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**PHYSICO-CHEMICAL FORMS OF NATURAL
RADIONUCLIDES IN DRILLED WELL WATERS
AND THEIR REMOVAL BY ION EXCHANGE**

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Academic Dissertation

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ABSTRACT

Appreciable concentrations of natural uranium and its daughter radionuclides may occur in drinking water obtained from drilled wells when the bedrock contains these nuclides. Effective methods are needed to remove these radionuclides.

A wide range of ion exchange materials, both organic and inorganic, were evaluated for the removal of $^{234,238}\text{U}$, ^{226}Ra , ^{210}Po and ^{210}Pb from ground waters. Screening tests were carried out, in which distribution coefficients (K_D) were determined for the ion exchangers. The ion exchangers that gave the highest K_D 's were tested in column-mode experiments for the removal of the radionuclides from drilled well water. The most efficient exchanger for the removal of U from neutral and slightly alkaline waters was the strong base anion resin. The chelating aminophosphonate resin removed uranium very efficiently from slightly acidic water. As well, it was an efficient exchanger for the removal of toxic and harmful transition metals from drilled well waters. The strong and weak acid cation resins and zeolite A removed radium most efficiently.

Large fractions of the total activity of polonium and lead were found to adsorb on equipment in the ion exchange studies. In investigation of this, the well waters were filtered through membranes to determine the soluble and particle-bound forms of $^{234,238}\text{U}$, ^{226}Ra , ^{210}Po and ^{210}Pb . Eight of the waters were of Ca-HCO₃ type and two were of Na-Cl type. Some of the waters also had high concentrations of Fe, Mn and humic substances. Uranium was present entirely in soluble form, probably as uranyl ion in soluble carbonate complexes. ^{226}Ra was in soluble form in the waters with low concentrations of Fe and Mn, but 10% of the total radium activity was bound to particles in Fe-Mn-rich waters. The speciation of Po is complex in natural waters; polonium was present in both soluble and particle-bound forms. A correlation was observed between the fractions of particle-bound ^{210}Po and the concentrations of iron in the raw waters. A considerable amount of the total activity of ^{210}Pb was found in the coarse particle fraction in iron-bearing water.

The results of the study show ion exchange to be an effective method for the removal of uranium and radium from drinking water. Efficient removal of polonium and lead will often require a second purification method.

PREFACE AND ACKNOWLEDGEMENTS

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LIST OF PUBLICATIONS

This thesis is based on the following publications:

- I Vaaramaa, K., Lehto, J. and Jaakkola, T., Removal of $^{234,238}\text{U}$, ^{226}Ra , ^{210}Po and ^{210}Pb from drinking water by ion exchange, *Radiochim. Acta* 88, 361-367 (2000).
- II Vaaramaa, K., Pulli, S. and Lehto, J., Effects of pH and uranium concentration on the removal of uranium from drinking water by ion exchange, *Radiochim. Acta* 88, 845-849 (2000).
- III Lehto, J., Kelokaski, P., Vaaramaa, K. and Jaakkola, T., Soluble and particle-bound ^{210}Po and ^{210}Pb in groundwaters, *Radiochim. Acta* 85, 149-155 (1999).
- IV Vaaramaa, K., Lehto, J. and Ervanne, H., Soluble and particle-bound $^{234,238}\text{U}$, ^{226}Ra and ^{210}Po in ground waters, *Radiochim. Acta* 91, 21-27 (2003).
- V Vaaramaa, K. and Lehto, J., Removal of metals and anions from drinking water by ion exchange, *Desalination*, in press.

The publications are referred to in the text by their Roman numerals. The original publications are reprinted with the permission of the publisher.

ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
DOC	Dissolved Organic Carbon
DVB	Divinylbenzene
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
MWCO	Molecular Weight Cutoff
PZC	Point of Zero Charge
SAC	Strong Acid Cation resin
SBA	Strong Base Anion resin
TOC	Total Organic Carbon
WAC	Weak Acid Cation resin
WBA	Weak Base Anion resin

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1. INTRODUCTION

1.1 Background

Most households today use tap water distributed by waterworks. Ground water is a very important source of the water, together with surface water. The proportion of ground water in total water use is expected to increase in future, and various types of ground water aquifers are under consideration as sources of ground water. In Finland the ground water distributed by waterworks mainly originates in porous gravel and sand aquifers.¹

Private well water is taken from wells dug in soil or from wells drilled into fractured bedrock. When the bedrock contains considerable amounts of uranium and its daughter radionuclides, drinking water taken from drilled wells may contain high concentrations of natural radionuclides. The concentrations are rarely significant in dug wells. Concentrations of natural radionuclides are high in drilled well waters in Europe, and especially in Finland, Sweden and Norway. The high concentrations in ground waters in the Nordic countries, appear to be associated with granitic and pegmatite rock.² Natural radioactivity in drinking water has been studied in Finland since the late 1960s.²⁻⁴

With respect to radiation dose, the most significant radionuclides that may occur in household water are the long-lived radioisotopes of uranium, radium, polonium and lead and short-lived radon, ²²²Rn. Radon is the source of the highest radiation dose to consumers of household water in Finland followed by ²¹⁰Po and ²¹⁰Pb. The major health effect of uranium is chemical toxicity rather than radiation hazard.⁵⁻⁸ ²²⁶Ra may add to the radiation dose in special cases, especially in saline drilled well waters.

Ion exchange is a useful method for the separation of radionuclides from water. If ion exchange is the primary method for the purification of water, the contaminant should be present in ionic form. The natural radionuclides differ in their physico-chemical properties, which means that use of a single material is often insufficient for the removal of all radioactive species from water.

1.2 Scope of the Study

This work was focused on the removal of major radionuclides (long-lived radioisotopes of U, Ra, Po and Pb) occurring in drinking water originating from drilled wells. A group of ion exchangers and the efficiency of the ion exchange process to remove these radionuclides were evaluated. The speciation and the presence of the radionuclides in particles of different size fractions were taken into consideration. Radon (^{222}Rn) is gaseous and cannot be removed by ion exchange and so was excluded from the study. Of the two radium isotopes, ^{226}Ra (from the uranium series) and ^{228}Ra (from the thorium series), only ^{226}Ra was included in the study, because chemical and ion exchange behaviour is similar for isotopes of the same element. Even though ^{228}Ra may be present in drilled well water in higher activity concentrations than ^{226}Ra , ^{226}Ra was chosen to represent the behaviour of radium because it is easier to analyse.

As reported in publication **I**, a wide range of ion exchange materials, both organic and inorganic and varying from strongly acidic to strongly basic in character, were evaluated for the removal of uranium, ^{226}Ra , ^{210}Po and ^{210}Pb from drilled well water. New groups of ion exchangers, not previously studied for this purpose, were included. The speciation of uranium is known to vary with pH. In most drilled well waters the pH of the water is near neutral, but some waters are slightly alkaline or slightly acid. Uranium concentration is exceptionally high in some drilled well waters in Finland. The effects of pH and uranium concentration on the removal of uranium with two ion exchange resins were reported in publication **II**. The aim of the study was to determine whether uranium, ^{226}Ra , ^{210}Po and ^{210}Pb are present in drilled well waters in ionic form and so might be removed with ion exchangers. Soluble and particle-bound forms of the radionuclides were studied in publications **III** and **IV**.

Where ion exchangers are used for water purification, it is important to ensure that the treatment process does not affect the quality of the drinking water. The removal from the waters of useful elements and of non-radioactive harmful and toxic elements in the ion exchange process was investigated in publication **V**.

2. NATURAL RADIONUCLIDES IN WATER

2.1 Uranium

2.1.1 Natural uranium

Natural uranium consists of three isotopes: ^{238}U (half-life 4.47×10^9 a), ^{234}U (half-life 2.47×10^5 a) and ^{235}U (half-life 7.04×10^8 a). ^{238}U is the parent isotope of the uranium series and ^{234}U is its decay product, while ^{235}U is the parent isotope of the actinium series. The uranium series begins with the nuclide ^{238}U and terminates, after eight alpha and six beta decay steps, at the stable end product ^{206}Pb (Table 1). ^{238}U is the main constituent of natural uranium in the earth's crust (99.275%), while the minor constituents, ^{234}U and ^{235}U , are present in the amounts of 0.005% and 0.72%, respectively. Uranium occurs in all rocks and soils, but continental igneous rocks, in particular silica-rich rock such as granite, contain high uranium concentrations (average 4 ppm).^{9,10} The parent isotope of the decay series, ^{238}U , may enter the aqueous phase by direct dissolution or leaching of the rock matrix or by selective dissolution or leaching of a mineral phase within which uranium is concentrated. The decay products of the uranium series may enter solution phase by (1) the decay of a parent isotope already in solution, (2) the alpha recoil process or (3) leaching from, or direct dissolution of, the rock matrix.¹¹

Table 1. The natural radioactive decay series for ^{238}U .¹²

Element	Half-life	Decay mode and particle energy	
^{238}U	4.47×10^9 a	α 4.196 (77%), 4.149 (23%)	MeV
^{234}Th	24.1 d	β^- 0.199 (73%), 0.104 (21%)	MeV
$^{234\text{m}}\text{Pa}$	1.18 min	β^- 2.29 (98%)	MeV
^{234}U	2.47×10^5 a	α 4.774 (72%), 4.723 (28%)	MeV
^{230}Th	8.0×10^4 a	α 4.688 (76%), 4.621 (23%)	MeV
^{226}Ra	1602 a	α 4.785 (94%), 4.602 (5.6%)	MeV
^{222}Rn	3.824 d	α 5.49 (100%)	MeV
^{218}Po	3.05 min	α 6.002 (99%)	MeV
^{214}Pb	26.8 min	β^- 0.65 (48%), 0.73 (42%), 1.03 (6%)	MeV
^{214}Bi	19.7 min	β^- 1.51 (40%), 1.02 (23%), 3.26 (19%)	MeV
^{214}Po	164×10^{-6} s	α 7.687 (100%)	MeV
^{210}Pb	22.3 a	β^- 0.015 (81%), 0.061 (19%)	MeV
^{210}Bi	5.013 d	β^- 1.161 (99%)	MeV
^{210}Po	138.38 d	α 5.305 (100%)	MeV
^{206}Pb	–	stable	

Percentage in parentheses is intensity of disintegration.

In general, a decay series is said to be in secular equilibrium if the radioactivity of all daughter nuclides of the series is equal to that of the parent. Radioactive disequilibrium occurs when the daughter nuclides have been lost from a geologic system by other processes than radioactive decay. Uranium series disequilibrium is common in natural waters, as a result of the different physico-chemical properties of the radionuclides: redox-sensitive uranium, gaseous radon, and particle-reactive lead and polonium (i.e. Pb and Po have a strong tendency to sorb onto particles).

2.1.2 Uranium complexes

The physico-chemical properties of the radionuclides control their occurrence and abundance in natural waters. The most important oxidation states of uranium in nature are U(IV) and U(VI). Uranous ion (U^{4+}) and its aqueous complexes predominate in anoxic waters i.e. in low Eh conditions. The uranous ion forms complexes with fluoride below pH 4, while uranous hydroxy complexes predominate at higher pH values. Because of the extremely low solubilities of the most common uranium(IV) ore minerals (uraninite, coffinite), the uranium (IV) concentrations in ground waters at low Eh are typically less than 10^{-8} mol/l.¹⁰

Uranium (VI) hydroxide and carbonate complexes

Uranium is transported in oxidising waters as highly soluble uranyl ion (UO_2^{2+}) and its complexes. The complexing of the uranyl ion depends on pH and the presence of other ions. In pure solutions, in the absence of carbonate and at a uranium concentration of 10^{-8} mol/l, mononuclear species (UO_2^{2+} , UO_2OH^+ and $UO_2(OH)_2^0$) dominate at all pH values. At higher U(VI) concentrations the polynuclear species (for example, $(UO_2)_3(OH)_5^+$) become the major hydroxyl complexes. In most natural waters, uranyl ion forms strong carbonate complexes. Uranyl carbonate complexes replace the U(VI)-hydroxyl complexes above pH 6 to 7 with a partial pressure of CO_2 of $10^{-3.5}$ bar (normal atmospheric pressure) and with a typical ground water CO_2 pressure (10^{-2} bar).^{10,13} The carbonate complexes are extremely important because they increase uranium mobility by limiting the extent of uranium adsorption in oxidised waters and by increasing the solubility of uranium minerals.^{10,14,15} In uranyl–hydroxide–carbonate system, the $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ complexes predominate in the pH range 6–8, while the uranyl di- and tri-carbonate complexes

predominate above pH 7.5.¹³⁻¹⁷ The $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ species appears in neutral pH range, varying in importance with the concentrations of carbonate and uranium in solution.^{13,15,17,18}

U(VI) fluoride, phosphate and sulphate complexes

Soluble U(VI) complexes are also formed in natural waters with fluoride, phosphate and sulphate. Uranyl fluoride complexes are important only at acidic pH. Phosphate and sulphate complexes are notable in uranium mining and milling areas (Saxony, Thuringia)^{19,20} and in areas of phosphate industry.²¹ Uranyl sulphate complexes UO_2SO_4^0 and $\text{UO}_2(\text{SO}_4)_2^{2-}$ determined by Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS) are reported to form at acidic pH.²² However, the concentration of sulphate in the solution was relatively high in this study, above 10^{-2} mol/l. Speciation studies of uranium in seepage waters of a mine tailing pile in Saxony (Germany) showed that uranyl carbonate complexes compete with sulphate around pH 5 and dominate above pH 6 (concentrations of U, sulphate and carbonate: 10^{-5} , 10^{-2} and 10^{-3} mol/l).²⁰ As well, uranyl phosphate complexes are important in natural waters, but again the carbonate complexes compete with phosphate in neutral pH range. In investigation of the solubility of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{s})$ and the formation of U(VI) phosphate complexes, Sandino and Bruno²³ found that the predominant species are $\text{UO}_2\text{HPO}_4(\text{aq})$ and UO_2PO_4^- in the pH range 4–9. In order for U(VI) phosphate complexes to dominate over carbonate complexes, the total concentration ratio $[\text{PO}_4^{3-}]_{\text{T}}/[\text{CO}_3^{2-}]_{\text{T}}$ should be greater than 10^{-1} .

U(VI) minerals and UO_2^{2+} sorption from solution

Uranium(VI) minerals such as schoepite ($\beta\text{-UO}_3 \cdot 2\text{H}_2\text{O}$) and the most important oxidised ore minerals of uranium, i.e. carnotite $[\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}]$, tyuyamunite $[\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5\text{-}8\text{H}_2\text{O}]$, uranophane $[\text{Ca}(\text{UO}_2)_2(\text{SiO}_3(\text{OH})_2) \cdot 5\text{H}_2\text{O}]$ and autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{-}12\text{H}_2\text{O}]$, are often products of the oxidation and weathering of primary uranium(IV) ore minerals.¹⁰ According to Langmuir,¹⁴ the uranyl minerals are least soluble in the pH range 5–8.5. This pH range is also the pH range of maximal sorption of UO_2^{2+} on most natural colloidal materials, including Fe(III) and Mn oxyhydroxides, zeolites, clays and organic matter. Sorption is generally more important than uranium mineral precipitation in the control of uranium mobility.^{14,15} Ferric oxides and oxyhydroxides strongly adsorb dissolved uranyl

species. The adsorption begins at pH 2–5 and increases up to pH 5–8 varying with the adsorbent and its concentration and the solution composition.^{13,15,24,25} When carbonate is present in solution, decrease of adsorption is observed from pH 6–7 to pH 7–9.^{13,15,25}

U(VI) humus complexes

Uranium(VI) complexation with organic matter has been discussed by many authors.^{26–35} Complexation of UO_2^{2+} with humic substances occurs mainly in acidic waters up to pH 6–7, while carbonate complexes predominate at higher pH. Shanbhag and Choppin,³⁰ in their investigations at pH 8 of the binding of uranyl ion to humic acid, found that, in the absence of carbonate, uranyl ion forms 1:1 and 1:2 complexes with humates and binds to the carboxyl (COO^-) group. When carbonate is present (10^{-5} mol/l), uranyl ion exists completely as carbonate complexes. Lenhart and co-workers³¹ found that, at pH 4 and 5, U(VI) is strongly bound to both humic and fulvic acids, and the binding of uranyl ion to humic acid is stronger than binding to fulvic acid. Lienert and co-workers³³ used model calculations for the determination of uranium speciation in shallow ground water and found that UO_2 –humate complexes predominate below pH 6.8, while uranyl–carbonate complexes predominate at higher pH.

2.2 Radium

Four radium isotopes occur naturally in ground waters and, of these, ^{226}Ra and ^{228}Ra have relatively long half-lives, 1602 years for ^{226}Ra and 5.8 years for ^{228}Ra . The half-lives of the other radium isotopes, ^{223}Ra and ^{224}Ra , are only 11.4 and 3.7 days, respectively. ^{226}Ra is a high-energy alpha emitter and ^{228}Ra is a low-energy beta emitter. ^{226}Ra is a member of the ^{238}U decay series (Table 1), while ^{228}Ra is the second member of the thorium series and has an extremely insoluble parent (^{232}Th). The $^{238}\text{U}/^{232}\text{Th}$ activity ratio is typically 0.8 for granites in which U and Th are enriched.¹⁰ $^{226}\text{Ra}/^{228}\text{Ra}$ activity ratios of 0.3 to 26 are reported for some Finnish ground waters.² The high ratios may relate to local enrichments of uranium in the aquifer rocks. Fuller studies have been made of ^{226}Ra and ^{228}Ra isotopes in natural waters than of the shorter lived isotopes, ^{223}Ra and ^{224}Ra (both alpha emitters). These shorter lived isotopes can be used to provide valuable information on the rate of various processes in ground water.^{36–38}

Radium exists primarily as noncomplexed Ra^{2+} cation in low salinity solutions, but may form weak complexes with chloride, sulphate and carbonate in concentrated waters. The solubility and mobility of radium will not thus be significantly affected by these weak complexes of radium in low salinity waters. But a significant amount of radium may be complexed in saline and sulphate-rich waters when the concentration of sulphate is over 20 mg/l and the chloride concentration is at least 5 g/l. Likewise, the $\text{RaCO}_3(\text{aq})$ complex is suggested to be significant in very alkaline waters ($\text{pH} > 10$) and at high carbonate concentrations (> 60 mg/l).³⁹ In general, among all the aqueous species and solids, only Ra^{2+} ion and $\text{RaSO}_4(\text{s})$ are likely to be of significance in the environment.⁴⁰ However, the concentrations of radium in natural waters are not high enough for radium to form insoluble RaSO_4 . The solubility product (K_{sp}) for $\text{RaSO}_4(\text{s})$ is reported^{40,41} to be 10^{-11} to $10^{-10.4}$. Radium concentrations in natural waters are limited either by adsorption or by solid solution formation or both.⁴² Trace radium may form solid solutions with barite (BaSO_4) and celestite (SrSO_4), which would reduce the concentration of radium in waters.^{40,42,43} Radium substitutes for barium in barite, and very effectively adsorbs onto iron and manganese hydroxides.⁴⁴⁻⁴⁶ A strong positive correlation between radium concentration and salinity of ground waters has several times been reported.^{11,39,41,47-51} Cation (Ca^{2+} , Na^+) saturation of sites that otherwise would be available for the sorption of radium could be a possible explanation.^{42,47-49}

2.3 Polonium

Seven radioactive isotopes of polonium occur in the natural decay series, but only the most long-lived isotope, ^{210}Po (the last radioactive member of the uranium series), is significant. The half-life of ^{210}Po is 138 days and it is an alpha-emitter. The other isotopes are extremely short-lived, their half-lives ranging from shorter than a microsecond to 3 minutes. The speciation of polonium in natural waters is highly complex and is still not well understood. Polonium is known to be highly particle-reactive. The oxidation states characteristic of polonium are -2 , $+2$, $+4$ and $+6$. In oxic conditions the most stable oxidation state of polonium is $+4$.^{52,53} However, Po^{4+} exists only in strongly acidic solutions. Polonium hydrolyses, forming $\text{PoO}(\text{OH})^+$, $\text{PoO}(\text{OH})_2$, and PoO_2 , in the slightly acidic to neutral pH regions, and forms PoO_3^{2-} in alkaline solutions.⁵⁴ Under reducing conditions polonium may exist as a divalent species.⁵⁵

The solubility of polonium species in natural waters is not known, but it is assumed to be very low. Figgins (1961) has reported a solubility product of 10^{-37} for $\text{Po}(\text{OH})_4$.⁵² Although the concentrations of polonium are low in natural waters, it cannot be excluded that Po may form intrinsic particles. More likely, however, it adsorbs on other particles, such as mineral colloids and humic substances.

Ulrich and Degueldre⁵⁴ studied the influence of ionic strength and pH on the sorption processes of ^{210}Po , ^{210}Bi and ^{210}Pb on montmorillonite (a three-layered silicate) and found that sorption of Po and Bi is independent of the ionic strength. They determined adsorption and desorption coefficients of Po and observed that polonium may form colloids in the liquid phase prior to the sorption step. This complicates the interpretation of the sorption process of polonium. In addition, they observed the sorption of polonium to be nearly irreversible for the species being sorbed from aqueous phase, whereas, for ^{210}Po generated by radioactive decay of sorbed ^{210}Pb , the desorption was significantly facilitated. Balistrieri and co-workers⁵⁶ studied the geochemical processes controlling the behaviour of polonium and lead in seasonally anoxic lake water, and proposed that co-cycling of Po and Mn in the water may occur through the sorption of Po onto Mn oxide phases and its subsequent release when the Mn oxide phase is reduced. Wei and Murray⁵⁷ assumed that biological particles rather than inorganic particles are major carrier phases for ^{210}Po in the Black Sea. In oxic layers of the Black Sea, dissolved ^{210}Po was deficient relative to dissolved ^{210}Pb , while in anoxic layers the amounts of particle bound polonium and lead were similar. The enrichment of ^{210}Po , ^{210}Pb and microbes at the $\text{O}_2/\text{H}_2\text{S}$ interface of a permanently anoxic fjord in Norway has also been reported.⁵⁵ Excess ^{210}Po has been observed in acidic sulphide-containing ground waters of central Florida by Harada and co-workers,⁵⁸ who suggested that the Po cycling may be closely tied to the microbial sulphur cycle in these waters. The behaviour of ^{210}Po and ^{210}Pb during anoxic conditions in Lake Sammamish (USA) has been proposed by Balistrieri and co-workers⁵⁶ to be influenced by sulphur cycling. In the study of the bacterial mobilization of polonium from waste gypsum, LaRock and co-workers⁵⁹ demonstrated that sulphate-reducing bacteria were effective at mediating polonium release from gypsum provided the sulphide levels resulting from their metabolism did not rise above $10 \mu\text{mol/l}$, in which case Po was evidently coprecipitated as a metal sulphide.

2.4 Lead

Three stable lead isotopes (^{206}Pb , ^{207}Pb and ^{208}Pb) and four radioactive isotopes occur in the natural decay series. Among these, ^{210}Pb is the most long-lived (half-life 22.3 a) and therefore the most significant. The half-lives of ^{211}Pb (^{235}U series), ^{212}Pb (^{232}Th series) and ^{214}Pb (^{238}U series) are 36 min, 10.6 h and 26.8 min, respectively. ^{210}Pb is a low-energy beta-emitter from the ^{238}U series (Table 1), which decays to the stable ^{206}Pb isotope via two daughter radioisotopes, ^{210}Bi and ^{210}Po . The oxidation states +2 and +4 are the most stable ones for naturally occurring lead, but +2 is the most prevalent.⁶⁰

Lead exists in natural waters in various inorganic forms, complexed with organic matter and adsorbed onto insoluble particles. Carbonate concentration and pH of the water are the primary factors affecting the formation of lead complexes.⁶¹ According to Naylor and Dague,⁶² lead dissolves in pure solutions having a pH less than 8 and precipitates as PbO in pH range 8–11. Above pH 11, PbO is replaced by soluble $\text{Pb}(\text{OH})_3^-$. In a lead–carbon dioxide–water system, lead can exist as Pb^{2+} ion in solution below pH 5, and it precipitates as PbCO_3 in the pH range 5–8.5. Between pH 8.5 and 12.5, lead will precipitate as either PbO or $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, while at pH values above 12.5, soluble lead hydroxide complexes will start to form. The minimum solubility for red PbO (the stable form) is 10^{-5} mol/l, but this phase is not likely to be the saturating form in natural systems.⁶⁰ Instead, the basic carbonate, the sulphide, the phosphate and lead silicate are the insoluble forms of Pb^{2+} in natural systems.

At a lead concentration of 10^{-5} mol/l, hydrolysis of lead commences above pH 6. Below pH 11 the prevalent soluble species are $\text{Pb}(\text{OH})^+$ and $\text{Pb}(\text{OH})_2$. The primary polynuclear species are $\text{Pb}_4(\text{OH})_4^{4+}$ and $\text{Pb}_6(\text{OH})_8^{4+}$, but they are only relevant at higher lead concentrations (0.1 mol/l).⁶⁰

High concentration of soluble ^{210}Pb has been reported in SSGF brine (Salton Sea Geothermal Field, California). Complexing of Pb^{2+} and Cl^- is assumed to keep ^{210}Pb in solution.^{38,49} Vertical profiles of ^{210}Pb in the Black Sea have shown that dissolved ^{210}Pb (Pb^{2+} ion) dominates in the oxic zone, while particulate ^{210}Pb is the major form in the deep sulphide-bearing anoxic zone; in other words, the redox conditions of the sea water column influence the fractionation of ^{210}Pb between dissolved and particulate phases.⁵⁷ Studies of Pb speciation

in a meromictic lake (Paul Lake, Michigan) have shown that Pb is scavenged by Fe-rich particles formed at the oxic–anoxic transition. The particles of hydrous iron oxides form complex aggregates with natural organic matter, and these species remove lead.⁶³ In the studies of the behaviour of lead in natural ground waters, Lieser and co-workers^{64,65} found that Pb was predominantly bound in the coarse particle fraction (> 0.45 µm) in both oxic and reducing waters. Coarse and colloidal particles were observed to consist mainly of clay minerals, polysilic acid and iron hydroxide. Large amounts of Pb were also found in the molecular fraction in the presence of organic compounds, i.e. humic and fulvic acids. According to Ulrich and Degueldre,⁵⁴ the sorption of Pb on montmorillonite is dependent on the ionic strength below pH 7 and independent of it at higher pH. Their sorption studies showed that the sorption of Pb was reversible. Results of studies on the ²¹⁰Pb/²²²Rn and ²¹⁴Pb/²²²Rn disequilibria in ground waters suggest very short residence times of lead isotopes, from a few minutes for ²¹⁴Pb to some days for ²¹⁰Pb.^{11,66}

2.5 Colloids and Particles

Natural radionuclides and stable trace metals entering aquatic systems interact with naturally occurring particles through sorption processes. Sorption changes the size and charge characteristics of the radionuclides and trace metals and thereby influences their transport, mobility and bioavailability. The radioactive and stable elements in natural waters may be associated with forms ranging from simple ions or molecules via hydrolysis products and polymers to colloids, pseudocolloids and suspended particles (Figure 1).⁶⁷ The amount and chemical composition of colloids and particles in ground waters differ from water to water.

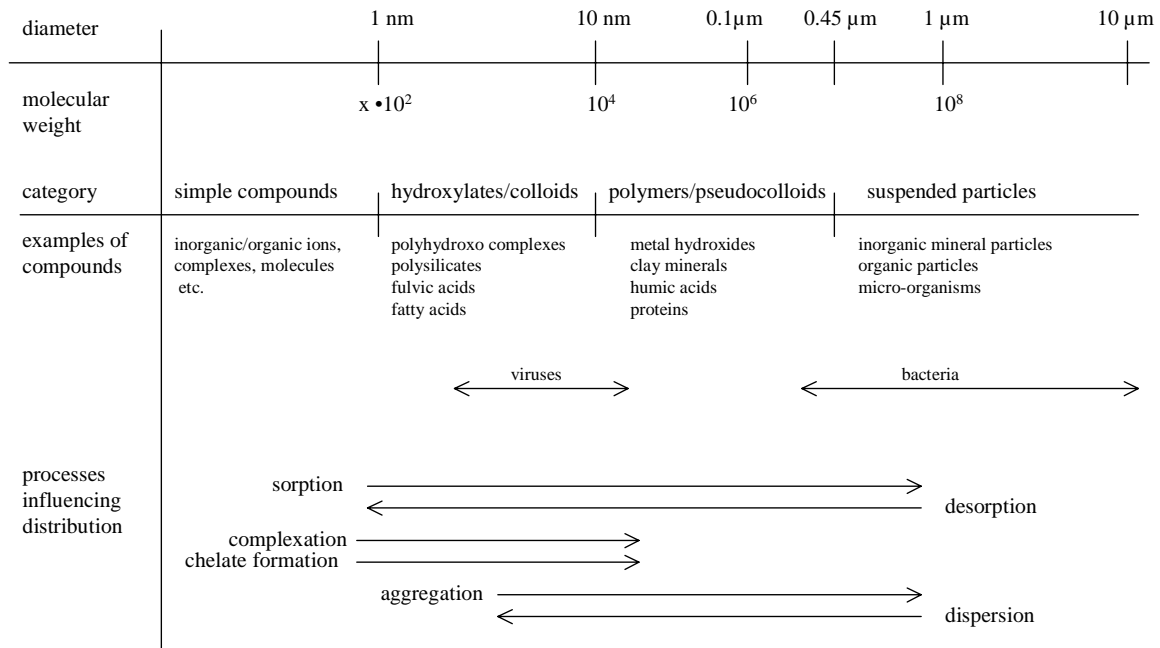


Figure 1. Association of trace elements with compounds in different size ranges.⁶⁷

Colloids may be of two kinds: Type I colloids, called “intrinsic colloids”, are compounds of an element formed mainly by condensation of mononuclear to polynuclear species. Polynuclear hydroxo complexes (colloidal hydroxides) and polyacids (such as colloidal silicic acid) are typical examples. Type II colloids, or “carrier colloids (pseudocolloids)”, are colloids in which ions or compounds of elements are sorbed by physical adsorption, chemisorption or ion exchange onto colloidal species of other composition present in the solution.⁶⁸

Trace elements and radionuclides may be introduced into ground water slowly, or they may be introduced all at once in a relatively high concentration that is then diluted by the ground water. In the case of slow dissolution, or leaching, the probability that the solubility limit of a sparingly soluble compound of the element may be exceeded is small. The probability of the formation of polynuclear complexes of the trace elements is also small. On the other hand, the probability of interaction of trace elements with colloids present in the water increases with the concentration of these colloids. At low concentrations of trace elements, the carrier colloids are strongly favoured.

When, in turn, a trace element enters the ground water in relatively high concentration, the probability of formation of sparingly soluble compounds of the trace element is high. These sparingly soluble compounds may then be stabilised as colloids. Alternatively, if the effect of stabilisation is low and solubility is high enough, they may be dissolved in the course of further dilution by ground water. However, if the effect of stabilisation is high and the solubility very low, the polynuclear complexes (e.g. hydroxo complexes) may persist in the water as intrinsic colloids. Stabilised colloids may thus be present at concentrations far below the solubility of the corresponding compounds.⁶⁴

Adsorption processes

According to Stumm and Morgan,⁶⁹ adsorption may result from short-range chemical forces (e.g. covalent bonding, hydrophobic bonding and hydrogen bridges) or long-range forces (electrostatic and van der Waals attraction forces). The chemisorption processes (ones that result from short-range chemical forces) are often irreversible, whereas electrostatic adsorption tends to be rapid and reversible.⁷⁰ Sorption of radionuclides will frequently be governed by electrostatic forces between nuclide species in aqueous solution and surface charges of the sorbent.⁷¹ Many suspended and colloidal solids in natural waters have surface charge, originating from ionizable functional groups (e.g. OH, COOH etc.), from lattice imperfections at the solid surface or isomorphous replacement within the lattice or from adsorption of surfactant ions (e.g. adsorption of an organic coating onto an inorganic surface). Most oxide and hydroxide surfaces exhibit an amphoteric behaviour; thus the charge is strongly dependent on pH. The positively charged species dominate at low pH while negatively charged species dominate at high pH. The surface charge will go from positive to zero to negative as the pH changes from low to high values.^{69,70}

Parameters controlling speciation

Oxidation state, hydrolysis and complexation are important speciation-controlling parameters. The redox potential, Eh, greatly influences the behaviour of uranium, for example. U(IV) oxidises to U(VI) under aerobic conditions and highly soluble UO_2^{2+} ion is formed. If the water enters a reducing zone, a reduction of U(VI) to +4 state leads to the formation of uranium colloids. In natural waters, pH varies from 6 to 8 and influences the chemical behaviour of elements that hydrolyse easily. The formation of complexes with the inorganic and organic ligands present in natural waters competes with the formation of hydroxo

complexes. High concentration of inorganic salts (high ionic strength) hinders the formation of colloids, and colloids already present coagulate. The anions in natural waters form stable complexes with cationic radionuclides, affecting their solubility, colloid formation and sorption behaviour.⁷²

Colloidal and particulate phases

Inorganic colloids and suspended (coarse) particles present in ground waters consist mainly of clay minerals, polysilicic acid and iron hydroxide.^{64,73} Colloids and particulates may also be made up of high molecular weight organic matter and metal oxides such as MnO₂, Fe₂O₃ and Al₂O₃. The most important organic compounds in natural waters are humic and fulvic acids, both degradation products of organic matter. Humic substances are organic polyelectrolyte macromolecules and contain carboxylic and phenolic hydroxyl groups. Usually they are classified according to their solubilities: fulvic acids are soluble at all pH values, humic acids are soluble above pH 3.5, and humin is insoluble in both alkali and acid.⁷⁴ Carrier colloids containing organic compounds and radionuclides may be formed in two different ways: by ion exchange or sorption of radionuclides on organic compounds or by sorption of organic complexes of the radionuclides on inorganic colloids.⁷² Natural uranium in the Gorleben glacial sand/silt ground water system is reported to be bound on humic colloids of nominal size larger than 1 nm diameter. Most of the colloid population occurred in the size range of 1.5–15 nm. The dissolved organic carbon (DOC) that passed through a 10 000 MWCO (molecular weight cutoff) filter, i.e. approximately 1.5 nm filter, consisted mainly of fulvic acid. The 1.5–15 nm fraction was composed of both humic and fulvic acids.^{34,75}

2.6 Natural Radionuclides in Drinking Water

2.6.1 Concentrations and radiation doses

Natural radionuclides are not a problem in surface waters, but high concentrations may exist in ground waters, especially in drilled well waters. In terms of radiation dose the most important radionuclides that may occur in household water are ²³⁴U, ²³⁸U, ²²⁶Ra, ²²²Rn, ²¹⁰Pb and ²¹⁰Po from the uranium decay series and, on occasion, ²²⁸Ra from the thorium series. High concentrations of natural radionuclides may occur in drinking water taken from drilled wells when the bedrock contains considerable amounts of natural radionuclides. In regard to

radiation protection, the most important radionuclide is ^{222}Rn . High radon concentrations in drilled wells occur in Finland, Sweden and Norway but, for the most part, not in other European countries. The high concentrations of radon are associated with uraniferous granitic rocks.^{76,77} High concentrations of ^{222}Rn are also reported for waters of drilled wells in granitic bedrock in the United States (Maine and New Hampshire).² In general, radioactive concentrations of household waters in different countries are not statistically comparable as the measurements are performed unsystematically, for example only in areas of high concentrations. The measurements of the concentrations of ^{222}Rn in waters of drilled wells in Finland, Sweden and Norway are comparable, however. For geographical and geological representative sampling, the average radon concentration in drilled wells in these countries varies from 210 Bq/l to 340 Bq/l (Table 2).⁷⁷ The highest radon concentration has been measured in Finland, 78 000 Bq/l. The number of consumers in Finland using water from drilled wells is about 200 000. The number permanent dwellings where water is drawn from private drilled wells is 70 000–100 000 in Finland, about 200 000 in Sweden and about 100 000 in Norway.

Table 2. Radon (^{222}Rn) concentrations in drilled wells in Finland, Sweden and Norway.⁷⁷

Country	Average concentration of ^{222}Rn , Bq/l		Maximum concentration of ^{222}Rn , Bq/l	^{222}Rn in water exceeding 1000 Bq/l, percentage of all drilled well users
Finland	590 ^a	310 ^b	78 000	10%
Sweden	–	210 ^b	57 000	4%
Norway	–	ca 340 ^b	32 000	6–8%

a) The mean of all measurement results is weighted by the number of drilled wells in the area

b) Geographical and geological representative sampling

The average concentrations of radionuclides from the uranium decay series in drinking water supplied by waterworks and private wells in Finland are presented in Table 3.⁷⁸ The concentrations are clearly highest in drilled wells. The radioactivity concentrations of gross (total) alpha including long-lived alpha emitters ($^{234,238}\text{U}$, ^{226}Ra , ^{210}Po) in drilled wells in Finland are shown in the map of Figure 2. According to Table 3, the average concentration of the gross alpha activity in drilled wells is 1.13 Bq/l. The radioactivity concentration of the

gross alpha is mainly composed of the concentration of uranium. If the salinity of the water is high, ^{226}Ra may exceed the radioactivity concentration of uranium.

Table 3. Average concentrations of radionuclides from the uranium decay series in drinking water supplied by waterworks and private wells in Finland. Maximum concentrations are in parentheses. The whole population mean is weighted by the number of users of each water type.^{77,78}

Radionuclide	Tap water of waterworks, Bq/l		Dug wells, Bq/l		Drilled wells, Bq/l		Whole population mean, Bq/l
^{222}Rn	27	(6500)	60	(3600)	590	(78000)	50
^{234}U	0.02	(3.1)	0.02	(1.5)	0.6	(230)	0.04
^{238}U	0.015	(1.8)	0.02	(1.1)	0.4	(150)	0.03
^{226}Ra	0.003	(1.3)	0.01	(2.0)	0.06	(49)	0.006
^{210}Po	0.003	(0.29)	0.01	(1.3)	0.07	(16)	0.007
^{210}Pb	0.003	(0.15)	0.04	(1.4)	0.06	(21)	0.008

With respect to radiation dose, after ^{222}Rn the most important radionuclides in household water in Finland are polonium (^{210}Po) and lead (^{210}Pb).^{3,78} Uranium may increase the radiation dose in some cases, but the health effect of uranium is assumed to be chemical kidney toxicity rather than radiation hazard.^{5,6} Radium may increase the radiation dose only in saline waters. Using the average concentrations of ^{222}Rn , $^{234,238}\text{U}$, ^{226}Ra , ^{210}Po and ^{210}Pb (Table 3), ingestion of drilled well water causes an average radiation dose of 0.5 mSv/a to adult consumers in Finland, while the corresponding value for ingestion of water from waterworks is only 0.02 mSv/a. The concentration of 1000 Bq/l of ^{222}Rn in water corresponds to about 0.6 mSv annual radiation dose (Table 2). The highest radiation dose of a drilled well water user from all nuclides in water has been 70 mSv/a.⁷⁸ The average annual radiation dose to the Finnish population from all sources is 3.7 mSv, of which 2 mSv is caused by radon in indoor air.

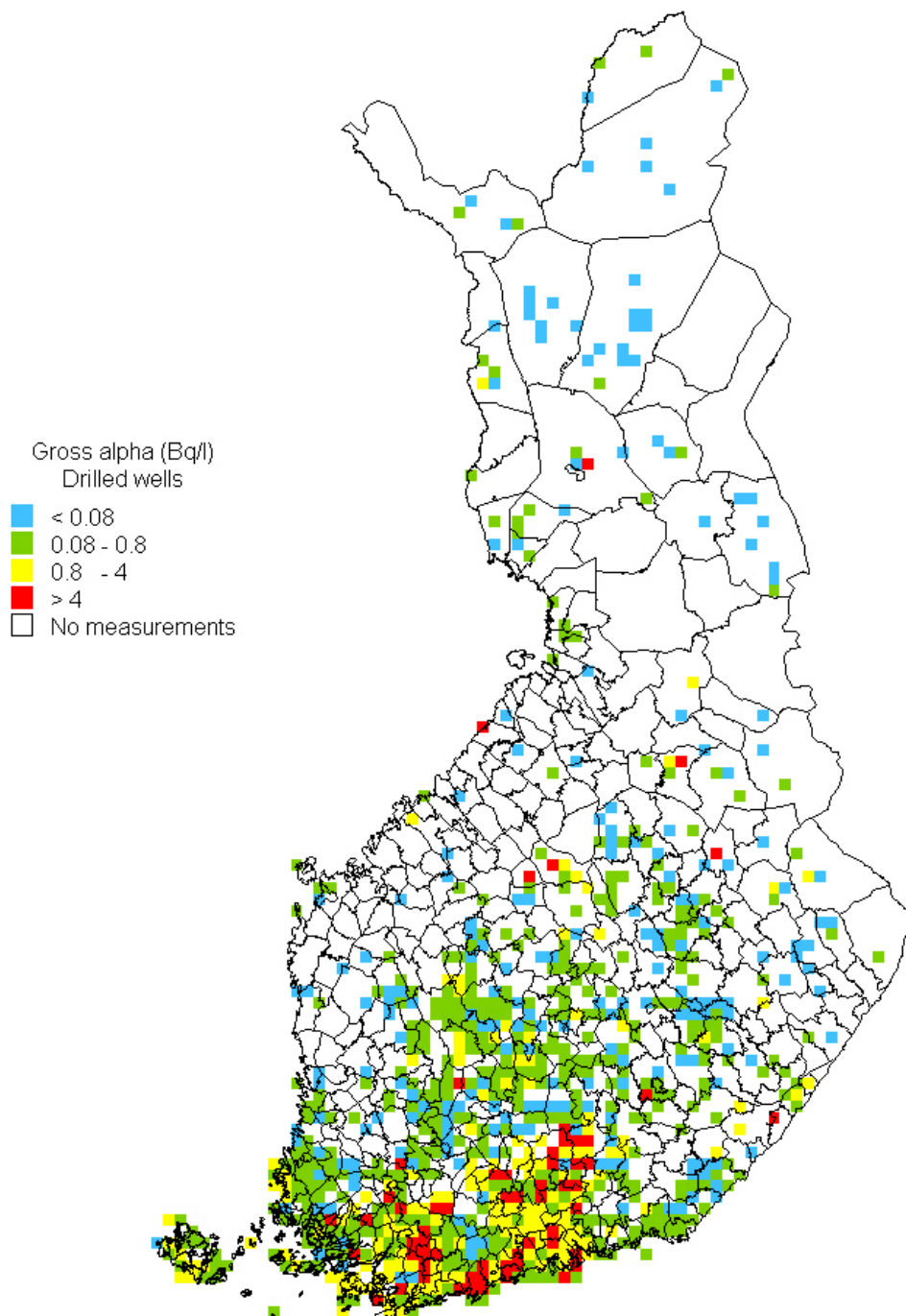


Figure 2. The gross alpha activities (Bq/l) in approximately 6000 drilled wells in Finland.⁷⁷

2.6.2 Health effects and proposed guidelines

Studies in the 1920s led to the conclusion that radon in the mine atmosphere was largely responsible for the lung disease of the miners, which was later diagnosed as lung cancer. By the 1950s, it was confirmed that the principal dose to the lung from inhalation of radon was due to the short-lived decay products.⁷⁹ At present, the indoor air ²²²Rn problem is well recognized, although risk estimations for lung cancer vary widely. In Finland, the radiation risk due to drinking water is, in general, smaller than that of indoor air radon. If radon exists in household water, it is released into the indoor air whenever water is used. It is estimated that the radiation risk for users of drilled well water is, on average, the same as for those who are exposed to indoor radon permeating from the soil into the room air.⁷⁶

Radiation effects have not been observed in man after exposure to natural uranium. The chemical toxicity of natural uranium is likely to be more dangerous for human health than the risk of cancer from radiation.⁵⁻⁸ Gilman and co-workers^{80,81} have concluded from laboratory animal studies that soluble uranium can produce specific tubular injury at relatively low doses. According to Finnish researchers,⁶ altered proximal tubulus function is weakly associated with natural uranium exposure, without a clear threshold. The study encompassed 300 consumers of drilled well water where median uranium concentration in the water was 28 µg/l (range from 0.001 to 1920 µg/l). Previous studies in humans have also shown that uranium in drinking water may affect kidney tubular function.^{82,83}

Radium was used intravenously for a variety of ills in the 1920s through to 1940. Bone cancer developed in many patients, as well as among painters of luminous dials who were exposed to radium by ingestion during the early years of last century.^{7,79} Mays and co-workers⁷ have estimated the cancer risk from a lifetime intake of radium isotopes and concluded that the cumulative lifetime risk to one million people, resulting from the daily ingestion of 0.185 Bq of a radium isotope, is 21 cancers for ²²⁶Ra and 22 for ²²⁸Ra. Elevated radiation doses due to ²¹⁰Po and ²¹⁰Pb have been found in the lichen–reindeer/caribou–human food chain. ²¹⁰Pb accumulated primarily to bone, and ²¹⁰Po exceeded concentrations of its precursor, ²¹⁰Pb, in soft tissues.^{84,85} Increase in cancer frequency due to the natural radionuclides in drinking water has not been demonstrated. However, since ²¹⁰Po and ²¹⁰Pb cause highest radiation

doses after radon via consumption of drilled well water, these radionuclides should be taken into consideration.

A proposal to restrict and monitor the radiation exposure from radioactive substances in drinking water in Finland suggests an action level of 300 Bq/l (0.2 mSv/a) for radon in waterworks. For other nuclides the action level is 0.1 mSv/a. The proposed guideline for radon in private wells is 1000 Bq/l (ca 0.6 mSv/a).⁷⁸ The EU directive for drinking water published in 1998 set a dose limit of 0.1 mSv/a from radioactive elements, excluding tritium, ⁴⁰K and radon and its daughter radionuclides.⁸⁶ Thus, doses due to ²¹⁰Po and ²¹⁰Pb were not regulated by the EU directive. A new recommendation, published by the EU Commission at the end of the year 2001, also takes into account radon and its long-lived daughter nuclides. According to the recommendation, it should be considered as a call for action if the concentrations of ²¹⁰Po and ²¹⁰Pb in waterworks exceed 0.1 Bq/l and 0.2 Bq/l, respectively. An action level of 1000 Bq/l for radon in private wells is also mentioned. Also according to the recommendation, concentrations of radon exceeding 100 Bq/l in waterworks call for the national government to set an action level.⁸⁷ Environmental Protection Agency (EPA) regulations in the United States limit the total radium content (combined ²²⁶Ra and ²²⁸Ra) of drinking water to 0.185 Bq/l.⁸⁸ Guideline values for uranium with respect to its chemical toxicity range from 2 µg/l to 100 µg/l.^{6,89} The World Health Organization (WHO) proposes the guideline value of 2 µg/l and the EPA 30 µg/l for the safe concentration of uranium in drinking water.^{88,89} The results of Finnish research suggest that the safe concentration of uranium in drinking water may lie within the range 2–30 µg/l.⁶ The amount of 30 µg/l (≈0.37 Bq/l) of natural uranium in water causes a radiation dose of 0.025–0.05 mSv/a assuming that the ²³⁴U/²³⁸U ratio is in the range of 1–3 and the consumption of water is on average two litres per day and using the dose conversion factors given by the Council of the EU (for adult 4.9×10^{-8} SvBq⁻¹ for ²³⁴U and 4.5×10^{-8} SvBq⁻¹ for ²³⁸U).⁹⁰

3. ION EXCHANGE

The general structural principle for ion exchangers is that they consist of a framework with electric surplus charge and mobile counter ions. However, hydrous metal oxides are often amorphous in character and hydroxyl groups cover their surface, causing the surface charge to depend on the pH of the solution. Many of these ion exchangers are amphoteric, i.e. anion exchangers at low pH and cation exchangers at high pH values.

Ion exchange materials are classified into natural materials and synthetic ion exchangers. The group of natural materials includes zeolites, clay and mica minerals and hydrous oxides. These naturally occurring inorganic materials can also be prepared synthetically. At present more than 100 zeolites have been synthesised and many of them do not have analogous structures to the known natural zeolites. Ion exchange resins are typically synthetic organic materials with polymer backbones. This section deals only with those ion exchange materials that were chosen for study in this work.

3.1 Ion Exchange Materials

Zeolites are hydrated aluminosilicates of the alkaline and alkaline earth cations.⁹¹ They have a porous three-dimensional framework structure, in which $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra are linked at their corners by oxygen bridges. The exchangeable cations move freely in the cavities and channels of the framework. The rigid and regular structure of a zeolite often acts as “a molecular sieve” which excludes molecules larger than the channels in the crystal lattice (Figure 3). Analcime, chabazite, clinoptilolite and mordenite are examples of naturally occurring zeolites, while zeolites A,X,Y and ZMS-5 are examples of synthesised zeolites. Zeolites are widely used as ion exchangers, catalysts and water softeners (e.g. zeolite A in the sodium form is commonly used for removing hardness from washing water).⁹² They are also used for the treatment of nuclear waste and the removal of radioactive fission products ^{90}Sr and ^{137}Cs at the Sellafield reprocessing plant in the United Kingdom.⁹³ The usefulness of zeolites in the decontamination of waste solutions is due to their high selectivity, thermal stability and resistance to radiation.⁹⁴ The ion exchange capacity of zeolites may be no higher than for organic ion exchange resins, but their selectivity is very much higher. The Si/Al ratio

affects the selectivity and capacity of the zeolites.⁹⁵ However, their application is limited to a narrow pH range (pH 5–10) because of their solubility in highly acidic and alkaline media.

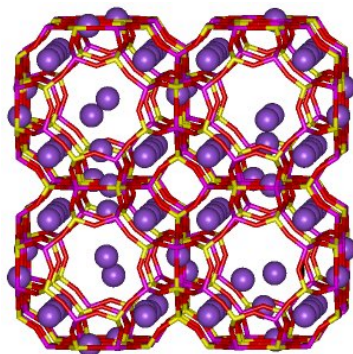


Figure 3. The structure of zeolite A in sodium form. Sodium (balls) is replaced by calcium and magnesium ions in water softening.⁹⁶

Clay and mica minerals, like zeolites, are aluminosilicates. Unlike the zeolites, however, they have layered structures and the exchangeable cations locate between the layers (Figure 4).⁹⁷ The structures of clay minerals are also more flexible than those of zeolites. A typical clay mineral is montmorillonite, which swells through widening of its interlayer distance. Higher ion exchange capacities than possessed by the natural clay minerals are obtained with the synthetic clays. Na-4-mica is a synthetic, highly charged sodium fluorophlogopite mica of nominal composition $\text{Na}_4\text{Al}_4\text{Si}_4\text{Mg}_6\text{O}_{20}\text{F}_4 \cdot x\text{H}_2\text{O}$, which is reported to take up radium selectively from sodium chloride solutions.⁹⁸

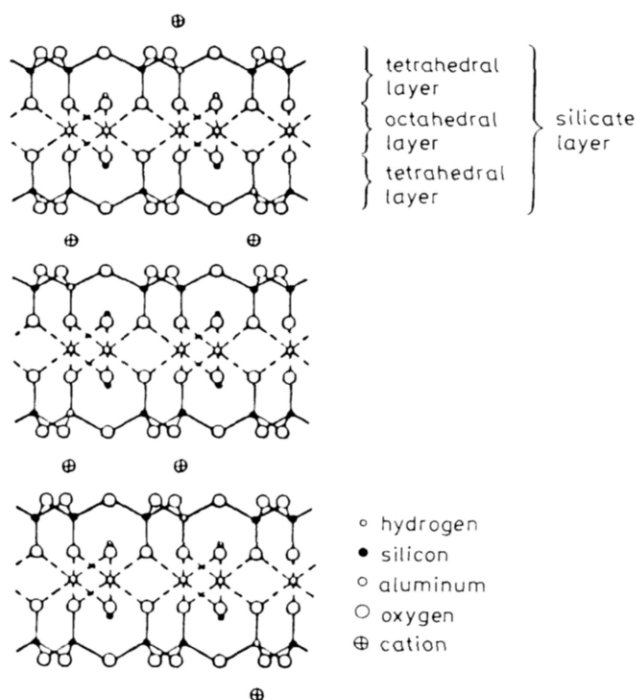


Figure 4. The structure of a dioctahedral mica-type clay mineral.⁹⁷

Also, hydrous **MnO₂** is sometimes used as an ion exchange material. MnO₂ has been applied for extracting ⁵⁴Mn, ⁶⁰Co and ⁶⁵Zn from reactor coolant waters and for removal of radium from natural waters.^{46,99} The point of zero charge (PZC) for δ-MnO₂ is 2.8. Zero charge is the proton condition where the surface charge is zero; thus above this pH value manganese oxide has negative surface charge and is able to take up cations.⁶⁹ **Sodium titanate**, Na₄Ti₉O₂₀·xH₂O, is a layered compound. Exchangeable sodium ions are located between the layers, which are constructed of TiO₆ octahedra.^{100,101} SrTreat[®] (Fortum Nuclear Services Oy, Finland) is a commercial highly selective sodium titanate for strontium, used to remove ⁹⁰Sr from basic waste solutions.¹⁰² As a weakly acidic exchanger it performs effectively for strontium only in alkaline solutions. Calcium ions strongly interfere with the strontium exchange. CoTreat is a commercial sodium titanate that is highly selective for radioactive cobalt and other activation corrosion products (e.g. ⁵⁴Mn, ⁵⁹Fe, ⁶⁵Zn, ⁶³Ni) contained in waste waters generated by nuclear power plants.¹⁰³

The framework (matrix) of the **organic ion exchange resins** consists of an irregular, macromolecular, three-dimensional network of hydrocarbon chains.⁹¹ Generally, the matrix (R) is composed of polystyrene (Figure 5) or acrylic acid crosslinked with divinylbenzene (DVB). The degree of crosslinking in commercial resins typically ranges from 2% to 20%. Increase in the degree of crosslinking results in greater chemical and mechanical stability and greater differences in selectivity for ions. In addition, a greater number of crosslinks makes the network more rigid and the resin has less tendency to swell. Two types of synthetic resins are available: macroporous resins and gel-type resins. Pores of macroporous resins can be as much as several hundred nanometers in diameter, whereas the pores of the gel-type resins are less than 10 nm (100 Å) diameter. Interlayer distances and sizes of the channels of the synthetic inorganic ion exchangers tend to be smaller, less than 10 Å.

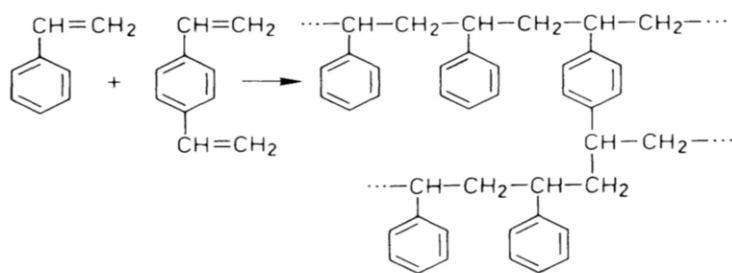
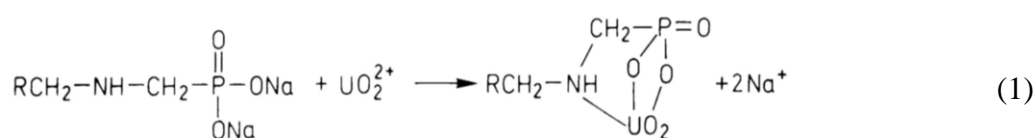


Figure 5. The crosslinked polystyrene divinylbenzene (product). The styrene (C_8H_8) is polymerized with itself and with divinylbenzene ($\text{C}_{10}\text{H}_{10}$).¹⁰⁴

The most common cation exchanger resins are the strong acid cation exchanger (SAC) with sulphonic acid groups ($-\text{SO}_3^-$) and the weak acid cation exchanger (WAC) with carboxylic acid groups ($-\text{COO}^-$). Sulphonic acid resin can be prepared by treatment of styrene–divinylbenzene copolymer with concentrated sulphuric acid where the ionic groups ($-\text{SO}_3^-$) are attached to the styrene rings. The most extensively used weak acid cation exchangers are crosslinked copolymers of acrylic or methacrylic acid.⁹¹

Cation exchangers with preference for specific cations can be made by introducing groups that form chelates with these cations. Commercial products of this kind are the chelating

aminophosphonate and iminodiacetate resins. In iminodiacetate resins, the iminodiacetate groups are attached to a styrene matrix and ions can be fixed forming metal chelate complexes. In aminophosphonate resins the two exchangeable ions (usually sodium) in the phosphonate groups can be replaced with a divalent ion, such as Zn^{2+} or UO_2^{2+} . Moreover, the free electron pairs of the oxygen atoms in the phosphonate group and the nitrogen atom in the amino group form a coordination bond with the metal, leading to a strong multi-ring chelate system. The chelating reaction for uranyl ion can be expressed as follows:¹⁰⁵



The strong base anion exchangers (SBA) and the weak base anion exchangers (WBA) are mainly prepared by chloromethylation of polystyrene. If the chloromethylated intermediate is treated with trimethylamine, the strong base anion exchanger is obtained with the ionic groups $-N^+(CH_3)_3$. Reaction with tertiary dimethylamine, in turn, gives the weak base amino groups. In general, the advantages of the organic resins over the inorganic ion exchangers are the high chemical and mechanical stability, high ion exchange capacity and fast ion exchange rate.

The organic resins are widely used in water treatment. Strong acid cation exchangers (SAC) are used to remove hardness (Ca^{2+} and Mg^{2+}).¹⁰⁶ Concurrently with hardness, they also effectively remove radium from ground water.^{107,108} In general, all cation exchange resins remove Ca and Mg effectively, but the SAC resins are preferred in many applications.¹⁰⁶ Chelating resins have been investigated for the purification of metallurgical process effluents. The aminophosphonate and iminodiacetate resins have proved to be highly effective in removing zinc and nickel from effluents in the metal plating industry.¹⁰⁹ Conventional organic resins – the strong acid cation and strong base anion exchangers – are used at nuclear power plants for purification of different water solutions (primary coolant water, spent fuel storage pond water).¹¹⁰ Recently, SAC and SBA resins have been applied for the removal of natural radionuclides from drinking water.

3.2 Ion Exchange Equilibria

An exchange of ions occurs when an ion exchanger with the counter ions B^{z_B} is contacted with a solution containing ions A^{z_A} . A binary ion exchange reaction between ion A and ion B can be expressed as



where A^{z_A} and B^{z_B} are ions in solution, \bar{B}^{z_B} and \bar{A}^{z_A} are the ions in a solid ion exchanger, and z_A and z_B are the ion charges. Ion exchange is a stoichiometric process; each ion that is removed from the exchanger is replaced by an equivalent amount (moles of unit charge) of another ion of the same sign.

The ion exchanger usually takes up certain counter ions in preference to others. Large ions may be excluded by sieve action. For example, with certain zeolites, Cs^+ ion is excluded because the ion is larger than the pore width of the zeolite. In organic resins the counter ion with smaller solvated equivalent volume is preferred because it causes less swelling than the larger one. The ion exchanger prefers the counter ion of higher valence (electroselectivity) and preference increases with dilution of the external solution. Ions that form strong complexes with the fixed ionic groups of the ion exchangers, and ions that associate least with the ions of the external solution, are also preferred. In organic resins, selectivity increases with increasing degree of crosslinking of the resin.⁹¹ The selectivity coefficient ($k_{A/B}$), the most commonly used equilibrium quantity for measuring the efficiency of the ion exchanger, is defined as

$$k_{A/B} = \frac{[\bar{A}]^{z_B} [B]^{z_A}}{[A]^{z_B} [\bar{B}]^{z_A}} \quad (3)$$

where $[A]$ and $[B]$ are concentrations of the ions in solution (mol/l) and $[\bar{A}]$ and $[\bar{B}]$ those in the exchanger (mol/kg dry exchanger). The selectivity coefficient ($k_{A/B}$) depends on the composition of the exchanger and the total concentration of the external solution.¹¹¹

The distribution coefficient (K_D) is often used to express the distribution of an ion between the exchanger and solution phase, especially in a trace component removal. Distribution coefficient K_D of ion A is defined as the ratio of the concentration in the exchanger to the concentration in solution:

$$K_D = \frac{[\bar{A}]}{[A]} \quad (4)$$

The distribution coefficient generally depends on the ionic composition of the exchanger and the solution. From equations (3) and (4) one obtains for binary exchange:

$$K_D = k_{A/B} \frac{1}{Z_B} \left(\frac{[\bar{B}]}{[B]} \right)^{\frac{Z_A}{Z_B}} \quad (5)$$

Hydrolysis of the ion exchanger and the cations in solution may interfere with ion exchange equilibria.¹¹² Weakly acidic ion exchangers prefer hydronium ions and take them up from water. Thus



which is a net reaction of Na^+/H^+ exchange and dissociation of water. Hydrolysis of the ion exchanger may increase the pH of the solution and, the change in pH may alter the speciation of the ions in the solution. Hydrolysis of cations in aqueous solutions may be expressed as in equation 7:



If the hydrolysed metal species is charged, it may undergo ion exchange reactions. In the case that hydrolysable ions are present, the ion exchange reactions and the concentrations of the different species should be known for the determination of the ion exchange equilibrium quantities.

3.3 Capacity

Radionuclides are usually present in water in trace concentrations. A trace radionuclide does not significantly alter the ionic composition of the exchanger, which in practice is in the ionic form of the macro ion in solution. Thus, it is not relevant in the case of trace ion exchange to determine the theoretical specific capacity (Q), which is defined by the number of ionogenic groups in the material (meq/g of dry exchanger).

Much more important is to determine the processing capacity of the ion exchanger. A column run is the preferred method for separating ions from water. A curve of the concentration of an ion in effluent as a function of effluent volume is called the breakthrough curve. The processing capacity of an ion exchanger can be estimated from the value of the distribution coefficient (K_D). The theoretical processing capacity is equal to the K_D value, which can easily be determined for trace ions by the batch method. In trace ion exchange, the K_D value corresponds to a breakthrough of 50% and it describes the volume of solution treatable with a kilogramme of exchanger. In real radionuclide separation processes, however, the column operation is usually discontinued once a measurable breakthrough value is obtained, which typically occurs well before the total processing capacity has been reached.¹¹¹ The processing capacity of an ion exchanger can be calculated at any arbitrary breakthrough level, e.g. at 1% or 10%.

In the case of binary uni-univalent exchange ($z_A = z_B = 1$), a simple relationship can be obtained between K_D and the feed composition ($[A]$, $[B]$) and selectivity coefficient $k_{A/B}$. By combining the equations (3) and (4) and inserting $[\bar{B}] = Q - [\bar{A}]$:

$$K_D = \frac{Q}{\frac{[B]}{k_{A/B}} + [A]} \quad (8)$$

where Q is the ion exchange capacity ($Q = [\bar{A}] + [\bar{B}]$), $k_{A/B}$ is the selectivity coefficient and $[B]$ is the macro ion concentration in solution. For example, for the Cs/Na exchange ($RNa + Cs^+ \rightleftharpoons RCs + Na^+$):

$$K_D = Q/([Na] / k_{Cs/Na} + [Cs]) \quad (9)$$

Because $[Cs] \ll [Na]$ in trace ion exchange, also $[Na]/k_{Cs/Na} \gg [Cs]$ and $Q \approx [Na]$. Under the special condition in which Cs is present in the solution in trace amount (e.g. as ^{137}Cs isotope), the capacity of the ion exchanger is independent of the trace ion Cs in solution but depends on Q and the concentration of Na (macro ion).

The shape of the column breakthrough curve depends on the operating conditions and is often described by various plate models. In general, the performance of the column improves as the number of theoretical plates (N) is increased. The film diffusion, particle diffusion and longitudinal diffusion contribute to the number of theoretical plates. Longitudinal diffusion is important only when flow rates are very low. Both the film diffusion and particle diffusion may simultaneously affect the kinetics of the ion exchange. The plate number N_f for film diffusion controlled exchange is¹¹³

$$N_f = A \frac{D_f s}{d^{3/2} u_0^{1/2}} \quad (10)$$

where A is an empirical factor, D_f is the diffusion coefficient, s is the column length, d is the particle diameter and u_0 is the linear flow rate. Correspondingly, the plate number N_p for particle diffusion controlled exchange is

$$N_p = B \frac{D_p s}{d^2 u_0} \quad (11)$$

where B is an empirical factor. The number of theoretical plates (N) can be increased by reducing the flow rate and the exchanger particle size and by increasing the column length.

Ion uptake on a resin with weak acid and weak base groups depends on pH because the dissociation of the groups is pH-dependent. The most common ionogenic group of a weak acid cation resin is carboxylic acid, which dissociates above the pK value of 4–6 ($\text{pK}_{\text{resin}} = -\log([R^-][H^+]/[RH])$). This means that, at pH above 6, the weak acid groups are completely ionised and active. Weak acid resins carrying phenolic acid groups do not dissociate until pH

9–10. Correspondingly, weak base anion resins dissociate in acidic pH and the ionogenic groups are completely ionised at pH values below 7.^{91,104} Ion exchangers with strongly acidic or strongly basic groups are completely dissociated over the whole pH range and they can be used under acidic, neutral and alkaline conditions. Many polyfunctional ion exchangers contain ionogenic groups that differ in their pK values. For example, at pH 1–6 the aminophosphonate resin is converted from the form $R-CH_2-NH_2^+-CH_2-PO_3H^-$ to the completely dissociated phosphonic group form $R-CH_2-NH_2^+-CH_2-PO_3^{2-}$. The protonated amino groups dissociate at pH above 6 where $R-CH_2-NH-CH_2-PO_3^{2-}$ forms.¹¹⁴

4. MATERIALS AND METHODS

4.1 Ground Waters

The ground water samples used in the column and filtration experiments were obtained from ten private drilled wells located in the southern part of Finland, where the granitic bedrock contains considerable amounts of uranium and its daughter radionuclides. A criterion for choosing the wells was that they contained high concentrations of natural radionuclides and were used as a source of drinking water. Today, half of the wells are still in use but the water is purified. Most of the waters studied can be categorised as Ca-HCO₃-bearing, which is a typical property of ground water in the granitic bedrock of Finland. Two of the waters had a high saline content and are of Na-Cl type. Some had high Fe, Mn and organic matter concentrations. The compositions of the ground waters used in the filtration experiments are shown in Table 4. More detailed descriptions of the compositions and the activity concentrations of the radionuclides in the ground waters used in the column and the filtration experiments can be found in publications **I** and **III–V**. The water samples were collected from sampling taps into plastic bottles at the site and were taken to the laboratory, without pretreatment, within three hours of sampling. All samples were bubbled with nitrogen gas (purity 99.5%) to expel radon.

Table 4. Chemical compositions of the ground waters in the filtration experiments.

Ground water	Fe (mg/l)	Mn (mg/l)	KMnO ₄ number ^b (mg/l)	TOC (mg/l)	Al (µg/l)	Cl (mg/l)	HCO ₃ (mmol/l)	pH
Water 1	0.011	0.015	3.2	n.d.	8.9	15	1.93	7.87
Water 2	0.018	0.011	8.5	n.d.	63	4.4	1.25	7.85
Water 3	1.1	1.1	24	n.d.	2.2	4.7	4.99	7.86
Water 4	1.1	0.25	13	n.d.	2.7	159	3.03	7.53
Water 5	1.8	0.85	16	n.d.	7.3	905	2.09	7.77
Water B	0.06 ^a	0.10	n.d.	1.9	< 1	4.8	0.68	7.01
Water L	0.40 ^a	0.15	n.d.	2.1	< 1	4.8	0.65	6.91
Water K	0.03	0.003	n.d.	1.8	35	45	1.55	7.81
Water I	0.13 ^a	0.26	n.d.	2.0	< 1	17	2.85 ^c	8.91

a) Before ICP-MS measurements, the sample was filtered through 0.45 µm filter and some iron may have been sorbed on the filter; thus the Fe concentration does not represent the initial concentration in the raw water (see text in **IV**). Concentrations of Fe in the other waters were determined in unfiltered water by AAS.

b) Amount of oxidised total organic matter is determined by KMnO₄ consumption.

c) The concentration of bicarbonate in water I is estimated from the equivalent amount of cations.

n.d. = not determined

Ground water simulants were used in the determination of radionuclide (U, Ra, Po) distribution coefficients (publications **I**, **II**) and in the column experiments (publication **II**). The compositions of the simulants are representative of the compositions of drilled well waters in Finland. One of the simulants represents a good quality drinking water but the element concentrations are nearly twice as high as in typical bedrock water.¹¹⁵ The doubled values help to bring out the differences between the various exchangers. A second simulant was an Fe–Mn-rich water and a third had elevated concentration of NaCl. A detailed description of the composition of the simulants can be found in publication **I**.

4.2 Ion Exchangers

At the beginning of the work, six organic and five inorganic ion exchangers were evaluated for the removal of uranium, radium and polonium from water (Table 5). The chelating aminophosphonate and iminodiacetate resins and the inorganic ion exchange materials had not previously been studied for this purpose.

Table 5. Ion exchangers tested.

Type	Name	Chemical composition	Manufacturer
Organic ion exchangers ^a			
Aminophosphonate	Purolite S950	R-CH ₂ NHCH ₂ PO ₃ H ₂	Purolite
Iminodiacetate	Purolite S930	R-N(CH ₂ COOH) ₂	Purolite
Strong acid cation	Purolite C145H	R-SO ₃ H	Purolite
Weak acid cation	Purolite C104	R-COOH	Purolite
Strong base anion	Purolite A500	R-N(CH ₃) ₃ OH	Purolite
Weak base anion	Purolite A105	R-N(CH ₃) ₂	Purolite
Inorganic ion exchangers			
Sodium titanate	CoTreat	–	Selion Oy ^b
Synthetic mica	Na-4-mica	Na ₄ Mg ₆ Al ₄ Si ₄ O ₂₀ F ₄ · xH ₂ O	Unilever Ltd ^c
Manganese dioxide	–	MnO ₂ · xH ₂ O	Reference ^d
Synthetic zeolite	Zeolite A (Si/Al=1.1)	Na ₁₂ [(AlO ₂) ₁₂ (SiO ₂) ₁₂] · 27H ₂ O	Laporte and Bayer
Synthetic zeolite	Mordenite (Si/Al=5)	Na _{7.8} [(AlO ₂) ₈ (SiO ₂) ₄₆] · 26H ₂ O	Laporte

R= Styrene-divinylbenzene

a) Macroporous types

b) At present Fortum Nuclear Services Oy

c) Obtained from Unilever Ltd, prepared according to reference 116

d) Prepared according to reference 117

4.3 Experimental Procedures

4.3.1 Batch and column experiments

Preliminary screening of the ion exchangers was carried out by determining the distribution coefficients (K_D) for uranium and radium in the ground water simulants. These tests (publication **I**), and the experiments on the effect of pH and uranium concentration on the removal of uranium (publication **II**), were carried out by the batch method. The K_D values were calculated according to the equation

$$K_D = \frac{[\bar{A}]}{[A]} = \frac{\text{concentration in ion exchanger}}{\text{concentration in solution}} = \frac{(A_0 - A) V}{A m} \quad (12)$$

where A_0 and A are radionuclide activities in solution before and after contact, V is the solution volume (ml) and m is the dry exchanger mass (g). V/m is called the batch factor. The uncertainty of the K_D value is caused mainly by the standard deviations of the activity

measurements. The error is high when the activity of the sample is near the background level. For example, when the K_D value exceeds one million (sample activity is low), the error varies from 10% to 60%, but for a K_D value of 10 000 ml/g the error is below 10% varying with the experimental conditions (concentration of A_0 , batch factor).

Processing capacities of the exchangers and the decontamination factors (DF) were determined in column experiments. The water simulant spiked with ^{238}U (publication **II**) and the drilled well waters (publications **I** and **V**) were passed through the ion exchanger bed and the breakthrough values of the radionuclides or inactive elements were determined as a function of the processed bed volumes (BV). The breakthrough values were calculated by dividing the ion concentration in the effluent by the ion concentration in the feed water and are expressed as percentages. The decontamination factor (DF) is defined as

$$DF = \frac{C_0}{C} \quad (13)$$

where C_0 and C are the ion concentrations in the feed and effluent, respectively. The DF value is the inverse value of the breakthrough level (e.g. a 0.1% breakthrough level corresponds to a decontamination factor value of one thousand).

The pretreatment of the ion exchangers for the batch and the column experiments is described in publications **I** and **II**. Before determination of the distribution coefficients (K_D) the ion exchangers were equilibrated with the non-radioactive ground water simulants in order to achieve equilibrium with respect to macro ions. The K_D values were then determined by spiking the simulants with ^{233}U , ^{226}Ra or ^{209}Po . The initial pH of the spiked simulant waters was approximately 8. The effect of pH was studied by adjusting the pH of the water with 1 M HCl. The concentration of uranium was adjusted between 0.02 mg/l (8.4×10^{-5} mmol/l) and 25 mg/l (0.1 mmol/l) at pH 8 with a ^{238}U solution (publication **II**). The simulant was also spiked with a ^{233}U tracer solution because the specific activity of the ^{238}U was not high enough for K_D determinations. The equilibration time in the determinations was three days, after which the exchanger was separated from the solution phase by centrifugation and filtration through 0.2 μm filters. The pH values of the supernatants were determined after equilibration. All experiments were carried out in duplicate.

Adsorption of the radionuclides on the walls of the equilibration vessels and filter materials was evaluated in blank tests by shaking spiked simulant waters for three days in plastic vessels and by filtering samples through different materials. Uranium and radium did not adsorb on the equipment significantly, but large fractions of polonium and lead adsorbed on both vessels and filters. As a result, no definite K_D values could be obtained for the radionuclides of polonium and lead.

The performance of the ion exchangers in the column-mode experiments for the removal of $^{234,238}\text{U}$, ^{226}Ra , ^{210}Po and ^{210}Pb from uranium-rich drilled well water is discussed in publication **I**. As the K_D values suggested that the processing capacities of the exchangers would be high, the tests were not run up to exhaustion of the exchanger. Instead, only 1800 bed volumes (BV; 1 BV = 10 ml) of drilled well water was processed through the exchanger beds. The average concentration of uranium in the feed water was 7 mg/l (0.03 mmol/l). The 18 litres processed correspond to a water consumption of 3–4 months in a typical Finnish single-family dwelling, assuming a usage rate of 5 m³/week and a 40-litre exchanger bed. Four different elution rates were used to investigate the effect of flow rate on element removal: first, 6 litres at 15 BV/h; then 4 litres at 40 BV/h; 4 litres at 60 BV/h; and, finally, 4 litres at 80 BV/h, all at pH 7–8. The particle size was 0.3–0.85 mm for the inorganic ion exchangers and 0.3–1.2 mm for the organic resins. The processing capacities of the ion exchangers for inactive elements (metals and anions) were determined simultaneously. A constant flow rate (20 BV/h) was also used for inactive elements (publication **V**). The metal concentrations and pH of the effluents were analysed.

The processing capacities of the strong base anion resin and the chelating aminophosphonate resin for uranium were investigated in the ^{238}U spiked water simulant at pH values 5 and 8 (publication **II**). The pH of the simulant water was 8 before it was adjusted to pH 5 with concentrated HNO_3 solution. The concentration of uranium in these experiments was 4.7 mg/l (0.02 mmol/l). A total of 2000 bed volumes of the spiked simulant water was processed through the resin beds at a flow rate of 20 BV/h.

4.3.2 Filtration experiments

The ground water samples for the filtration experiments were obtained from nine drilled wells. The presence of ^{210}Po and ^{210}Pb in particles in ground waters from four different locations is discussed in publication **III** and the presence of $^{234,238}\text{U}$, ^{226}Ra and ^{210}Po in five drilled well waters in publication **IV**.

Water samples of 50 or 250 ml were filtered through a Sartorius Ultrasart[®] Cell 50 ml pressure filtration system, with use of a magnetic stirrer to prevent filter clogging. Polyethersulphone filters were 47 mm in diameter and of pore size 5 kD, 10, 50, 100, 450 and 800 nm. 5 kD corresponds to approximately 1 nm in pore size. The overpressure in the system was 0.5–2 bar. Since it was noticed in the filtration experiments of publication **III** that the activity concentrations in the sample vessels did not remain constant, subsequent filtrates (publication **IV**) were immediately acidified with concentrated HCl to pH 1. Subsamples of the unfiltered water (raw ground water) were also acidified. The results of the filtrations were confirmed with two parallel determinations.

$^{234,238}\text{U}$, ^{226}Ra , ^{210}Po and ^{210}Pb were desorbed from the filters by shaking the filters in plastic bottles with concentrated acid. The activity fraction retained in the filters may represent particles or adsorbed ionic species. An approximate value of the ionic adsorption was obtained by equilibrations of unused filters with each ground water in a plastic bottle. In study **III**, the filters were treated with acid solution after equilibration. The desorbed ^{210}Po and ^{210}Pb was assumed to have been taken up by adsorption of non-particulate polonium and lead. As the adsorption of uranium and radium was expected to be very low, a different procedure was used in study **IV**. After equilibration (and with filters discarded), the waters were acidified with concentrated HCl to pH 1. The activities in these acidified samples were then compared with the activities in the acidified raw waters, and the difference was taken as a measure of the adsorption of non-particulate radionuclides to the filters. The activity fractions adsorbed on the filtration system were determined by washing the equipment with HCl solution and counting the solutions for $^{234,238}\text{U}$, ^{226}Ra , ^{210}Po or ^{210}Pb .

Fractions retained in the filter were calculated as

$$A_{i,F} = A_{i,Tot} - (A_{i,E} + A_{i,ADS_s}) \quad (14)$$

where i is the radionuclide, $A_{i,F}$ the fraction retained in the filter, $A_{i,Tot}$ the total activity in the raw water, $A_{i,E}$ the activity in the filtrate and A_{i,ADS_s} the activity of the fraction adsorbed on the filtration system. Activity of the nuclides retained in the filter was also determined in actual activity measurements, but the inaccuracy is great and the values obtained from equation 14 were used instead.

The proportions of radionuclides bound in different particle fractions were calculated in a similar manner in publications **III** and **IV**, except that in publication **IV** the fractions of the radionuclides in the filtrates were calculated by comparing the filtrate activities with the activities of the raw water, while, in publication **III** the filtrate activities were compared with the summed activities of the filtrate, the activity in the filter and the activity adsorbed in the filtration system.

4.4 Determination of Radioactive and Inactive Elements

The methods of determining ^{210}Po and ^{210}Pb are described in detail in publication **III**. ^{210}Po activities were determined by alpha spectrometry. Polonium was spontaneously deposited on a silver disc and a ^{209}Po tracer was used for the determination of the chemical yield. The samples of ^{210}Pb were purified by ion exchange with SrResin[®] (EiChrom). Lead carrier was added before the purification for the determination of the yield, and the concentration of lead was determined by atomic absorption spectrophotometry. ^{210}Bi was allowed to grow for one to two weeks in the purified lead sample, during which time 62–85% ingrowth of ^{210}Bi from its equilibrium state occurred. The summed activity of ^{210}Pb and ^{210}Bi was determined with a low background liquid scintillation counter 1220 Quantulus[™] (Wallac).

The activities of ^{226}Ra were derived from the total (gross) alpha spectra determined with the low background liquid scintillation counter, using pulse shape analysis. The total alpha activities were determined in the column and the filtration experiments as described by

Salonen and Hukkanen.¹¹⁸ The activity concentration of ^{226}Ra was determined from its daughter, ^{214}Po . The water sample (40 ml) was evaporated in a teflon-coated polyethylene vial. The residue was dissolved in 1 ml of 1 M HCl to which 20 ml of scintillation cocktail (Wallac, OptiPhase ‘Hisafe 3’) was added. The sample volume was lower (5 ml) in the case of water of high salt content because high salt concentration interferes with the separation of the ^{214}Po peak from the total (gross) alpha peak (publication **IV**). The radium samples were measured one month after sample preparation, when ^{214}Po was in equilibrium with ^{226}Ra . Figure 6 shows the liquid scintillation alpha spectrum of a drilled well water in which the activity concentration of ^{226}Ra was very high (22 Bq/l). The alpha peaks of U (^{238}U 4.20 MeV, ^{234}U 4.77 MeV), ^{226}Ra (4.78 MeV), ^{210}Po (5.31 MeV), ^{222}Rn (5.49 MeV) and ^{218}Po (6.00 MeV) are located in channels 525–700, while ^{214}Po (7.69 MeV) is seen at higher channels (up to 765).

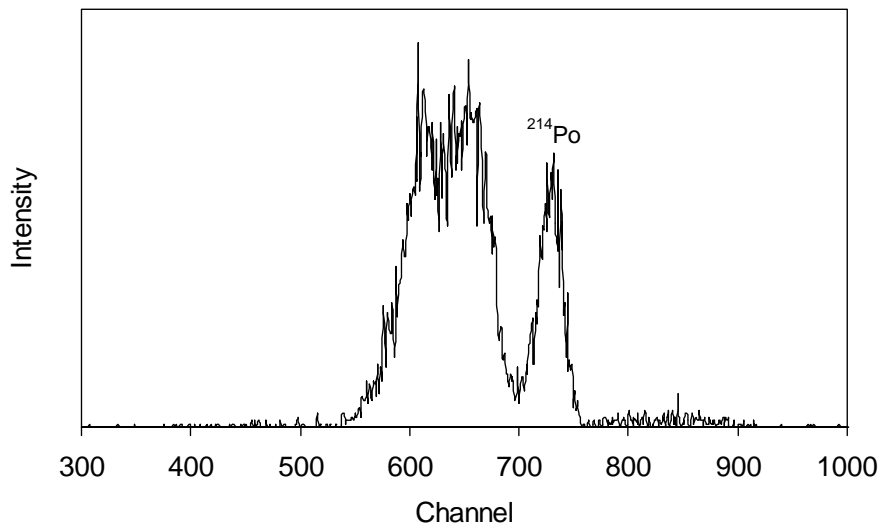


Figure 6. A low-background liquid scintillation alpha spectrum (QuantulusTM) of a saline drilled well water.

The activity concentration of ^{226}Ra was calculated as follows:

$$A_{\text{Ra}} = \frac{R_{\text{Po}}}{60 \times V \times E} \quad (15)$$

where R_{Po} is the count rate of ^{214}Po , V is the sample volume and E is the counting efficiency for ^{214}Po . Except for ^{214}Po , the counting efficiencies of alphas in the liquid scintillation counting are usually close to 100%. A standard sample of ^{226}Ra (85 ± 1.67 Bq/g) was used for the determination of the counting efficiency for ^{214}Po , which was 86%.

In the experiments with the simulant waters (publications **I** and **II**), the activity of uranium was usually measured with the low background liquid scintillation counter. In K_D determinations of publication **I** some of the uranium and radium activities were measured with a 1219 Rackbeta scintillation counter (Wallac). The concentration of uranium ($^{234,238}U$) in the column experiments of publication **I** was calculated by subtracting the counts due to ^{226}Ra , ^{222}Rn , ^{218}Po , ^{214}Po and ^{210}Po from the counts in the alpha window of the Quantulus spectrum. This can be done when the samples are counted one month after sample preparation, when ^{214}Po is in equilibrium with ^{226}Ra . ^{210}Po activities were determined by the radiochemical method. All activity concentrations of uranium ($^{234,238}U$) reported in publication **IV** were determined by a radiochemical method. The sample was purified by ion exchange with Dowex[®] 1x4¹¹⁹ and precipitated with cerium fluoride.¹²⁰ Finally, the activity of uranium ($^{234,238}U$) was determined by alpha spectrometry with PIPS semiconductor detectors. The uncertainties given for the liquid scintillation counting and α spectrometry are 1σ counting errors.

Inactive metal concentrations of the ground waters were mainly determined by inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma atomic emission spectrometry (ICP-AES) and the anions (Br^- , Cl^- , F^- , NO_3^- , SO_4^{2-}) were determined by ion chromatography. Atomic absorption spectrophotometry (AAS) was used for determinations of the metal concentrations of the simulant waters and for iron and manganese concentrations in ground waters. Concentrations of phosphate were determined by UV spectrophotometry, and concentrations of bicarbonate and the $KMnO_4$ number by titrimetry. The $KMnO_4$ number was used as a measure of the total organic matter and describes the amount of humic substances in the waters (publication **IV**). Total organic carbon (TOC) was determined in the experiments of publication **III**. The error of determination for AAS is 15%. The uncertainty for the determinations of anions is 5–15% (2σ error) and the uncertainty for ICP-MS/AES 10–20% (2σ error) varying with the concentration and the element in question.

5. RESULTS AND DISCUSSION

5.1 Removal of $^{234,238}\text{U}$, ^{226}Ra , ^{210}Po and ^{210}Pb by Ion Exchange Method

Various ion exchange materials were tested for the removal of uranium, ^{226}Ra , ^{210}Po and ^{210}Pb from water. Screening tests were carried out by determining K_D values for the ion exchangers by batch method. The ion exchangers that showed the best performance in K_D experiments were further tested in column-mode experiments. Polonium and lead were found to adsorb on the equipment and the results of the column experiments suggested that they are present in water mainly in particle form.

5.1.1 Screening of the ion exchangers

In all three water simulants the highest distribution coefficients for uranium were obtained with the strong base anion resin (Table 6). The weak base anion resin also gave relatively high K_D values. Uranium was present in the water simulants as anionic carbonate complexes, and the anion exchange resins were able to take up uranium efficiently. The Na-4-mica was the only inorganic ion exchanger that took up uranium reasonably well.

The strong and weak acid cation resins took up radium fairly efficiently (Table 7). However, the inorganic ion exchangers, especially manganese dioxide and sodium titanate, were clearly more efficient than the organic resins. The K_D values were in the order of a million for manganese dioxide and sodium titanate.

Table 6. ^{233}U distribution coefficients for organic and inorganic ion exchangers in three ground water simulants (Fe–Mn-rich water, good quality water and saline water).

Exchangers	K_D (ml/g) Fe–Mn-rich water simulant	pH_{eq}	K_D (ml/g) good quality water simulant	pH_{eq}	K_D (ml/g) saline water simulant	pH_{eq}
Organic resins						
Strongly acidic resin	14	8.49	0	8.23	44	8.29
Weakly acidic resin	2220	7.61	0	8.34	190	8.33
Strongly basic resin	15×10^6	8.53	29×10^6	8.18	4.4×10^6	8.26
Weakly basic resin	2.1×10^6	8.46	880 000	8.22	165 000	8.32
Aminophosphonate	13 450	7.72	41 050	8.35	32 500	8.33
Iminodiacetate	53 000	7.73	n.d.	n.d.	n.d.	n.d.
Inorganic exchangers						
Na-4-mica	35 300	8.50	n.d.	n.d.	n.d.	n.d.
Zeolite A	82	8.26	0	8.29	107	8.36
Mordenite	49	8.17	n.d.	n.d.	n.d.	n.d.
Manganese dioxide	650	7.93	n.d.	n.d.	n.d.	n.d.
Sodium titanate	7600	7.91	2140	8.02	2550	8.13

n.d.= not determined

eq = equilibrium

Table 7. ^{226}Ra distribution coefficients for organic and inorganic ion exchangers in three ground water simulants (Fe–Mn-rich water, good quality water and saline water).

Exchangers	K_D (ml/g) Fe–Mn-rich water simulant	pH_{eq}	K_D (ml/g) good quality water simulant	pH_{eq}	K_D (ml/g) saline water simulant	pH_{eq}
Organic resins						
Strongly acidic resin	15 200	8.59	19 900	8.08	21 700	8.31
Weakly acidic resin	5230	7.84	8060	8.19	8250	8.28
Strongly basic resin	0	8.58	0	8.32	100	8.32
Weakly basic resin	0	8.38	0	8.30	86	8.35
Aminophosphonate	1800	7.26	3220	8.29	3060	8.31
Iminodiacetate	980	7.73	n.d.	n.d.	n.d.	n.d.
Inorganic exchangers						
Na-4-mica	146 000	8.36	n.d.	n.d.	n.d.	n.d.
Zeolite A	106 000	8.51	153 000	8.27	116 300	8.34
Mordenite	45 600	8.57	n.d.	n.d.	n.d.	n.d.
Manganese dioxide	5.4×10^6	7.89	n.d.	n.d.	n.d.	n.d.
Sodium titanate	2.0×10^6	7.84	1.4×10^6	8.11	1.5×10^6	8.21

n.d.= not determined

eq = equilibrium

Exchangers were selected for further testing on the basis of the K_D results in batch experiments. Manganese dioxide and Na-4-mica were excluded from the column experiments since they are not commercial products and their performances were not appreciably better than those of sodium titanate and zeolite A, respectively. The chelating aminophosphonate resin was chosen for testing for the removal of uranium in column operations because it has been reported to be efficient for the separation of pure uranyl ion.¹²¹

5.1.2 Column experiments

Five organic (the strong and weak base anion resins, the strong and weak acid cation resins and the aminophosphonate resin) and two inorganic (sodium titanate and zeolite A) ion exchangers were tested in column-mode experiments. The activity concentrations of the radionuclides in the drilled well water are reported in publication **I** and the chemical compositions in publication **V**.

Uranium

Taking into account the total processed 1800 bed volumes, clearly the most effective exchanger for the removal of uranium was the strong base anion resin (SBA) (Fig.7a). The flow rate had some effect on the breakthrough of $^{234,238}\text{U}$: the breakthrough level increased with the flow rate from 0.87% to 5% (simultaneously, the decontamination factor decreased from 120 to 20). The SBA resin was distinctly better for uranium removal than the weakly basic anion resin (WBA) (Fig. 2 in **I**). Probably breakthrough of uranium had taken place with the WBA resin. Strong base anion resin has been reported to have an enormous capacity for uranium carbonate complexes. For example, Zhang and Clifford¹²² found that the strong base anion resin (SBA), without regeneration, still removed 95% of the uranium from a neutral-pH, sulphate-free water containing 120 $\mu\text{g/l}$ of uranium after a 16-month run. This corresponded to 302 000 bed volumes of throughput with the flow rate of 20–30 BV/h. Before 260 000 BV, the removal efficiency was more than 99%.

Use of the NEA thermodynamic data base¹⁸ and calculations with the HYDRAQL speciation program¹²³ showed that complexes $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ predominate in the water in pH range 7–8. Since uranium was present mainly as anionic carbonate complexes, it is understandable that the strong cation exchanger and zeolite A cannot take up uranium (Figs. 7b and 7e). However, the weak acid cation exchanger, sodium titanate (CoTreat) and the aminophosphonate resin took up uranium to some extent (Fig. 7c, 7d and 7f). The removal efficiency of WAC before the breakthrough was only modest, but both CoTreat and the aminophosphonate resin took up uranium efficiently at low processed water volumes. Below 200 BV, the breakthrough level of uranium from the CoTreat column was as low as 0.15%, and from the aminophosphonate resin it was only 0.67% up to 600 BV (the DF was 150). These levels are lower than for the SBA resin. The cation exchangers may have been able to strip the carbonate complexes and take up uranium as uranyl cation.

Radium

The anion exchangers took up ^{226}Ra poorly, presumably because it was mainly present in the ground water as cationic Ra^{2+} (Fig. 7a, SBA). The strong acid cation resin (SAC), and especially the weak acid cation resin (WAC) at low flow rates, took up ^{226}Ra considerably better (Fig. 7b and 7c). With the WAC resin the flow rate had a clear effect on the breakthrough of ^{226}Ra : the breakthrough levels increased with flow rate (Fig. 7c). The much stronger effect of flow rate with the WAC than the SAC resin (Fig. 7b) is in good agreement with the generally accepted poorer kinetics of WAC than SAC. In contrast to our results, Subramonian and co-workers¹⁰⁸ found the SAC resin (in Ca form) to have a higher affinity for radium than the WAC resin (in hydronium form). In their study the breakthrough of radium occurred at 8300 BV with the SAC resin and at just 750 BV with the WAC resin. The fact that, in the present study, both the SAC resin and the WAC resin were initially in sodium form may explain the discrepancy in the results. In addition, Subramonian and co-workers¹⁰⁸ used a constant flow rate of about 20 BV/h, whereas in our study the flow rate was increased from 15 BV/h to 80 BV/h.

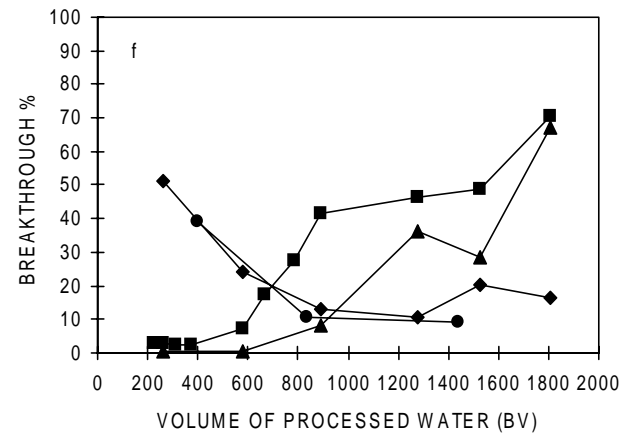
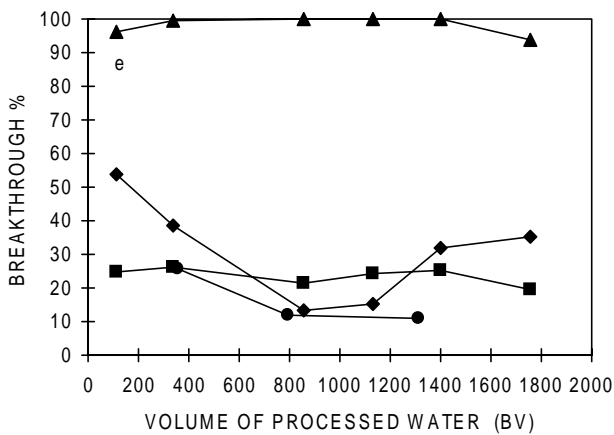
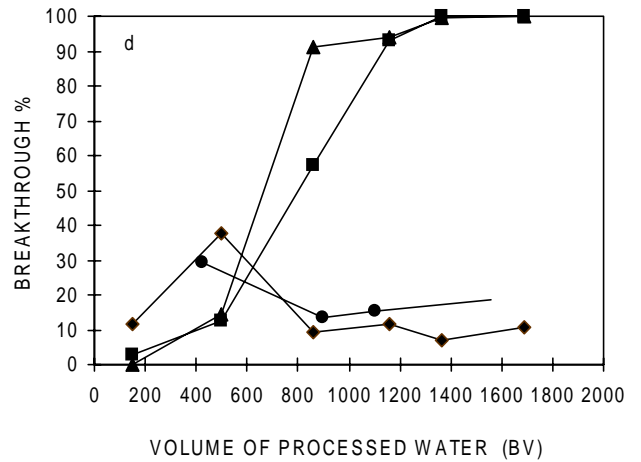
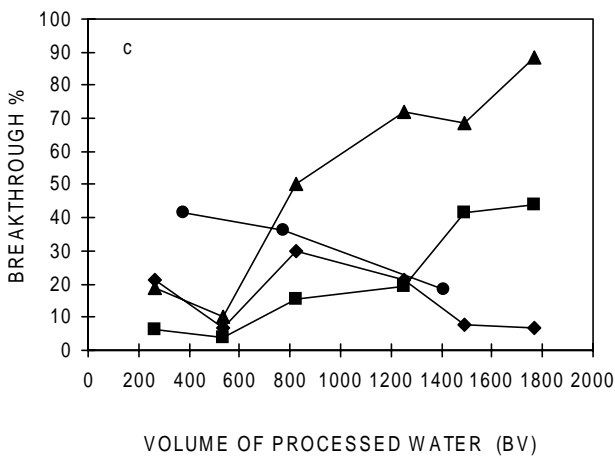
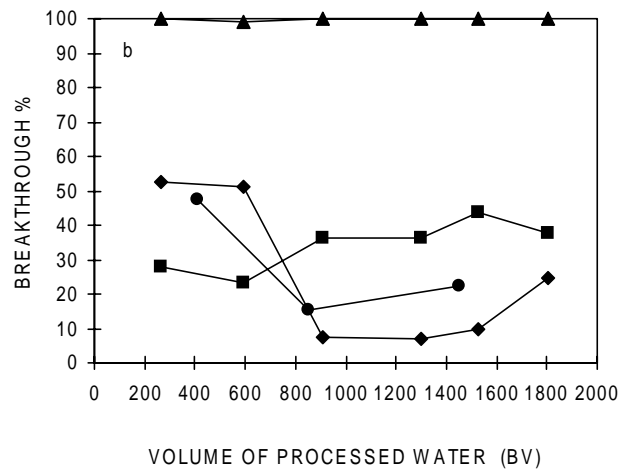
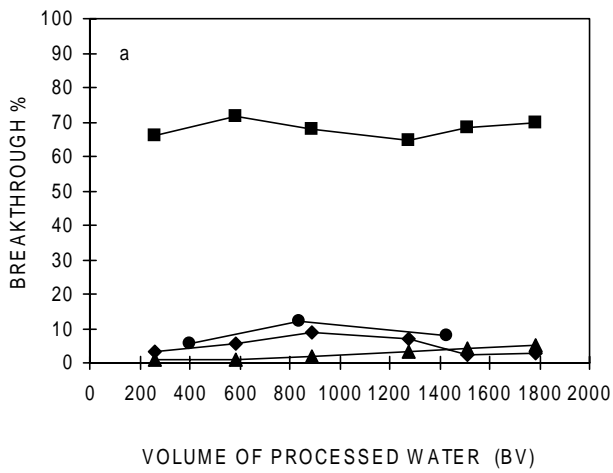


Figure 7a–f. Breakthrough curves for $^{234,238}\text{U}$ (▲), ^{226}Ra (■), ^{210}Po (◆) and ^{210}Pb (●) in drilled well water with a: the strong base anion exchanger (SBA), b: the strong acid cation exchanger (SAC), c: the weak acid cation exchanger (WAC), d: sodium titanate (CoTreat), e: synthetic zeolite (zeolite A) and f: the chelating aminophosphonate resin.

The KMnO_4 number in the feed water was 6 mg/l, which indicates that organic matter was present. Complexation of some of the radium with carboxylate ligands of the organic matter could explain why the breakthrough level of radium remained at about 70% for the SBA resin (Fig. 7a) and at about 30% for the SAC resin (Fig. 7b). If the organic matter is removed by ion exchange, the complexed radium will, of course, also be removed. However, the water also contained macro concentrations of Ca and Mg, which can be assumed to have competed with radium for the carboxylate ligands. The polycarboxylate stability constants of Ca and Mg are estimated to be greater than the stability constant for radium, so that Ca and Mg would bid for the ligands more strongly than radium does.⁹⁹ In fact, the breakthrough levels of Ca and Mg were almost 100% for the SBA resin (water 6 in publication V), which argues against the formation of Ca and Mg complexes. The results (publication I) suggest that there is some anionic Ra species present in addition to Ra^{2+} cation, and in that case a mixed bed containing SAC and SBA resin could be useful for the removal of both forms.

The decontamination factor (DF) for radium with the synthetic zeolite A was only moderate (3–5) and the flow rate had no influence on the breakthrough level (Fig. 7e). The processing capacity of the sodium titanate, CoTreat, was rather low; the breakthrough of ^{226}Ra occurred below 200 bed volumes (Fig. 7d). Before breakthrough, however, the decontamination factor was one of the highest for all the exchangers (DF 36).

It cannot be decided from the results whether the chelating aminophosphonate resin bed was saturated with radium or whether the flow rate had an influence on the breakthrough level (Fig. 7f). Both factors may play a role, as the kinetics of metal-ion exchange on aminophosphonate resin is rather slow. At low processed water volumes (< 300 BV), the breakthrough level was only 3%, which is lower than with WAC and of the same order as with CoTreat.

Polonium and lead

The breakthrough of ^{210}Po and ^{210}Pb varied considerably from one eluent fraction to another and even decreased with increasing bed volume (Fig. 7a–f). This suggested that both radionuclides were present in the water as particles. The assumption was confirmed in the filtration experiments (publications III and IV), as well as in the column mode experiment for inactive lead (publication V). Of all the exchangers, the anion exchange resins took up ^{210}Po

and ^{210}Pb most efficiently. Evidently, the polonium and lead are present in particles that have an anionic surface charge; they may, for example, be sorbed on humic substances. In most cases, sorption of ^{210}Po and ^{210}Pb increased as the column run progressed, probably because of improving filtering properties of the column bed.

Table 8 summarises the percentage uptakes of uranium, ^{226}Ra , ^{210}Po and ^{210}Pb by the ion exchangers from the drilled well water in the column experiments.

Table 8. Column-mode experiments for the removal of $^{234,238}\text{U}$, ^{226}Ra , ^{210}Po and ^{210}Pb from drilled well water, with uptakes in percentages (at 300, 600, 1000 and 1600 bed volumes).

Exchangers	Uptake (%)			
	$^{234,238}\text{U}$ Bed Volumes 300, 600, 1000,1600	^{226}Ra Bed Volumes 300, 600, 1000,1600	^{210}Po Bed Volumes 300, 600, 1000,1600	^{210}Pb Bed Volumes 300, 600, 1000,1600
Strongly acidic resin	0, 0, 0, 0%	70, 75, 65, 60%	50, 50, 93, 60%	n.d, 65%, 85%, n.d.
Weakly acidic resin	80, 80, 50, 25%	94, 94, 83, 57%	80, 90, 70, 93%	n.d, 60%, 70%, n.d.
Strongly basic resin	99, 99, 98, 95%	30, 30, 35, 30%	96, 94, 92, 98%	n.d, 92%, 90%, n.d.
Weakly basic resin	98, 97, 90, 65%	30, 30, 33, 25%	91, 93, 90, 96%	n.d, 95%, 90%, n.d.
Aminophosphonate	99, 99, 85, 65%	97, 93, 58, 50%	55, 77, 88, 80%	n.d, 75%, 90%, n.d.
Zeolite A	0, 0, 0, 0%	75, 77, 77, 78%	60, 75, 86, 66%	n.d, 75%, 88%, n.d.
Sodium titanate	95, 70, 8, 0%	95, 80, 30, 0%	80, 70, 90, 90%	n.d, 80%, 86%, 80%

n.d. = not determined

5.2 Physico-Chemical Forms of U, ^{226}Ra , ^{210}Po and ^{210}Pb and Their Influence on Ion Exchange

The speciation of uranium in natural waters is considerably affected by pH. As is well known, conventional strong base anion resins have an enormous processing capacity for uranium in neutral and slightly alkaline waters, where it is present mainly as anionic uranyl carbonate complexes. At slightly acidic pH values, where carbonyl complexes do not occur, the aminophosphonate resin was expected to perform better than the SBA resin owing to its selectivity for the uranyl ion. Extremely high uranium concentrations may be present in Finnish drilled well waters and affect the uranium separation. It was important, therefore, to

evaluate the effect not only of pH but also of U concentration on the removal of uranium. Large fractions of polonium and lead were found to adsorb on equipment in the ion exchange experiments and no definite K_D values could be obtained for Po and Pb. Although it was assumed that uranium and radium were mainly in ionic form in the waters, this was verified in filtration studies. Particle-bound species can interfere in the ion exchange process by sorbing on or passing through the exchanger beds. It was important, therefore, to determine the presence of radionuclides in particles of different size fractions.

5.2.1 Effects of pH and U concentration on the removal of uranium

Uranium concentration

Figure 8 presents the distribution coefficients of uranium on the aminophosphonate resin and the strong base anion resin (SBA) as a function of equilibrium uranium concentration at pH 8. The K_D value is more or less constant up to equilibrium uranium concentrations of 0.82 mg/l for the aminophosphonate resin and 0.054 mg/l for the SBA resin, but as the uranium concentration increases beyond these values, the K_D values start to decrease. Maximum uranium uptake was obtained at pH 8 with the SBA resin, but not with the aminophosphonate resin (see Figure 9).

The ion exchange system in the present study is not simple because of the several ions involved. In addition, there are interfering coexisting solution phase equilibria, such as the complexation of uranium with carbonate, which affect the ion exchange. In general (Equation 8), at low concentrations of the exchanging ions (uranium in this case) the K_D value is constant because, as is evident from Equation 16, macro ions (B), which are present at constant level, determine the value of K_D .

$$K_D = Q / ([B] / k_{U/B} + [U]) \quad (16)$$

However, once a certain concentration value is exceeded, the concentration of the exchanging ion (uranium) begins to dominate, which appears as a decrease in the K_D value (see Figure 8). The equilibrium pH values for the aminophosphonate resin dropped below pH 8 at high uranium concentrations (Fig. 8) and these points were corrected to pH 8 with the aid of the curves in Fig. 9, which present the uranium K_D as a function of pH.

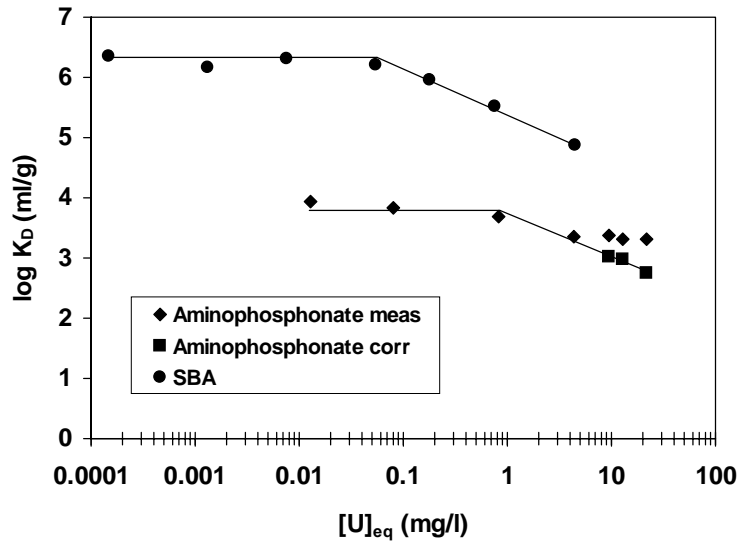


Figure 8. Distribution coefficients (K_D) of uranium on the chelating aminophosphonate resin and the strong base anion resin (SBA) as a function of equilibrium uranium concentration. The squares are points corrected to pH 8 and the diamonds are experimental results at pH 8 obtained with the aminophosphonate resin (II).

The highest concentration of uranium found in drilled well water in Finland is 12 mg/l (150 Bq/l, Table 3). As the experiments at different uranium concentrations show, such an extremely high level will have a strong decreasing effect on the removal of uranium. However, relatively high processing capacities can still be obtained with the SBA resin, as the K_D value is higher than ten thousand (Fig. 8).

Effect of pH

The aminophosphonate resin is an efficient exchanger for the removal of uranium in the pH range 5–6.5 (Fig. 9): the distribution coefficients are higher than one million. As the pH increases, the K_D values decrease and are only about 10 000 ml/g at pH 8. The trend is opposite for the SBA resin (Fig. 9): the K_D values are higher than one million in pH range 6.8–8, but decrease linearly to a value of almost 10 000 ml/g as the pH approaches 5.

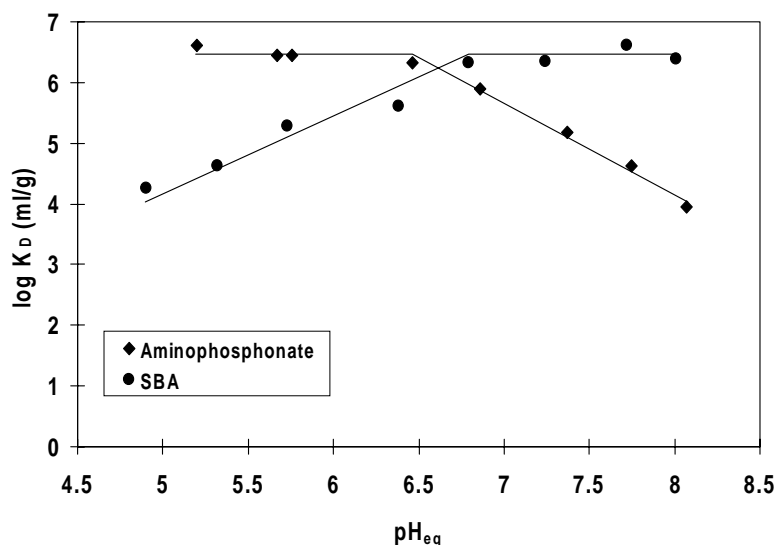


Figure 9. Distribution coefficients (K_D) of uranium on the chelating aminophosphonate resin and the strong base anion resin (SBA) as a function of pH (II).

The behaviour of both resins can be explained by the speciation of uranium and also the different functionality of the exchangers. At pH values close to 5, uranium exists in solution as the uranyl ion (UO_2^{2+}) and it can replace the two exchangeable ions in the phosphonate groups of the aminophosphonate resin. In addition, a strong chelate is formed between the uranyl ion and the free electron pairs of the oxygen atoms of the phosphonate group and the nitrogen atom in the amino group.¹²¹ At pH values where uranium is present mostly as an anionic complex, the aminophosphonate resin is still able to take up uranium since it is able to strip the uranyl ion from its complex. The SBA resin cannot efficiently remove uranium at pH 5, since the uranium is then present as cationic uranyl ion. However, the SBA resin has enormous capacity for uranium removal at pH 8 where the uranium is present as anionic uranyl carbonates.

The K_D values for the SBA resin at pH 5 are still in order of 10^4 (Fig. 9), although uranium is mainly present in the solution as cationic uranyl ion. Calculations with the speciation program¹²³ showed that only one anionic species, UO_2F_3^- , is present at pH 5, but it comprises less than 1% of the total uranium concentration.

Column experiments were carried out at pH values 5 and 8 to verify the performance of the aminophosphonate and the SBA resin. The aminophosphonate resin was an efficient exchanger for the removal of uranium at pH 5 (Figure 5 in **II**); Altogether 2000 bed volumes were processed and the uptake of uranium was 99.8% and higher, which corresponds to a high DF value of about 600. The aminophosphonate resin works much better than a conventional SAC resin at pH 5. Lee and co-workers^{124,125} have reported 60–70% uranium removal for the SAC resin, while the value for the aminophosphonate resin in the present study was 99.8%.

The SBA resin was the more efficient at feed pH 8: no uranium breakthrough was observed and uranium uptake was 99.7% and higher, which corresponds to an approximate DF value of 330 (Figure 6 in **II**). The concentration of uranium in the feed water was 4.7 mg/l. Though this high concentration has a marked effect on the K_D , high processing capacities could still be obtained (up to 100 000 ml/g, Fig. 8).

5.2.2 Adsorption on the filtration system and filters

The distribution of U, Ra, Po and Pb in particles of different size fractions was investigated in filtration studies with the drilled well waters. Adsorption on the filtration system, filters and storage vessels needs to be considered in filtration studies of radionuclides. To minimise adsorption on storage vessels, the samples should be filtered as soon as possible after sample collection and the filtrates and subsamples of the unfiltered water (raw water) should be acidified.

Adsorption in filtration studies

The oxidation states of **uranium** were determined in waters 1 and 4 (publication **IV**) and, in both, uranium was in +6 state. On the basis of the composition of the other waters (waters 2, 3 and 5) it can be assumed that +6 was the predominant oxidation state for uranium in these waters as well (carbonate concentrations and pH in Table 4). The fraction of ^{234,238}U adsorbed on the filtration system and filters was insignificant (0–1%). The calculations with the HYDRAQL speciation program¹²³ support the assumption that uranium is mostly complexed with carbonate in these waters. If the water system is exposed to atmospheric CO₂ (open system), soluble $UO_2(OH)_2^0$ may be important along with the carbonate complexes in the pH

range 7–8. Adsorption of ^{226}Ra on the filtration system and on the filters was below 3% and 10%, respectively.

Polonium adsorption on the filtration system was below 10% in waters 1–5 and somewhat higher in waters B, L and K. Adsorption of polonium on filters was high (17–26%) with all waters and water composition had no effect on this. Adsorption of ionic species of ^{210}Pb on filters was fairly low (3–10%) in waters L, K and I, but the sorption of ^{210}Pb on the filtration system was high (17–30%).

5.2.3 Fractions of radionuclides in soluble form

$^{234,238}\text{U}$ was present in soluble form in waters 1–5; that is, it passed through even the smallest pore size (5 kD). As mentioned above, uranium was complexed with carbonate, and the complexation with carbonate kept the uranium in soluble form even where the concentrations of humic substances and iron were high, as in waters 3, 4 and 5 (Table 4). According to Shanbhag and Choppin,³⁰ at pH 8 uranyl ion binding to carbonate displaces binding of uranyl ion to humic acid at the carbonate concentration of 10^{-5} mol/l, and in the present study the carbonate concentrations are as much as two orders of magnitude higher (10^{-3} mol/l).

Table 9 shows the proportions of ^{210}Po , ^{210}Pb and ^{226}Ra present in soluble form. ^{226}Ra was almost totally present in soluble form in waters 1 and 2, in which the concentrations of humus, Fe and Mn were low (Table 4). In the Fe–Mn-rich waters 3, 4 and 5, 85–88% of the total ^{226}Ra activity was in the soluble fraction. Since iron and manganese oxides and hydroxides sorb radium very effectively, probably part of the radium was sorbed on hydrated oxides and hydroxides. Moore and Reid⁴⁶ found that acrylic fibres impregnated with manganese oxide-dioxide were much more efficient in uptake of radium than the same fibres treated with iron hydroxide. On the other hand, most of the manganese in these waters is probably present as the soluble metal cation. A look at the breakthrough curves for the cation exchangers with water 3 (Figures 12a–c) suggests that Mn is present mostly as soluble Mn^{2+} ion. It cannot be excluded, however, that manganese oxides/oxohydroxides were also present. The theoretical Eh (mV) of $\text{MnO}_2/\text{Mn}^{2+}$ oxidation–reduction couples is rather high (around 540 mV) at pH 7 and Mn concentration of 1 mg/l.¹⁰ Thus the Eh values of waters 3, 4 and 5 would have to be rather high in order to oxidise Mn^{2+} to MnO_2 . It is also possible that

colloidal γ -MnOOH was present in the waters.¹²⁶ This species is formed at lower Eh values than MnO₂ (around 350 mV).⁶⁹

The concentrations of Fe and Mn were higher in water 5 than water 4; the concentration of Mn was over three times and that of Fe almost twice as high in water 5 as in water 4. From this, one would have expected the fraction of soluble radium to be lower in water 5 than in water 4. But, as can be seen from Table 9, the fractions were similar. Evidently, the results are also affected by salinity: the salinity of water 5 is much higher than that of water 4 and high salinity increases the solubility of radium in ground waters.^{11,47-51}

Table 9. Fractions of ²¹⁰Po, ²¹⁰Pb and ²²⁶Ra in soluble form in the ground waters (III, IV).

Water	Soluble ²¹⁰ Po (%)	Soluble ²¹⁰ Pb (%)	Water	Soluble ²¹⁰ Po (%)	Soluble ²²⁶ Ra (%)
B	2.0 ± 0.7	n.d.	1	68 ± 9	98 ± 2
L	1.0 ± 0.7	1.2 ± 0.1	2	43 ± 5	100 ± 7
K	20 ± 8	26 ± 4	3	32 ± 3	85 ± 3
I	n.d.	1.0 ± 0.3	4	4.9 ± 0.3	88 ± 2
			5	7.5 ± 0.6	88 ± 2

n.d. = not determined

Speciation of ²¹⁰Po is complex in natural water and varies from water to water. In the filtration studies of waters B, L and K, the highest fraction of ²¹⁰Po in soluble form (20%) was found in water K, and it was assumed that the greater salinity of this water enhanced the solubility of polonium. At the same time, however, the concentrations of Fe and Mn were lower in water K than waters B and L (Table 4), and further reflection suggested this as the more likely cause of the higher solubility of ²¹⁰Po in water K (Tables 4 and 9). Similarly, the solubility of ²¹⁰Pb was much greater in water K (26%) than in waters L and I (1.2 and 1%) (see Tables 4 and 9). The TOC values for the raw waters B, L, K and I were determined (Table 4), but not the KMnO₄ number (i.e. KMnO₄ consumption). However, the mean values of the KMnO₄ numbers of different batches from the same wells were close to those of waters 1 and 2, from which it could be concluded that waters B, L, K and I were not as humus-rich as waters 3, 4 and 5 (Table 4).

In the filtration study of waters 1–5, polonium was least soluble in waters 4 and 5, where the chloride concentrations were clearly higher than in water K (Table 4). Maiti and co-workers¹²⁷ found that no colloid formation for ²³⁸U, ²²⁶Ra, ²³²Th or lead in briny (high ionic strength) ground water, but colloid formation of ²¹⁰Po occurred. Besides chloride, the concentrations of humus, Fe and Mn were much higher in waters 4 and 5 than in water K. The concentrations of humus, Fe and Mn alone do not explain the solubility of ²¹⁰Po in waters, however. In water 3, where the concentrations were high (Table 4), as much as 32% of polonium was in soluble form (Table 9). In waters 1 and 2, with their clearly lower concentrations of Fe and Mn than in waters 3–5, amounts of polonium in soluble form were higher (Table 9).

5.2.4 Radionuclides in particle-size fractions

As discussed above, ^{234,238}U was in soluble form in all five drilled well waters, studied in filtration experiments, i.e. all of the U activity passed through the 5 kD filter. The values for ²²⁶Ra bound in the different particle fractions are given in Table 10. Of the total radium activity, 10% was bound on particles in the Fe–Mn-rich waters (waters 3, 4 and 5). Iron hydroxides and probably manganese species sorb radium, but at the same time the salinity of the water enhances radium solubility. As noted already, the concentrations of Fe and Mn were higher in water 5 than water 4, but the amounts of ²²⁶Ra bound on particles in the two waters were the same. Evidently the higher salinity of water 5 hinders the sorption of radium. The requirement for the sorption of radium by manganese is that the manganese is present in the water as oxides or oxohydroxides. Waters 3, 4 and 5 were also humus-rich (Table 4) and radium may have been bound to humic substances as well.

Table 10. Distribution of ²²⁶Ra activity (%) on particles of different size in the ground waters (IV).

Particle size	Water 1 (%)	Water 2 (%)	Water 3 (%)	Water 4 (%)	Water 5 (%)
> 450 nm	0.28 ± 0.07	0	0	7.6 ± 1.3	7.7 ± 1.0
450–50 nm	0.44 ± 0.001	0	1.3 ± 0.01	0	0
50 nm–5kD	0.29 ± 0.001	0	4.5 ± 0.03	4.2 ± 0.04	2.6 ± 0.02
< 5 kD	98 ± 2	100 ± 7	85 ± 3	88 ± 2	88 ± 2

The values for ^{210}Po bound in the different particle fractions in waters 1–5 are given in Figure 10 and those for ^{210}Pb in waters L, K and I in Figure 11. In water B about 40% of ^{210}Po was bound in particles coarser than $0.45\ \mu\text{m}$ (Figure 5 in **III**). In water L a significant proportion of Po total activity was adsorbed on particles of sizes between $0.45\ \mu\text{m}$ and $100\ \text{nm}$, while in water K polonium was more evenly distributed in the different particle-size fractions (Figure 5 in **III**). The behaviour of polonium is clearly complex and depends strongly on the water composition, and other factors affect speciation of ^{210}Po as well. Water 1 represents a good quality ground water in its concentrations of Fe, Mn and humus (Table 4), but even in this water, 10% of the total activity of polonium was bound in particles (Figure 10). In all nine waters the chemical concentration of polonium was lower than or equal to $2\text{--}3 \times 10^{-16}\ \text{mol/l}$. The adsorption of polonium species on colloids or larger particles of other elements is probable, but it cannot be excluded that polonium forms intrinsic precipitates at this concentration. The solubility of polonium species is not known but is probably very low.

As can be seen in Figure 10, most of the ^{210}Po was bound in particles in the waters with high concentrations of Fe, Mn and humus (waters 3–5). A general correlation is apparent between the concentrations of Fe and the fractions of particle-bound polonium in all waters: as the concentrations of Fe increased (Table 4), the fractions of particle-bound polonium increased (Fig. 10). Only water 4 departs from the trend: the fraction of particle-bound polonium was highest in water 4, although the concentration of Fe was of the same order as in water 3 and lower than in water 5. The reason for this discrepancy may be that water 4 was unique in not having been used for a long time; the others were being consumed daily as household water. It is worth noting, too, that 70% of the polonium in water 4 was bound in coarser particles ($> 0.45\ \mu\text{m}$, Fig. 10). It was suggested in publication **III**, on the basis of the ICP-MS analyses of the metals in filtrates, that iron and aluminium particles sized between $0.45\ \mu\text{m}$ and $5\ \text{kD}$ may adsorb polonium and lead. About 20% of the polonium in water K and in water 2 was bound in particles coarser than $0.45\ \mu\text{m}$. One significant difference between waters K and 2 and the other waters is that the aluminium concentrations were clearly higher in waters K and 2 (Table 4). At the same time the Fe and Mn concentrations were low. The waters were not acidified before filtering ($0.45\ \mu\text{m}$ filter) for the ICP-MS measurements, however, so the Al values for waters K and 2 do not represent initial concentrations in the raw waters. Later (publication **V**) water samples (water 3) were acidified before filtering because it was found that some Al may otherwise be retained on the filter. The coarser particles that bind Po in

waters K and 2 may, thus, contain aluminium. Definitive conclusions cannot, however, be drawn solely from the compositions of the ground water.

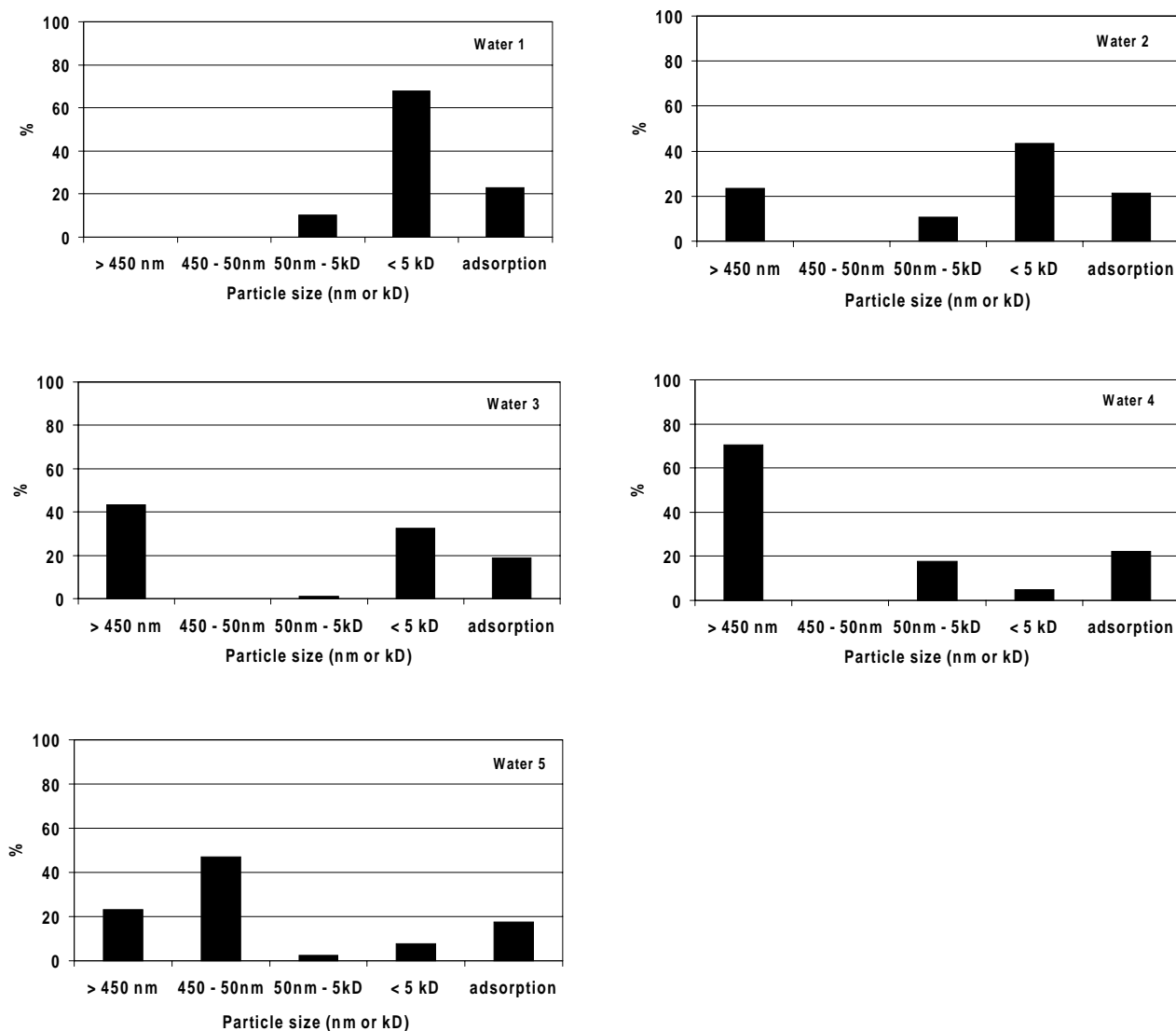


Figure 10. Distribution of ²¹⁰Po activity (%) in different particle-size fractions in ground waters 1–5 (IV).

About 80% of the ²¹⁰Pb in water I was bound in particles coarser than 0.45 μm (Figure 11). Lieser and co-workers^{64,65} found that most of the total ²¹⁰Pb activity in ground waters was bound in particles coarser than 0.45 μm, which included iron hydroxides. The iron concentration of water I was high, so the coarse particles here may have consisted of Fe(III) hydroxides as well. In waters K and L, ²¹⁰Pb was more evenly distributed in different particle-

size fractions. The concentrations of Pb (10^{-9} mol/l) in the waters were much higher than those of Po (10^{-16} mol/l). The solubility product of PbCO_3 is 7.5×10^{-14} mol/l¹²⁸ and PbCO_3 may be formed in pH range 5–8.5.⁶² With the carbonate and lead concentrations of waters L, K and I, intrinsic lead carbonate particles should not be formed at the pH values of the waters, based on the solubility product of the pure metal system. The possibility that lead precipitates cannot be excluded in complex systems such as natural waters, especially in water L in which the lead concentration was highest (25 nmol/l).

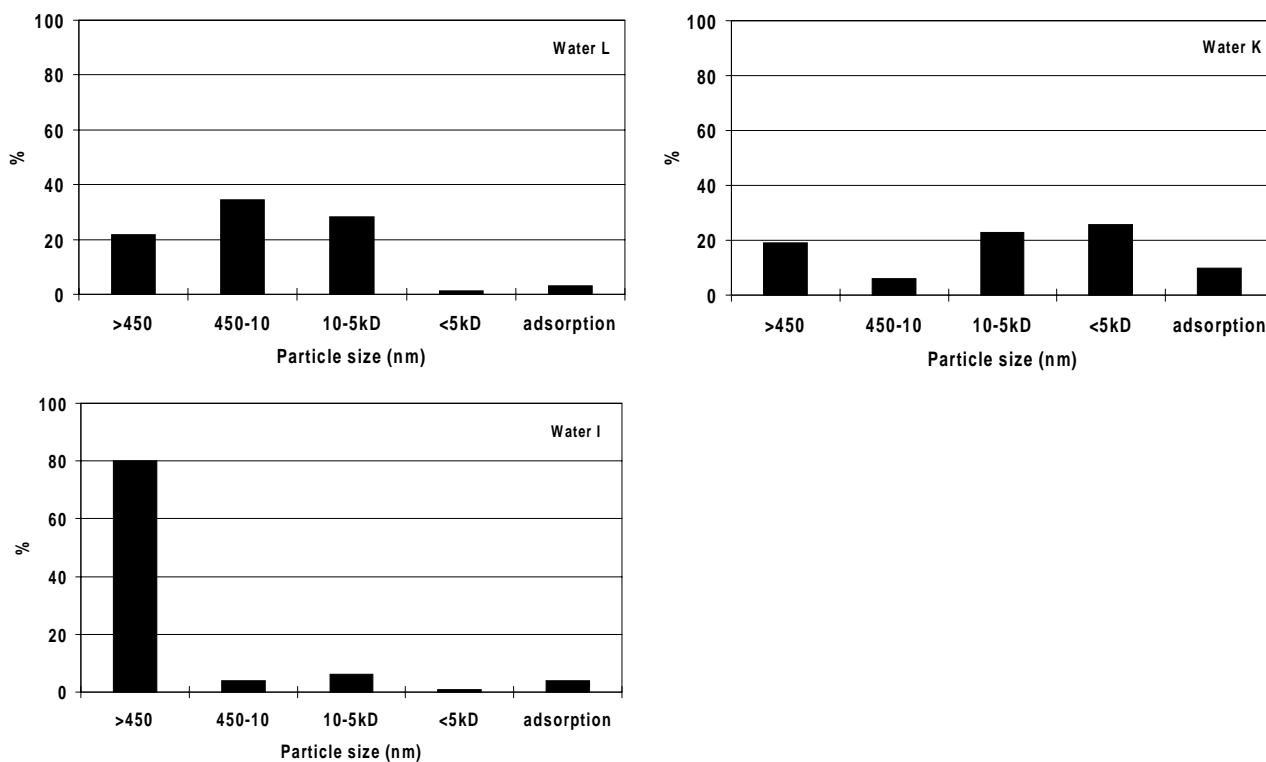


Figure 11. Distribution of ²¹⁰Pb activity (%) in different particle-size fractions in ground waters L, K and I (III).

5.3 Removal of Metals and Anions from Ground Waters by Ion Exchange

It is important that the quality of drinking water after the ion exchange process be studied. An extra advantage would be gained if the exchangers removed other toxic and harmful elements as well as radionuclides. At the same time, the exchangers should not be overly effective in removing useful elements.

The strong and weak base anion resins, the strong and weak acid cation resins, the aminophosphonate resin and the sodium titanate and zeolite A were evaluated for the removal of metals and anions from waters of two drilled wells. The flow rate was increased during the run of one experiment (water 6) and the other experiment was performed at constant flow rate (water 3).

Overall, the sodium titanate (CoTreat) and the aminophosphonate resin were the most efficient exchangers in removing toxic and harmful transition metals from the waters. CoTreat performed best for almost all the transition metals. The breakthrough level of manganese was below 1% with CoTreat even when its concentration in the feed water was high (1 mg/l). The decontamination factor of CoTreat for Mn was as high as 1075 up to 1300 BV, and still 108 at 1750 BV. The processing capacity of the strong acid cation resin (SAC), which is the usual choice for removing Mn from water, was significantly lower than that of the other exchangers. When the concentration of Mn in the feed water was 1 mg/l, the breakthrough of Mn with the SAC resin occurred below 400 BV. The weak acid cation resin (WAC) took up transition metals relatively efficiently (Fig. 12a).

CoTreat and the aminophosphonate resin exhibited similar separation efficiencies for the transition metals with water 3 (Figs. 12b and 12c). Separation efficiencies were highest for Mn, lowest for Fe and Ni and more or less the same for Cd, Zn and Cu. With the WAC resin, the breakthrough of Mn clearly occurred at 500 BV (Fig. 12a). Most likely the flow rate had an increasing effect on the breakthrough of Zn with the WAC resin and on the breakthrough of Ni with the chelating aminophosphonate resin (water 6, Tables 5 and 6 in **V**).

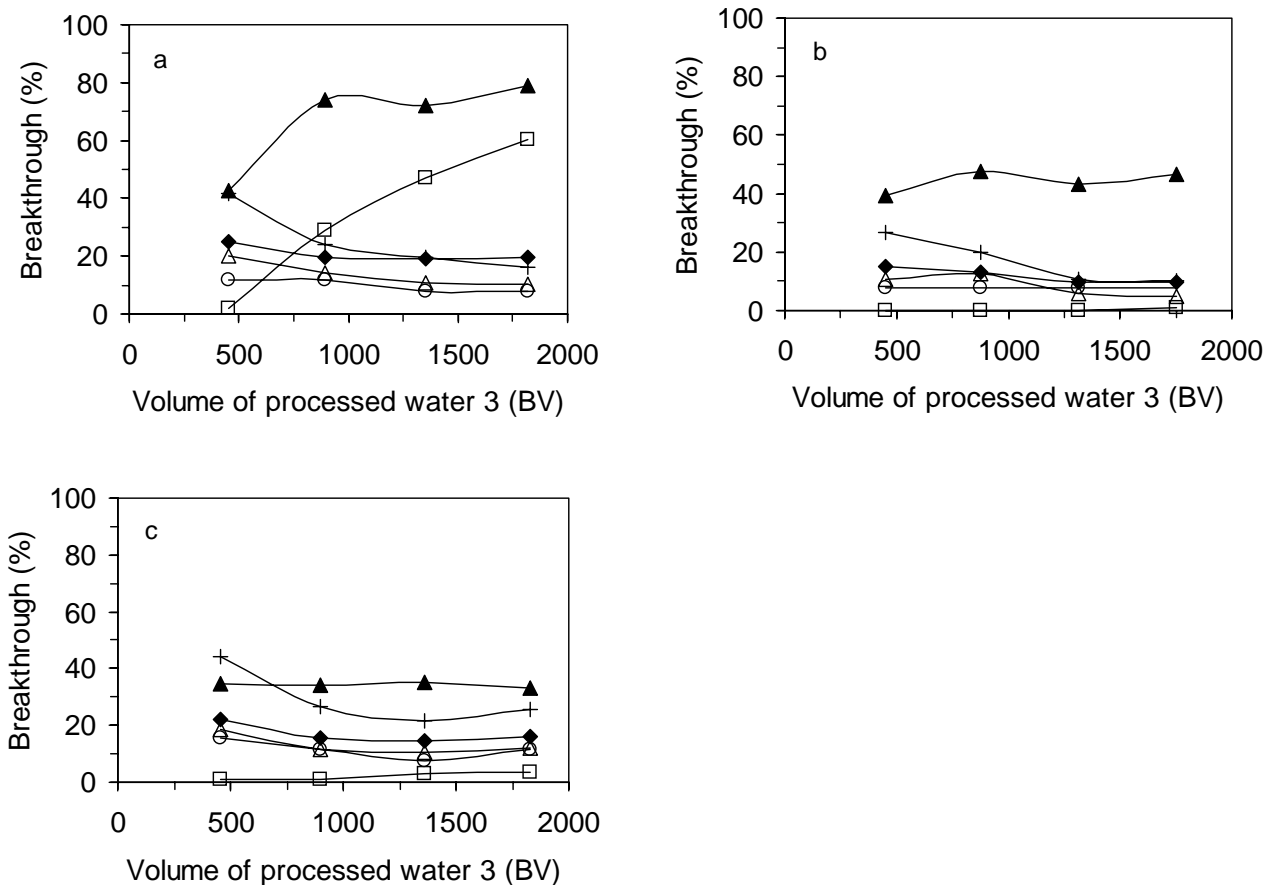


Figure 12a–c. Breakthrough curves of the transition metals Mn (□), Fe (+), Ni (▲), Cu (◆), Zn (Δ), and Cd (○) for a: the weak acid cation exchanger (WAC) b: sodium titanate (CoTreat) and c: the chelating aminophosphonate resin as a function of the processed bed volumes with water 3 (V).

The exchangers behaved similarly in the uptake of both inactive lead (Table 3 in V) and radioactive lead (I). Both ^{210}Pb and inactive lead were concluded to be present in water 6 as particles, which were adsorbed on the exchanger beds.

Iron, probably present as Fe(III) hydroxide, was taken up well by the cation exchangers; the breakthrough values were below 45%. Somewhat unexpectedly, the cation exchangers also removed arsenic from water. The breakthrough curves of the cation exchangers were similar for Fe and As (Figures 2 and 3 in V). Arsenic is typically present in ground waters as a neutral H_3AsO_3 molecule and H_2AsO_4^- and HAsO_4^{2-} species. Arsenic may have been sorbed on iron species,¹²⁹ which were adsorbed and filtered by the exchanger beds.

Most of the cation exchangers took up calcium and magnesium at low processed water volumes (< 400 BV), which is not desirable if water is soft and especially when it is acidic, because of corrosion problems. Although all the cation exchangers (which initially were in sodium form) released sodium into the treated water, the limit set for drinking water was not exceeded. The removal of calcium from the feed water and the release of sodium into the treated water can be avoided by using resins in calcium form.

The removal of Br^- , Cl^- , F^- , NO_3^- and SO_4^{2-} was studied in column experiments with water 6. Changes in concentrations were observed only with the SBA resin (Fig. 13). The percentage above 100% (Figure 13) indicates the relative amount of chloride released from the exchanger. This is caused by the “chromatography effect”: at lower processed water volumes, the exchanger takes up several anions, whereas at higher volumes, when the exchanger capacity is being exceeded, it continues to take up the anions it prefers, but releases the ones that are less preferred. The quality of the treated water with respect to its chloride concentration was reasonably good. At low processed water volumes, the SBA took up nitrate, bromide and sulphate very efficiently (< 700 BV; breakthrough values were 6.5%, 0.1% and 8%, respectively). Fluoride was not taken up by any of the exchangers tested.

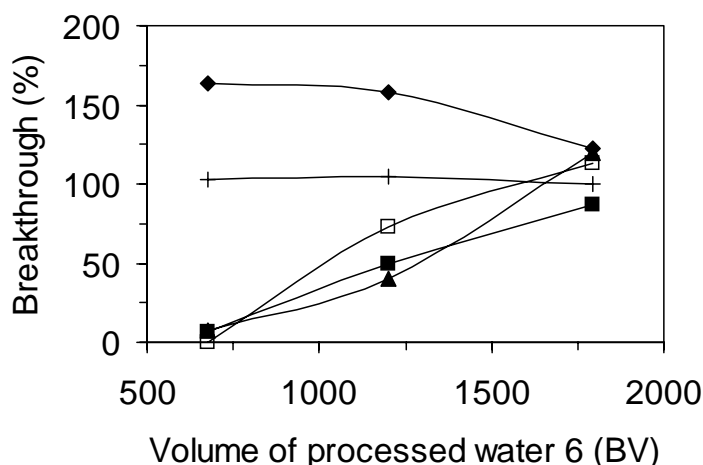


Figure 13. Breakthrough curves of the anions NO_3^- (■), SO_4^{2-} (▲), F^- (+), Cl^- (◆), and Br^- (□) for the strong base anion exchanger (SBA) as a function of processed bed volumes with water 6 (V).

6. CONCLUSIONS

Drinking water taken from drilled wells may contain high concentrations of natural radionuclides when the bedrock contains uranium and its daughter radionuclides. Various ion exchange materials were tested for the removal of $^{234,238}\text{U}$, ^{226}Ra , ^{210}Po and ^{210}Pb from ground waters. Strong base anion resin is known to have enormous capacity for uranium carbonate complexes. In this work the strong base anion resin proved to be the most efficient exchanger for uranium removal in neutral and slightly alkaline waters, in which uranium was present as anionic carbonate complexes. Strong base anion resin is currently being used in Finland for the removal of uranium from drilled well waters. In some drilled wells the water pH is slightly acidic in which case carbonate complexes are not present. The chelating aminophosphonate resin – which had not earlier been studied for this purpose – was found to remove uranium very efficiently from slightly acidic water. On the basis of this result, the aminophosphonate resin can be recommended for uranium decontamination of acidic drinking waters. Besides removal of uranium, this resin was also an efficient exchanger for the removal of toxic and harmful transition metals from drilled well waters.

The highest processing capacities for radium were provided by the ordinary strong and weak acid cation resins and zeolite A. Though the capacity of the aminophosphonate resin was lower the decontamination factor was higher than that of SAC, WAC or zeolite A.

Study was made of the distribution of $^{234,238}\text{U}$, ^{226}Ra , ^{210}Po and ^{210}Pb in particles of different sizes. Uranium was present entirely in soluble form in the waters. Radium was mainly in soluble form, though 10% of the total radium activity was bound to particles in the Fe–Mn-rich waters. Polonium and lead were present both as particles and in soluble form. Most of the total ^{210}Po and ^{210}Pb activity was bound on particles in the Fe–Mn-rich waters. ^{210}Pb was probably sorbed on iron hydroxides. Speciation of ^{210}Po in natural water is complex and varies from water to water. Although polonium is highly particle-reactive, in the waters studied a significant proportion of the total polonium activity was in soluble form, even where high concentrations of Fe, Mn and humus were present. A positive correlation was observed between the concentration of iron in the raw ground water and the fraction of particle-bound polonium.

Uranium and radium were almost completely in ionic form in the waters and thus the primary method of removal for these radionuclides would be ion exchange. It is clear that the selection of ion exchangers must be governed by the properties of the water. In most cases the combination of SBA plus SAC or WAC resins would remove both uranium and radium. Polonium and lead were present both in soluble form and bound in particles. Thus the ion exchange method would remove part of the polonium and lead, but membrane filtration would also be required. Better understanding is needed of the speciation of ^{210}Po and ^{210}Pb . Polonium and lead may form intrinsic precipitates in natural waters and the possibility of this occurring should be considered. It is as well to use a combination of various analytical techniques in speciation studies of radionuclides.

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