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# Electrodialysis as part of the integrated membrane process for landfill leachate treatment

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## ABSTRACT

Desalination of leachates from municipal and hazardous waste landfills using electrodialysis was studied experimentally. The process was integrated into the complex technology for leachate treatment to reduce the concentration of inorganic salts prior to the reverse osmosis (RO). The technology principle is as follows: electrodialysis minimizes osmotic pressure of RO feed, thus the process can be operated economically using low-pressure and fouling-resistant RO membranes and low salinity RO concentrate can be easily recycled back into the landfill body. The pilot batch electrodialysis experiments were carried out with several types of leachate wastewaters which were collected from two municipal waste landfills and one landfill for the disposal of hazardous waste. The results of the experiments demonstrate that the electrodialysis integrated into the treatment system allows the reduction of the dissolved solids content in the leachate to 18%–27% of the initial value. Most of the organic matter remains in the leachate (diluate) together with multivalent ions, especially $Fe^{3+}$, $Ba^{2+}$, $Sr^{2+}$ and $B^{3+}$. If the concentrate pH was kept as low as necessary to achieve Langelier saturation index below –0.2, then it was possible to realize the process with the minimum ratio of the concentrate to diluate volume. An effective method to recover the system from physical and chemical reversible fouling using alkaline cleaning in place was also found and verified.

*Keywords:* Electrodialysis; Wastewater treatment; Leachate; Scaling; Membrane fouling

## 1. Introduction

Leachate from municipal waste landfills is considered a serious pollutant of soil, and both surface and ground waters [1,2]. It is formed by liquids which are generated during the decomposition of the waste within the landfill and the water that infiltrates into the landfill site during rains and eventually from the underground water. A landfill site produces leachate throughout its working life and also for several decades after it is decommissioned. The control of the leachate level and an appropriate treatment of the leachate excess are of great importance for current and future protection of surrounding natural resources.

Leachate is generally a dark colored liquid, with a strong odor, which contains a high organic and inorganic load. The content of each pollutant depends on the age of the landfill, the seasonal climatic conditions, the hydrogeology of the landfill site and the type of waste. The characteristics of the landfill leachate can usually be represented by basic parameters such as chemical oxygen demand (COD), 5-d biochemical oxygen demand ($BOD_5$), $BOD_5$/COD ratio, pH, electrical conductivity (G), ammonium nitrogen, total nitrogen (TN) and

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heavy metals content. Young acidogenic landfill leachate is commonly characterized by both high $BOD_5$ and COD values, moderate strength of ammonium nitrogen and pH value below 6.5. Biodegradable volatile low molecular organic compounds characterized by linear chains, which are substituted by carboxyl and alcoholic groups, appear to be major constituents of the young leachate. As the landfill matures, the methanogenic degradation occurs. Volatile fatty acids are converted to biogas and the organic fraction in the leachate becomes dominated by non-biodegradable complex compounds such as humic substances. As a result, the ratio of $BOD_5$/COD decreases rapidly from a value slightly smaller than one to several hundredths during the aging of the landfills [3,4]. Both the total leachate salinity and the ammonia concentration do not follow the same decreasing trend and may constitute the major long-term pollutants in the landfill leachate [5]. The content of heavy metals in the old leachates is generally extremely low as a result of sorption and precipitation processes that take place within the disposed waste.

Reverse osmosis (RO) seems to be one of the most promising and efficient methods for landfill leachate treatment. In the past, a number of studies [6–8], performed both on a laboratory and industrial scale, demonstrated high RO performance. Depending on the leachate composition, the type of membrane module and the operating pressure, permeate recovery rates were found in a range from 60% to 90%. The retention efficiency primarily depended upon the molecular weight and polarity of contaminants. The values of the membrane rejection coefficient higher than 98% were reported. These were usually referred to the COD parameter, electrical conductivity, total salinity or heavy metal concentration. Two- or three-stage RO facilities were also employed which achieved contaminant removal rates better than 99.9%. The RO permeate meets nearly potable water standards and can easily be discharged to water bodies. It is suitable for irrigation without the risk of over-salinity build-up.

The economic sustainability of the adoption of leachate treatment, based on the reverse osmosis, is dominantly connected to the management of the resulting concentrated leachate. The concentrate off-site disposal to an incinerator, licensed to accept hazardous liquid wastes, is normally prohibitively expensive. Throughout the European Union (EU), the co-treatment of leachate with domestic sewage in municipal wastewater treatment plants (WWTPs), after its transportation by lorries is a common practice [9]. Reducing the volume of leachate using on-site treatment with the reverse osmosis facility enables a decrease in the concentrate transport costs. Due to low biodegradability and high salinity of leachate concentrate it is often difficult to mix these types of wastewater in a ratio that would guarantee safe and effective conditions for the treatment [10–13]. Also, increasingly stringent WWTP emission limits represent a significant threat to the sustainability of co-treatment of leachate with municipal wastewater [9]. Disposal of RO leachate concentrate by re-circulation into the landfill body under controlled reinjection is another and certainly the cheapest way of the leachate treatment. There is relatively little scientific research on this topic and opinions are often conflicting. In some countries, this process is looked at critically or it is limited by approval authorities within special boundary conditions [9]. The experimental results [14,15] indicated that the re-circulation of the concentrate accelerated the decomposition of organic matter, and this was particularly noticeable on the landfill sites with more fresh waste. According to Ledakowicz and Kaczorek's study [16], recirculation can generate additional quantities of landfill gas and methane from waste degraded under methanogenic anaerobic conditions. The RO concentrate disposed to landfill can in contrary result in a continually rising salinity and contaminant strength in the leachate, which seems to contravene all ideas of flushing the landfill clean, because ultimately, all salinity above the natural background salinity needs to be flushed out before the landfill will become fully safe for the environment. According to Džolev's study [17], over a 10-year period of recirculating concentrated leachate back into the landfill the concentration of certain parameters ($NH_4^+$, $Cl^-$ and $SO_4^{2-}$) was found to be higher in the leachate recovered after recirculation compared with the period before recirculation. In systems with high ammonia levels, landfill gas produced by methanogenic organisms may be inhibited and landfill gas yield reduced or poisoned [16,17]. Logically, after some years, the RO separation also became less and less efficient due to rising salinity levels in the leachate and the consequent need for higher pressure differences to overcome the generated osmotic pressure.

This contribution deals with the study of complex leachate treatment system integrating membrane electrodialysis into the separation process. The idea is that upstream electrodialysis (ED) will reduce the salinity of the landfill leachate. The diluate containing mainly organic matter is further fed into the RO unit. The RO concentrate is recycled back into the landfill body (long-term salinity of landfill body decreases) and high quality permeate is produced. Most important benefit of the electrodialysis, used in this combination with RO, will be minimization of RO feed osmotic pressure, thus the RO process can be operated economically using low-pressure and fouling-resistant RO membranes. Very little information is available in the current literature regarding the desalination of leachates with ED [18,19]. The main objective of this investigation was therefore to evaluate ED performance for the desalination of several types of landfill leachate and to determine the fouling potential of the leachate for heterogeneous ED membranes as well as membrane cleaning strategies. A simplified process flow chart of the integrated leachate treatment is presented in Fig. 1.

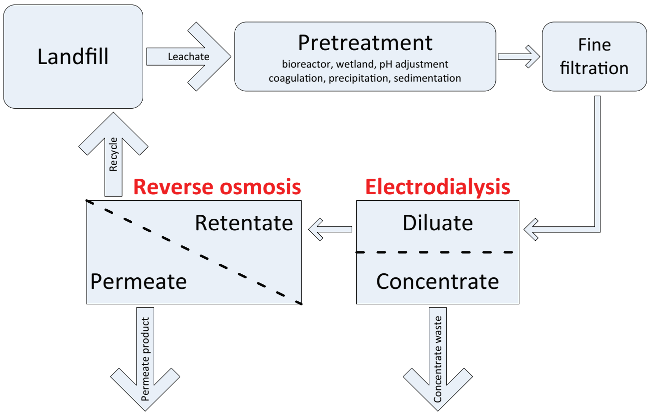

Fig. 1. Process flow chart of the integrated leachate treatment system.

## 2. Materials and methods

### *2.1. Leachates*

Real leachates used in the experimental investigation were collected from two municipal waste landfills and one landfill for the disposal of hazardous waste. The first landfill site, which is managed by Ekoservis Ralsko (Czech Republic) in Svébořice, has been in operation since 1996. Municipal waste from surrounding smaller towns and villages is deposited in the landfill. The capacity of the original landfill was filled in 2004 and its reclamation was completed. A new section with a storage capacity of 185,000 m$^3$ was opened in 2005. The municipal waste does not undergo any biomechanical pre-treatment, sorting or crushing. The leachates were first pumped from the retention basin, which serves to separate leachates from the open section of the landfill. The leachates were then processed using constructed wetland technology, which included two bioreactors (aerobic and anaerobic) and a vegetation basin. The technology was managed by an external company (Aquatest, Czech Republic). The basic composition of raw leachate is shown in Table 1. The leachate can be specified as young, which is characterized by considerable portion of biodegradable organic substances.

The second landfill of municipal waste is operated in Zdechovice (Bohemian Waste Management, Czech Republic) serving mainly for the disposal of municipal waste from the larger cities Pardubice and Hradec Králové. The newer part has been in operation since 1994. The municipal waste is first treated using a mobile drum screen sorting technology in order to obtain both the metal and the combustible components of the waste for further processing and to achieve the best possible homogenization of remaining waste for its efficient compaction into the landfill. Excessive landfill leachates are collected in a large retention basin where are mixed with leachates from all other landfill sections, that is, the opened and the enclosed. The leachate samples used in the laboratory experiments were taken from this basin. The composition of raw leachate is shown in Table 1. In this case, it is a mixture of young and old leachates. The content of organic and inorganic compounds is higher in comparison with other leachates.

The third sample of leachate was collected from the Tušimice hazardous waste landfill site. The landfill is primarily focused on deposition of materials contaminated by organic solvents, oils and paints. The basic composition of the raw leachate is shown in Table 1. Produced landfill leachate can be characterized by a lower level of pollution. The leachate contains, however, considerable amounts of calcium, magnesium and ammonium ions.

Prior to the processing on the electrodialysis unit, the raw leachates were treated with respect to the amount of their initial contamination. The leachates from the Svébořice and Tušimice landfills were acidified by sulfuric acid and the solid particles were removed using sedimentation and a polymeric candle filter (5 μm). The leachate from the Zdechovice landfill, containing a higher amount of organic substances, especially non-biodegradable humic acids, was first coagulated using ferric sulfate. The resulting flakes were then removed by sedimentation and, for maximum efficiency, also filtered through a polymeric candle filter (5 μm). Alternatively, the electrodialysis with Zdechovice's leachate feed was performed, while the leachate was only treated with acidification to pH = 6.3 followed by fine candle filtration.

### *2.2. Electrodialysis unit and membranes*

Electrodialysis (ED) pilot unit P1 EDR-Y/4 (MemBrain, Czech Republic) was used for the leachate desalination experiments. The unit was equipped with EDR-Y/50-0.8 module that contained two series-coupled membrane bundles with 50 pairs of heterogeneous ion exchange membranes (cationic CMH - PES and anionic AMH - PES membranes [MEGA a.s., CR]). The total active membrane area was 4 m$^2$ (dimension of active area a single membrane was 0.1 ´ 0.4 m). There were also three circulation pumps, safety cartridge filters, heat exchanger, chemical dosage pumps, DC drive, internal and external product vessels, and an electrical switchboard with

Table 1
Basic characteristics of the leachates measured

| | Municipal waste | | Hazardous waste |
|---|---|---|---|
| | Zdechovice landfill | Svébořice landfill | Tušimice landfill |
| pH | 7.8–8.2 | 9.01–8.8 | 6.8–8.3 |
| Electrical conductivity (*G*), mS/cm | 18.6–23 | 11.5–12.1 | 3.3–7.4 |
| Total dissolved substances (TDS), g/L | 9.8–15.6 | 8.5–9.6 | 2.1–5.2 |
| Total carbon (TC), mg/L | 2,700–3,300 | 900–1,300 | 170–200 |
| Total inorganic carbon (TIC), mg/L | 1,100–1,650 | 236–501 | 52–60 |
| Total organic carbon (TOC), mg/L | 1,600–1,700 | 680–800 | 115–150 |
| Total nitrogen (TN), mg/L | 800–1,600 | 350– 600 | 6.5–75 |
| B, mg/L | 10.2–13 | 8.5–11.2 | 2.5–3 |
| Ca, mg/l | 52.3–95.3 | 89.1–95.6 | 105–221 |
| Mg, mg/L | 60–70 | 111–129 | 64.6–138 |
| Ba, mg/L | 0.40–0.60 | 0.2– 0.25 | 0.05–0.096 |
| Sr, mg/L | 0.51–0.60 | 0.637–0.654 | 0.68–1.37 |
| Fe, mg/L | 2.99–6.04 | 3.26–4.12 | 0.05–0.14 |
| $SO_4^{2-}$, mg/L | 230.6–311 | 269.6–341.5 | 674–1,279 |

PLC and touchscreen control in the unit assembly. The salt ions were passed through the membranes at a constant voltage of 55 V from the diluate to the concentrate circuit.

### 2.3. Experimental procedure and analytical methods

Experiments were performed in the batch mode. Pure water (e.g., RO permeate from the leachate reverse osmosis unit) of a volume of 9 L was introduced at the beginning of the experiment into the concentrate vessel and 400 L of leachate into the feed (diluate) vessel of the ED unit. Sodium sulfate solution was used as electrode rinse solution. The feed, concentrate, and electrode rinse solutions were circulated through the ED stack at flow rates of approximately 700 L/h. The electricity was switched on and voltage, current, conductivity, pH, both the diluate and concentrate volume and temperature were monitored. The desalination of the leachate was terminated at a conductivity of 2 mS/cm in the diluate process stream. The maximum electrical conductivity value of 60 mS/cm and a pH below 8 were maintained in the concentrate stream. If one of these limits was exceeded during the experiment, deionized water (RO permeate) or sulfuric acid was added.

Reference salt tests were conducted before and after both the ED runs and the cleaning in place (CIP) procedures, which use a sodium sulfate solution (20 g/L), to determine the degree of membrane fouling. The membrane cleaning was initially performed by flushing with deionized water, removing coarse impurities and water-soluble substances. The sodium hydroxide solution (10 g/L) was subsequently used, which was circulated in the system for 30 min. Upon completion of these chemical cleaning steps, a rinse with deionized water was done to remove all traces of chemicals from the cleaning. An acidic cleaning was begun at this point, if needed, using nitric acid followed again by careful water rinsing.

The analytical studies of the composition of the studied leachate, as well as of the leachate samples, taken at various stages of the integrated treatment technology, were carried out according to the standardized methods for the examination of water and wastewater. Total carbon (TC), total organic carbon (TOC), total inorganic carbon (TIC) and TN were measured according to ČSN EN 1484 using the TOC-TN analyzer (Skalar, NL). The total dissolved substances (TDS) were determined according to ČSN EN 15216. Conductivity (*G*) and pH were determined using ProfiLine 3310 (WTW, Germany). Concentrations of selected cations and anions were determined using ICP analysis (Integra XL2 and Avanta Ultra Z, GBC Australia) and ion chromatography (DIONEX ICS-5000, Thermo Scientific, US). The electron scanning microscopy (Quanta 250 FEG, FEI, CR) was used for analyses of solid material (i.e., membranes and precipitates).

### 2.4. Data analysis

In order to evaluate the influence of the operating parameters on the performance of the ED desalination process, the separation percentage, current efficiency (CE), specific energy consumption (EC) and ion permeation flux (*J*) were calculated by procedures described, for example, in Gherasim et al. [20]. Due to the high concentrations of $Ca^{2+}$, $Ba^{2+}$, $Sr^{2+}$, $SO_4^{2-}$ and $CO_3^{2-}$ in the process streams, it was possible that the scaling at the diluate and/or concentrate side of the membrane could affect the ED system operation. The saturation levels of $CaSO_4$, $BaSO_4$, $SrSO_4$ and $CaCO_3$ in the experimented waters were, therefore, calculated using standard software ROSA and TorayDS2. Langelier (LSI) and Stiff–Davis (SDSI) saturation indexes were used to indicate the scaling potential of water containing carbonates, which are expressed by

$$\text{LSI (or SDSI)} = \text{pH} - \text{pH}_S \tag{1}$$

where $\text{pH}_S$ is the "saturation pH" at which the water is saturated with calcium carbonate [21,22]. Values of both LSI and SDSI lower than –0.2 were taken as the non-scaling conditions.

## 3. Results and discussion

### 3.1. Pretreatment of raw leachate

Landfill leachates, acquired from three different waste disposals, were pretreated prior to electrodialysis processing. The pretreatment depended especially on the leachate degree of pollution. Young leachates from the communal and dangerous waste disposals of the towns Svébořice and Tušimice, respectively, were initially biologically pretreated in bioreactors and the tanks equipped with vegetation, which replaces general wetland technology. Such pretreatment predominantly decreases the biologically decomposable organic content.

Values of TOC were decreased by 20% and the total nitrogen content was decreased by 25%. This pretreatment had no influence on the content of inorganic salts. The content of calcium and magnesium ions, in contrast, was increased due to the presence of a pebble in the tanks. Biologically pretreated leachates and one sample of non-pretreated real leachate taken from the Zdechovice waste disposal were acidified at laboratory conditions. Acidification of the leachate (pH decrease) is needed to prevent the risk of ammonia elution in an alkali environment and an equilibrium shift of $CO_3^{2-}/HCO_3^-$. A sample of Zdechovice's leachate was also treated by the physico-chemical method (coagulation), because the basis of this leachate consists of an old and young leachate mixture. Acidic iron sulfate (PREFLOC, Precheza, Czech Republic) was used as the coagulation agent. The best coagulation results were obtained during experiments at pH = 5.8. High-molecular humin compounds were removed by sedimentation of the coagulated leachate. pH decrease also enables transfer of carbonates to gaseous $CO_2$, which escapes to the environs. Low-molecular fulvic acids remain in the solution. Coagulation pretreatment decreases TC content in the processed solution by 80%. Details of this pretreatment are described in our previous work [23].

### 3.2. Prediction of scaling and membrane fouling

Risks of calcium carbonate precipitation on the membrane surface during the electrodialysis process were evaluated on the basis of LSI and SDSI index measurements. The SDSI index is preferentially suggested in case of highly salted solutions. The calculation results point to the comparability of both indexes, but the SDSI index obtains slightly lower values than LSI. Based on this fact, the worse LSI value was then taken to estimate the influence on the precipitation in the investigated system. Raw and untreated leachates have positive index values which signify the high risk of carbonate precipitation. Indexes for all electrodialysis process streams are calculated in Table 2. With respect to Table 2 data, it is observable that acidification decreases indexes value, however, acquisition of LSI = –0.2 requires a further pH decrease (see the model pH values in Table 2). Diluate stream of electrodialysis evinces noticeably negative LSI values in all cases, which means that the risk of membrane fouling by calcium carbonate precipitation is negligible. Precipitation in the electrodialysis concentrate streams is, in contrast, possible and thus careful monitoring of this process stream and continuous pH control are needed. A testing experiment, without acidification of the concentrate stream, acquired from processing of young leachate taken from Svébořice demonstrated that the white crystal precipitate arises in the stream at solution conductivity exceeding 70 mS/cm and pH higher than 8.25. An analysis confirmed that the crystal precipitate consists of calcium carbonate, magnesium ions, sulfates, chlorides and some metals (Fig. 2).

The results obtained from vessel tests, focused on the stability of ammonium ions and precipitation of organic compounds (humins), indicate that the amount of acid used for the pretreatment also influences precipitation of other compounds by the LSI value (Table 2). In the case of Tušimice leachates (Table 2), for example, acidification with a small amount of sulfuric acid (0.05–0.3 mL per 1 L of leachate) the LSI reaches very low values, while following sulfate ions increase threats by precipitation of sulfates. This was confirmed by experiments where different solid sulfates (white precipitates) are excluded in the concentrate stream. Based on these observations, it is important to use an alternative acid for acidification, that is, hydrochloric acid which does not increases saturation indexes which depend on the sulfate ion concentration in the leachate.

Barium sulfate has a low solubility coefficient ($1.08 \times 10^{-10}$) and therefore precipitates at extremely low concentrations. In addition, its precipitation equilibrium is shifted by the presence of sulfate ions supplied during acidification with sulfuric acid. Such acidification results in a definite prediction of barium sulfate precipitation in all the process streams. The presence of barium ions was not detected, however, in Fig. 2 which could be caused by higher detection limits of the used analytical method or because of the presence of fulvic acids (high affinity to metal ions), which can bind barium ions to their functional groups and prevent barium ions from binding with sulfates. The work of Martyniuk and Więckowska [24] described the possibilities of humin compounds in barium ions removal. If this hypothesis will be confirmed by further experiments,

Table 2
Calculation and modeling of saturation parameters for ED separation of leachates

| Sample No. | Process stream | TDS (g/L) | LSI | SDSI | pH Experimental | Model pH for LSI (–0.2) | $Mg(OH)_2$ saturation (%) | $CaSO_4$ saturation (%) | $BaSO_4$ saturation (%) | $SrSO_4$ saturation (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Svébořice feed, filtered | 9.57 | –0.13 | –0.434 | 7.16 | 7 | 0.0025 | 5.3 | 1,128 | 2 |
| 1 | Svébořice diluate | 2.61 | –1.83 | –1.793 | 6.56 | 8 | 0.0001 | 1.9 | 2,300 | 2 |
| 1 | Svébořice concentrate | 51.9 | 1.66 | 0.724 | 7.51 | 5.7 | 0.8000 | 41.8 | 4,011 | 10 |
| 2 | Svébořice feed, filtered | 9.08 | 0.42 | 0.086 | 7.43 | 6.8 | 0.0026 | 5.5 | 1,187 | 2 |
| 2 | Svébořice diluate | 2.56 | –1.5 | –0.732 | 7.08 | 8 | 0.0001 | 1.8 | 2,301 | 2 |
| 2 | Svébořice concentrate | 44.4 | 2.27 | 1.478 | 8.33 | 5.9 | 0.8200 | 8 | 1,650 | 5 |
| 1 | Tušimice feed, filtered | 4.86 | 0.51 | 0.361 | 7.58 | 6.9 | 0.0001 | 21.4 | 791 | 7 |
| 1 | Tušimice diluate | 0.884 | –3.05 | –2.662 | 6.2 | 9 | 0.0001 | 1.5 | 505 | 1 |
| 1 | Tušimice concentrate | 47.58 | 1.77 | 0.004 | 7.69 | 5.7 | 0.2600 | 192.3 | 4,731 | 40 |
| 2 | Tušimice feed, filtered | 2.57 | –0.87 | –0.843 | 6.9 | 7.6 | 0.0002 | 11.8 | 563 | 4 |
| 2 | Tušimice diluate | 0.868 | –4.22 | –4.148 | 5.23 | 9 | 0.0001 | 2.2 | 516 | 1 |
| 2 | Tušimice concentrate | 25.337 | 1.48 | 0.777 | 7.91 | 6.3 | 0.1400 | 133.9 | 3,988 | 26 |
| 3 | Tušimice feed, filtered | 5.43 | –8.36 | –8.45 | 3.21 | 8.3 | 0.1230 | 32.5 | 1,526 | 12 |
| 3 | Tušimice diluate | 0.874 | –8.48 | –7.33 | 3.57 | 9 | 0.0001 | 1.6 | 593 | 1 |
| 3 | Tušimice concentrate | 50.7 | –8.67 | –7.946 | 2.58 | 8.8 | 0.9300 | 160 | 9,453 | 69 |
| 1 | Zdechovice feed, coagulated | 15 | –0.18 | –0.803 | 6.69 | 6.7 | 0.0002 | 15.4 | 5,086 | 3 |
| 1 | Zdechovice diluate | 3.25 | –3.81 | –3.763 | 5.81 | 9 | 0.0001 | 0.3 | 888 | 2 |
| 1 | Zdechovice concentrate | 59.7 | 1.36 | 0.279 | 7.83 | 6.3 | 0.0400 | 45.9 | 2,827 | 6 |
| 2 | Zdechovice, feed filtered | 11.2 | –1.31 | –1.239 | 6.34 | 7.5 | 0.0003 | 12.9 | 1,247 | 6 |
| 2 | Zdechovice diluate | 2.665 | –0.62 | –0.453 | 7.58 | 8 | 0.0005 | 1.8 | 4,800 | 3 |
| 2 | Zdechovice concentrate | 42.82 | 1.87 | 0.946 | 8.25 | 6.2 | 0.2600 | 10.9 | 6,109 | 4 |

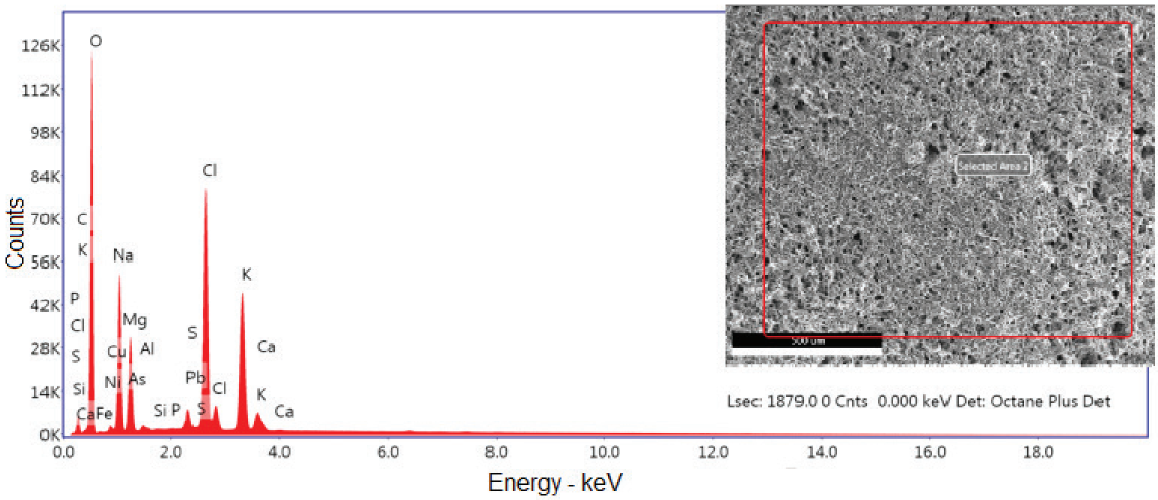

Fig. 2. Representation of the elements in the precipitate and an image of the resulting precipitate in the ED concentrate at 70 mS/cm (electron microscope).

then the fulvic acids can be considered a natural antiscalant, which shifts the precipitation equilibrium and prevents barium sulfate from precipitating on the membrane surface at certain concentrations.

Irreversible membrane fouling can also be caused by the long-term presence of ferric ions in the leachate. Based on experience from long-term running of membrane technologies, the maximal concentration of iron ions in the processed waters should not exceed 0.3 mg/L. The studied leachates exceed this value in their raw form up to 15 times. According to our previous measurements [23], it is apparent that the iron ions content can be significantly reduced by aimed chemical pretreatment completed by the creation of insoluble humin complexes with multivalent ions. A possible alternative is preprocessing by iron removal filters although these can be clogged by certain high-molecular humin compounds. No membrane clogging by iron ions was observed during our short-term experiments.

Fouling of ion exchange membranes by an organic matter (humates) present in leachate is also expected. Humic substances are electronegative because of their carboxyl content. There is, therefore, a possibility that they were also removed from the feed solution by an anion exchange membrane similarly to inorganic anions. Both internal and external fouling can increase the resistance of ED membrane. When internal fouling occurs, the transport of salt ions through the membrane is hindered by slow mobility or adsorption of organic molecules in the membrane. External fouling occurs when the layer of precipitated or adsorbed organic molecules on the membrane surface provides additional transport resistance.

### *3.3. Batch ED tests*

Experiments were carried out with several objectives: (1) to evaluate the performance of ion exchange membranes selected under various process conditions with the aim of determining the most convenient operating parameters; (2) to verify the potential of membranes for fouling and scaling; and (3) to test membrane cleaning (CIP) procedures.

#### *3.3.1. ED separation efficiency*

The expected benefit of the electrodialysis is predominantly a decrease in leachate salinity before reverse osmosis processing. RO then can be run at lower pressure differences and higher conversion ratios. Produced desalinated permeate can be utilized in the disposal humidification. Produced retentate with a high content of organic compounds and a lower content of salts can be recirculated back to the disposal without the risk of long-term salt accumulation. We focused in our experiments on specific compounds which represent limiting agents for long-term use of membrane technologies, especially the reverse osmosis. We also focused on compounds which represent a potential problem when recirculated back to disposal, that is, ammonium ions and chlorides. An additional monitored compound was boron, which is known by a small rejection when processed by reverse osmosis [25]. Releasing of water with a higher boron content into surface water is not legislatively limited (the limits are only for drinkable water) but this release should not be negligible any more from the long-term point of view.

The cumulative parameters and concentration of individual species in the electrodialysis technological streams are summarized in Tables 2 and 3. The overall salinity (TDS) of the diluate stream decreases to 18%–27% of the initial value. TOC values, however, decrease to only 64%–88% of the initial value. This fact demonstrates that a significant part of organic compounds remains in the diluate and part of TDS could be formed by soluble organic compounds (fulvic acids). It is apparent that with the high separation efficiency (around 80%), the total nitrogen content also decreased. Residual TN is composed of nitrate and nitrite ions. The selectivity of the used membranes depends dominantly on properties of ion exchange resins and Donnan equilibrium. The results for the investigated systems show that potassium, sodium, magnesium, and calcium cations and chloride, carbonate, and sulfate anions has similar transport properties and were very effectively removed from the diluate stream. A lesser removal efficiency was evinced by multivalent ions of $Fe^{3+}$, $Ba^{2+}$, $Sr^{2+}$ and $B^{3+}$.

In addition to the transport of ions through the ED membrane, the water balance was a significant factor influencing ED efficiency. A significant contribution of electroosmotic water transport that resulted from the migration of hydrated ions under the gradient of electrochemical potential was monitored during the experiments. On the other hand, in some cases, it was necessary to dilute the concentrate to overcome the scaling conditions for some compounds. For example, in the case of Svébořice feed, the volume of concentrate was changed from the initial 9 L to 45 L at the end of experiment; 30% of this was water from the electroosmotic transport.

The removal rate and the degree of desalination of the individual leachate samples primarily depends on the composition, temperature, membrane resistance and changes of current densities caused by changing ion content during the processing. CE of the process ranges from 36% to 72.9% and specific energy consumption ranges from 0.98 to 3.79 kWh/m$^3$ of leachate. Typical values of flux *J* are presented in Fig. 3.

### 3.3.2. Membrane fouling and cleaning procedures

Experiments aimed at an evaluation of the membrane fouling degree and testing the efficiency of the CIP procedures were also carried out. Fig. 3 shows both the reference salt permeation flux and the process permeation flux in different stages of the testing procedure. The testing began with a reference salt test (RST) using new ED membranes. The entire research scheme was consequently carried out for 2 months as can be seen in Fig. 3.

Only membrane clogging by humin compounds was visually observed during electrodialysis experiments. Yellow colored fulvic acids, which have a lower molar weight, were predominantly removed to the concentrate stream by the anion exchange membrane. This fact is confirmed by a high concentration of TOC in the concentrate stream (Table 3). If the pretreatment does not remove high-molecular humin compounds, then the risk of the surface membrane fouling increases and also some parts can be irreversibly integrated to the membrane inner structure, which decreases the membrane separation properties. Based on this fact, the membrane cleaning takes place after each experiment finished. CIP were carried out with a 1% solution of sodium hydroxide which dissolves humin compounds. The membrane module was then flushed by demineralized water. Several experiments were only completed with demineralized water flushing for the comparison. The results of the RSTs, which characterize the membrane cleaning process quality, are present in Fig. 3. It is obvious that apart from the last experiment with the non-pretreated Zdechovice leachate the cleaning of the membranes resulted in complete flux restoration.

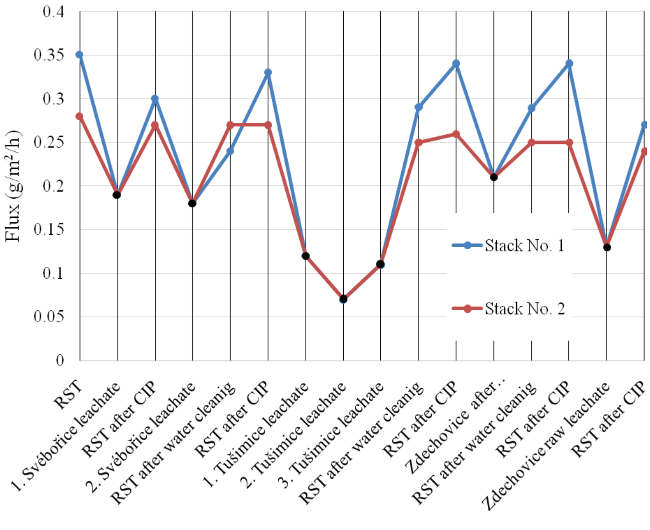

Fig. 3. Course of follow-up experiments and reference salt tests (RSTs) (short time horizon batch test).

### 3.4. ED concentrate amount and management

The designed membrane system creates an enclosed cycle, which manifests one problem of processing and utilization of the produced ED concentrate stream. The ED concentrate circuit in the batch experiments was kept at a certain concentration (conductivity 60 mS/cm) by continuous addition of demineralized water (RO permeate) to prevent the risk of the precipitation. In this case, the volume of the resulting concentrate was approximately 13.5%–14% of the diluate volume. If there is a continuous process of monitoring and the concentrate pH is kept low to achieve LSI below –0.2 (Table 2), then it will be possible to realize the process at a higher concentration degree which results in higher conductivities in the ED concentrate stream. It can be determined that the concentrate volume should be lower to the order of percent units of diluate volume. Technology waste (ED concentrate – hazardous waste) could be eliminated by incineration, or thanks to a higher content of ammonium ions and nitrate nitrogen, it could be mixed with sewage water and biologically processed in wastewater treatment plants.

## 4. Conclusions

Integrated landfill leachate treatment technology was developed combining advanced membrane processes with efficient conventional pretreatment methods. In the system electrodialysis reduces the salinity of landfill leachate which is consequently treated by conventional low-pressure reverse osmosis. Desalinated RO concentrate can be recycled back into the landfill body.

In order to verify the technology, the batch electrodialysis experiments were carried out with several types of leachate wastewaters which were collected from two municipal waste landfills and one landfill for the disposal of hazardous waste. The results can be summarized as follows:

- heterogeneous ion selective membranes from Mega a.s. demonstrated good selectivity and resistance against irreversible membrane fouling,
- excellent removal of TDS was found; the TDS content in the diluate was reduced to 18%–27% of the initial value,
- $K^+$, $Na^+$, $Mg^{2+}$, $NH_4^+$ and $Ca^{2+}$ cations were effectively separated as well as $Cl^-$, $CO_3^{2-}$ and $SO_4^{2-}$ anions,
- separation of multivalent ions, especially $Fe^{3+}$, $Ba^{2+}$, $Sr^{2+}$ and $B^{3+}$, and organic substances (TOC) was performed with low efficiency,
- acidifying the ED streams by HCl to LSI < –0.2 was a good alternative method to prevent membrane scaling,

Table 3
Chemical compositions of ED feed, diluate and concentrate for treatment of individual leachates (TDS and pH values are given in Table 2)

| Sample No. | Process stream | G (mS/cm) | TC (mg/L) | TIC (mg/L) | TOC (mg/L) | TN (mg/L) | B (mg/L) | Ba (mg/L) | Ca (mg/L) | Fe (mg/L) | Mg (mg/L) | Sr (mg/L) | $SO_4^{-2}$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Svébořice feed, filtered | 12.4 | 776 | 113 | 663 | 414 | 9.83 | 0.25 | 91 | 3.83 | 109 | 0.69 | 1,092 |
| 1 | Svébořice diluate | 2.25 | 606 | 21.7 | 584 | 114 | 9.4 | 0.25 | 20.4 | 4.35 | 19 | 0.25 | 530.3 |
| 1 | Svébořice concentrate | 64.3 | 1,450 | 574 | 872 | 2,760 | 9.27 | 0.54 | 375 | 0.25 | 550 | 2.52 | 7,519 |
| 2 | Svébořice feed, filtered | 12.6 | 908 | 212 | 696 | 499 | 8.45 | 0.25 | 95.3 | 4.12 | 110 | 0.65 | 1,020 |
| 2 | Svébořice diluate | 2.26 | 614 | 48.8 | 565 | 102 | 7.6 | 0.25 | 19 | 4.51 | 15.8 | 0.25 | 524.2 |
| 2 | Svébořice concentrate | 58.2 | 2,360 | 1,720 | 637 | 2,080 | 6.15 | 0.25 | 89.4 | 0.25 | 526 | 1.49 | 5,422 |
| 1 | Tušimice feed, filtered | 6.9 | 181 | 45.9 | 135 | 72.3 | 2.64 | 0.08 | 187 | 0.18 | 119 | 1.13 | 1,201 |
| 1 | Tušimice diluate | 1.1 | 106 | 5 | 105 | 9.2 | 2.57 | 0.05 | 17.1 | 0.36 | 11.7 | 0.11 | 335.5 |
| 1 | Tušimice concentrate | 56.7 | 419 | 233 | 186 | 715 | 0.1 | 0.25 | 701 | 0.25 | 764 | 4.15 | 17,795 |
| 2 | Tušimice feed, filtered | 3.64 | 129 | 22.5 | 107 | 7.04 | 2.2 | 0.05 | 98.3 | 0.36 | 64.6 | 0.62 | 793.9 |
| 2 | Tušimice diluate | 1.07 | 99.5 | 5 | 99.4 | 6.52 | 2.25 | 0.05 | 24 | 0.37 | 13.8 | 0.15 | 350.5 |
| 2 | Tušimice concentrate | 32.9 | 250 | 105 | 144 | 220 | 0.1 | 0.25 | 629 | 0.25 | 640 | 3.82 | 8,778 |
| 3 | Tušimice feed, filtered | 7.75 | 130 | 0.672 | 129.3 | 53.6 | 2.62 | 0.11 | 204 | 0.34 | 148 | 1.4 | 1,896 |
| 3 | Tušimice diluate | 1.1 | 99.6 | 0.5 | 99.4 | 8.4 | 2.09 | 0.05 | 15.7 | 0.18 | 11.2 | 0.1 | 382.5 |
| 3 | Tušimice concentrate | 59.7 | 165 | 5 | 165 | 754 | 0.1 | 0.62 | 741 | 3.42 | 1,640 | 9.09 | 13,481 |
| 1 | Zdechovice feed coagulated | 23.7 | 587 | 154 | 433 | 1,100 | 9.56 | 0.05 | 43.9 | 1.02 | 65.1 | 0.17 | 6,800 |
| 1 | Zdechovice diluate | 2.7 | 287 | 9.83 | 277 | 112 | 9.12 | 0.05 | 1.59 | 0.92 | 3.38 | 0.3 | 868 |
| 1 | Zdechovice concentrate | 73.8 | 418 | 319 | 99 | 4,310 | 0.1 | 0.11 | 127 | 0.05 | 254 | 0.45 | 22,500 |
| 2 | Zdechovice, feed filtered | 19.7 | 1,430 | 522 | 908 | 1,240 | 6.94 | 0.25 | 62.8 | 25 | 70.2 | 0.26 | 4,373 |
| 2 | Zdechovice diluate | 4.07 | 712 | 71.9 | 640 | 238 | 8.35 | 0.25 | 8.83 | 14.3 | 7.63 | 0.25 | 1,414 |
| 2 | Zdechovice concentrate | 62.9 | 2,410 | 1,670 | 739 | 4,180 | 0.1 | 0.25 | 32.9 | 0.25 | 263 | 0.34 | 17,495 |

- organic compounds, that is, fulvic substances found in the raw leachate as well as in various process ED streams, were the dominant fouling substances,
- effective method to recover the systems from physical and chemical reversible fouling, using alkaline CIP, was found and verified.

High overall water recovery can be achieved from the integrated RO–ED system suggested. Thus, in this case, ED can both technically and environmentally be a good option to desalinate RO feeds.

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## Symbols

| | | |
|---|---|---|
| $BOD_5$ | — | 5-d biochemical oxygen demand |
| CE | — | Current efficiency |
| CIP | — | Cleaning in place |
| COD | — | Chemical oxygen demand |
| EC | — | Specific energy consumption |
| ED | — | Electrodialysis |
| $G$ | — | Conductivity |
| LSI | — | Langelier saturation index |
| RO | — | Reverse osmosis |
| RST | — | Reference salt test |
| SDSI | — | Stiff–Davis saturation index |
| TC | — | Total carbon |
| TDS | — | Total dissolved substances |
| TIC | — | Total inorganic carbon |
| TN | — | Total nitrogen |
| TOC | — | Total organic carbon |
| WWTP | — | Wastewater treatment plant |

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