally by comparing the operation of a cell pair with and without a spacer. Generally the effect of the spacer on the current density can be estimated within an error range of about 5% (Lee et al., 2001).

1.7.6. Current utilization

The current utilization in ED is determined by three different terms, e.g.,: (1) the selectivity of the membranes, (2) the water transport through the membranes due to osmosis and electroosmosis and (3) current leakage through the manifold of the stack. For relatively low concentrations as treated in brackish water desalination, all three effects are rather low and the selectivity of the membrane is the most important parameter, which is obtained for a certain concentration range from the membrane manufactures (Lee et al., 2001).

1.7.7. Current efficiency

Current efficiency is a measure of how effective ions are transported across the ion exchange membranes for a given applied current. Typically current efficiencies >80% are desirable in commercial stacks to minimize energy operating costs. Low current efficiencies indicate water splitting in the diluate or concentrate streams, shunt currents between the electrodes, or back-diffusion of ions from the concentrate to the diluate could be occurring (Davis, 1990)

Current efficiency is calculated according to:

$$\xi = \frac{zFQ_f\,(C_{inlet}^{d} - C_{outlet}^{d})}{NI} \qquad (1.20)$$

where

ξ = current utilization efficiency

z = charge of the ion

F = Faraday constant, 96,485 Amp-s/mol

Q_f= diluate flow rate, L/s

$C_{inlet}{}^{d}$= diluate ED cell inlet concentration, mol/L

$C_{outlet}{}^{d}$= diluate ED cell outlet concentration, mol/L

N = number of cell pairs

I = current, Amps.

Current efficiency is generally a function of feed concentration.

1.7.8. Different types of electrodialysis processes

1.7.8.1. Batch mode electrodialysis

The simplest case, a batch desalination process, is carried out by circulating the solution through the stack until the conductivity of the tank solution has its target conductivity. As a result, the power consumption rises also within the process because the voltage drop over the cell increases. The production rate is, therefore, dependent on the concentration of dissolved minerals in the raw feed water and on the degree of demineralization desired (Heitmann, 1990).

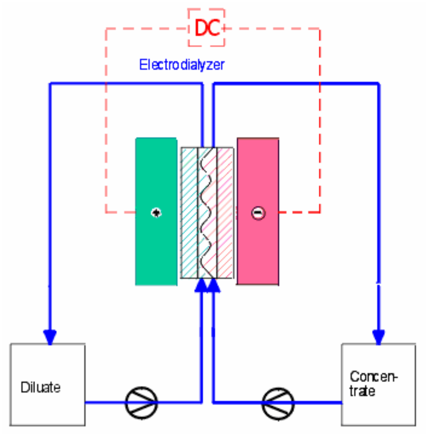

Figure 1.13. Batch mode ED system (PCA Company, 2007)

1.7.8.2. Continuous mode electrodialysis

It is also possible to run an ED process continuously. To decide whether a batch or a continuous process should be performed, the stack design has to be taken into account. To run in a continuous mode, the module has to treat the solution in one go. Because you need a certain time and a certain velocity of solution, this corresponds with a certain process length.

Advantages of this system are having minimal specific energy consumption and simple design with respect to piping and control (Rauthenbach et al., 1989).

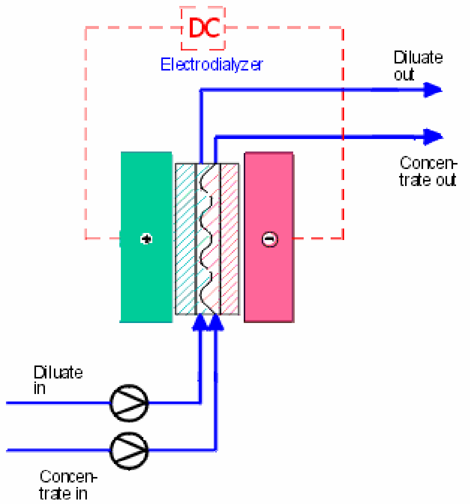

Figure 1.14. Continuous mode ED system (PCA Company, 2007)

1.7.8.3. <u>Feed and bleed mode electrodialysis</u>

The third commercially avaible system is undirectional continuous type electrodialysis. In this system, product water is recirculated to the holding tank through the demineralizing spacers of a single stack until the desired final purity is obtained (Rauthenbach et al., 1989).

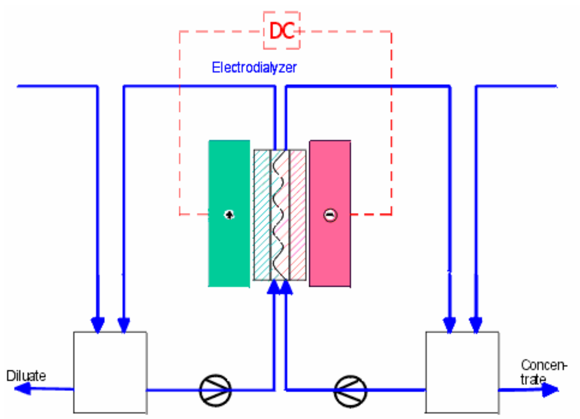

Figure 1.15. Feed and bleed mode ED system (PCA Company, 2007)

1.7.9. Advantages of electrodialysis

- Variability of ED system operation
- Easy operation of ED equipment
- Demineralization of biological solutions without affecting the quality and quality of proteins and hydrocarbons
- Energetically advantageous separation without phase changes and additional chemicals (www.mega.cz)

1.7.10. Limitations

Electrodialysis has inherent limitations, working best at removing low molecular weight ionic components from a feed stream. Non-charged, higher molecular weight and less mobile ionic species will not typically be significantly removed.

Also, in contrast to RO, electrodialysis becomes less economical when extremely low salt concentrations in the product are required and with sparingly conductive feeds: current density becomes limited and current utilization efficiency typically decreases as the feed salt concentration becomes lower, and with fewer ions in solution to carry current, both ion transport and energy efficiently greatly declines.

Consequently, comparatively large membrane areas are required to satisfy capacity requirements for low concentration (and sparingly conductive) feed solutions. Innovative systems overcoming the inherent limitations of electrodialysis (and RO) are available; these integrated systems work synergistically, with each sub-system operating in its optimal range, providing the least overall operating and capital costs for a particular application (www.en.wikipedia.org/wiki/electrodialysis).

1.7.11. Application areas of electrodialysis

- Pharmaceutical industry
  - Purification of fermented solution, serums and vaccines
- Chemical industry
  - Separation of inorganic and organic solutions
  - Purification of organic substances, e.g. amino acids
  - Waste water treatment, recycling of chemical substances
- Food industry
  - Demineralization of milk whey
  - Wine stabilization
  - Desalination of fruit juices
- Other uses
  - Desalination and conservation of sea and brackish water and industrial waters
  - Regeneration and recycling of galvanic baths (Strathman, 1992; Strathman, 2006; Sata, 2004).

1.8. Removal of Fluoride by Modified Zeolites Loaded with Metal Ions

1.8.1. Properties of zeolites

Zeolites are naturally occurring hydrated aluminosilicate minerals. They belong to the class of minerals known as “tectosilicates.” Most common natural zeolites are formed by alteration of glass-rich volcanic rocks (tuff) with fresh water in playa lakes or by seawater (Almaraz et al., 2003).

The structures of zeolites consist of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium, or calcium). These cations are exchangeable with certain cations in solutions such as lead, cadmium, zinc and manganese (Barer, 1987).

Clinoptilolite is the most abundant natural zeolite and has the chemical formula $Na_{0.1}K_{8.57}Ba_{0.04}(Al_{9.31}Si_{26.83}O_{72})x19.56\ H_2O$. Its characteristic tabular morphology shows an open reticular structure of easy access, formed by open channels of 8- to 10-membered rings. Considerable research has been conducted to characterize the chemical, surface, and ion-exchange properties of clinoptilolite. The ion-exchange capacity of natural zeolite (clinoptilolite) has been investigated by many authors. The clinoptilolite samples from different regions show different behavior in ion-exchange processes (Erdem et al., 2004).

1.8.2. Applications of zeolites

Zeolites are extremely useful as catalysts for several important reactions involving organic molecules. The most important are cracking, isomerisation and hydrocarbon synthesis (Wallce 1997; Jeanerette 1997).

Zeolites are used to adsorb a variety of materials. This includes application in drying, purification, and separation (Miller 1994).

Hydrated cations within the zeolite pores are bound loosely to zeolite framework, and can readily exchange with other cations when in aqueous media. The highly selective cation exchange capacity makes zeolites especially beneficial in controlling specific cationic levels in water systems, agriculture and many other areas (Chen 1989; Braun et. al. 1996).

2. EXPERIMENTAL

2.1. Materials

2.1.1. Water samples

- Drinking waters (Pinar, Ozsu, Bornova, Manisa, Balikliova. Salihli)
- Mineral waters (Kula, Ozgu, Salihli Eges, Schweppes, Akmina, Sarıkız)
- Balçova geothermal water

The geothermal water was obtained from Balçova Powerplant; İzmir. Composition of the geothermal water was shown in Table 2.1. All water samples were collected in clean fluoride-free plastic bottles.

Table 2.1. Characteristics of the geothermal water

Ion Species (Cations)	**Concentration (mg/L)**	**Ion Species (Anions)**	**Concentration (mg/L)**
*Na^+	353.50	■Cl^-	208.96
*K^+	26.55	■SO_4^{2-}	176.56
*Ca^{2+}	28.17	♦F^-	7.72
*Mg^{2+}	2.14	NO_3^-	•N.M
▲B (mg/L)		8.5-9.5	
TDS (mg/L)		1026	
Salinity		0.9	
pH= 8.42		EC=1651µS/cm	

*AAS ♦ ISE ■ IC ▲ Spectrophotometric •N.M: Not measured

2.1.2. Chemicals

All reagents were of analytical grade and high quality ultra pure water was used for preparing all solutions.

Model Balçova geothermal water solutions were prepared by dissolving NaF, NaCl, KCl, Na_2SO_4, Na_2CO_3, $NaHCO_3$, H_3BO_3 in deionized water.

Clinoptilolite type samples of zeolite (<45 µm) which were obtained from open pit mine in Manisa-Gördes in Western Anatolia were used. Chemical composition and physical properties of zeolite sample was given in Table 2.2.

Table 2.2. Chemical composition and physical properties of zeolite sample (Samatya, 2006)

Chemical composition	(%)	Physical properties	
SiO_2	70.90	Appearance porosity (%)	44.20
Al_2O_3	12.40	Appearance density (g/cm^3)	2.25
Fe_2O_3	1.21	Weight of per unit volume	1.32
CaO	2.54	Water adsorpsion (original), (%)	31.30
MgO	0.83	Water adsorpsion (grinding), (%)	105
Na_2O	0.52	Oil absorpsion (g oil/100 g sample)	66
K_2O	4.46	Whiteness (%)	68
SO_3	0.10	Original bleaching (g sample/g tonsil)	1.90
H_2O	6.88	Active bleaching (g sample/g tonsil)	1.70
Si/Al	4.66	pH 7.5	

Aluminum and zirconium solutions were prepared by using their nitrate salts; $Al(NO_3)_3.9H_2O$, $ZrO(NO_3)_2.xH_2O$. Fluoride solutions were prepared by NaF standard solutions (WTW 10.0g F^-/L) and TISAB (WTW Total Ionic Strength Adjustment Buffer) solution which contains glacial acetic acid, sodium chloride, CDTA (trans-1,2-cyclohexylendinitrilo tetraacetic acid) and NaOH (pH=5-5.5) was used as a buffer.

2.2. Equipments

2.2.1. Electrodialysis equipment

TS-1-10 batch-type electrodialysis unit (Tokuyama Co., Japan) was used for experimental studies (Figure 2.1).

Figure 2.1. Batch-mode electrodialysis unit

The ED stack contained 10 pairs of anion- and cation exchange Neosepta CMX (strongly acidic cation exchange) and AMX (strongly basic cation exchange) membranes, providing for each an effective membrane area of 1 dm^2.

The equipment has three pumps with a capacity of max 1.6 L/min and three solution tanks (each of them have 1 L capacity and holding dilute, concentrate and electrode rinse solutions). DC power at constant voltage (max 18 V) or current (max 3 A) is provided by a rectifier. Concentrate and dilute solution transfer lines have been provided with a couple of rotameters. The electrodes are platinum-plated titanium (anode) and stainless steel (cathode).

Characteristics of the Neosepta membranes used are given in Table 2.3.

Table 2.3. Properties of Neosepta membranes (Samatya, 2006)

Grade	AMX	CMX
Type	Strongly basic anion permeable	Strongly acidic cation permeable
Characteristic	High mechanical Strength (Cl form)	High mechanical Strength (Na form)
Electric resistance (Ω-cm^2)	2.0 ~3.5	1.8 ~3.8
Burst strength (kgf/cm^2)	≥0.30	≥0.40
Thickness (mm)	0.12 ~ 0.18	0.14~0.20
Application	Demineralization of whey Purification of organics Concentration of inorganics Demineralization of sucrose Desalination of ground water	Demineralization of whey Purification of organics Concentration of inorganics

2.2.2. Equipments for instrumental analyses

The analysis of fluoride, chloride, sulfate ions were performed by Shimadzu model ion chromatography equipment (model LC 10 Ai). Also, F-ISE (WTW F800 Fluoride Combination Electrode) was used for fluoride measurements.

WTW LF-330/SET conductometer was used for conductivity measurements and Metrohm 691 model pH meter was used for pH measurements.

Na^{+}, K^{+}, Mg^{2+}, Ca^{2+} ions concentrations have been determined by Varian 10 Plus Model Atomic Absorption Spectrophotometer.

2.3. Fluoride Analysis by Ion Selective Electrode

The fluoride concentration was measured using a Fluoride Combination Electrode (WTW F800) connected to the WTW inoLab pH/ION 735 electrometer.

Figure 2.2. WTW F800 Fluoride Combination Electrode

2.3.1. Direct measurement

In this method a series of fluoride standards are prepared in a background matrix of TISAB. The unknown sample is prepared using TISAB.

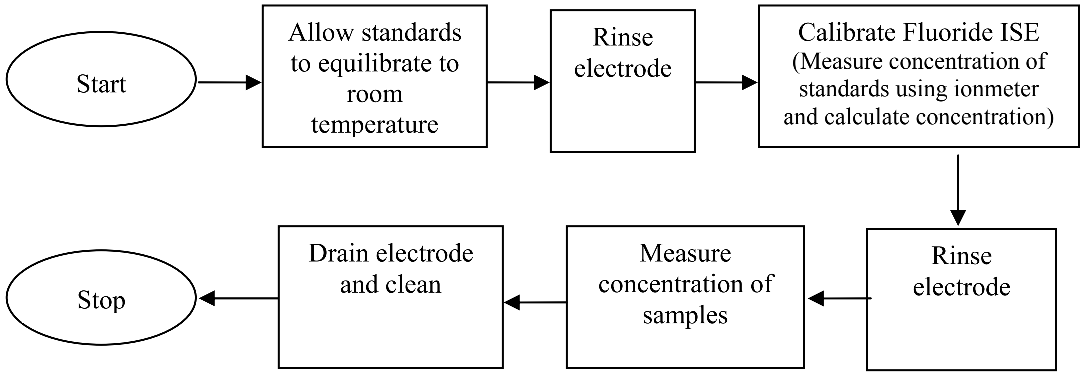

Figure 2.3. Procedure of direct measurement

Since E = K + S log C a plot of E vs. log C should yield a working curve that can be used to measure an unknown.

Figure 2.4 shows the calibration curve prepared from the measurement of the potential (mV) of 7 standard solutions (0.020, 0.050, 0.100, 0.200, 0.500, 1.000, 2.000 mg/L). Two replicates of each sample were analyzed (slope= -54.8 mV at 26^{o}C). A sample size of 100.0 mL was utilized, to which 1.0 ml of TISAB buffer was added.

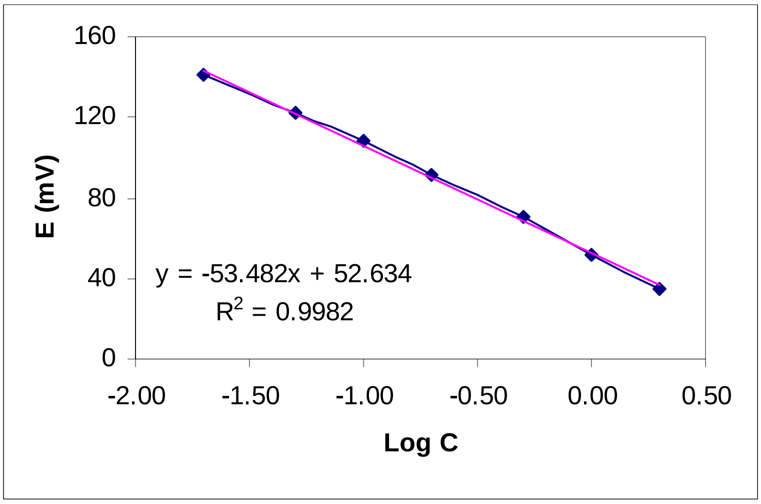

Figure 2.4. Calibration curve

2.3.2. Standard addition method

Standard addition must be used whenever the matrix of a sample changes the analytical sensitivity of the method. A constant volume of the standard solution (1mg F^-/L) is added to each of volumetric flasks of volume V_{flask}. Then each flask is made up to the mark with deionized water and mixed well. Prepared solutions are placed in a beaker and potential measured and concentration values calculated.

2.4. Fluoride Analysis by Ion Chromatography

The analyses of fluoride were carried out using a Shimadzu model ion chromatography equipment which consist of an LC 10Ai liquid delivery pump, a CDD 6A conductivity detector, a CTA 10A oven, and a CBM 10A system controller.

Figure 2.5. Shimadzu LC-10 A*i* model Ion Chromatography

In the studies, Shim-pack IC-A1 analytical column (4.6mm i. d. x 100mm stainless-stell column), packed with an anion-exchange resin on polymethacrylate support incorporating a quaternary ammonium base as a functional group, was used. A Shim-pack guard column (4.6 mm I.D x 10 mm) is attached to the main column.

The mobile phase is 2.5 mM Pthalic acid and 2.4 mM Tris (hydroxymethyl)-aminomethane at a 1.5 mL/min, which is degassed prior to use. The temperatures of column and detector are set at 40^oC.

The other column we used in our studies was MCI GEL column (4. 6 mm I.. D x 150 mm). MCI GEL columns are packed with MCI GEL packing materials (hydrophilic polymer) which are spherical packings with a narrow particle size distribution. This column provides excellent separation and short analysis time. Functional group of these columns is NR_3^+ and mobil phase is 3.0 mM Vanillic Acid, 2.8 mM N-Methyldiethanolamine (pH: 6.2) at a 1.2 mL/min.

The injection port of an ion chromatography commonly consists of an injection valve and the sample loop. The sample is typically dissolved in the mobile phase before injection into the sample loop. The sample is then drawn into a syringe and injected into the loop via the injection valve. A rotation of the valve rotor closes the valve and the loop in order to inject the sample into the stream of the mobile phase. Loop volume of 20 μL was used.

Filtration of the eluents before operation works to remove small particulates that may contaminate the pump check valves and cause erratic flow rates. Therefore, all natural samples must be prefiltered through 0.25 μm membrane filters before use.

The resolution of chloride and sulfate using isocratic conditions with 2.5 mM pthalic acid and 2.4 mM Tris (hydroxymethyl)-aminomethane as eluent.

The standards solutions were analyzed by ion chromatography, a calibration curve constructed and concentrations of unknown samples are calculated from the calibration curve obtained (Figures 2.6-8).

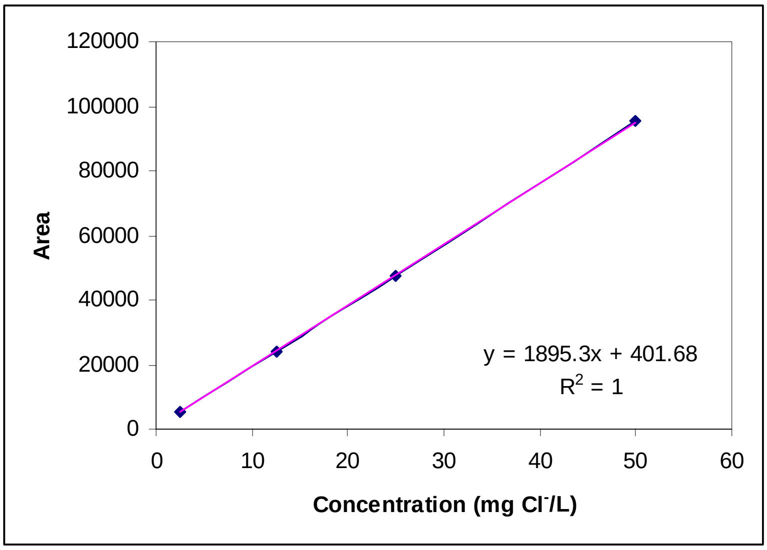

Figure 2.6. Calibration curve of chloride

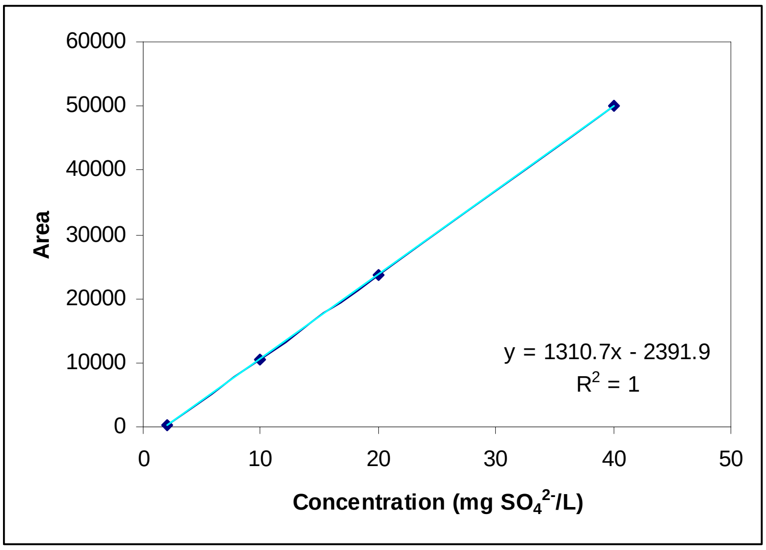

Figure 2.7. Calibration curve of sulfate

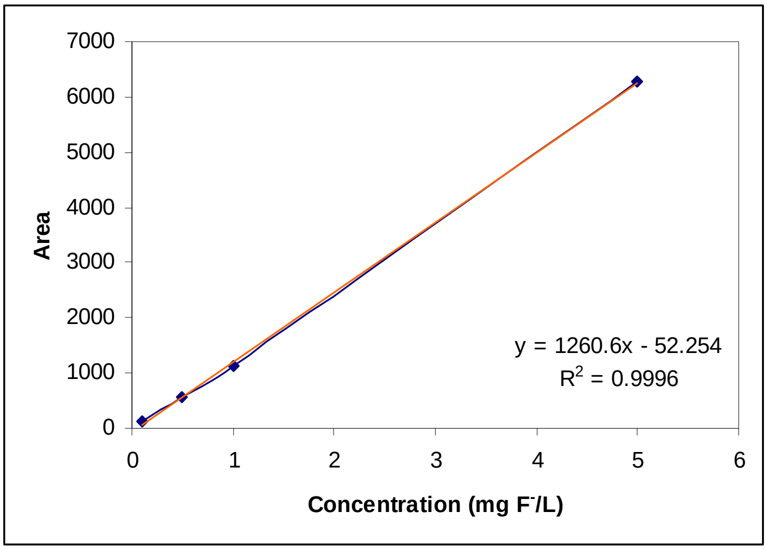

Figure 2.8. Calibration curve of fluoride

Figure 2.9 shows retention time of fluoride, chloride and sulfate for Balçova geothermal water. During the analysis MCI GEL column was used and the mobile phase was 2.5 mM Pthalic acid and 2.4 mM Tris (hydroxymethyl)- aminomethane at a 1.5 mL/min.

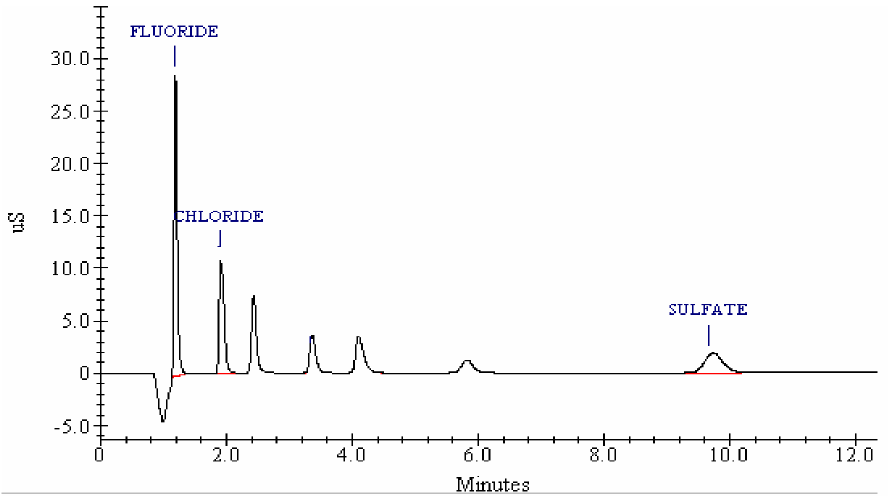

Figure 2.9. Peaks for fluoride, chloride and sulfate

The high sensitivity of the instrument makes it imperative to use only ultra pure water in all operations.

2.5. Separation of Fluoride by Metal Loaded Zeolite Adsorbents

2.5.1. Pretreatment of natural zeolite

2.5.1.1. Pretreatment with HNO_3, $NaNO_3$, NaOH solutions

15.0 g of natural zeolite sample was treated with 100.0 mL of 2 M HNO_3 solution. This mixture was continuously stirred at 40°C for 4 h. after this period, it was filtered, washed. Then, it was contacted with 100.0 mL 2 M $NaNO_3$ aqueous solution, pH was adjusted to 8-8.5 with 2 M NaOH, and then the sample was continuously stirred for 4 h. Later pH was adjusted to 6.5-7 with HNO_3 solution. It was filtered, washed and dried at 105°C for 24 h. Thus prepared sample was defined as ZEO-1 (Samatya, 2006).

2.5.1.2. Pretreatment with $NaNO_3$ solution

15.0 g of zeolite sample was treated with 100.0 mL 2 M $NaNO_3$ solution for 4 h with a continuous stirrer. The treated sample was filtered, washed and dried at 105°C for 24 h. It was as ZEO-2 (Samatya, 2006).

2.5.2. Preparation of metal loaded zeolite adsorbents

In the experiments, pretreated zeolite samples (ZEO-1, ZEO-2) were used. An amount of 12.0 g zeolite samples was conducted with 200.0 mL of 1000 mg-Al/L and 2000 mg-Zr/L solution at 30^{o}C for 24 h with a continuous shaking.

Table 2.4. Adsorption of metal ions on zeolite (Samatya, 2006)

Modified zeolite	**mg metal/g-zeolite**
Zr-ZEO-1	21.25
Zr-ZEO-2	19.38
Al-ZEO-1	2.44
Al-ZEO-2	1.65

2.5.3. Batch mode sorption tests

Batch experiments were performed twice and fluoride concentration in each sample was analyzed by ion selective electrode. The results were given as average of obtained values from two tests.

2.5.4. Effect of zeolite amount

Various amounts of Zr-ZEO-1, Zr-ZEO-2, Al-ZEO-1 and Al-ZEO-2 type metal loaded zeolite (0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.80, 1.00, 1.20, 1.40, 1.60 g) was contacted with 25.0 mL of Balçova geothermal water at 30^{o}C for 24 h with continuous shaking in shaker. Effect of zeolite amount on fluoride removal from Balçova geothermal water was investigated. Experiments were done twice and samples were analyzed using ISE method.

2.5.5. Kinetic tests

Kinetic tests were carried out in a 500.0 mL of three neckled glass flask placed in a water bath at 25^{o}C. 500 mL of Balçova geothermal water containing 7.72 mg F^-

/L was put into the flask. The experiments were performed by using 24.0 g of Zr-ZEO-2 immersed into the solution. The system was stirred by a mechanical stirrer at 250 RPM. The fluoride concentration was monitored after 0, 3, 5, 10, 15, 20, 30, 45, 60, 90, 120, 150, 180, 240, 300, 360, 420, 480, 540 and 1440 min periods by taking 3.5 mL of supernatant from the solution.

2.6. Separation of Fluoride by Electrodialysis

2.6.1. Limiting current measurements

Before performance tests, limiting current measurements were carried out for each solution. Desalting electrodialysis unit was employed for the measurements of limiting current (LC). The applied currents were changed keeping the solution concentration constant. The feed and permeate solutions pumped from the same reservoir were circulated through the feed and permeate compartments, respectively, and then recycled to the reservoir. By doing this way, the solution concentration in the feed could be maintained constant at a desired level during the experiments. If the applied current changes, obtained potential values will change linearly until limiting current density point. After this point, there is a sharp change in slope. This switching point is determined as limiting current point.

2.6.2. Separation tests by electrodialysis

The ED operation to remove fluoride was carried out with fluoride-rich Balçova geothermal water containing 1026 mg/L of TDS and 7.72 mg/L of fluoride. The main characteristics of this water were given in Table 2.1.

Because of higher concentration of bivalent salts in the geothermal water, the risk of precipitation of these salts, especially sulfate and carbonate in the concentrate compartment by exceeding solubility, becomes very important. In this case the performances of the ED operation fall down by decreasing the recovery rate of water and the overall rejection of ions and the membranes can be damaged by scaling and fouling.

During our tests, the ED operation was carried out according to three methods:

l) With a model solution
2) Without pretreatment of Balçova geothermal water
3) With a chemical pretreatment of Balçova geothermal water

2.6.2.1. <u>Removal of fluoride from model solution by electrodialysis</u>

Tests with model solution containing boron

Electrodialysis process was conducted with a model solution which doesn't contain Ca^{2+} and Mg^{2+} ions. Main components of the model solution were shown in Table 2.5.

Table 2.5. Main characteristics of the model solution

Ion Species (Cations)	Concentration (mg/L)	Ion Species (Anions)	Concentration (mg/L)
*Na^+	353.40	■Cl^-	209.00
*K^+	26.52	■SO_4^{2-}	174.01
NO_3^-	•N.M	♦F^-	7.72
▲B (mg/L)		9.20	
TDS (mg/L)		827	
Salinity		0.7	
pH= 8.48		EC=1698µS/cm	

*AAS ♦ ISE ■ IC ▲ Spectrophotometric •N.M: Not measured

Separation tests were carried out applying 8.67 V as voltage (LC) and 1.6 L/min as flow rate at room temperature. Water samples were taken from exit of the membrane stack in the time interval of 2 minutes. About 10 mL of samples were taken from the drain of concentrate and dilute reservoirs into the plastic tubes and fluoride analysis of each sample was performed using ISE and IC method.

Tests with model solution in the absence of boron

To investigate the effect of boron on fluoride removal, electrodialysis process was carried out with a model solution in the absence of boron. Main components of the model solution were shown in Table 2.6.

Table 2.6. Characteristic of the model solution

Ion Species (Cations)	Concentration (mg/L)	Ion Species (Anions)	Concentration (mg/L)
*Na^+	353.50	■Cl^-	208.90
*K^+	26.53	■SO_4^{2-}	174.30
NO_3^-	•N.M.	♦F^-	7.72
TDS (mg/L)		824	
Salinity		0.7	
pH= 8.45		EC=1698µS/cm	

*AAS ♦ ISE ■ IC ▲Spectrophotometric •N.M: Not measured

The ED operation was carried out with the model solution at 12.15 V as voltage (LC) and with a flow rate of 1.6 L/min. About 10 mL water sample was taken from exit of the membrane stack in the time interval of 2 minutes, pH and conductivity measurements were performed. In each run, process was carried out until the current drops to 0.01 A and fluoride concentration of all samples was determined by ISE method and IC.

2.6.2.2. Fluoride removal from geothermal water by electrodialysis without a chemical pretreatment

To minimize the precipitation risk, before electrodialysis operation pH of the Balçova geothermal water was adjusted to 7.0-7.5 by addition of 12 M HCl.

The main characteristics of Balçova geothermal water were given in Table 2.1. Table 2.7 shows the characteristics of this water after adjusting of pH.

Table 2.7. Characteristics of the Balçova geothermal water after HCl addition

Ion Species (Cations)	Concentration (mg/L)	Ion Species (Anions)	Concentration (mg/L)
$*Na^+$	353.00	▪Cl^-	211.50
$*K^+$	26.50	▪SO_4^{2-}	176.50
$*Ca^{2+}$	28.10	♦F^-	7.72
$*Mg^{2+}$	2.13	NO_3^-	•N.M
▲B (mg/L)		9.20	
TDS (mg/L)		1026	
Salinity		0.9	
pH= 7.01		EC=2140μS/cm	

*AAS ♦ ISE ▪ IC ▲Spectrophotometric •N.M: Not measured

For each run of experiment, concentrate, dilute and electrode rinse reservoirs were filled with 1 L feed solution. Separation tests were carried out applying 10.02 V as voltage (LC) and 1.6 L/min as flow rate at room temperature. Water samples were taken from exit of the membrane stack in the time interval of 2 minutes. About 10 mL of samples were taken from the drain of concentrate and dilute reservoirs into the plastic tubes. The pHs and conductivities of the samples were measured by pH meter and conductometer, respectively.

In each run, process was carried out until the current drops to 0.01 A. In all experiments, the rectifier was stopped immediately afterwards the current becomes 0.01 A in order to prevent the electrolysis of water. Fluoride concentration of all samples was determined by ISE method and IC.

2.6.2.3. <u>Removal of fluoride from geothermal water by ED after a chemical pretreatment</u>

Before ED operation, a chemical pretreatment of Balçova geothermal water was carried out to precipitate the calcium ions. This was achieved by the successive addition of a predetermined amount of Na_2CO_3 (1.06 g) and NaOH (3.0 mL, 5 M). After one day of waiting for settling, the water was filtered and the pH was adjusted to 7.0-7.5 by addition 12 M HCI (4.0 mL).

The ED operation was carried out with the pretreated water at 10.63 V as voltage (LC) and with a flow rate of 1.6 L/min. About 10 mL of water samples was taken from exit of the membrane stack in the time interval of 2 minutes, pH and conductivity measurements were performed. In each run, process was carried out until the current drops to 0.01 A. The concentration of fluoride for all samples was determined by ISE method and IC.

Table 2.8 shows the main characteristics of pretreated Balçova geothermal water.

Table 2.8. Main characteristics of pretreated Balçova geothermal water

Ion Species (Cations)	Concentration (mg/L)	Ion Species (Anions)	Concentration (mg/L)
*Na^+	259.01	▪Cl^-	307.95
*K^+	26.44	▪SO_4^{2-}	157.01
*Ca^{2+}	5.42	♦F^-	7.72
*Mg^{2+}	1.85	NO_3^-	•N.M
▲B (mg/L)		8.40	
TDS (mg/L)		956	
Salinity		0.9	
pH= 7.09		EC=2010µS/cm	

*AAS ♦ ISE ▪ IC ▲Spectrophotometric •N.M: Not measured

3. RESULTS AND DISCUSSION

3.1. Water Analyses

Determination of fluoride concentration in water samples were performed by ion chromatography and ion selective electrode methods. The obtained data were given in Table 3.1. As we could see in Table 3.1, both methods gave the similar data. Fluoride concentration in Balçova geothermal water was found to be the highest.

Table 3.1. Fluoride concentration of water samples

Water type	Concentration (mg F^-/L)	
	ISE	IC
Pinar	0.286±0.001	0.280 ±0.002
Ozsu	0.090 ±0.002	0.094 ±0.001
Balikliova (Tap water)	0.993 ±0.008	0.996 ±0.001
Manisa (Tap water)	0.339 ±0.002	0.321 ±0.001
Bornova (Tap water)	0.128 ±0.003	0.130 ±0.012
Balçova (Geothermal water)	7.723 ±0.044	7.72 ±0.009
Kula (mineral water)	0.354 ±0.004	*N.M
Akmina (mineral water)	0.530 ±0.040	N.M
Ozgu (mineral water)	2.546 ±0.062	N.M
Salihli Eges (mineral water)	0.190 ±0.001	N.M
Schweppes (mineral water)	0.513 ±0.003	N.M

*N.M: Not measured

3.2. Removal of Fluoride from Balçova Geothermal Water by Metal Loaded Zeolite

3.2.1. Batch mode sorption tests

3.2.1.1. Effect of the metal loaded zeolite amount on fluoride removal from Balçova geothermal water

In order to find the optimum amount of modified zeolite on fluoride removal from geothermal water, various amounts of modified zeolites (Zr-ZEO-1, Zr-ZEO-2, Al-ZEO-1, Al-ZEO-2) were contacted with 25.0 mL Balçova geothermal water at 30°C for 24 h with a continuous shaking. The results were shown in Figures 3.1-4.

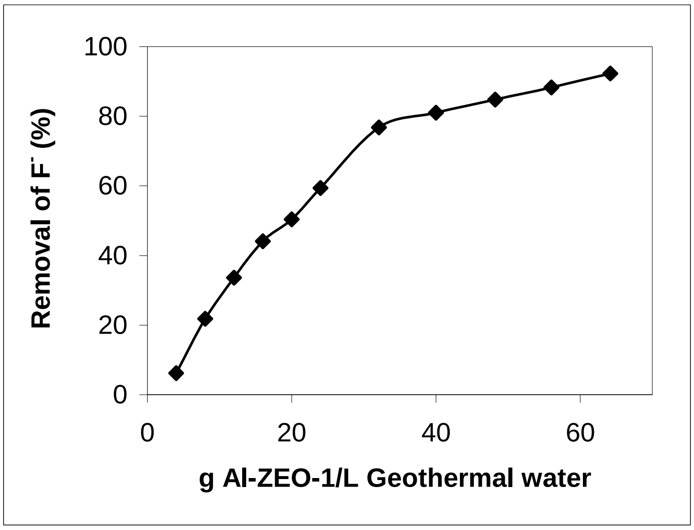

Figure 3.1. Effect of metal loaded zeolite amount on fluoride removal from geothermal water by Al-ZEO-1

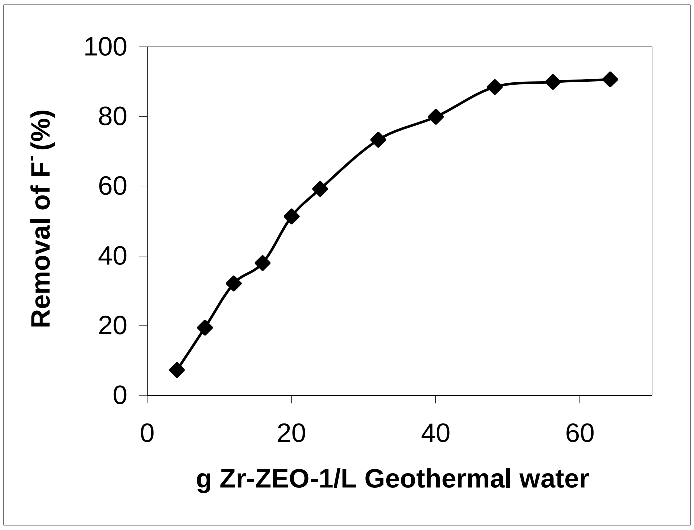

Figure 3.2. Effect of metal loaded zeolite amount on fluoride removal from geothermal water by Zr-ZEO-1

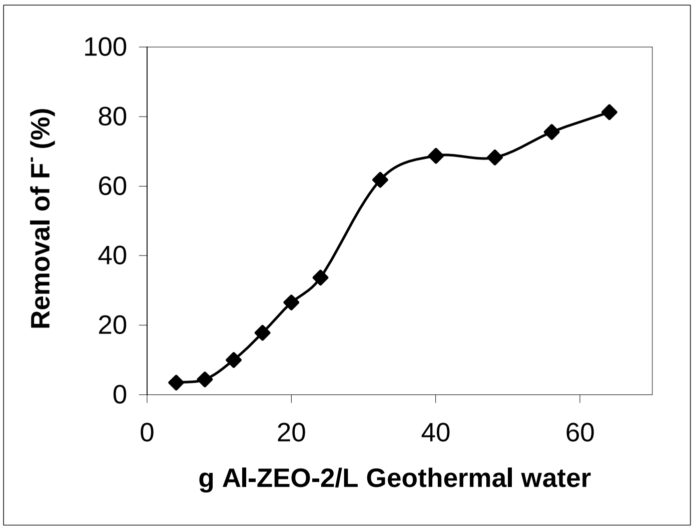

Figure 3.3. Effect of metal loaded zeolite amount on fluoride removal from geothermal water by Al-ZEO-2

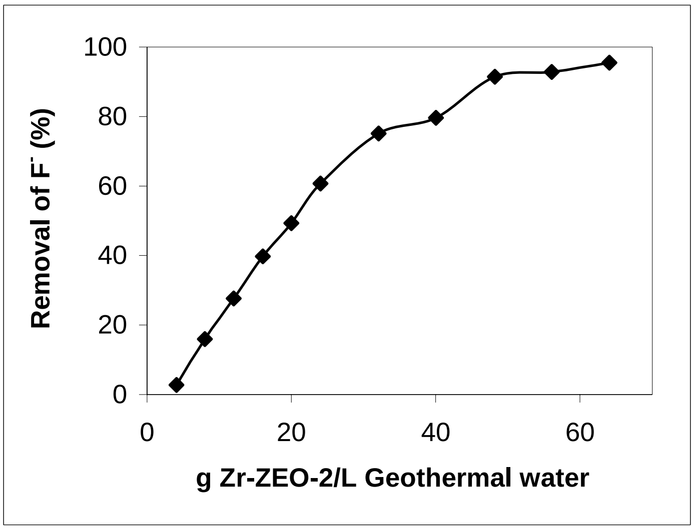

Figure 3.4. Effect of metal loaded zeolite amount on fluoride removal from geothermal water by Zr-ZEO-2

Optimum zeolite amounts and fluoride removal efficiencies were shown in Table 3.2.

Table 3.2. Optimum adsorbent amount and fluoride removal capacity of each zeolite adsorbent

Zeolite type	Removal of F^- (%)	Optimum zeolite concentration (g/L)
Zr-ZEO-1	88.5	48.200
Zr-ZEO-2	91.5	48.200
Al-ZEO-1	84.8	48.200
Al-ZEO-2	81.3	64.080

As shown in Table 3.2 and Figures 3.1-4, fluoride removal increased with an increase in metal loaded zeolite amount and leveled off at a zeolite amount of 48.20 g/L-geothermal water with more than 90% of fluoride removal for Zr-ZEO-2 type zeolite adsorbent.

3.2.2. Kinetic tests

Kinetic tests were performed using 24.0 g of Zr-ZEO-2. Fluoride concentration in Balçova geothermal water was monitored for 0, 3, 5, 10, 15, 20, 30, 45, 60, 90, 120, 150, 180, 240, 300, 360, 420, 480, 540 and 1440 minutes periods.

Figure 3.5 illustrates the relative concentration decrease of fluoride versus time. The removal of fluoride increased with time and reached the equilibrium in 120 min with a 87.7 % of fluoride removal.

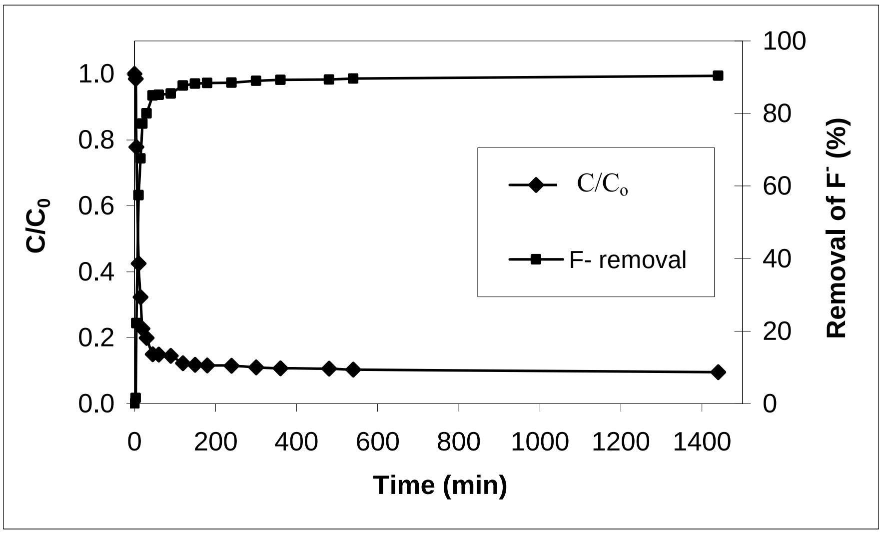

Figure 3.5. Kinetic performance of Zr-ZEO-2 for fluoride removal

3.3. Removal of Fluoride from Balçova Geothermal Water by Electrodialysis

The fluoride separation tests were carried out with Balçova geothermal solutions containing 7.72 mg F^{-}/ L and applying 1.6 L/min as flow rate at room temperature. Limiting current measurement was carried out before the performance test.

The flow rate is kept constant (1.6 L/min) during the test. The concentrated (C) and dilute (D) streams were monitored for concentration of anions (fluoride, chloride and sulfate), current and conductivity values by time. The measured data were converted to their dimensionless forms by dividing them by their initial values. Their graphical presentations are given in Figures 3.6-41.

3.3.1. Removal of fluoride from model solution by electrodialysis

3.3.1.1. Tests with model solution containing boron

The characteristics of model solution before and after 30 minutes of electrodialysis operation were given in Table 3.3

Table 3.3. Characteristics of the model solution before and after electrodialysis

		Concentration (mg/L) Before ED	Concentration (mg/L) After ED
Ion Species	Na^+	353.40	8.80
	K^+	26.52	0.34
	Cl^-	209.00	0.50
	SO_4^{2-}	174.01	21.10
	F^-	7.72	0.07
	NO_3^-	*N.M.	*N.M.
	B	9.20	8.40
TDS (mg/L)		827	25
Salinity		0.7	0.0
pH		8.48	6.03
EC (µS/cm)		1698	40

*N.M: Not measured

Changes in fluoride concentration, current, conductivity and pH during electrodialysis experiment by time were shown in Figures 3.6-7. Fluoride concentrations were determined by ion chromatography method.

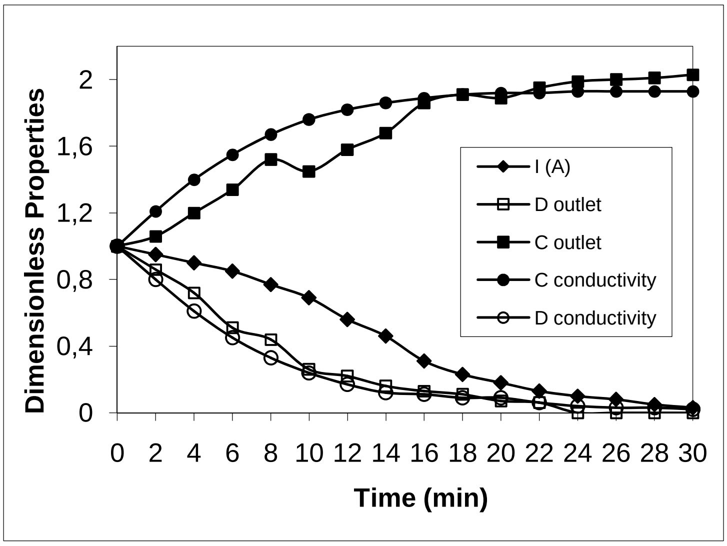

Figure 3.6. Dimensionless properties vs. time graph for model solution containing boron (IC method) C: Concentrate, D: Dilute compartments

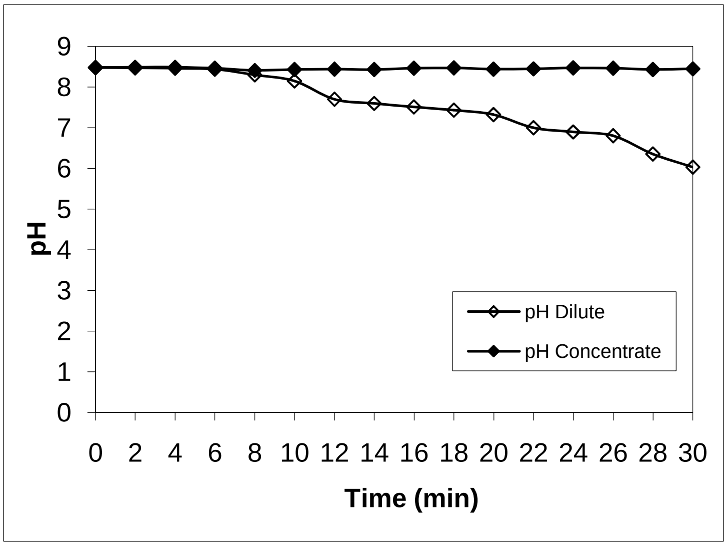

Figure 3.7. pH changes during electrodialysis test

Variations of chloride and sulfate ions by time during electrodialysis experiment were monitored. Figures 3.8-10 shows the obtained data. After the fourth minute of the experiment, removal rate of sulfate ions decreased. Because, as mentioned in our previous studies (İpek, 2005), removal of monovalent ions was faster than divalent ions.

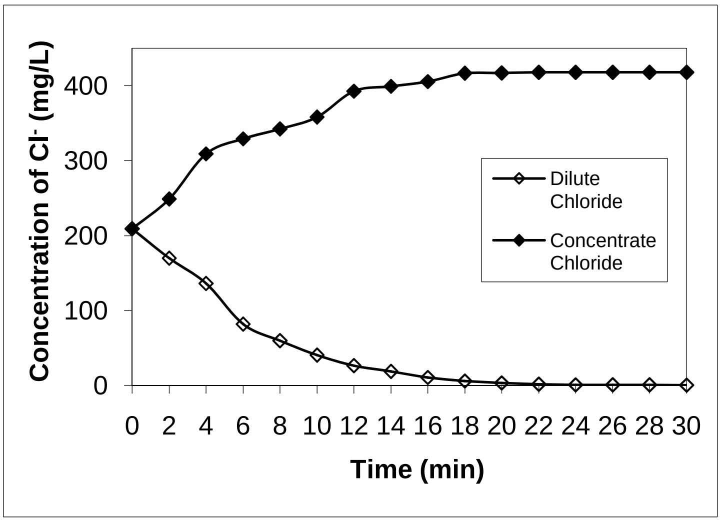

Figure 3.8. Variations of chloride contents vs time

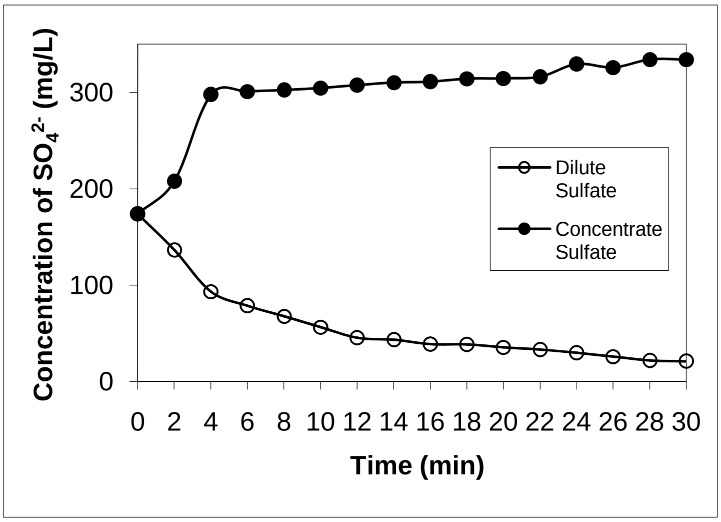

Figure 3.9. Variations of sulfate contents vs time

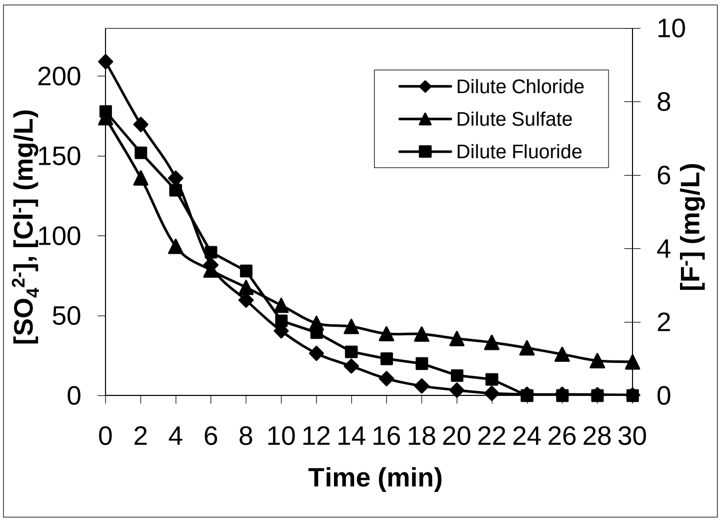

Figure 3.10. Variations of anion contents vs time

Figure 3.11 shows the changes in fluoride concentration, current, conductivity and pH during electrodialysis experiment by time. Fluoride concentrations were determined by ion selective electrode method this time.

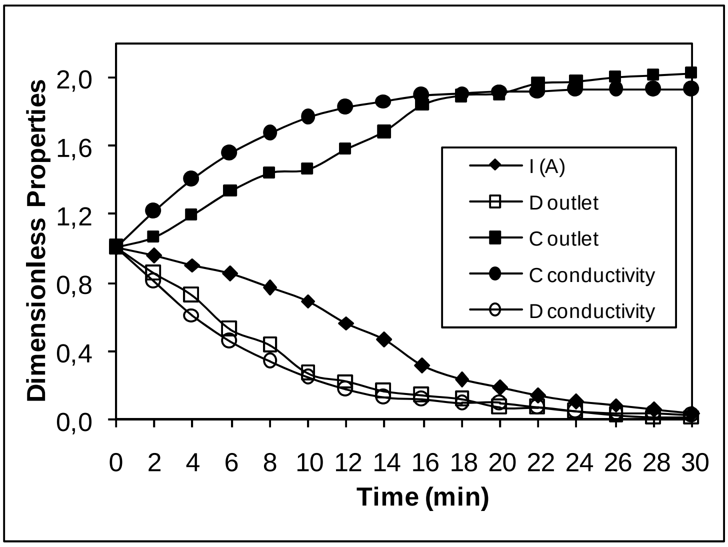

Figure 3.11. Dimensionless properties vs. time graph for model solution containing boron (ISE method) C: Concentrate, D: Dilute compartments

Figure 3.12 shows the change in concentration of fluoride, chloride and sulfate ions vs time in dilute compartment. Fluoride and chloride ions were removed from Balçova geothermal water effectively by electrodialysis. Concentration of fluoride, chloride and sulfate ions decreased to 0.07, 0.50 and 21.10 mg/L in 30 minutes respectively.

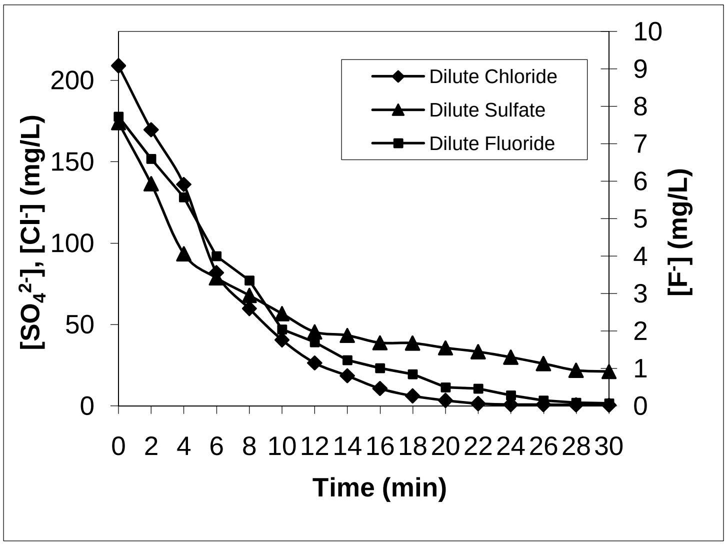

Figure 3.12. Variations of anion contents vs time

Figure 3.13 shows the percentage of removal for fluoride, chloride and sulfate ions during electrodialysis experiment. At the end of the experiment, approximately 99 % of removals for fluoride and chloride, 88 % of removal for sulfate were obtained.

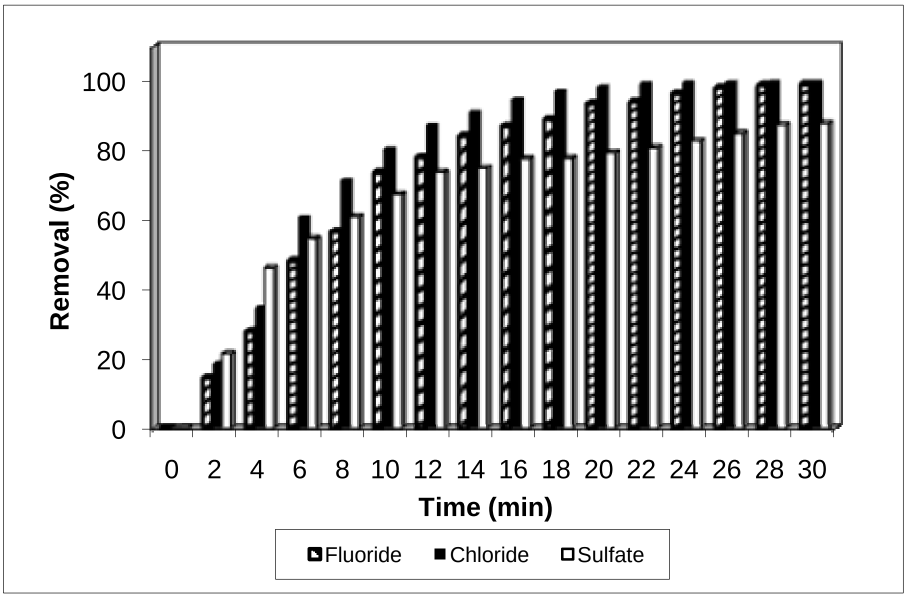

Figure 3.13. Removal of anions F^-, Cl^-, SO_4^{2-} from model solution (containing boron)

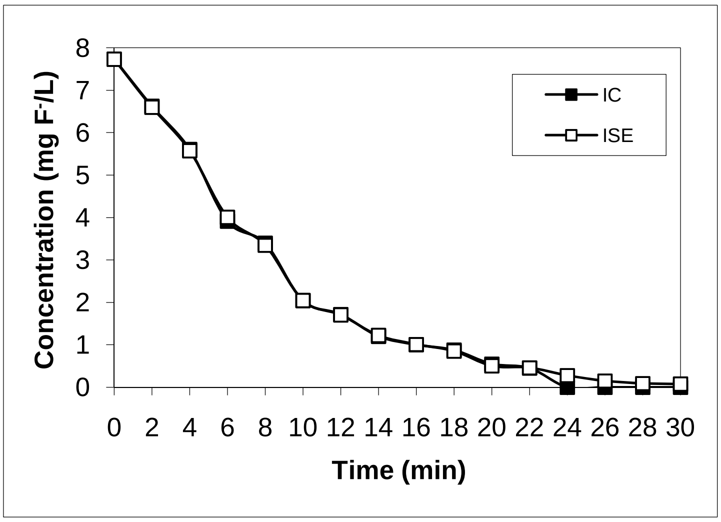

Figure 3.14. Comparison of ion chromatography and ion selective electrode methods for fluoride analysis

As a result, fluoride ions could be removed easily from model solution containing boron by electrodialysis process. The results of fluoride concentrations obtained by two different methods (ISE and IC) agreed to each other very well as shown in Figure 3.14.

3.3.1.2. Tests with model solution in the absence of boron

The characteristics of model solution before and after 24 minutes of electrodialysis operation were given in Table 3.4.

Table 3.4. Characteristics of the model solution before and after ED

		Concentration (mg/L) Before ED	**Concentration (mg/L) After ED**
Ion Species	Na^+	353.50	8.83
	K^+	26.53	0.31
	Cl^-	208.90	0.52
	SO_4^{2-}	174.30	21.33
	F^-	7.72	0.10
	NO_3^-	*N.M.	*N.M.
TDS (mg/L)		824	34
Salinity		0.7	0.0
pH		8.45	6.03
EC (µS/cm)		1698	48

*N.M.: Not measured

Changes in fluoride concentration, current, conductivity and pH during electrodialysis experiment by time were shown in Figures 3.15-16. Fluoride concentrations were determined by ion chromatography method.

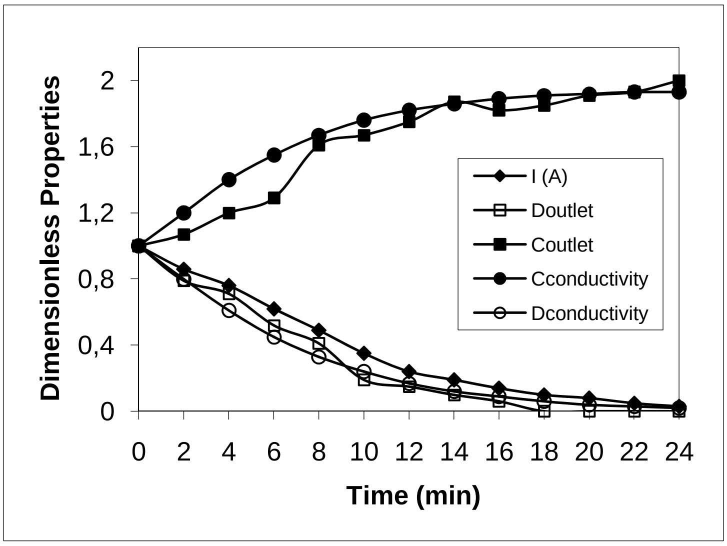

Figure 3.15. Dimensionless properties vs. time graph for model solution (IC method)
C: Concentrate, D: Dilute compartments

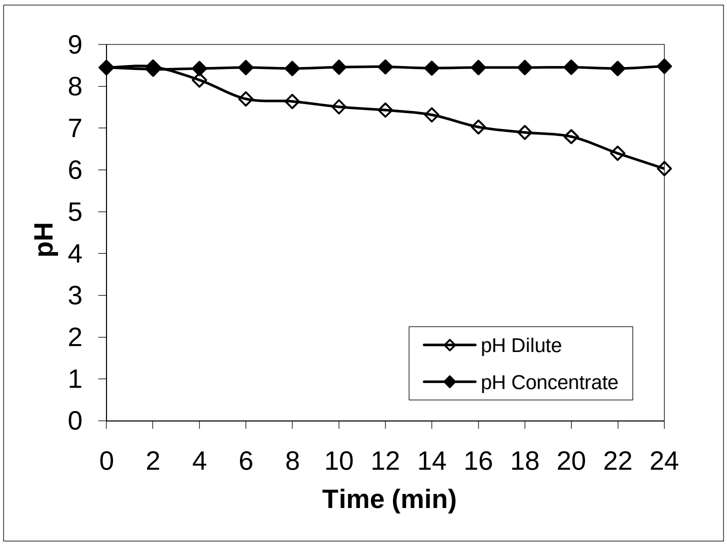

Figure 3.16. pH changes during electrodialysis test

Variations of chloride and sulfate ions by time during electrodialysis experiment were monitored. Figures 3.17-19 shows the obtained data.

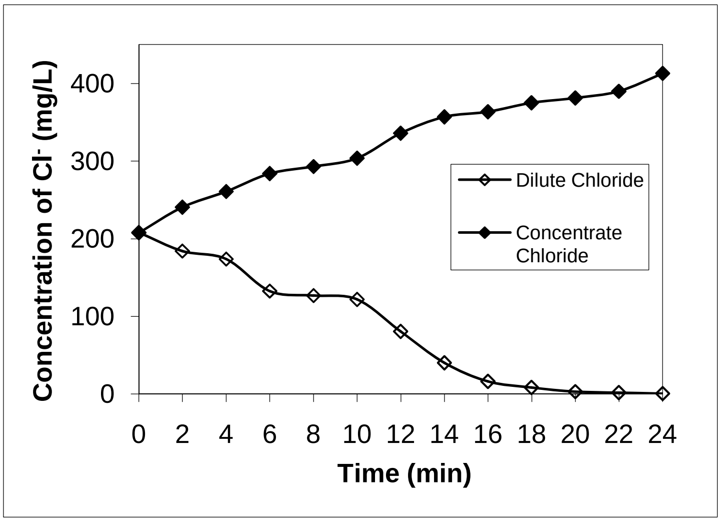

Figure 3.17. Variations of chloride contents vs time

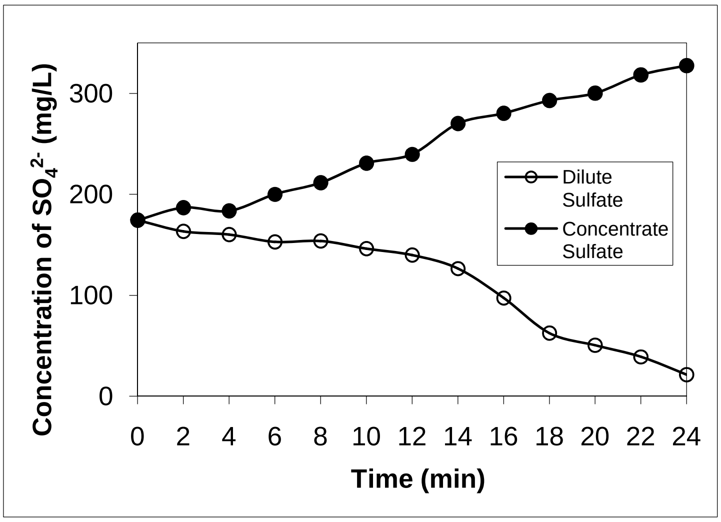

Figure 3.18. Variations of sulfate contents vs time

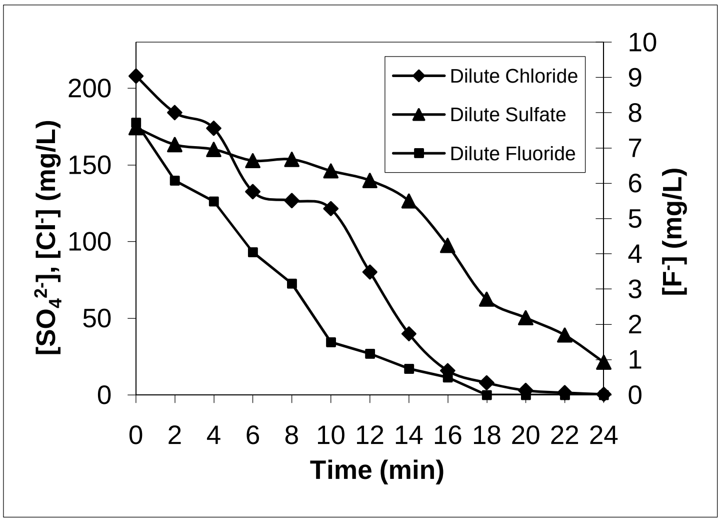

Figure 3.19. Variations of anion contents vs time

Figure 3.20 shows the changes in fluoride concentration, current, conductivity and pH during electrodialysis experiment by time. Fluoride concentrations were determined by ion selective electrode method.

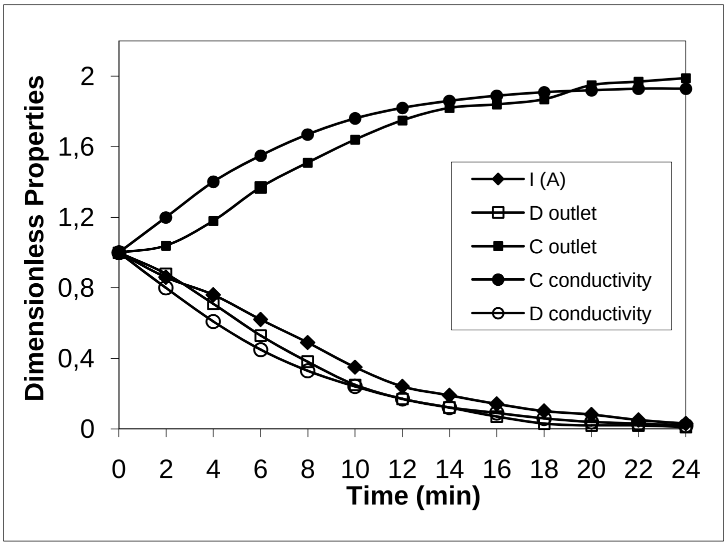

Figure 3.20. Dimensionless properties vs. time graph for model solution (ISE method)
C: Concentrate, D: Dilute compartments

Figure 3.21 shows the variations of fluoride, chloride and sulfate ion contents vs time during electrodialysis experiment.

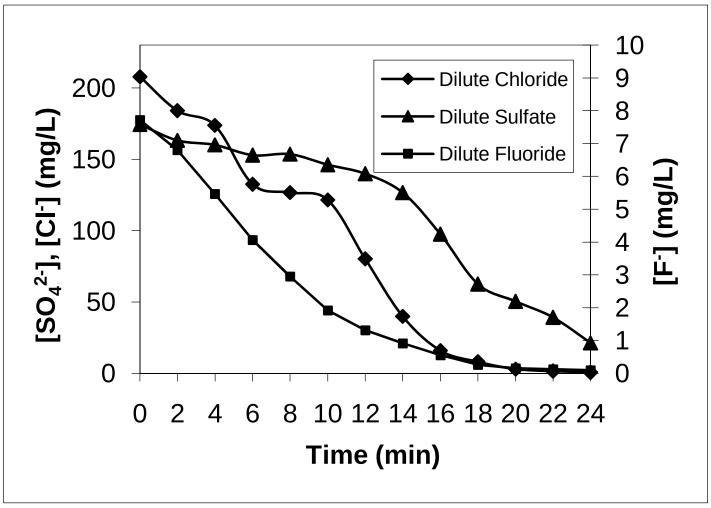

Figure 3.21. Variations of anion contents vs time

Figure 3.22 shows the percentage of removal for fluoride, chloride and sulfate ions during electrodialysis experiment. At the end of the experiment, 98.70 % of removal for fluoride, 99.75 % of removal for chloride and 87.77 % of removal for sulfate were obtained.

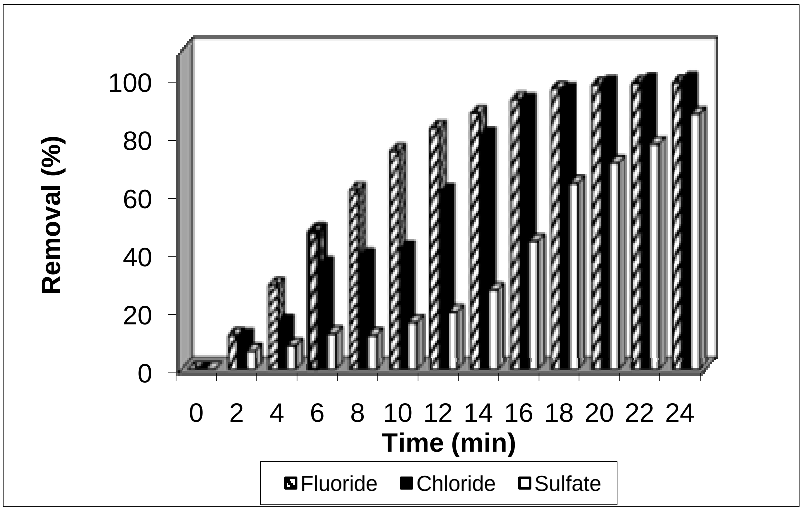

Figure 3.22. Removal of anions F^-, Cl^-, SO_4^{2-} from model solution (absence of boron)

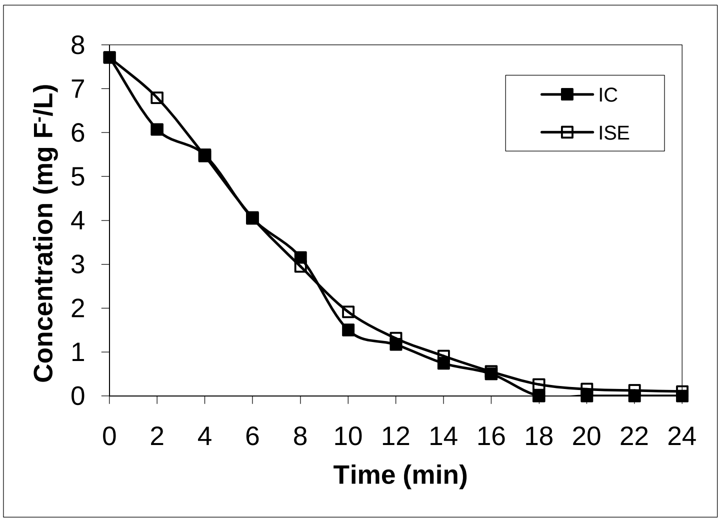

Figure 3.23. Comparison of ion chromatography and ion selective methods

Fluoride ions were removed effectively from model solution by electrodialysis. The results obtained with two techniques (ISE and IC) almost agreed to each other although the data obtained between 10-16 min were different to some extent (Figure 3.23).

3.3.2. Fluoride removal from geothermal water by electrodialysis without a chemical pretreatment

To minimize the precipitation risk, before electrodialysis operation pH of the Balçova geothermal water was adjusted to 7.0-7.5 by addition of 12 M HCl. The characteristics of geothermal water before and after 29 minutes of electrodialysis operation were given in Table 3.5.

Table 3.5. Characteristics of the Balçova geothermal water* before and after ED

		Concentration (mg/L) Before ED	Concentration (mg/L) After ED
Ion Species	Na^+	353.00	15.10
	K^+	26.50	0.70
	Ca^{2+}	28.10	0.21
	Mg^{2+}	2.13	0.10
	Cl^-	211.50	0.50
	SO_4^{2-}	176.55	17.04
	F^-	7.72	0.06
	NO_3^-	N.M	N.M.
	B	9.20	8.30
TDS (mg/L)		1026	33
Salinity		0.9	0.0
pH		7.01	6.05
EC (µS/cm)		2140	73

* pH was adjusted to 7.0 by addition of HCl before ED.

Changes in fluoride concentration, current, conductivity and pH during electrodialysis experiment by time were shown in Figures 3.24-25. Fluoride concentrations were determined by ion chromatography method.

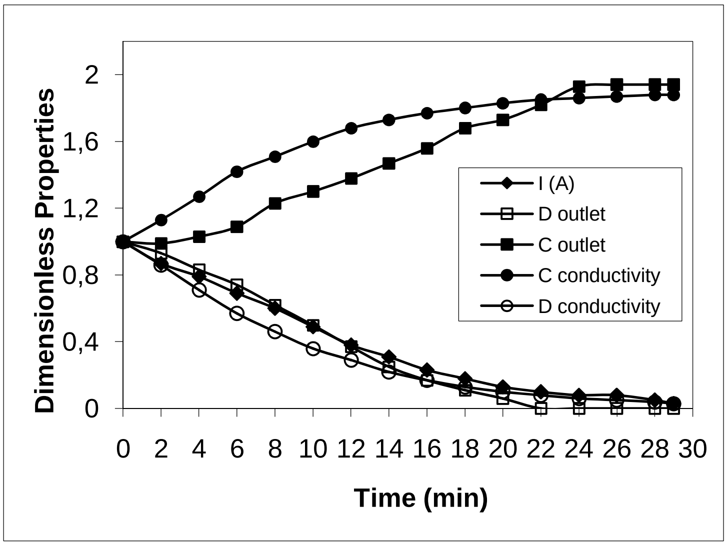

Figure 3.24. Dimensionless properties vs. time graph for Balçova geothermal water (pH was adjusted to 7.0 before ED) (IC method) C: Concentrate, D: Dilute compartments

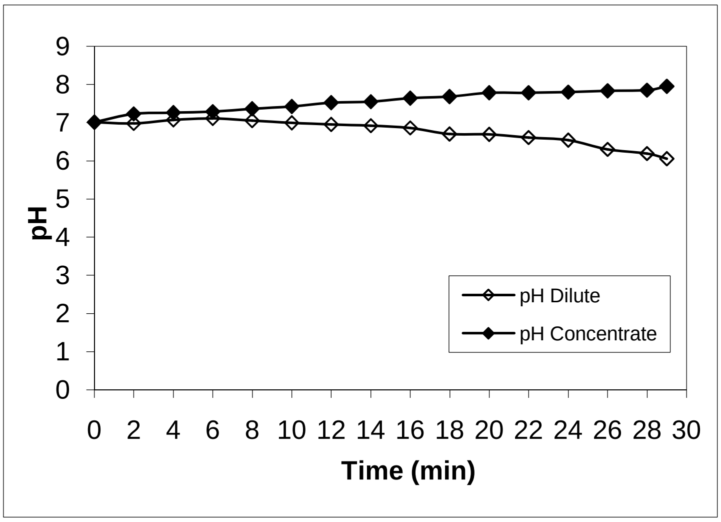

Figure 3.25. pH changes during electrodialysis test

Variations of chloride and sulfate ions by time during electrodialysis experiment were monitored. Figures 3.26-28 show the obtained data.

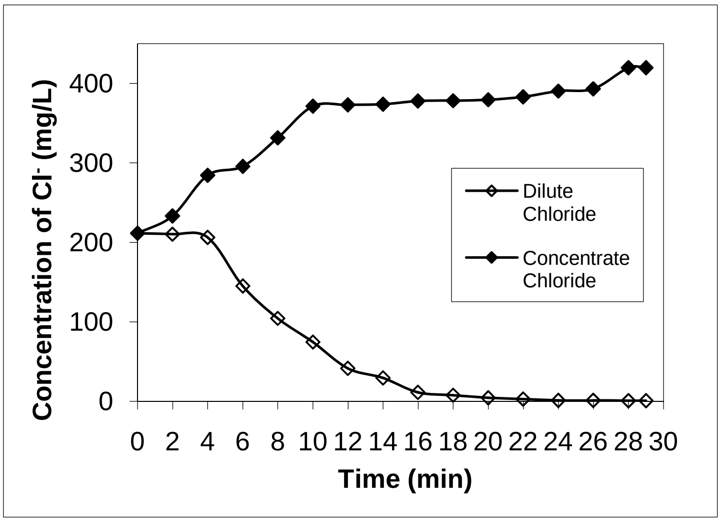

Figure 3.26. Variations of chloride contents vs time

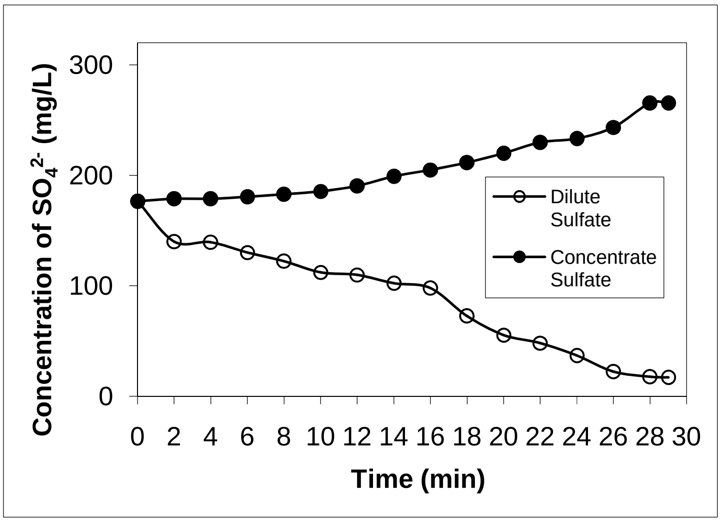

Figure 3.27. Variations of sulfate contents vs time

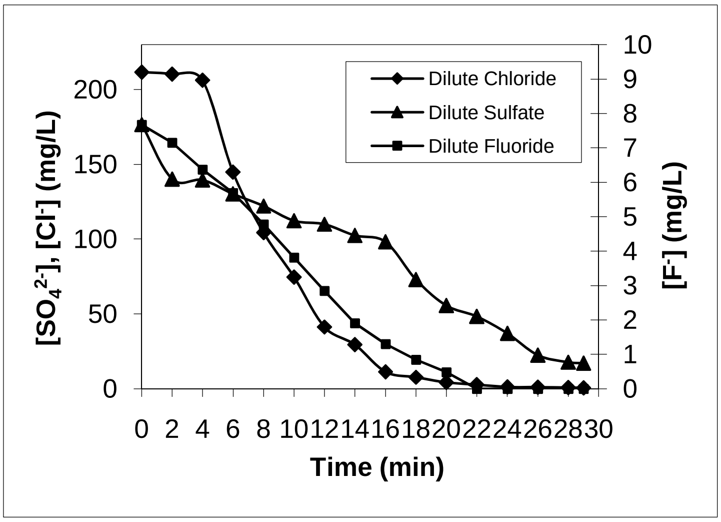

Figure 3.28. Variations of anion contents vs time

Figure 3.29 shows the changes in fluoride concentration, current, conductivity and pH during electrodialysis experiment by time. Fluoride concentrations were determined by ion selective electrode method.

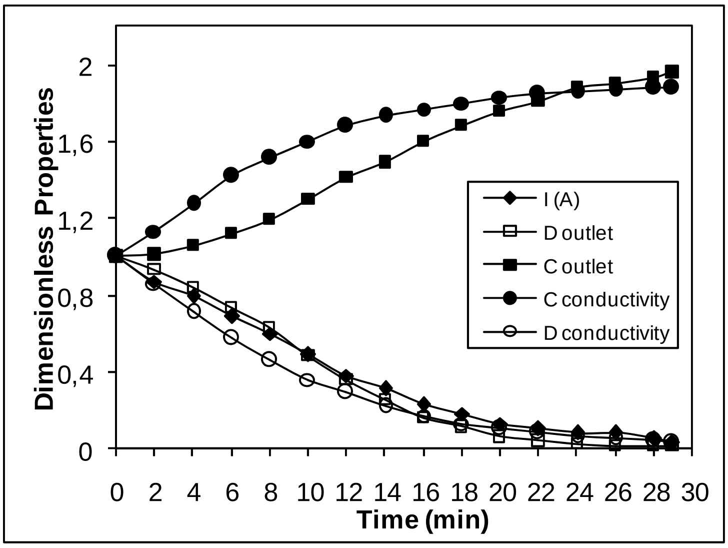

Figure 3.29. Dimensionless properties vs. time graph for Balçova geothermal water (pH was adjusted by HCl) (ISE method) C: Concentrate, D: Dilute compartments

Figure 3.30 shows the variations of fluoride, chloride and sulfate ion contents vs time during electrodialysis experiment.

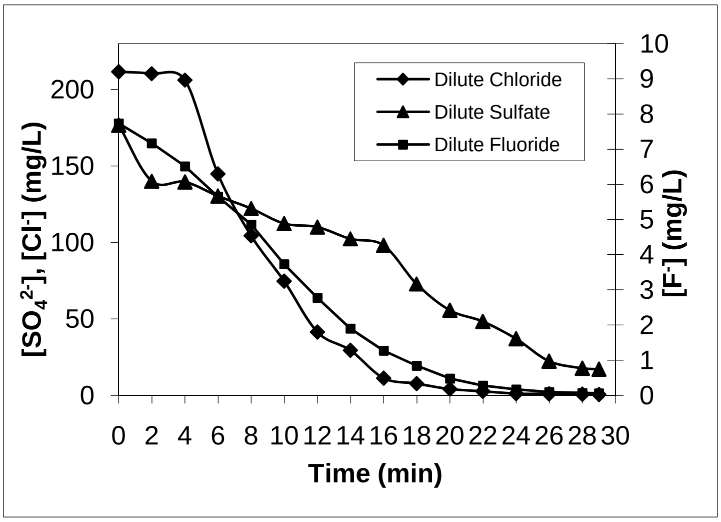

Figure 3.30. Variations of anion contents vs time

Figure 3.31 shows the percentage of removal for fluoride, chloride and sulfate ions during electrodialysis experiment. At the end of the experiment, 99.22 % of removal for fluoride, 99.76 % of removal for chloride and 90.35 % of removal for sulfate were obtained.

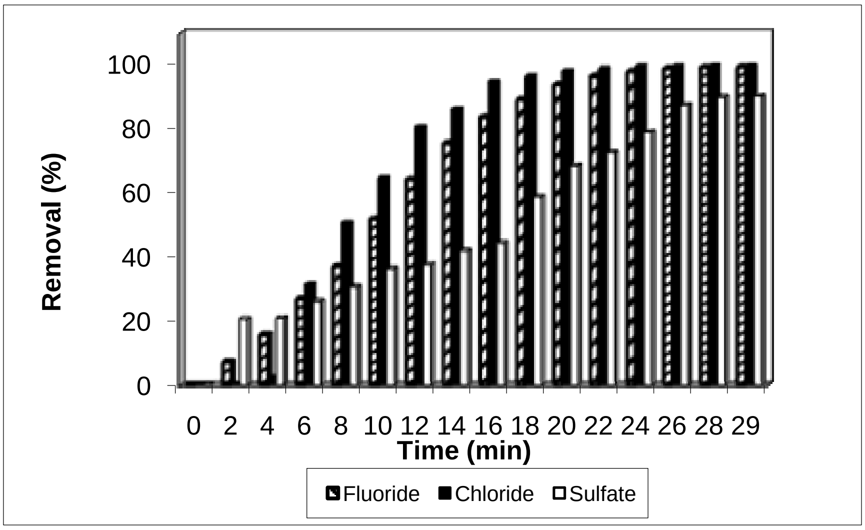

Figure 3.31. Removal of anions F^-, Cl^-, SO_4^{2-} from Balçova geothermal water (pH was adjusted by HCl)

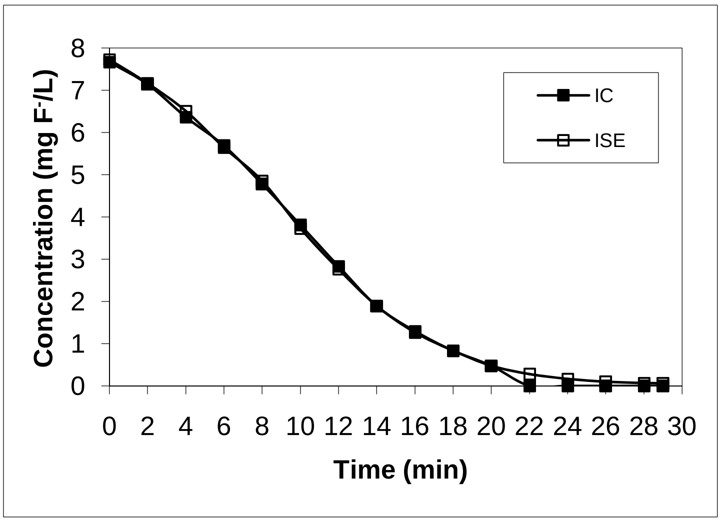

Figure 3.32. Comparison of ion chromatography and ion selective methods

As a result, fluoride ions could be removed easily from Balçova geothermal water by electrodialysis. The results of fluoride analysis with two methods agreed well with each other as shown in Figure 3.32.

3.3.3. Removal of fluoride from geothermal water by electrodialysis after a chemical pretreatment

Before ED operation, a chemical pretreatment of Balçova geothermal water was carried out to precipitate the calcium ions in geothermal water. The characteristics of model solution before and after 24 minutes of electrodialysis operation were given in Table 3.6.

Table 3.6. Characteristics of the pretreated Balçova geothermal water before and after ED

		Concentration (mg/L) Before ED	Concentration (mg/L) After ED
Ion Species	Na^+	259.01	10.06
	K^+	26.44	0.54
	Ca^{2+}	5.42	0.03
	Mg^{2+}	1.85	0.01
	Cl^-	307.95	0.98
	SO_4^{2-}	157.01	18.68
	F^-	7.72	0.07
	NO_3^-	N.M	N.M.
	B	8.40	7.60
TDS (mg/L)		956	32
Salinity		0.9	0.0
pH		7.09	6.15
EC (µS/cm)		2010	66

Changes in fluoride concentration, current, conductivity and pH during electrodialysis experiment by time were shown in Figures 3.33-34. Fluoride concentrations were determined by ion chromatography method.

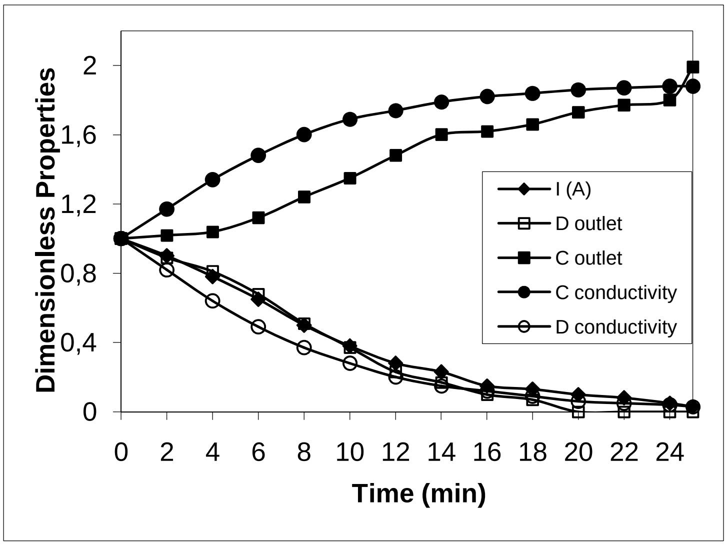

Figure 3.33. Dimensionless properties vs. time graph for Balçova geothermal water after pretreatment (IC method) C: Concentrate, D: Dilute compartments

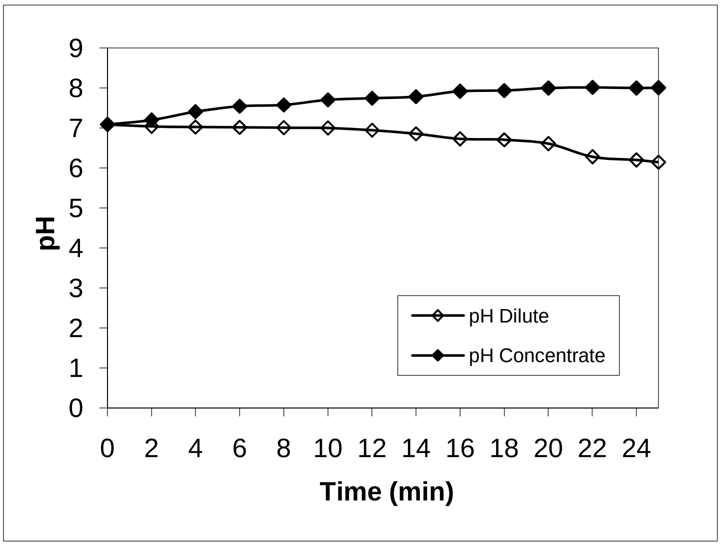

Figure 3.34. pH changes during electrodialysis test

Variations of chloride and sulfate ions by time during electrodialysis experiment were monitored. Figures 3.35-37 shows the obtained data. After eight minutes, removal rate of sulfate ions decreased. Because removal of fluoride and chloride ions were faster than sulfate ions.

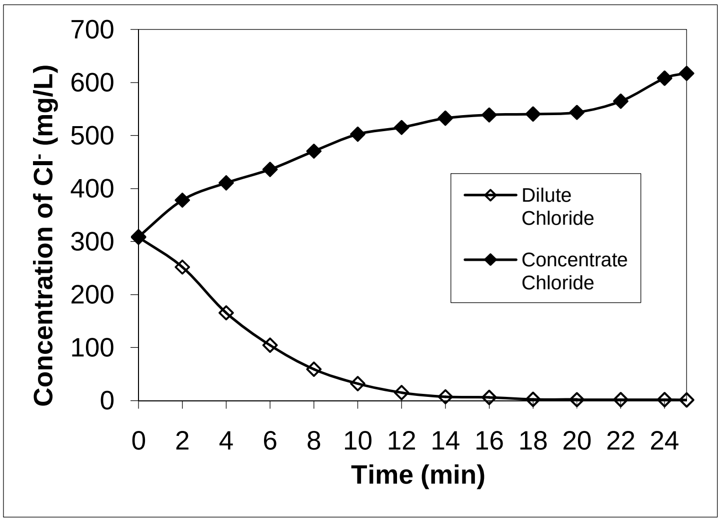

Figure 3.35. Variations of chloride contents vs time

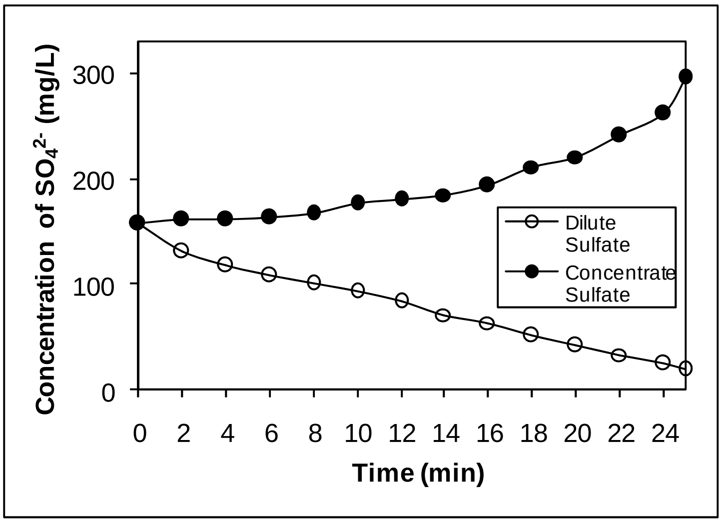

Figure 3.36. Variations of sulfate contents vs time

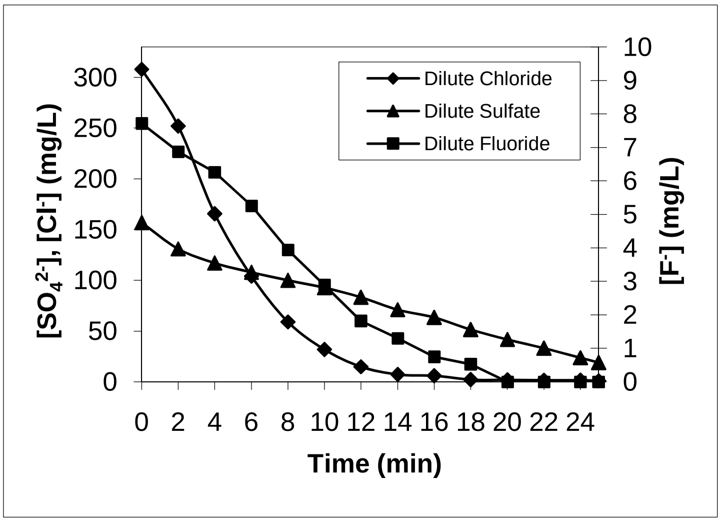

Figure 3.37. Variations of anion contents vs time

Figure 3.38 shows the changes in fluoride concentration, current, conductivity and pH during electrodialysis experiment by time. Fluoride concentrations were determined by ion selective electrode method.

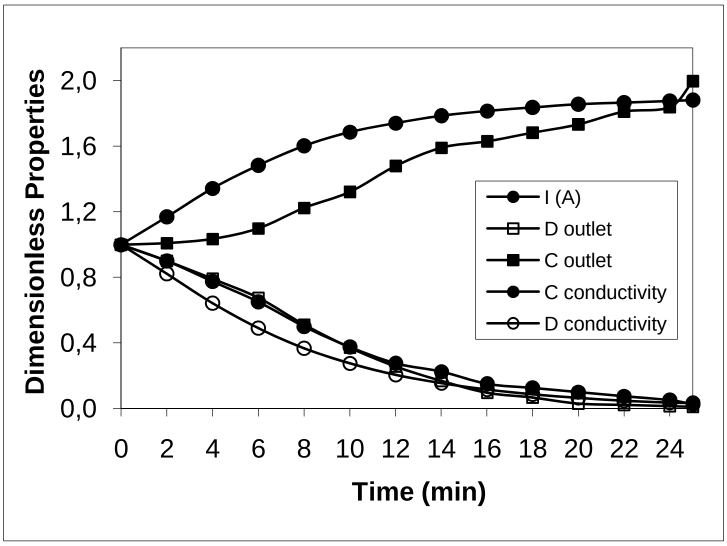

Figure 3.38. Dimensionless properties vs. time graph for Balçova geothermal water after pretreatment (ISE method) C: Concentrate, D: Dilute compartments

Figure 3.39 shows the variations of fluoride, chloride and sulfate ion contents vs time during electrodialysis experiment.

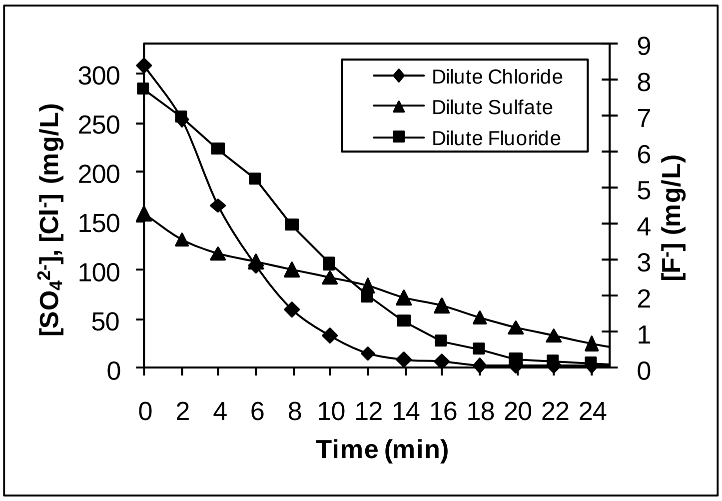

Figure 3.39. Variations of anion contents vs time

Figure 3.40 shows the percentage of removal for fluoride, chloride and sulfate ions during electrodialysis experiment. At the end of the experiment, 99.09 % of removal for fluoride, 99.68 % of removal for chloride and 88.07 % of removal for sulfate were obtained.

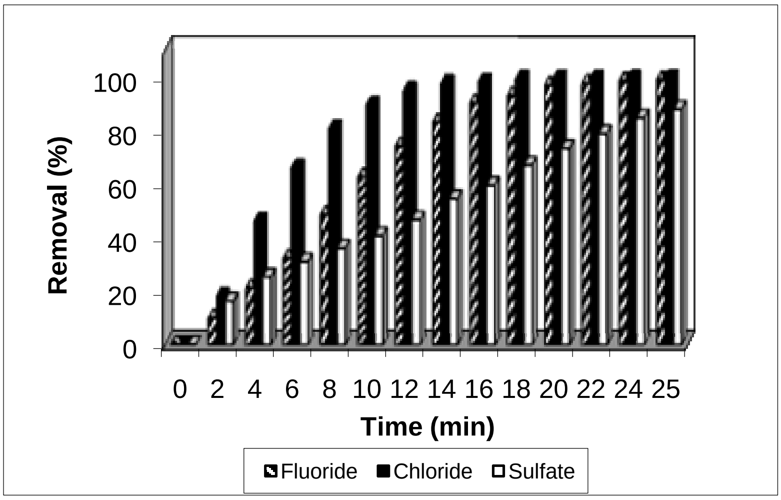

Figure 3.40. Removal of anions F^-, Cl^-, SO_4^{2-} from pretreated Balçova geothermal water

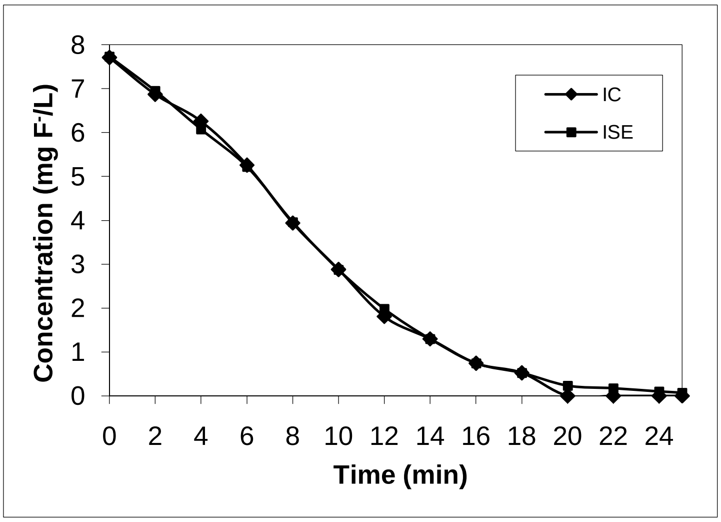

Figure 3.41. Comparison of ion chromatography and ion selective methods

Fluoride ions were removed from geothermal water by electrodialysis. The results obtained with two techniques (ISE and IC) agreed well with each as shown in Figure 3.41.

At the end of the electrodialysis experiments, for pretreated Balçova geothermal water, pH adjusted Balçova geothermal water, Balçova model solution which contains boron and Balçova model solution in the absence of boron, fluoride concentrations were found as 0.06 mg/L, 0.06 mg/L, 0.07 mg/L and 0.10 mg/L, respectively.

For Balçova model solution in the absence of boron and pretreated Balçova geothermal water, electrodialysis experiments took 24 minutes. For Balçova model solution which contains boron and Balçova geothermal water after pH adjustment, electrodialysis experiments took 30 and 29 minutes, respectively. Difference in the time of electrodialysis experiments can be connected applied potential values and number of ionic species in the solutions.

3.3.4. Specific power consumption (SPC)

The efficiencies of each run were evaluated as specific power consumption with the electrical energy consumed only in stack. If the potential difference U is maintained across a resistor, the power, or rate at which energy is supplied to the resistor is given by;

$$P = UI \tag{3.1.}$$

Total energy requirement during electrodialysis process can be written as;

$$E = \int_0^t UI((t)dt \tag{3.2}$$

If total energy requirement is divided by the volume of reservoir, specific power consumption obtained as;

$$SPC = E/V \tag{3.3}$$

Substituting Equation 3.2 into Equation 3.3, Equation 3.4 is obtained. Specific power consumption for each set of potential and flow rate was calculated as follows.

$$SPC = \frac{U\int_0^t I(t)dt}{V_D} \tag{3.4}$$

where E is the applied potential, I the current, V_D the dilute stream volume, t time.

For each run Integral part of this equation was computed using numerical integration (Trapezoidal Rule) and then specific power consumption (SPC) values were calculated (Samatya, 2006).

$$\text{Trapezoidal Rule: } \int_0^t I(t)dt = \frac{\Delta X}{2}\left[I_{first} + I_{final} + (2I_{others})\right] \tag{3.5}$$

The calculated specific power consumption (SPC) values were shown in Table 3.7.

Table 3.7. Specific power consumption (SPC) values

Solution	SPC (Wh/L)
Balçova Model Solution (in the presence of boron)	0.76
Balçova Model Solution (in the absence of boron)	0.66
Balçova Geothermal Water (pH was adjusted with HCl to 7.0)	0.71
Balçova Geothermal Water (pretreated)	0.56

According to the result obtained, one could conclude that the difference in specific power consumption values is due to difference in applied potential values and number of ionic species in the solution.

4. CONCLUSIONS

Determination of fluoride in various mineral and natural waters was investigated by using fluoride selective electrode and ion chromatography methods. The results of two methods (ISE and IC) agreed well with each other.

Removal of fluoride from Balçova geothermal water was investigated by using Al^{3+} and ZrO^{2+} loaded natural zeolites. The capacity of Zr-ZEO-2 type zeolites found higher than that of Al-ZEO-1, Al-ZEO-2 and Zr-ZEO-1 types zeolites. In a series of batch experiments, the optimum amount of zeolites (Al-ZEO-1, Zr-ZEO-1, Zr-ZEO-2) was found as 48.20 g-zeolite/L solution for fluoride removal from Balçova geothermal water. In a kinetic study using Zr-ZEO-2 the removal of fluoride increased with time and reached the equilibrium in 120 min with a 87.7 % of fluoride removal. The results show that metal loaded zeolite can be used for the removal of fluoride from geothermal water.

Removal of fluoride from Balçova geothermal water containing 7.72 mg F^-/L has been carried out using electrodialysis system. After electrodialysis, fluoride contents of samples were determined by ion chromatography and fluoride selective electrode methods. Fluoride was effectively removed from Balçova geothermal water by electrodialysis. In each solution, we obtained approximately 98-99 % of removal for fluoride at the end of the electrodialysis experiments.

For Balçova model solution which contains boron and Balçova geothermal water after pH adjustment, fluoride concentrations were found below 1.00 mg/L after 18 minutes of electrodialysis experiment. For Balçova model solution in the absence of boron and pretreated Balçova geothermal water, fluoride concentrations were found below 1.00 mg/L after 14 minutes of electrodialysis experiment.

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6. APPENDIX

6.1. Removal of Fluoride from Balçova Geothermal Water by Metal Loaded Zeolite

Table 6.1. Result of determination of optimum amount for Al-ZEO-1

Resin amount(g)	Resin concentration (g/L)	C_{eq} (mg F^-/L)	Removal of F^- (%)	mg F^- removed
0.100	4.012	7.347	4.872	0.009
0.200	8.016	6.247	19.114	0.037
0.300	12.032	5.327	31.026	0.060
0.400	16.000	4.467	42.162	0.082
0.500	20.024	3.587	53.556	0.103
0.600	24.000	3.100	59.862	0.116
0.803	32.120	1.790	76.813	0.148
1.000	40.000	1.467	80.997	0.156
1.205	48.200	1.175	84.780	0.164
1.401	56.040	0.906	88.264	0.170
1.605	64.200	0.595	92.29	0.178

Table 6.2. Result of determination of optimum amount for Zr-ZEO-1

Resin amount(g)	Resin concentration (g/L)	C_{eq} (mg F^-/L)	Removal of F^- (%)	mg F^- removed
0.103	4.128	7.166	7.215	0.014
0.200	8.020	6.222	19.464	0.038
0.300	12.000	5.247	32.062	0.062
0.400	16.012	4.793	37.941	0.073
0.500	20.016	3.760	51.316	0.099
0.600	24.000	3.158	59.175	0.114
0.801	32.040	1.751	73.319	0.149
1.001	40.040	1.549	79.935	0.154
1.205	48.200	0.899	88.484	0.171
1.406	56.240	0.779	89.909	0.174
1.605	64.200	0.725	90.609	0.175

Table 6.3. Result of determination of optimum amount for Al-ZEO-2

Resin amount(g)	**Resin concentration (g/L)**	**C_{eq} (mg F^-/L)**	**Removal of F^- (%)**	**mg F^- removed**
0.100	4.016	7.453	3.499	0.007
0.200	8.016	7.380	4.444	0.008
0.301	12.028	6.947	10.051	0.019
0.400	16.012	6.347	17.820	0.034
0.500	20.012	5.673	26.546	0.051
0.600	24.012	5.120	33.707	0.065
0.808	32.320	2.950	61.788	0.119
1.000	40.032	2.420	68.653	0.132
1.205	48.200	2.450	68.264	0.133
1.402	56.080	1.885	75.583	0.146
1.602	64.080	1.445	81.282	0.157

Table 6.4. Result of determination of optimum amount for Zr-ZEO-2

Resin amount(g)	**Resin concentration (g/L)**	**C_{eq} (mg F^-/L)**	**Removal of F^- (%)**	**mg F^- removed**
0.101	4.060	7.507	2.799	0.005
0.201	8.020	6.487	16.007	0.031
0.301	12.032	5.587	27.660	0.053
0.401	16.032	4.653	39.753	0.077
0.500	20.004	3.913	49.335	0.095
0.600	24.016	3.033	60.729	0.117
0.802	32.080	1.920	75.130	0.145
1.000	40.012	1.574	79.611	0.154
1.205	48.200	0.660	91.451	0.177
1.402	56.080	0.555	92.811	0.179
1.602	64.080	0.345	95.531	0.184

6.2. Removal of Fluoride from Balçova Geothermal Water by Electrodialysis

6.2.1. Tests with model solution containing boron

Table 6.5. Concentration, conductivities and pH's for model solution containing boron (IC method) at 8.67V and 1.6 L/min (Figures 3.7 and 3.14)

EXPERIMENTAL RESULTS											
Time (min)	I (A)	D_{outlet} (mg/L)	C_{outlet} (mg/L)	C_{EC} (µS/cm)	D_{EC} (µS/cm)	pH_D	pH_C	D_{Cl^-} (mg/L)	C_{Cl^-} (mg/L)	$D_{Sulfate}$ (mg/L)	$C_{Sulfate}$ (mg/L)
0	0.39	7.74	7.73	1698	1698	8.48	8.48	209.00	208.98	174.01	174.02
2	0.37	6.62	8.19	2054	1360	8.47	8.49	169.74	248.91	136.36	207.90
4	0.35	5.60	9.25	2381	1030	8.46	8.49	136.12	309.23	93.39	297.81
6	0.33	3.91	10.34	2640	767	8.44	8.46	81.79	329.27	78.56	301.03
8	0.30	3.39	11.72	2840	558	8.30	8.41	59.70	342.25	67.79	302.50
10	0.27	2.04	11.22	2990	400	8.15	8.43	40.53	358.22	56.57	304.61
12	0.22	1.72	12.20	3090	285	7.70	8.44	26.44	392.88	45.44	307.48
14	0.18	1.20	12.98	3160	205	7.60	8.43	18.55	399.24	43.34	310.30
16	0.12	1.00	14.36	3212	195	7.51	8.46	10.70	405.73	38.79	311.06
18	0.09	0.87	14.74	3240	150	7.43	8.47	6.05	416.60	38.53	314.27
20	0.07	0.55	14.61	3260	146	7.32	8.44	3.39	416.96	35.67	314.59
22	0.05	0.45	15.10	3265	105	7.00	8.45	1.42	417.86	33.23	316.18
24	0.04	0.00	15.41	3270	70	6.90	8.47	0.83	417.80	29.83	329.39
26	0.03	0.00	15.49	3272	55	6.80	8.46	0.79	417.86	25.98	325.89
28	0.02	0.00	15.51	3274	48	6.35	8.43	0.69	417.86	21.86	334.22
30	0.01	0.00	15.69	3274	40	6.03	8.45	0.50	417.87	21.10	334.22

Table 6.6. Dimensionless properties for model solution containing boron (IC method) at 8.67V and 1.6 L/min (Figure 3.6)

DIMENSIONLESS PROPERTIES											
t	**I**	D_{outlet}	C_{outlet}	C_{EC}	D_{EC}	pH_D	pH_C	D_{Cl^-}	C_{Cl^-}	$D_{Sulfate}$	$C_{Sulfate}$
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.95	0.86	1.06	1.21	0.80	1.00	1.00	0.81	1.19	0.78	1.19
4	0.90	0.72	1.20	1.40	0.61	1.00	1.00	0.65	1.48	0.54	1.71
6	0.85	0.51	1.34	1.55	0.45	1.00	1.00	0.39	1.58	0.45	1.73
8	0.77	0.44	1.52	1.67	0.33	0.98	0.99	0.29	1.64	0.39	1.74
10	0.69	0.26	1.45	1.76	0.24	0.96	0.99	0.19	1.72	0.33	1.75
12	0.56	0.22	1.58	1.82	0.17	0.91	1.00	0.13	1.88	0.26	1.77
14	0.46	0.16	1.68	1.86	0.12	0.90	0.99	0.09	1.91	0.25	1.78
16	0.31	0.13	1.86	1.89	0.11	0.89	1.00	0.05	1.94	0.22	1.79
18	0.23	0.11	1.91	1.91	0.09	0.88	1.00	0.03	2.00	0.22	1.81
20	0.18	0.07	1.89	1.92	0.09	0.86	1.00	0.02	2.00	0.20	1.81
22	0.13	0.06	1.95	1.92	0.06	0.83	1.00	0.01	2.00	0.19	1.82
24	0.10	0.00	1.99	1.93	0.04	0.81	1.00	0.00	2.00	0.17	1.89
26	0.08	0.00	2.00	1.93	0.03	0.80	1.00	0.00	2.00	0.15	1.87
28	0.05	0.00	2.01	1.93	0.03	0.75	0.99	0.00	2.00	0.13	1.92
30	0.03	0.00	2.03	1.93	0.02	0.71	1.00	0.00	2.00	0.12	1.92

Table 6.7. Concentration, conductivities and pH's for model solution containing boron (ISE method) at 8.67V and 1.6 L/min (Figures 3.12-14)

EXPERIMENTAL RESULTS											
Time (min)	**I (A)**	D_{outlet} (mg/L)	C_{outlet} (mg/L)	C_{EC} (µS/cm)	D_{EC} (µS/cm)	pH_D	pH_C	D_{Cl^-} (mg/L)	C_{Cl^-} (mg/L)	$D_{Sulfate}$ (mg/L)	$C_{Sulfate}$ (mg/L)
0	0.39	7.73	7.73	1698	1698	8.48	8.48	209.00	208.98	174.01	174.02
2	0.37	6.60	8.17	2054	1360	8.47	8.49	169.74	248.91	136.36	207.90
4	0.35	5.57	9.23	2381	1030	8.46	8.49	136.12	309.23	93.39	297.81
6	0.33	4.00	10.31	2640	767	8.44	8.46	81.79	329.27	78.56	301.03
8	0.30	3.35	11.10	2840	558	8.30	8.41	59.70	342.25	67.79	302.50
10	0.27	2.04	11.30	2990	400	8.15	8.43	40.53	358.22	56.57	304.61
12	0.22	1.70	12.19	3090	285	7.70	8.44	26.44	392.88	45.44	307.48
14	0.18	1.22	12.95	3160	205	7.60	8.43	18.55	399.24	43.34	310.30
16	0.12	1.01	14.23	3212	195	7.51	8.46	10.70	405.73	38.79	311.06
18	0.09	0.85	14.60	3240	150	7.43	8.47	6.05	416.60	38.53	314.27
20	0.07	0.50	14.65	3260	146	7.32	8.44	3.39	416.96	35.67	314.59
22	0.05	0.46	15.16	3265	105	7.00	8.45	1.42	417.86	33.23	316.18
24	0.04	0.28	15.26	3270	70	6.90	8.47	0.83	417.80	29.83	329.39
26	0.03	0.15	15.45	3272	55	6.80	8.46	0.79	417.86	25.98	325.89
28	0.02	0.09	15.50	3274	48	6.35	8.43	0.69	417.86	21.86	334.22
30	0.01	0.07	15.65	3274	40	6.03	8.45	0.50	417.87	21.10	334.22

Table 6.8. Dimensionless properties for model solution containing boron (ISE method) at 8.67V and 1.6 L/min (Figure 3.11)

DIMENSIONLESS PROPERTIES											
t	I	D_{outlet}	C_{outlet}	C_{EC}	D_{EC}	pH_D	pH_C	D_{Cl^-}	C_{Cl^-}	$D_{Sulfate}$	$C_{Sulfate}$
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.95	0.85	1.06	1.21	0.80	1.00	1.00	0.81	1.19	0.78	1.19
4	0.90	0.72	1.19	1.40	0.61	1.00	1.00	0.65	1.48	0.54	1.71
6	0.85	0.52	1.33	1.55	0.45	1.00	1.00	0.39	1.58	0.45	1.73
8	0.77	0.43	1.44	1.67	0.33	0.98	0.99	0.29	1.64	0.39	1.74
10	0.69	0.26	1.46	1.76	0.24	0.96	0.99	0.19	1.72	0.33	1.75
12	0.56	0.22	1.58	1.82	0.17	0.91	1.00	0.13	1.88	0.26	1.77
14	0.46	0.16	1.68	1.86	0.12	0.90	0.99	0.09	1.91	0.25	1.78
16	0.31	0.13	1.84	1.89	0.11	0.89	1.00	0.05	1.94	0.22	1.79
18	0.23	0.11	1.89	1.91	0.09	0.88	1.00	0.03	2.00	0.22	1.81
20	0.18	0.06	1.90	1.92	0.09	0.86	1.00	0.02	2.00	0.20	1.81
22	0.13	0.06	1.96	1.92	0.06	0.83	1.00	0.01	2.00	0.19	1.82
24	0.10	0.04	1.97	1.93	0.04	0.81	1.00	0.00	2.00	0.17	1.89
26	0.08	0.02	2.00	1.93	0.03	0.80	1.00	0.00	2.00	0.15	1.87
28	0.05	0.01	2.01	1.93	0.03	0.75	0.99	0.00	2.00	0.13	1.92
30	0.03	0.01	2.02	1.93	0.02	0.71	1.00	0.00	2.00	0.12	1.92

6.2.2. Tests with model solution in the absence of boron

Table 6.9. Concentration, conductivities and pH's for model solution in the absence of boron (IC method) at 12.15V and 1.6 L/min (Figures 3.16-19 and 3.23)

EXPERIMENTAL RESULTS											
Time (min)	I (A)	D_{outlet} (mg/L)	C_{outlet} (mg/L)	C_{EC} (µS/cm)	D_{EC} (µS/cm)	pH_D	pH_C	D_{Cl^-} (mg/L)	C_{Cl^-} (mg/L)	$D_{Sulfate}$ (mg/L)	$C_{Sulfate}$ (mg/L)
0	0.37	7.72	7.72	1698	1698	8.45	8.45	207.89	207.39	174.35	174.35
2	0.32	6.08	8.28	2040	1352	8.47	8.41	184.06	240.54	163.26	186.80
4	0.28	5.49	9.30	2380	1037	8.15	8.43	173.83	260.86	160.14	183.46
6	0.23	4.05	9.95	2640	765	7.70	8.45	132.52	283.83	152.85	200.21
8	0.18	3.16	12.40	2840	558	7.64	8.43	126.70	293.07	153.64	211.38
10	0.13	1.50	12.87	2980	403	7.51	8.46	121.60	303.54	146.19	230.77
12	0.09	1.17	13.51	3090	285	7.43	8.47	80.26	335.88	139.86	239.84
14	0.07	0.74	14.42	3160	205	7.32	8.44	39.92	356.83	126.61	270.15
16	0.05	0.50	14.07	3210	146	7.03	8.45	15.93	363.54	97.49	280.13
18	0.04	0.00	14.26	3240	105	6.90	8.45	7.99	375.05	62.50	292.87
20	0.03	0.00	14.71	3260	73	6.80	8.46	2.92	381.20	50.37	300.12
22	0.02	0.00	14.87	3270	53	6.40	8.43	1.42	390.12	39.13	318.33
24	0.01	0.00	15.43	3270	48	6.03	8.48	0.52	413.20	21.33	327.37

Table 6.10. Dimensionless properties for model solution in the absence of boron (IC method) at 12.15V and 1.6 L/min (Figure 3.15)

DIMENSIONLESS PROPERTIES											
t	I	D_{outlet}	C_{outlet}	C_{EC}	D_{EC}	pH_D	pH_C	D_{Cl^-}	C_{Cl^-}	$D_{Sulfate}$	$C_{Sulfate}$
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.86	0.79	1.07	1.20	0.80	1.00	0.99	0.89	1.16	0.94	1.07
4	0.76	0.71	1.20	1.40	0.61	0.96	0.99	0.84	1.26	0.92	1.05
6	0.62	0.52	1.29	1.55	0.45	0.91	1.00	0.64	1.37	0.88	1.15
8	0.49	0.41	1.61	1.67	0.33	0.90	0.99	0.61	1.41	0.88	1.21
10	0.35	0.19	1.67	1.76	0.24	0.89	1.00	0.58	1.46	0.84	1.32
12	0.24	0.15	1.75	1.82	0.17	0.88	1.00	0.39	1.62	0.80	1.38
14	0.19	0.10	1.87	1.86	0.12	0.87	0.99	0.19	1.72	0.73	1.55
16	0.14	0.06	1.82	1.89	0.09	0.83	1.00	0.08	1.75	0.56	1.61
18	0.10	0.00	1.85	1.91	0.06	0.82	1.00	0.04	1.81	0.36	1.68
20	0.08	0.00	1.91	1.92	0.04	0.81	1.00	0.01	1.84	0.29	1.72
22	0.05	0.00	1.93	1.93	0.03	0.76	0.99	0.01	1.88	0.22	1.83
24	0.03	0.00	2.00	1.93	0.02	0.71	1.00	0.00	1.99	0.12	1.88

Table 6.11. Concentration, conductivities and pH's for model solution in the absence of boron (ISE method) at 12.15V and 1.6 L/min (Figures 3.21-23)

EXPERIMENTAL RESULTS											
Time (min)	I (A)	D_{outlet} (mg/L)	C_{outlet} (mg/L)	C_{EC} (µS/cm)	D_{EC} (µS/cm)	pH_D	pH_C	D_{Cl^-} (mg/L)	C_{Cl^-} (mg/L)	$D_{Sulfate}$ (mg/L)	$C_{Sulfate}$ (mg/L)
0	0.37	7.72	7.73	1698	1698	8.45	8.45	207.89	207.39	174.35	174.35
2	0.32	6.80	8.07	2040	1352	8.47	8.41	184.06	240.54	163.26	186.80
4	0.28	5.47	9.09	2380	1037	8.15	8.43	173.83	260.86	160.14	183.46
6	0.23	4.06	10.56	2640	765	7.70	8.45	132.52	283.83	152.85	200.21
8	0.18	2.95	11.65	2840	558	7.64	8.43	126.70	293.07	153.64	211.38
10	0.13	1.92	12.67	2980	403	7.51	8.46	121.60	303.54	146.19	230.77
12	0.09	1.31	13.53	3090	285	7.43	8.47	80.26	335.88	139.86	239.84
14	0.07	0.91	14.06	3160	205	7.32	8.44	39.92	356.83	126.61	270.15
16	0.05	0.55	14.23	3210	146	7.03	8.45	15.93	363.54	97.49	280.13
18	0.04	0.26	14.49	3240	105	6.90	8.45	7.99	375.05	62.50	292.87
20	0.03	0.15	15.08	3260	73	6.80	8.46	2.92	381.20	50.37	300.12
22	0.02	0.12	15.26	3270	53	6.40	8.43	1.42	390.12	39.13	318.33
24	0.01	0.10	15.41	3270	48	6.03	8.48	0.52	413.20	21.33	327.37

Table 6.12. Dimensionless properties for model solution in the absence of boron (ISE method) at 12.15V and 1.6 L/min (Figure 3.20)

DIMENSIONLESS PROPERTIES											
t	I	D_{outlet}	C_{outlet}	C_{EC}	D_{EC}	pH_D	pH_C	D_{Cl^-}	C_{Cl^-}	$D_{Sulfate}$	$C_{Sulfate}$
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.86	0.88	1.04	1.20	0.80	1.00	0.99	0.89	1.16	0.94	1.07
4	0.76	0.71	1.18	1.40	0.61	0.96	0.99	0.84	1.26	0.92	1.05
6	0.62	0.53	1.37	1.55	0.45	0.91	1.00	0.64	1.37	0.88	1.15
8	0.49	0.38	1.51	1.67	0.33	0.90	0.99	0.61	1.41	0.88	1.21
10	0.35	0.25	1.64	1.76	0.24	0.89	1.00	0.58	1.46	0.84	1.32
12	0.24	0.17	1.75	1.82	0.17	0.88	1.00	0.39	1.62	0.80	1.38
14	0.19	0.12	1.82	1.86	0.12	0.87	0.99	0.19	1.72	0.73	1.55
16	0.14	0.07	1.84	1.89	0.09	0.83	1.00	0.08	1.75	0.56	1.61
18	0.10	0.03	1.87	1.91	0.06	0.82	1.00	0.04	1.81	0.36	1.68
20	0.08	0.02	1.95	1.92	0.04	0.81	1.00	0.01	1.84	0.29	1.72
22	0.05	0.02	1.97	1.93	0.03	0.76	0.99	0.01	1.88	0.22	1.83
24	0.03	0.01	1.99	1.93	0.02	0.71	1.00	0.00	1.99	0.12	1.88

6.2.3. Fluoride removal from geothermal water by electrodialysis without a chemical pretreatment

Table 6.13. Concentration, conductivities and pH's for Balçova geothermal water (pH was adjusted to 7.0 before ED) (IC method) at 10.01 V and 1.6 L/min (Figures 3.25-28 and 3.32)

EXPERIMENTAL RESULTS											
Time (min)	I (A)	D_{outlet} (mg/L)	C_{outlet} (mg/L)	C_{EC} (µS/cm)	D_{EC} (µS/cm)	pH_D	pH_C	D_{Cl-} (mg/L)	C_{Cl-} (mg/L)	$D_{Sulfate}$ (mg/L)	$C_{Sulfate}$ (mg/L)
0	0.39	7.67	7.72	2140	2140	7.01	7.01	211.50	211.50	176.56	176.55
2	0.34	7.15	7.62	2420	1833	6.98	7.23	210.32	233.16	140.05	178.80
4	0.31	6.37	7.92	2720	1518	7.07	7.26	206.14	284.23	139.50	178.92
6	0.27	5.69	8.40	3030	1215	7.11	7.29	144.77	295.50	130.25	180.62
8	0.23	4.78	9.52	3240	993	7.05	7.36	104.32	331.49	122.22	182.83
10	0.19	3.81	10.01	3430	779	6.99	7.42	74.55	371.38	112.30	185.66
12	0.15	2.84	10.66	3590	610	6.95	7.52	41.30	372.82	109.99	190.38
14	0.12	1.90	11.33	3700	479	6.92	7.55	29.33	373.65	102.37	199.12
16	0.09	1.30	12.08	3790	373	6.86	7.64	11.23	377.65	98.04	205.10
18	0.07	0.84	12.95	3860	288	6.70	7.68	7.66	378.30	72.81	211.58
20	0.05	0.48	13.35	3910	224	6.69	7.78	4.20	379.54	55.54	220.05
22	0.04	0.00	14.06	3950	173	6.61	7.78	2.61	383.04	48.27	229.80
24	0.03	0.00	14.90	3980	131	6.54	7.80	1.08	390.37	36.87	233.29
26	0.03	0.00	14.99	4000	102	6.30	7.83	0.97	392.92	22.30	243.59
28	0.02	0.00	14.99	4020	79	6.19	7.85	0.70	419.52	17.70	265.45
29	0.01	0.00	14.98	4030	73	6.05	7.95	0.50	419.53	17.04	265.46

Table 6.14. Dimensionless properties for Balçova geothermal water (pH was adjusted to 7.0 before ED) (IC method) at 10.01 V and 1.6 L/min (Figure 3.24)

DIMENSIONLESS PROPERTIES											
t	I	D_{outlet}	C_{outlet}	C_{EC}	D_{EC}	pH_D	pH_C	D_{Cl^-}	C_{Cl^-}	$D_{Sulfate}$	$C_{Sulfate}$
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.87	0.93	0.99	1.13	0.86	0.99	1.03	0.99	1.10	0.79	1.01
4	0.79	0.83	1.03	1.27	0.71	1.01	1.04	0.97	1.34	0.79	1.01
6	0.69	0.74	1.09	1.42	0.57	1.01	1.04	0.68	1.40	0.74	1.02
8	0.60	0.62	1.23	1.51	0.46	1.00	1.05	0.49	1.57	0.69	1.04
10	0.49	0.50	1.30	1.60	0.36	0.99	1.06	0.35	1.76	0.64	1.05
12	0.38	0.37	1.38	1.68	0.29	0.99	1.07	0.20	1.76	0.62	1.08
14	0.31	0.25	1.47	1.73	0.22	0.99	1.08	0.14	1.77	0.58	1.13
16	0.23	0.17	1.56	1.77	0.17	0.98	1.09	0.05	1.79	0.56	1.16
18	0.18	0.11	1.68	1.80	0.13	0.96	1.10	0.04	1.79	0.41	1.20
20	0.13	0.06	1.73	1.83	0.10	0.95	1.11	0.02	1.79	0.31	1.25
22	0.10	0.00	1.82	1.85	0.08	0.94	1.11	0.01	1.81	0.27	1.30
24	0.08	0.00	1.93	1.86	0.06	0.93	1.11	0.01	1.85	0.21	1.32
26	0.08	0.00	1.94	1.87	0.05	0.90	1.12	0.00	1.86	0.13	1.38
28	0.05	0.00	1.94	1.88	0.04	0.88	1.12	0.00	1.98	0.10	1.50
29	0.03	0.00	1.94	1.88	0.03	0.86	1.13	0.00	1.98	0.10	1.50

Table 6.15. Concentration, conductivities and pH's for Balçova geothermal water (pH was adjusted to 7.0 before ED) (ISE method) at 10.01 V and 1.6 L/min (Figures 3.30-32)

EXPERIMENTAL RESULTS											
Time (min)	I (A)	D_{outlet} (mg/L)	C_{outlet} (mg/L)	C_{EC} (μS/cm)	D_{EC} (μS/cm)	pH_D	pH_C	D_{Cl-} (mg/L)	C_{Cl-} (mg/L)	$D_{Sulfate}$ (mg/L)	$C_{Sulfate}$ (mg/L)
0	0.39	7.73	7.74	2140	2140	7.01	7.01	211.50	211.50	176.56	176.55
2	0.34	7.17	7.82	2420	1833	6.98	7.23	210.32	233.16	140.05	178.80
4	0.31	6.51	8.20	2720	1518	7.07	7.26	206.14	284.23	139.50	178.92
6	0.27	5.65	8.67	3030	1215	7.11	7.29	144.77	295.50	130.25	180.62
8	0.23	4.86	9.21	3240	993	7.05	7.36	104.32	331.49	122.22	182.83
10	0.19	3.73	10.06	3430	779	6.99	7.42	74.55	371.38	112.30	185.66
12	0.15	2.77	10.91	3590	610	6.95	7.52	41.30	372.82	109.99	190.38
14	0.12	1.90	11.53	3700	479	6.92	7.55	29.33	373.65	102.37	199.12
16	0.09	1.27	12.38	3790	373	6.86	7.64	11.23	377.65	98.04	205.10
18	0.07	0.84	13.00	3860	288	6.70	7.68	7.66	378.30	72.81	211.58
20	0.05	0.48	13.62	3910	224	6.69	7.78	4.20	379.54	55.54	220.05
22	0.04	0.28	14.01	3950	173	6.61	7.78	2.61	383.04	48.27	229.80
24	0.03	0.17	14.55	3980	131	6.54	7.80	1.08	390.37	36.87	233.29
26	0.03	0.10	14.71	4000	102	6.30	7.83	0.97	392.92	22.30	243.59
28	0.02	0.07	14.94	4020	79	6.19	7.85	0.70	419.52	17.70	265.45
29	0.01	0.06	15.17	4030	73	6.05	7.95	0.50	419.53	17.04	265.46

Table 6.16. Dimensionless properties for Balçova geothermal water (pH was adjusted to 7.0 before ED) (ISE method) at 10.01 V and 1.6 L/min (Figure 3.29)

DIMENSIONLESS PROPERTIES											
t	I	D_{outlet}	C_{outlet}	C_{EC}	D_{EC}	pH_D	pH_C	D_{Cl^-}	C_{Cl^-}	$D_{Sulfate}$	$C_{Sulfate}$
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.87	0.93	1.01	1.13	0.86	0.99	1.03	0.99	1.10	0.79	1.01
4	0.79	0.84	1.06	1.27	0.71	1.01	1.04	0.97	1.34	0.79	1.01
6	0.69	0.73	1.12	1.42	0.57	1.01	1.04	0.68	1.40	0.74	1.02
8	0.60	0.63	1.19	1.51	0.46	1.00	1.05	0.49	1.57	0.69	1.04
10	0.49	0.48	1.30	1.60	0.36	0.99	1.06	0.35	1.76	0.64	1.05
12	0.38	0.36	1.41	1.68	0.29	0.99	1.07	0.20	1.76	0.62	1.08
14	0.31	0.25	1.49	1.73	0.22	0.99	1.08	0.14	1.77	0.58	1.13
16	0.23	0.16	1.60	1.77	0.17	0.98	1.09	0.05	1.79	0.56	1.16
18	0.18	0.11	1.68	1.80	0.13	0.96	1.10	0.04	1.79	0.41	1.20
20	0.13	0.06	1.76	1.83	0.10	0.95	1.11	0.02	1.79	0.31	1.25
22	0.10	0.04	1.81	1.85	0.08	0.94	1.11	0.01	1.81	0.27	1.30
24	0.08	0.02	1.88	1.86	0.06	0.93	1.11	0.01	1.85	0.21	1.32
26	0.08	0.01	1.90	1.87	0.05	0.90	1.12	0.00	1.86	0.13	1.38
28	0.05	0.01	1.93	1.88	0.04	0.88	1.12	0.00	1.98	0.10	1.50
29	0.03	0.01	1.96	1.88	0.03	0.86	1.13	0.00	1.98	0.10	1.50

6.2.4. Removal of fluoride from geothermal water by electrodialysis after a chemical pretreatment

Table 6.17. Concentration, conductivities and pH's for Balçova geothermal water after pretreatment (IC method) at 10.63 V and 1.6 L/min (Figures 3.34-37 and 3.41)

EXPERIMENTAL RESULTS											
Time (min)	I (A)	D_{outlet} (mg/L)	C_{outlet} (mg/L)	C_{EC} (µS/cm)	D_{EC} (µS/cm)	pH_D	pH_C	D_{Cl^-} (mg/L)	C_{Cl^-} (mg/L)	$D_{Sulfate}$ (mg/L)	$C_{Sulfate}$ (mg/L)
0	0.40	7.71	7.72	2010	2010	7.09	7.09	307.95	308.88	156.58	157.01
2	0.36	6.87	7.84	2350	1650	7.04	7.20	251.85	378.23	130.89	16056
4	0.31	6.26	8.04	2700	1291	7.03	7.41	165.51	410.32	116.82	161.02
6	0.26	5.26	8.65	2980	983	7.02	7.55	104.09	435.93	107.83	162.34
8	0.20	3.94	9.54	3220	738	7.01	7.58	58.98	470.63	99.95	166.44
10	0.15	2.88	10.39	3390	554	7.00	7.71	31.75	502.49	92.59	175.75
12	0.11	1.81	11.41	3500	412	6.95	7.75	14.78	515.43	83.19	179.35
14	0.09	1.30	12.35	3590	310	6.86	7.79	7.13	532.43	70.98	184.19
16	0.06	0.74	12.49	3650	232	6.73	7.92	5.80	538.96	63.23	193.51
18	0.05	0.52	12.80	3690	173	6.71	7.94	1.96	540.21	51.25	210.82
20	0.04	0.00	13.33	3730	129	6.61	8.00	1.69	543.77	41.63	220.15
22	0.03	0.00	13.70	3750	96	6.28	8.02	1.56	544.75	32.98	240.45
24	0.02	0.00	13.86	3770	71	6.20	8.00	1.34	607.91	23.67	261.23
25	0.01	0.00	15.40	3780	66	6.15	8.01	0.98	617.38	18.68	295.02

Table 6.18. Dimensionless properties for Balçova geothermal water after pretreatment (IC method) at 10.63 V and 1.6 L/min (Figure 3.33)

DIMENSIONLESS PROPERTIES											
t	**I**	**D_{outlet}**	**C_{outlet}**	**C_{EC}**	**D_{EC}**	**pH_D**	**pH_C**	**D_{Cl^-}**	**C_{Cl^-}**	**$D_{Sulfate}$**	**$C_{Sulfate}$**
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.90	0.89	1.02	1.17	0.82	0.99	1.02	0.82	1.22	0.84	102.26
4	0.78	0.81	1.04	1.34	0.64	0.99	1.05	0.54	1.33	0.75	1.03
6	0.65	0.68	1.12	1.48	0.49	0.99	1.06	0.34	1.41	0.69	1.03
8	0.50	0.51	1.24	1.60	0.37	0.99	1.07	0.19	1.52	0.64	1.06
10	0.38	0.37	1.35	1.69	0.28	0.99	1.09	0.10	1.63	0.59	1.12
12	0.28	0.23	1.48	1.74	0.20	0.98	1.09	0.05	1.67	0.53	1.14
14	0.23	0.17	1.60	1.79	0.15	0.97	1.10	0.02	1.72	0.45	1.17
16	0.15	0.10	1.62	1.82	0.12	0.95	1.12	0.02	1.74	0.40	1.23
18	0.13	0.07	1.66	1.84	0.09	0.95	1.12	0.01	1.75	0.33	1.34
20	0.10	0.00	1.73	1.86	0.06	0.93	1.13	0.01	1.76	0.27	1.40
22	0.08	0.00	1.77	1.87	0.05	0.89	1.13	0.01	1.76	0.21	1.53
24	0.05	0.00	1.80	1.88	0.04	0.87	1.13	0.00	1.97	0.15	1.66
25	0.03	0.00	1.99	1.88	0.03	0.87	1.13	0.00	2.00	0.12	1.88

Table 6.19. Concentration, conductivities and pH's for Balçova geothermal water after pretreatment (ISE method) at 10.63 V and 1.6 L/min (Figures 3.39-41)

EXPERIMENTAL RESULTS											
Time (min)	**I (A)**	**D_{outlet} (mg/L)**	**C_{outlet} (mg/L)**	**C_{EC} (µS/cm)**	**D_{EC} (µS/cm)**	**pH_D**	**pH_C**	**D_{Cl^-} (mg/L)**	**C_{Cl^-} (mg/L)**	**$D_{Sulfate}$ (mg/L)**	**$C_{Sulfate}$ (mg/L)**
0	0.40	7.73	7.73	2010	2010	7.09	7.09	307.95	308.88	156.58	157.01
2	0.36	6.95	7.80	2350	1650	7.04	7.20	251.85	378.23	130.89	160.56
4	0.31	6.08	8.00	2700	1291	7.03	7.41	165.51	410.32	116.82	161.02
6	0.26	5.22	8.50	2980	983	7.02	7.55	104.09	435.93	107.83	162.34
8	0.20	3.96	9.46	3220	738	7.01	7.58	58.98	470.63	99.95	166.44
10	0.15	2.87	10.21	3390	554	7.00	7.71	31.75	502.49	92.59	175.75
12	0.11	1.98	11.43	3500	412	6.95	7.75	14.78	515.43	83.19	179.35
14	0.09	1.30	12.30	3590	310	6.86	7.79	7.13	532.43	70.98	184.19
16	0.06	0.74	12.59	3650	232	6.73	7.92	5.80	538.96	63.23	193.51
18	0.05	0.52	13.00	3690	173	6.71	7.94	1.96	540.21	51.25	210.82
20	0.04	0.23	13.39	3730	129	6.61	8.00	1.69	543.77	41.63	220.15
22	0.03	0.17	14.00	3750	96	6.28	8.02	1.56	564.75	32.98	240.45
24	0.02	0.10	14.21	3770	71	6.20	8.00	1.34	607.91	23.67	261.23
25	0.01	0.07	15.43	3780	66	6.15	8.01	0.98	617.38	18.68	295.02

Table 6.20. Dimensionless properties for Balçova geothermal water after pretreatment (ISE method) at 10.63 V and 1.6 L/min (Figure 3.38)

DIMENSIONLESS PROPERTIES											
t	**I**	**D_{outlet}**	**C_{outlet}**	**C_{EC}**	**D_{EC}**	**pH_D**	**pH_C**	**D_{Cl^-}**	**C_{Cl^-}**	**$D_{Sulfate}$**	**$C_{Sulfate}$**
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.90	0.90	1.01	1.17	0.82	0.99	1.02	0.82	1.22	0.84	1.02
4	0.78	0.79	1.03	1.34	0.64	0.99	1.05	0.54	1.33	0.75	1.03
6	0.65	0.68	1.10	1.48	0.49	0.99	1.06	0.34	1.41	0.69	1.03
8	0.50	0.51	1.22	1.60	0.37	0.99	1.07	0.19	1.52	0.64	1.06
10	0.38	0.37	1.32	1.69	0.28	0.99	1.09	0.10	1.63	0.59	1.12
12	0.28	0.26	1.48	1.74	0.20	0.98	1.09	0.05	1.67	0.53	1.14
14	0.23	0.17	1.59	1.79	0.15	0.97	1.10	0.02	1.72	0.45	1.17
16	0.15	0.10	1.63	1.82	0.12	0.95	1.12	0.02	1.74	0.40	1.23
18	0.13	0.07	1.68	1.84	0.09	0.95	1.12	0.01	1.75	0.33	1.34
20	0.10	0.03	1.73	1.86	0.06	0.93	1.13	0.01	1.76	0.27	1.40
22	0.08	0.02	1.81	1.87	0.05	0.89	1.13	0.01	1.76	0.21	1.53
24	0.05	0.01	1.84	1.88	0.04	0.87	1.13	0.00	1.97	0.15	1.66
25	0.03	0.01	2.00	1.88	0.03	0.87	1.13	0.00	2.00	0.12	1.88

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