Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Zirconium and Hafnium Separation, Part 3. Ligand-Enhanced Separation of Zirconium and Hafnium from Aqueous Solution using Nanofiltration

L. Poriel[a]; F. Chitry[a]; S. Pellet-Rostaing[a]; M. Lemaire[a]; A. Favre-Réguillon[b]
[a] Laboratoire de Catalyse et Synthèse Organique, CPE, Université Claude Bernard Lyon, Villeurbanne, France [b] Laboratoire de Chimie Organique, Conservatoire National des Arts et métiers, Paris, France

To cite this Article Poriel, L. , Chitry, F. , Pellet-Rostaing, S. , Lemaire, M. and Favre-Réguillon, A.(2006) 'Zirconium and Hafnium Separation, Part 3. Ligand-Enhanced Separation of Zirconium and Hafnium from Aqueous Solution using Nanofiltration', Separation Science and Technology, 41: 13, 2883 — 2893

To link to this Article: DOI: 10.1080/01496390600725810

URL: http://dx.doi.org/10.1080/01496390600725810

Separation Science and Technology, 41: 2883–2893, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600725810

Zirconium and Hafnium Separation, Part 3. Ligand-Enhanced Separation of Zirconium and Hafnium from Aqueous Solution using Nanofiltration

L. Poriel, F. Chitry, S. Pellet-Rostaing, and M. Lemaire
Laboratoire de Catalyse et Synthèse Organique, CPE, Université Claude
Bernard Lyon, Villeurbanne, France

A. Favre-Réguillon
Laboratoire de Chimie Organique, Conservatoire National des Arts et
métiers, Paris, France

Abstract: Membrane filtration equipment was used to evaluate zirconium and hafnium separation efficiency by a membrane separation process. High rejection of Zr and Hf species in aqueous solution were obtained with nanofiltration and ultrafiltration membranes. This high rejection could be explained by the formation of high molecular weight polynuclear species. Enhanced transportation across the nanofiltration and ultrafiltration membranes was observed when aminocarboxylic ligands, like EDTA, were introduced in the solution. This enhancement could be explained by a depolymerization process of the polynuclear complexes induced by the ligands. The rejection of Zr and Hf was markedly influenced by the counter anions and the EDTA/metal ratio. By using Zr and Hf oxynitrates instead of oxychlorides a difference of rejection of up to 20% was observed for Zr and Hf

Received 26 October 2005, Accepted 7 March 2006

Address correspondence to A. Favre-Réguillon, Laboratoire de Chimie Organique, UMR CNRS 7084, CNAM, 2 rue Conté, 75003 Paris, France. E-mail: alain.favre-reguillon@univ-lyon1.fr and M. Lemaire, Laboratoire de Catalyse et Synthèse Organique, UMR CNRS 5181, CPE, Université Claude Bernard Lyon 1, 43 boulevard du 11 novembre 1918, 69622 Villeurbanne, France. E-mail: marc.lemaire@univ-lyon1.fr

indicating that the membrane separation process could be an alternative process for Zr and Hf separation.

Keywords: Zirconium, hafnium, separation, nanofiltration

INTRODUCTION

Zirconium has a very low absorption cross-section for thermal neutrons and is therefore used for nuclear energy applications such as cladding of nuclear fuel rods. However, hafnium has a good absorption cross-section for thermal neutrons (almost about 600 times that of zirconium) and is used as control rods in the reactors. Thus the presence of one element, even in trace quantities, with the other could exert a profound influence on the nuclear properties of the system. However, zircon sand ($ZrSiO_4$), the major mineral for zirconium metal production, contains 1% hafnium. There is a substitution of Hf into the Zr sites of the mineral lattice. In part 1 and 2 of this set of papers regarding the Zr and Hf separation, liquid/liquid and solid/liquid extraction have been reviewed and studied (1, 2). Numerous alternative processes have been proposed for the separation of Hf from Zr, like the flotation technique (3, 4), crystallization of potassium fluorozirconate (5), and anhydrous Zr-Hf separation techniques (6, 7). However, these processes have not been applied on a commercial scale with the exception of the fractional cristallization process (5) and extractive distillation of zirconium and hafnium tetrachloride in molten potassium chloride-aluminum chloride (Cezus process) (8–10).

Membrane processes, particularly nanofiltration (NF) and ultrafiltration (UF), have been found to be very useful in recent years in wastewater treatment and drinking water production (11). The ability of membrane processes for the rejection (12–14) or fractionation of mono- and multi-valent cations (15, 16) leads the way to potential applications for ion separation. To increase the ion separation, the NF process can be associated with a preliminary selective complexation step of the target ions with water soluble ligands. Thus, the resulting complexes could be rejected by the membrane, whereas the non-complexed ions pass through it. It is this principle of nanofiltration assisted by complexation (17–21) which was applied to various ion separations.

To understand the separation characteristics of Zr and Hf species under the conditions of membrane processes and hence to evaluate these processes for the separation of these elements, experiments were conducted using different membranes with varying molecular weight cut-offs (MWCO). The effect of a water-soluble chelating agent and counter-ion on the Zr and Hf rejection by nanofiltration and ultrafiltration membranes were then evaluated.

EXPERIMENTS

The mixture of zirconium (IV) and hafnium (IV) chloride ($Zr/(Zr + Hf) = 0.71$ molar ratio) was provided by CEZUS. The preparation of zirconyl and hafnyl(IV) nitrate hydrate from $ZrCl_4/HfCl_4$ (Zr/(Zr + Hf) = 0.71 molar ratio) was made according to described procedure (22). The aqueous phases were prepared by dissolving the Zr/Hf mixture in aqueous solution. The pH of the solutions was adjusted by addition of concentrated hydrochloric or nitric acid. Zr and Hf analysis was carried out by ICP-AES spectrometry with a SpectroD ICP spectrometer.

Ethylenediaminetetraacetic acid (EDTA) and Triethylamine hydrochoride (TEA-HCl) (Aldrich) were used as received.

Membrane experiments have been performed with a lab-scale membrane cell where the schematic flow diagram of the system has been previously described (16). The nanofiltration organic membrane Desal G10 is a thin film composite membrane manufactured by Osmonics. The membrane area is 150 cm^2 and the MWCO is 2500 Da (23). The active layer of the G10 membrane (1.2 μm) is made from polyamide. The spectra, used to identify functional groups, were obtained with an attenuated total refractive Fourier transform infrared (ATR-FTIR) spectrophotometer (Bruker Equinox 55) equipped with a diamond ATR unit (24). Before starting experiments, the membrane is activated and conditioned as already described (16). The ultrafiltration inorganic membranes, Pall 1 and Pall 5, are tubular membranes manufactured by Pall Exekia. The tubular membrane area is 50 cm^2 and the MWCOs are 1 and 5 kDa, respectively.

The feed is kept at a constant composition during the experiments by totally recycling the permeate and the retentate. The rejection (*R* %) of a substance *i* was defined according to Eq. (1):

$$R_i(\%) = \left(1 - \frac{C_{ip}}{C_{ir}}\right) \times 100 \qquad (1)$$

where C_{ir} is the concentration of i in the retentate and C_{ip} is the concentration of i in the permeate. The ability of a solute to pass through the membrane (transmission) can be expressed according to Eq. (2):

$$T_i(\%) = \frac{C_{ip}}{C_{ir}} \times 100 = (1 - R_i) \times 100 \qquad (2)$$

The separation selectivity of two solutes by the membrane can be represented by the ratio of their transmissions. Thus the selectivity of the separation of compounds i and j can be defined according to Eq. (3):

$$S_{i/j} = \frac{T_i}{T_j} \qquad (3)$$

where T_i represents the transmission of i.

RESULTS

Zr and Hf Rejection by NF and UF Membranes

High rejections of Zr and Hf with NF and UF membranes were achieved from mixtures of the two elements (Table 1). This high rejection could be explained by special hydrolysis chemistry of Zr(IV) and Hf(IV) compared to other heavy-metal ions like Th(IV) or Pu(IV) (25, 26). The chemistry of Zr (and by extension of Hf) in aqueous media is dominated by the complexation of Zr^{4+} with OH^- (27). Zr and Hf are chemical species that show a high tendency to polymerize in aqueous solutions through reactions that depend on experimental conditions, such as pH, concentration, nature, and concentration of the mineral acid, age of the solutions and temperature (26, 28). For both metals, the formation of polynuclear hydroxo-bridged compounds in acidic solutions ($[H^+] = 1-2\,\mathrm{mol\,L^{-1}}$) occurred even in very dilute solutions ($10^{-3}-10^{-4}\,\mathrm{mol\,L^{-1}}$) (25, 29). The presence of tetranuclear aqua-hydroxo-complexes, i.e. $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, in acidic aqueous solutions has been confirmed both by proton NMR, Raman spectrometry (26). Furthermore, recently, a crystal structure of Zr and Hf tetranuclear aqua hydroxo complexes was obtained from $MOCl_2$ in 2 M HCl in the presence of macrocyclic cavitand cucurbituril (M=Zr or Hf) (30). The tetranuclear cation $[M_4(OH)_8(H_2O)_{16}]^{8+}$ forms a slightly distorted square with Zr or Hf at all corner. The length of the side is close to 3.5 Å (30), and size difference between Zr and Hf tetranuclear cations is less than 0.5%.

The aqueous chemistry of Zr has been more extensively studied than that of Hf. However, due to their close chemical similarity, the expected behavior of the dissolved Hf can often be deduced from the knowledge of analogous Zr solutions. Thus, these oligomeric charged species are highly rejected by NF and UF membranes. As expected lower rejection of Zr and Hf were found using Pall 5 membranes with a MWCO of 5 KDa (Table 1).

Table 1. Rejection of Zr and Hf oxychloride as the function of the membrane studied

	Rejection (%)	
Membrane	Zr	Hf
Desal G-10[a]	99 ± 2	98 ± 5
Pall 1[b]	96 ± 2	95 ± 2
Pall 5[b]	22 ± 2	23 ± 2

[a] pH = 2; [Zr] = 0.126 mmol/L; [Hf] = 0.048 mmol/L $\Delta P = 1$ bar, retentate flux: 9L/min., 20°C.

[b] pH = 1; [Zr] = 27 mmol/L; [Hf] = 11 mmol/L $\Delta P = 0.5$ bar, retentate flux: 9L/min., 20°C.

Influence of the Chelating Agent on Zr and Hf Rejection

Aminocarboxylic ligands, like EDTA, are known to form complexes with a great variety of heavy-metal ions (31). Aminocarboxylate ligands bind strongly to Zr(IV), and complexes have been reported, some of which have been crystallized from aqueous solutions (32). Zr(IV) and Hf(IV) complexes with EDTA are characterized by a high thermodynamic stability (Log K = 28.1 and log K = 29.5 for Zr and Hf respectively) (31) even if the behaviour of Zr and Hf differs in macro- and microconcentrations (33). Therefore, we studied the influence of the organic chelating agent on the rejection of Zr and Hf with NF and UF membranes.

Fig. 1a shows the rejection of Zr and Hf with increasing concentration of EDTA with the inorganic Pall 1 membrane. The rejection of Zr and Hf decreased from 95% to 35% on increasing EDTA/metal ratio. Thus, the enhancement of the transport of Zr and Hf across the membrane induced by EDTA was demonstrated. This could be explained by a depolymerisation process of the tetranuclear complexes induced by EDTA according to Eq. (4).

$$[Zr_4(OH)_8]Cl_8 + n\ EDTA \rightleftharpoons n[EDTA \sim Zr] + [Zr_{4-n}(OH)_{8-2n}]Cl_{8-2n} + 2nHCl + 2nH_2O \qquad (4)$$

with n = 1 to 4.

The EDTA/Zr or Hf complexes thus formed have a molecular weight and charge lower than the tetranuclear aqua-hydroxo-complexes and the transport of Zr or Hf across the membrane could thus be improved.

Membrane transport (12, 34–37) could be modified by numerous factors, and among them, organic solute interactions with the membrane are believed to play a crucial role (38). To confirm the depolymerization hypothesis (Eq. 4), we studied the influence of non-chelating charged organic salts on Zr and Hf rejection. The same experiment was performed using triethylamine hydrochoride (TEA-HCl) as a non-chelating organic solute (Fig. 1b). Under these conditions, the rejection of Zr and Hf slowly decreased from 95% to 85% with increasing TEA-HCl/metal ratio. For an organic salt/metal ratio of 0.3 a Zr/Hf rejection of 35% and 92% were obtained with EDTA and TEA-HCl, respectively. Thus, the decrease of the rejection could be attributed to a depolymerization process according to Eq. (4.) However, under these conditions, no difference between the rejection of Zr and Hf was observed.

The same trend was observed with the organic NF membrane (Fig. 2). As expected from the MWCO of the organic membrane the rejection of Zr or Hf was higher than that observed with inorganic membranes. The rejection for Zr and Hf was 65% with an EDTA/total metal ratio of 1 and under those conditions no Zr/Hf separation was observed.

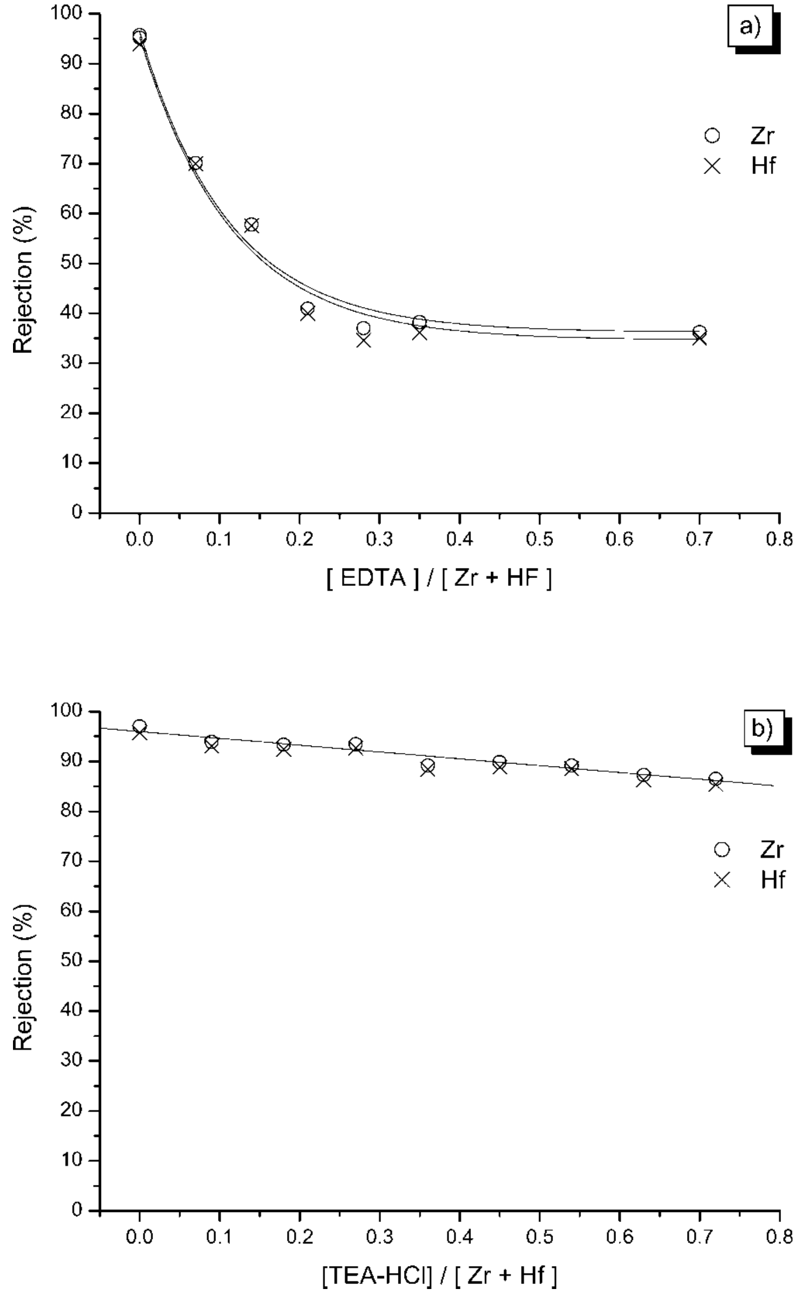

Figure 1. Rejection coefficient of Zr and Hf oxychloride ($Zr/(Zr + Hf) = 0.71$) on inorganic membrane Pall 1 as a function on EDTA a) or TEA b)/[Zr + Hf] metal ratio. pH = 1, [Zr] = 27 mmol/L, [Hf] = 11 mmol/L, $\Delta P = 0.5$ bar, retentate flux: 9 L/min., 20°C.

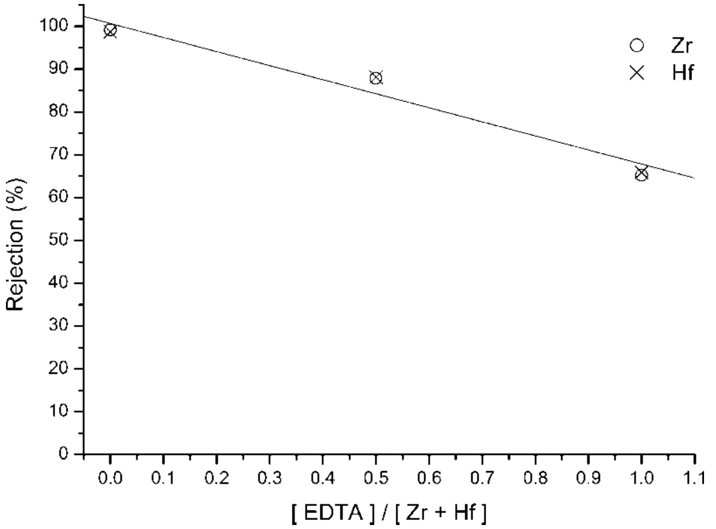

Figure 2. Retention coefficient of Zr and Hf oxychloride ($Zr/(Zr + Hf) = 0.71$) on the organic membrane Desal G10 as a function of EDTA/[Zr + Hf] ratio $pH = 2$, $[Zr] = 27$ mmol/L, $[Hf] = 11$ mmol/L, $\Delta P = 1$ bar, retentate flux: 9 L/min., 20°C

Influence of Counter-Ion on Zr and Hf Rejection by NF Membranes

The counter-ion influence on Zr and Hf rejection was then studied. The Zr and Hf oxynitrates were prepared from the mixture of Zr and Hf tetrachloride according to a published procedure (22). The Zr and Hf oxynitrates were then dissolved in water and the pH was adjusted with nitric acid to 2. Figure 3 shows the rejection of Zr and Hf with increasing concentration of EDTA with the organic G10 membrane.

The rejection of Zr and Hf oxynitrate is still high with the organic Desal G10 membrane (>98%) as previously reported in the hydrochlorohydric media. The rejection of Zr and Hf decreased with increasing EDTA concentration, but in the case of Zr and Hf oxynitrate, the transport across the membrane was higher for Hf than for Zr. This could be explained by the difference between the thermodynamic stability constants of EDTA with Zr or Hf (31). Thus Hf, which has a higher stability constant with EDTA, was preferably depolymerized and transported across the membrane. The Hf/Zr selectivity calculated according to Eq. (3) was higher than 2.5 for an EDTA/metal cation ratio of 0.2.

CONCLUSION

Taking into account the experimental observations reported above, Zr and Hf polynuclear hydroxo-bridged species are highly retained by nanofiltration and

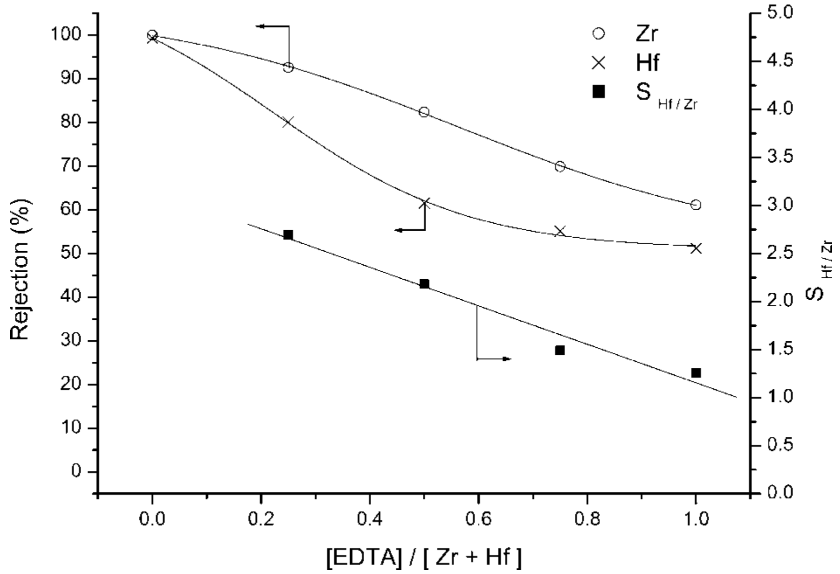

Figure 3. Rejection of Zr and Hf oxynitrate ($Zr/(Zr + Hf) = 0.71$) and Hf/Zr selectivity on organic membrane Desal G10 as a function of EDTA/metal ratio $pH = 2$, $[Zr] = 27$ mmol/L, $[Hf] = 11$ mmol/L, $\Delta P = 1$ bar, retentate flux: 9 L/min., 20°C

ultrafiltration membranes. In a hydrochloric aqueous solution, the introduction of a soluble organic ligand with a high thermodynamic stability constant towards Zr and Hf (i.e. EDTA) enhanced the transport of both Zr and Hf across the membranes. The same trend was observed in nitric solution media, but [EDTA-Hf] complexes are formed preferentially to [EDTA-Zr] complexes and thus a Hf/Zr selectivity higher than 2.5 was obtained. The data obtained with the oxynitrate of Zr and Hf demonstrates that the ligand-enhanced separation of Zr and Hf from aqueous solution using membranes is applicable.

ACKNOWLEDGEMENTS

This work was supported by Framatome through a Ph.D. grant to L.Poreil. Zr and Hf samples from Cezus are gratefully acknowledged.

REFERENCES

1. Poriel, L., Favre-Réguillon, A., Pellet-Rostaing, S., and Lemaire, M. (2006) Zirconium and hafnium separation, part 1. Liquid/liquid extraction in hydrochloric acid aqueous solution with Aliquat 336. Submitted to *Sep. Sci. Technol.*, 41 (9): 1927–1940.

2. Poriel, L., Favre-Réguillon, A., Pellet-Rostaing, S., and Lemaire, M. (2006) Zirconium and hafnium separation, part 2. Solid/liquid extraction in hydrochloric acid aqueous solution with anion exchange resins. Submitted to *Sep. Sci. Technol.*, 41 (12): 2711–2722.
3. Kabili, M.A., Akl, M.A., Abdallah, A.M., and Ismail, D.S. (2000) Selective separation-flotation of hafnium from zirconium and their determination in real samples. *Anal. Sci.*, 16: 713–718.
4. Akl, M.A., Kabil, M.A., Abdallah, A.M., and Ismail, D.S. (2001) Use of eriochrome cyanine R for separation-flotation and microdetermination of hafnium and zirconium in real samples. *Sep. Sci. Technol.*, 36: 2747–2760.
5. Baluev, V.A., Butya, E.L., and Kunaev, N.A., Shtutsa, M.G., Kotrekhov, V.A., Cheremnykh, G.S., and Efimov, Y.N. (07.20.2001) Method of preparing potassium fluorozirconate with low hafnium content. Russ. Patent 2170702.
6. Skaggs, R.L., Rogers, D.T., and Hunter, D.B. (1984) "Review of anhydrous zirconium-hafnium separation techniques," *Boulder City Eng. Lab., Bur. Mines.*
7. Pickles, C.A. and Flengas, S.N. (1997) Separation of $HfCl_4$ from $ZrCl_4$ by reaction with solid and liquid alkali chlorides under non-equilibrium conditions. *Can. Metall. Q.*, 36: 131–136.
8. Besson, P., Guerin, J., Bakes, M., and Brun, P. (10.11.1973) Continuous separation of mixtures of zirconium tetrachloride and hafnium tetrachloride. French Patent 2250707.
9. Moulin, L., Thouvenin, P., and Brun, P. (1984) New process for zirconium and hafnium separation. *ASTM Spec. Tech. Publ.*, 824: 37–44.
10. Delons, L., Picard, G., and Tigreat, D. (24.10.2002) Separation of zirconium and hafnium tetrachlorides by using a molten salt solvent. PCT Int. Appl. WO 02083960.
11. Van der Bruggen, B., Vandecasteele, C., Van Gestel, T., Doyen, W., and Leysen, R. (2003) A review of pressure-driven membrane processes in wastewater treatment and drinking water production. *Environ. Prog.*, 22: 46–56.
12. Schaep, J., Van Der Bruggen, B., Vandecasteele, C., and Wilms, D. (1998) Influence of ion size and charge in nanofiltration. *Sep. Purif. Technol.*, 14: 155–162.
13. Qin, J.-J., Oo, M.H., Lee, H., and Coniglio, B. (2004) Effect of feed pH on permeate pH and ion rejection under acidic conditions in NF process. *J. Membr. Sci.*, 232: 153–159.
14. Paugam, L., Taha, S., Dorange, G., Jaouen, P., and Quemeneur, F. (2004) Mechanism of nitrate ions transfer in nanofiltration depending on pressure, pH, concentration and medium composition. *J. Membr. Sci.*, 231: 37–46.
15. Seidel, A., Waypa, J.J., and Elimelech, M. (2001) Role of charge (Donnan) exclusion in removal of arsenic from water by a negatively charged porous nanofiltration membrane. *Environ. Eng. Sci.*, 18: 105–113.
16. Favre-Reguillon, A., Lebuzit, G., Foos, J., Guy, A., Sorin, A., Lemaire, M., and Draye, M. (2005) Selective rejection of dissolved uranium carbonate from seawater using cross-flow filtration technology. *Sep. Sci. Technol.*, 40: 623–631.
17. Gaubert, E., Barnier, H., Nicod, L., Favre-Reguillon, A., Foos, J., Guy, A., Bardot, C., and Lemaire, M. (1997) Selective cesium removal from a sodium nitrate aqueous medium by nanofiltration-complexation. *Sep. Sci. Technol.*, 32: 2309–2320.
18. Chitry, F., Pellet-Rostaing, S., Gozzi, C., and Lemaire, M. (2001) Separation of lanthanides(III) by nanofiltration-complexation in aqueous medium. *Sep. Sci. Technol.*, 36: 605–618.

19. Sorin, A., Pellet-Rostaing, S., Favre-Reguillon, A., and Lemaire, M. (2004) Cs+/Na+ Separation by nanofiltration-complexation with resorcinarene. *Sep. Sci. Technol.*, 39: 2577–2595.
20. Lin, S.-H., Wang, T.-Y., and Juang, R.-S. (2004) Metal rejection by nanofiltration from diluted solutions in the presence of complexing agents. *Sep. Sci. Technol.*, 39: 363–376.
21. Sorin, A., Favre-Reguillon, A., Pellet-Rostaing, S., Sbai, M., Szymczyk, A., Fievet, P., and Lemaire, M. (2005) Rejection of Gd(III) by nanofiltration assisted by complexation on charged organic membrane: Influences of pH, pressure, flux, ionic strength and temperature. *J. Membr. Sci.*, 267: 41–49.
22. Favotto, C. (2001) Synthèse par chimie douce et caractérisation d'oxynitrate de hafnium $HfO(NO_3)_2,xH_2O$. *Ann. Chim. Sci. Mat.*, 26: 71–78.
23. Afonso, M.D., Hagmeyer, G., and Gimbel, R. (2001) Streaming potential measurements to assess the variation of nanofiltration membranes surface charge with the concentration of salt solutions. *Sep. Purif. Technol.*, 22–23: 529–541.
24. Sorin, A. (2006) "Séparation actinides(III)/lanthanides(III) par nanofiltration assistée par complexation". Thesis N° 01-2006, Université Claude Bernard: Villeurbanne, France, Lyon 1.
25. Singhal, A., Toth, L.M., Lin, J.S., and Affholter, K. (1996) Zirconium(IV) tetramer/octamer hydrolysis equilibrium in aqueous hydrochloric acid solution. *J. Am. Chem. Soc.*, 118: 11529–11534.
26. Hannane, S., Bertin, F., and Bouix, J. (1990) Raman spectrometric and proton NMR study of zirconium(IV) hydrolysis in aqueous solution. I. Qualitative study: number and type of species occuring. *Bull. Soc. Chim. Fr.*, 127: 43–49.
27. Veyland, A., Dupont, L., Pierrard, J.-C., Rimbault, J., and Aplincourt, M. (1998) Thermodynamic stability of zirconium(IV) complexes with hydroxy ions. *Eur. J. Inorg. Chem.*, 11: 1765–1770.
28. Biswas, R.K. and Hayat, M.A. (2002) Solvent extraction of zirconium(IV) from chloride media by D2EHPA in kerosene. *Hydrometallurgy*, 63: 149–158.
29. Aberg, M. (1977) An X-Ray investigation of some aqueous zirconium(IV) halide, a hafnium(IV) chloride, and some zirconium (IV) perchlorate solutions. *Acta Chem. Scand.*, 31: 171–181.
30. Mit'kina, T.V., Gerasko, O.A., Sokolov, M.N., Naumov, D.Y., and Fedin, V.P. (2004) Syntheses and crystal structures of supramolecular compounds of tetranuclear ZrIV and HfIV aqua hydroxo complexes with macrocyclic cavitand cucurbituril. *Russ. Chem. Bull., Int. Ed.*, 53: 80–85.
31. Anderegg, G. (1977) *In Critical Survey of Stability Constants of EDTA Complexes: Critical Evaluation of Equilibrium Constants in Solution*. Pergamon Press: Oxford.
32. Zhong, W., Parkinson, J.A., Parsons, S., Oswald, I.D.H., Coxall, R.A., and Sadler, P.J. (2004) Structure and dynamics of dinuclear zirconium(IV) complexes. *Inorg. Chem.*, 43: 3561–3572.
33. Ivanov, P.I., Bojikov, G.A., Priemyshev, A.N., Bontchev, G.D., Maslov, O.D., Milanov, M.V., and Dmitriev, S.N. (2003) Behavior of zirconium and hafnium ions in ultramicroconcentrations investigated by horizontal zone electrophoresis in free electrolyte. *J. Radioanal. Nucl. Chem.*, 258: 639–643.
34. Bowen, W.R. and Mukhtar, H. (1996) Characterization and prediction of separation performance of nanofiltration membranes. *J. Membr. Sci.*, 112: 263–74.
35. Wiesner, M.R. and Buckley, C.A. (1996) Principles of rejection in pressure-driven membrane processes. *Water Treatment Memb. Process.*, 5.1–5.17.

36. Tu, S.-C., Ravindran, V., Den, W., and Pirbazari, M. (2001) Predictive membrane transport model for nanofiltration processes in water treatment. *AIChE Journal*, 47: 1346–1362.

37. Hilal, N., Al-Zoubi, H., Darwish, N.A., and Mohammad, A.W. (2005) Nanofiltration of magnesium chloride, sodium carbonate, and calcium sulphate in salt solutions. *Sep. Sci. Technol.*, 40: 3299–3321.

38. Bellona, C., Drewes, J.E., Xu, P., and Amy, G. (2004) Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review. *Water Res.*, 38: 2795–2809.