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Nanofiltration of salt solutions and landfill leachate

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Abstract

Nanofiltration (NF) has attracted increasing attention during recent years due to the development of new applications. The advantage of NF compared with reverse osmosis (RO) and ultrafiltration (UF) is that it is possible to separate organic substances from some types of salts. It is, furthermore, also possible to separate different kinds of salts due to the negatively charged groups on the membrane. The retention of sulphate salts by the membranes used in this investigation was 88–96%, while the retention of chloride salts was only 12–47% at low salt concentrations. This difference in retention is due to the charge density of the anion. The retention of NaCl was found to be strongly related to the concentration. The retention decreased from 45% to 7% when the concentration was increased from 0.05 M to 1 M. Although the repulsion of the anion mainly determines the retention of salt solutions, it was observed that the cation can affect the retention, especially in salt solutions with a high concentration of monovalent anions. It was found that the retention of divalent cations was three times higher than that of monovalent cations in this type of salt solution. In chloride solutions with mixed cations, it was shown that a monovalent cation passed through the membrane preferentially to the divalent cations, to such an extent that the retention became negative. NF was utilized to treat a landfill leachate with an extremely high salt content from a waste cell containing mainly ash because of the good separation of cations. Most of the heavy metals, which are multivalent cations, are rejected while the monovalent cations, which are rather harmless substances, pass through the membrane. The retention of, for example, cadmium, zinc, lead and chromium was found to be higher than 70%, while the retention of potassium and sodium was less than 10%. Since the transmembrane osmotic pressure was low, due to the low retention of the monovalent ions, the flux was several times higher than for RO membranes. The flux of the leachate, with a conductivity of 6800 mS/m, was above 50 l/m^2h at 3 MPa and 25°C.

Keywords: Nanofiltration; Salt; Retention; Landfill leachate; Ash; Waste water

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1. Introduction

The treatment of landfill leachate has been the subject of increasing interest during recent years, and several commercial RO leachate treatment plants have been installed in, e.g., Germany, the Netherlands and Switzerland. At the Spillepeng landfill in Malmö, Sweden, a new landfilling technology is being used where the waste is divided into three different categories and deposited in waste cells with separate leachate-collecting systems. The waste is divided into industrial waste, biodegradable waste and special waste. This gives different types of leachates with different characteristics. In a previous study [1] where leachates from the biodegradable waste cell and a conventional landfill were treated with RO, a good correlation was found between flux and the conductivity of these leachates, irrespective of origin. It was, however, also observed that the conductivity, and thus the osmotic pressure, was too high in the leachate from the cell containing special waste for RO to be a suitable treatment process for this type of leachate.

The high salt content in the leachate from the special waste cell arises to a great extent from monovalent ions such as chloride, sodium and potassium, although the concentration of heavy metals is also relatively high. NF is therefore a very interesting method of treatment for this type of leachate, as the retention of monovalent, rather harmless, ions is low, whereas heavy metals are usually present as multivalent ions, are well hydrated, and therefore have a higher retention [2].

NF is already used to treat conventional landfill leachates in combination with biological treatment and RO [3]. The purpose of using NF in combination with biological treatment is to recycle most of the concentrate, which contains recalcitrant and non-biodegradable organics, from the NF to the biological process. This results in a higher rate of biodegradation without increasing the hydraulic residence time.

The objective of the work presented in this paper was to investigate the possibility of using NF when treating a landfill leachate with a high salt content. However, leachates are very complex waste waters containing a mixture of many different inorganic ions and organic components, varying in concentration, thus influencing the performance of the NF membranes. The influence of the charge density of anions and cations on flux and retention was therefore studied using reference solutes.

2. Nanofiltration

Nanofiltration is a membrane process between RO and UF. During NF, substances are rejected by two principles: the rejection of neutral species by size (molecules larger than 200–300 g/mole are rejected), and the rejection of inorganic ions due to electrostatic interactions between the ions and the membrane [4–9]. It is thus possible to separate organic substances from monovalent inorganics, and NF was in fact originally designed to desalt whey. The area of application has, however, increased into other fields such as water softening, decolourization of textile dye house wastes, decolourization of citrus and sugar molasses, treatment of metal-containing waste waters from metal finishing industries and removal of sulphate from sea-water in off-shore oil well applications [2,7–16].

Various types of commercial NF membranes are available, and the separation performance of these membranes varies greatly [4,7,8,11,17]. Most NF membranes are thin-film composite membranes of hydrophobic polymers with negatively charged groups incorporated [8].

Since the membranes are negatively charged, it is the anion repulsion which mainly determines the solute retention of salt solutions. The degree of retention increases with increasing valency of the anion due to the increased repulsion by the membrane (e.g., the retention of sulphate ions is considerably higher than the retention of chloride ions). The cations are rejected to the same extent as the anions due to the requirement of electroneutrality.

However, the degree of retention can decrease with increasing valency of the cations, since high-valency cations cause membrane charge shielding. This would, for example, result in a lower retention of $CaCl_2$ than of NaCl [5,6,17,18]. The charge of the anion, however, still dominates the degree of retention.

The degree of hydration can also influence the retention. The retention of $NaNO_3$ is lower than of NaCl because the nitrate ion is more hydrated in aqueous solution than the chloride ion. This reduces its effective charge, which in turn reduces the retention [18].

The mechanism of retention is more complex in mixed salt solutions. In a mixed solution with NaCl and Na_2SO_4, the concentration of the divalent anion influences the monovalent anion retention. When Na_2SO_4 is added to a solution of constant NaCl concentration, the retention of Cl^- decreases as the concentration of Na_2SO_4 increases. The Na^+ ions which readily pass through the membrane must be accompanied by a negatively charged ion in order to maintain electroneutrality. The negatively charged ions are, however, repelled by the negatively charged membrane. The Cl^- ions with the lower potential are forced to permeate preferentially compared with the SO_4^{2-} ions, and even a negative retention of Cl^- has been observed. This is known as the Donnan effect [4,7,19]. The same phenomenon is observed with a mixture of NO_3^- and SO_4^{2-} ions [19].

3. Materials and methods

3.1. Landfill leachate

The leachate used in the investigation was collected at the Spillepeng landfill in Malmö, Sweden. The landfill is managed by SYSAV (Southwest Scania Solid Waste Company) and includes an older, conventional landfill and a new type of landfill. At the new Spillepeng landfill brought into operation in 1990, the waste is divided into three different categories and deposited in waste cells with separate leachate-collecting systems. The waste is divided into industrial waste, biodegradable waste and special waste, which mainly contains ashes (55% by weight). The leachate studied was that from the special waste cell. Treatment of the other types of leachates by RO have been investigated in a previous study [1].

The leachate from the special waste is characterized by an extremely high conductivity, as shown in Fig. 1, partly due to a very high chloride concentration. Concentrations above 55 g chloride/l have been measured. The conductivity of the leachate, which is related to the salt concentration, is an important parameter in membrane processes due to the relation between salt concentration and osmotic pressure.

The chemical oxygen demand (COD) content in the leachate is surprisingly high (also shown in Fig. 1). The high COD content may be derived from special wastes other than ashes with a high organic content which are also deposited in this cell. The high COD levels measured may also be due to the high concentration of chlorides which may interfere with the analysis of COD.

The leachate from the special waste cell is also characterized as a leachate with high concentrations of heavy metals. The concentration variations for cadmium, copper, zinc and lead are shown in Fig. 2.

The leachates used in the experiments described in this paper were collected on different occasions. Before treatment with NF the leachate was filtered through a 0.35 mm mesh.

3.2. Reference solutes

The reference solutes used to study the influence of anion charge density and cation interaction were solutions of NaCl, KCl, $CaCl_2$, $MgCl_2$, Na_2SO_4 and $MgSO_4$. All salts were of puriss grade.

3.3. Membranes

Two types of tubular NF membranes were used in the investigation: AFC30 and a newly

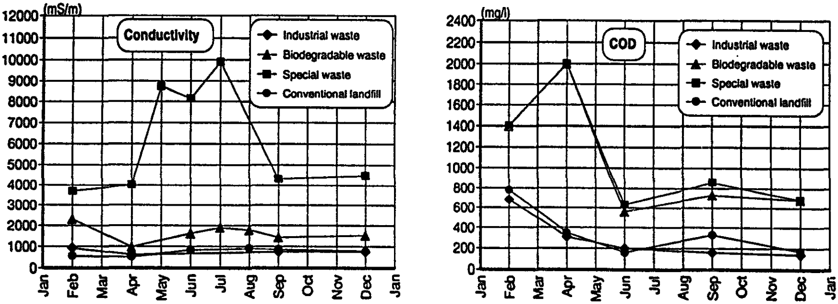

Fig. 1. Conductivity and COD in four different types of leachate at the Spillepeng landfill during 1993. The results are from the SYSAV landfill leachate analysis programme.

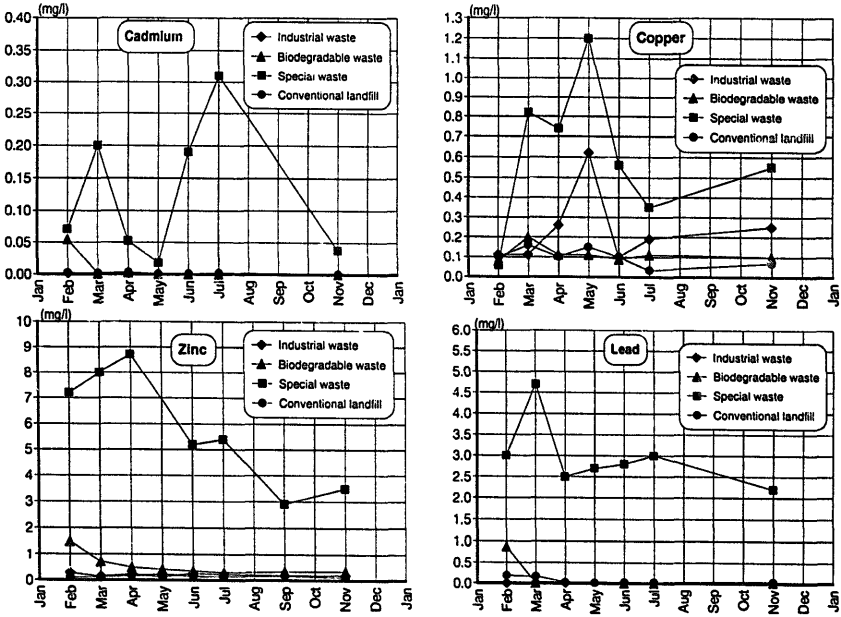

Fig. 2. Concentration of cadmium, copper, zinc and lead in four different types of leachate at the Spillepeng landfill during 1993. The results are from the SYSAV landfill leachate analysis programme.

developed membrane, AFC40. Both membranes are manufactured by PCI Membrane Systems. These NF membranes are thin-film composite membranes with negatively charged groups.

3.4. Equipment

The experiments were performed in a pilot-plant unit equipped with single-tube modules. In this way the two types of membranes could be tested simultaneously. Four membrane tubes, two of each type, were connected in series. The membrane area of each tube was 0.04 m^2.

The temperature was maintained at 25°C, and the cross-flow velocity was 2.8 m/s. The operating transmembrane pressure difference was 2 MPa, except in one experiment in which the pressure varied between 1.5 and 3 MPa.

The membranes were cleaned before and after each test with an enzyme cleaning agent, 0.5% Ultrasil 53 from Henkel at 40–45°C for about 60 min. The system was rinsed with deionized water before and after cleaning. After every cleaning procedure the pure water flux was measured in order to check the condition of the membrane. The salt retention was tested with a 0.5% Na_2SO_4 solution. The membranes were stored in a 0.05% sodium bisulphite solution when not being used.

3.5. Analyses

The conductivity of the feed and permeate was measured with a Phillips PW9526 conductivity meter. The concentration of metals was determined by inductively coupled plasma emission spectroscopy (ICP ES).

4. Results

4.1. Anion separation efficiency

The retention of calcium chloride was found to be about the same as that of sodium chloride, while the retention of sodium sulphate was about the same as that of magnesium sulphate, as shown in Fig. 3. The degree of retention increased with increasing valency of the anion, due to the increased electrostatic repulsion by the membrane, which is a characteristic property of NF membranes. There is, however, a slightly lower retention for anions with divalent cations compared with monovalent cations as high-valency cations cause membrane charge shielding.

The flux of the salt solutions, shown in Fig. 4, was approximately the same, with the exception of the NaCl solution which exhibited a flux that was even higher than the pure water flux.

The retention of sodium chloride decreased with increasing sodium chloride concentration, as shown in Fig. 5. The higher the concentration of salt, the more cations are available to shield the negative charges on the membrane, making it easier for the anions to pass through the membrane [5–7,9,16]. The sulphate ion has, however, a higher charge density than the chloride ion and is almost completely repelled by the membrane, even in high-ionic-strength solutions such as sea water or 4% magnesium sulphate solution [9].

4.2. Cation separation efficiency

Studies of the influence of cation interactions during NF are scarce in the literature. The influence of one cation on the retention of other cations was therefore studied in this investigation. To be able to evaluate the variation in retention for different cations, it was necessary to choose salts with an anion with low retention. All the tests with different cations were therefore performed with the chloride salt of the cations. A constant chloride concentration of approximately 1 M was used in all tests, since the chloride concentration should not influence the retention of the cations. The concentration of salt was chosen to be as high as 1 M with respect to chloride because it corresponds approximately to the chloride concentration in the leachate. The high concentration results in a very low retention of the chloride ions, as shown in Fig. 5. Under these conditions

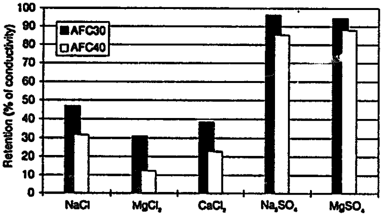

Fig. 3. Retention of salts with mono- and divalent anions in 50 mM single-salt solutions.

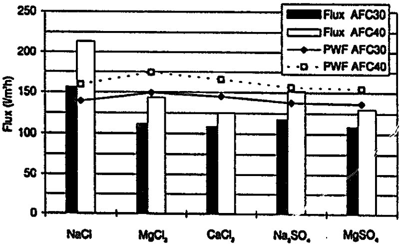

Fig. 4. Flux of salts with mono- and divalent anions in 50 mM single-salt solutions and the pure water flux (PWF) before the test.

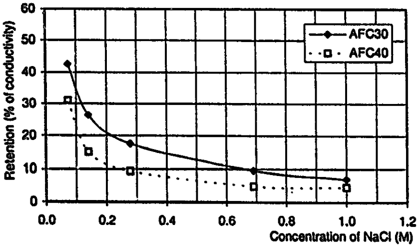

Fig. 5. Influence of NaCl concentration on retention.

the cation, and not the anion, mainly influences the retention.

The retention and flux of cations in single-salt solutions are shown in Fig. 6. The retention is approximately three times higher for the divalent

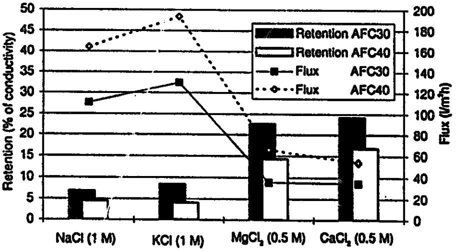

Fig. 6. Flux and retention of different cations in four different 1 M chloride solutions.

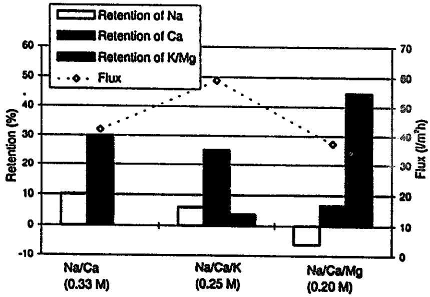

Fig. 7. Flux and retention of different cations in mixed cation solutions. The concentration of chloride was 1 M in all three solutions. $[Na^+]=[Ca^{2+}]$ in the first test, $[Na^+]=[Ca^{2+}]=[K^+]$ in the second test and $[Na^+]=[Ca^{2+}]=[Mg^{2+}]$ in the last test. The results in the figure are for the AFC30 membrane. Similar results were obtained with the AFC40 membrane.

cations than for the monovalent cations. This higher retention can be correlated to a lower diffusion coefficient (see Table 1), but the diffusion coefficient is probably just one cause among many of the higher retention. In this test the concentrations of the monovalent cations and the divalent cations differed due to the restriction of a constant chloride concentration. The same difference in retention was still found in a mixed salt solution of sodium and calcium with equimolar amounts of the cations, as is shown in Fig. 7.

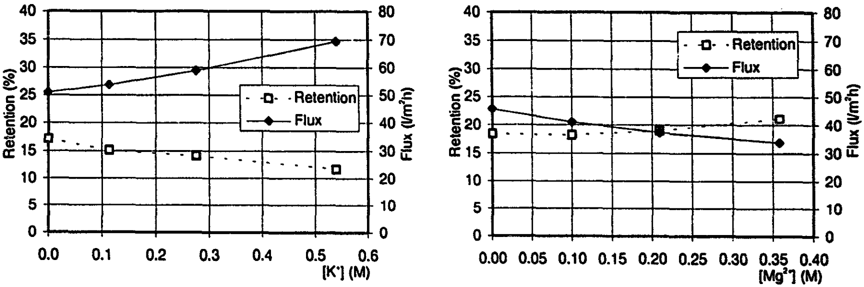

Fig. 8. Retention (% of conductivity) and flux of mixed salt solutions. The concentration of chloride was 1 M and [Na$^+$]=[Ca^{2+}] in all solutions. The results in the figure are for the AFC30 membrane. Similar results were obtained with the AFC40 membrane.

Table 1
Ionic diffusion coefficients in water at 25°C and infinite dilution

Metal ion	Diffusion coefficient (cm^2/s)
Potassium	$1.96\cdot10^{-5}$
Sodium	$1.33\cdot10^{-5}$
Calcium	$0.79\cdot10^{-5}$
Magnesium	$0.71\cdot10^{-5}$

The effect of lower retention due to shielding of the negatively charged groups on the membrane caused by the higher charge density of divalent cations in single-salt solutions, which was mentioned earlier (see Fig. 3), is eliminated by the high concentration of cations.

The flux of single-salt solutions is much higher for the monovalent salts than the divalent, as shown in Fig. 6, partly due to a lower osmotic pressure difference. The same tendency is found for mixed solutions with three different cations. In Fig. 8 it can be seen that the retention is reduced and the flux increased when the proportion of monovalent cations is increased and vice versa for an increasing proportion of divalent cations.

Fig. 7 shows that the addition of potassium influences the retention of sodium and calcium to a minor extent. However, the retention of sodium and calcium was found to be dramatically affected by the addition of magnesium.

Most of the negatively charged groups on the membrane are shielded by cations at high salt concentration, and therefore the chloride ions can readily pass through the membrane. The chloride ions are accompanied by the cations which most easily pass through the membrane. Therefore, potassium does not influence the retention of calcium and sodium, as there is already a cation, sodium, present in the solution, which easily passes through the membrane together with the chloride ion. In the system with sodium, calcium and magnesium, the amount of cations that easily passes through the membrane decreases when magnesium is added to the solution. Sodium is the cation which passes through the membrane preferentially to the other two metals in the solution. Sodium even has a negative retention and magnesium a higher retention than in the single-salt solution, as shown in Fig. 7. The negative retention of sodium implies that there is a negative concentration gradient. Fig. 9 shows how the retention of sodium and calcium is drastically altered when magnesium is added. The retention of calcium is also reduced when magnesium is added, as is also shown in the figure.

The effect of the most retained cation is analogous to the earlier discussion of the reducing

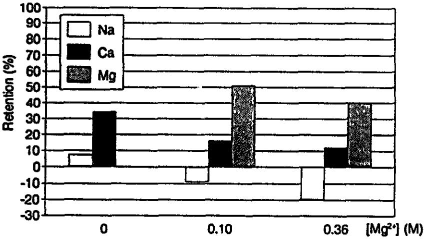

Fig. 9. The retention of sodium, calcium and magnesium at various magnesium concentrations. The concentration of chloride was 1 M and $[Na^+]=[Ca^{2+}]$ in all solutions. The results in the figure are for the AFC30 membrane. Similar results were obtained with the AFC40 membrane.

retention of NaCl at increasing concentration of Na_2SO_4.

4.3. *Landfill leachate*

The reduction in flux with time when treating landfill leachate was studied. Both retentate and permeate were recycled to the feed tank. The initial flux of the AFC30 and AFC40 membranes at 2 MPa was 40 and 65 l/m^{2}h, respectively, and after 4 days 16 and 30 l/m^{2}h. The flux decline with time is shown in Fig. 10. The flux was recovered after cleaning.

The reduction in the concentration of metals was, of course, lower than during RO [1], but the reduction in most of the hazardous metals was still high, as shown in Table 2. The retention of the different metals can be found in Fig. 11.

The chloride ion is the dominating ionic species in this type of leachate, with a concentration of 0.93 M on this occasion. The high concentration of chloride and the mixture of monovalent and multivalent cations makes it possible to compare the results with the tests with the reference solutions of cations. Fig. 11 shows that the retention of monovalent cations is very low, while most of the divalent cations are rejected, analogous to the results from the tests with the reference solutions of cations. Metals such as cadmium, chromium, nickel, lead and zinc have a retention higher than 70% and potassium and sodium a retention less than 10%. The calculation of the retention of the metals is based on the results in Table 2; as can be seen, the concentration of some metals in the permeate was too low to be detectable, which explains the low retention of, for example, copper. The retention of total organic content (TOC) was relatively high, about 55%, which gives a concentration of less than 70 mg TOC/l in the permeate.

The flux increases with increasing transmem-

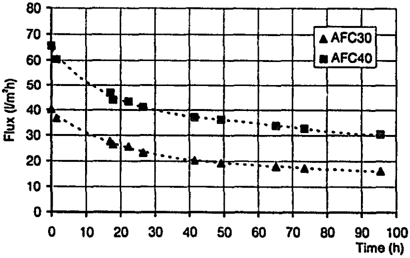

Fig. 10. The flux reduction with time at 25°C and 2 MPa. The leachate was prefiltered, but no other pretreatment was performed. As the pH was below 6.5, no pH adjustment was made to prevent precipitation of $CaCO_3$. The conductivity of the leachate was 6100 mS/m.

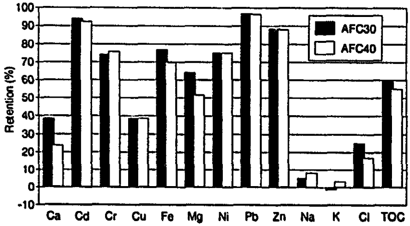

Fig. 11. Retention of different metal ions in the landfill leachate. Note that the retention is based on the results from Table 2 and that the retention of some metals is probably higher than indicated in this figure as the detection limit of some metals was reached.

Table 2
Reduction in the metal concentration by nanofiltration of leachate

Substance	Feed (mg/l)	Permeate AFC30 (mg/l)	Permeate AFC40 (mg/l)
Calcium	12,887	7,918	9,822
Cadmium	0.033	0.002	0.003
Chloride	37,054	27,689	30.791
Chrome	0.029	0.008	<0.007
Copper	0.011	<0.007	<0.007
Iron	85.80	19.74	25.85
Potassium	3,940	4,004	3,813
Magnesium	243.5	87.6	117.9
Sodium	6,400	6.068	5,874
Nickel	0.016	<0.004	<0.004
Lead	0.609	<0.020	0.022
Zinc	0.495	0.058	0.060
TOC	142	57	64

brane pressure, as shown in Fig. 12. With a leachate feed conductivity of 6800 mS/m, the flux was 55 and 75 l/m^{2}h for the AFC30 and AFC40 membranes at 3 MPa and 25°C. This can be compared with the RO membrane flux of 2 l/m^{2}h, when treating the same leachate with a conductivity of 8750 mS/m at 5 MPa and 20°C [1].

The retention, based on the conductivity, increased slightly with the pressure, as shown in Fig. 12. The retention of most of the metals and TOC was found to follow the same tendency, and therefore it can be concluded that the pressure can be increased to achieve higher capacity without risk of poorer separation.

The AFC40 membrane exhibited a higher flux but a lower retention than the AFC30 membrane when treating both the reference solutions and the leachate. The difference in retention of the heavy metals was, however, very small. It therefore seems to be most economical to choose the AFC40 membrane for the treatment of landfill leachate.

5. Conclusions

When treating salt solutions with NF, it was shown that the retention of sulphate salts was significantly higher than the retention of chloride salts, due to the larger electrostatic repulsion of the multivalent anion by the negatively charged membrane. Although the electrostatic repulsion of the anion mainly determines the retention of salt solutions, it was found that the retention of multivalent cations was about three times higher than the retention of monovalent cations in solutions with a high concentration of monovalent anions.

In solutions with different cations and a high concentration of monovalent anions, the passage of cations was determined by the highest rejected species, analogous to the behaviour in mixtures of

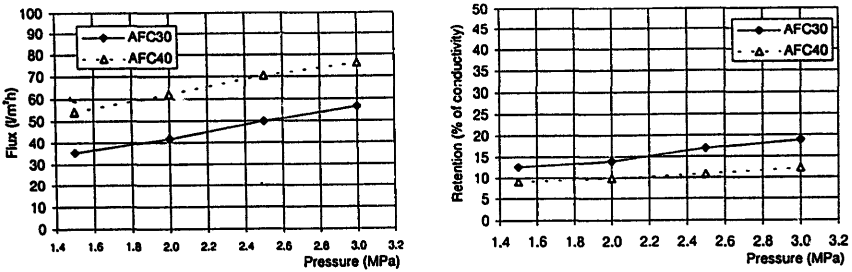

Fig. 12. Flux and retention related to the pressure at 25°C and a feed conductivity of 6800 mS/m.

anions. In a mixture of sodium and calcium ions the retention decreased dramatically for both sodium and calcium when magnesium ions was added to the system. Magnesium is the cation most retained in the mixture and forces the other two cations to pass through the membrane to a greater extent. This results in a negative retention of sodium and a higher retention of magnesium than in a pure magnesium chloride solution.

A landfill leachate with an extremely high salt content was treated by NF. Most of the heavy metals, multivalent cations, were rejected while the monovalent, rather harmless, cations passed through the membrane. The retention of, for example, cadmium, zinc, lead and chromium was higher than 70%, while the retention of potassium and sodium was less than 10%. The transmembrane osmotic pressure was low due to the low retention of the monovalent ions, and the flux several times higher than for RO membranes. These results show that NF is a very promising method of treatment for this type of waste water.

6. Acknowledgements

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