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Technology for the removal of radionuclides from natural water and waste management: state of the art

Rein Munter

Department of Chemical Engineering, Tallinn Technical University, Ehitajate tee 5, 19086 Tallinn; rein.munter@ttu.ee

Abstract. The paper provides an overview of natural radionuclides in surface water and groundwater, their maximum permissible concentrations, health effects, different processes of removal (aeration, coagulation and co-precipitation, filtration, adsorption, ion exchange, membrane separation), treatment costs, and options of radioactive waste management.

Key words: groundwater, radionuclides, radon, radium, uranium, technology of removal, costs, waste management.

INTRODUCTION

Our planet has been continuously radioactive since it was formed some 5 billion years ago. In nature, over 80 radionuclides can be found in detectable concentrations [1]. There are four naturally occurring decay series beginning with the long-lived ^{238}U, ^{235}U, ^{232}Th, and ^{237}Np, which were already present when the Earth was formed (Table 1) [2]. The natural decay series of ^{238}U, ^{235}U, and ^{232}Th contain 45 natural radioisotopes [1]. Human radiation exposure is mainly dominated by natural radiation (Table 2) [3]. Radon alone contributes to more than half of the annual radiation exposure to humans. The global average of the effective dose attributed to natural radiation has been estimated to be about 2.4 mSv/yr [4].

Contamination of drinking water with radionuclides has become a significant, emerging issue. Natural sources have been the primary cause of contamination.

Table 1. Properties of four natural decay series of actinides [2]

Series	Initial nuclide	Half-life, years	Stable endmember
Thorium	^{232}Th	1.405×10^{10}	^{208}Pb
Neptunium	^{237}Np	2.140×10^{6}	^{209}Bi
Uranium	^{238}U	4.470×10^{9}	^{206}Pb
Actinium	^{235}U	7.038×10^{8}	^{207}Pb

Table 2. Distribution of the contribution of radiation sources [3]

Radiation source	Exposure, %
Radon	54
Medical X-rays	11
Internal	11
Terrestrial	8
Cosmic	8
Nuclear medicine	4
Consumer products	3
Other	1

Table 3 [2] lists ten natural radionuclides that may occur in potable waters in harmful concentrations. In summary, only isotopes of uranium, radium, and radon, and in some cases also long-lived radon decay products (^{210}Pb, ^{210}Po) are of relevance in the drinking water supply. Among the radionuclides listed in Table 3 the majority, i.e. ^{222}Rn, ^{224}Ra, ^{226}Ra, ^{238}U, ^{234}U, ^{235}U, ^{210}Po, and ^{231}Pa, are alfa emitters, while ^{228}Ra and ^{210}Pb are beta emitters.

Radon is a naturally occurring radioactive gas that emits ionizing radiation. Inhalation of indoor air with high radon levels causes risk of lung cancer. Radon in drinking water does not present a major health concern compared to radium and uranium. However, permanent ingestion of drinking water that contains dissolved radon

Table 3. Significant radionuclides in the drinking water supply [2]

^{238}U decay series	^{232}Th decay series	^{235}U decay series
^{238}U	^{228}Ra	^{235}U
^{234}U	^{224}Ra	^{231}Pa
^{226}Ra		
^{222}Rn		
^{210}Po		
^{210}Pb		

also presents a risk of internal organ cancers, primarily stomach cancer [5].

Radium isotopes ^{226}Ra and ^{228}Ra are natural groundwater contaminants, which usually occur at trace levels. Radium is one of the most hazardous elements with respect to internal radiation exposure. At high exposure levels both radium isotopes can cause osteoporosis, anemia, kidney and liver disease, and bone cancer in humans and are believed to cause stomach, lung, and other cancers as well [6].

Uranium is a naturally occurring radioactive contaminant, which is found not only in groundwater, but also in surface waters. Uranium has no known metabolic function in the human body and is considered relatively non-essential [7]. However, US Environmental Protection Agency (US EPA) believes that uranium can be toxic to the kidneys [8].

The determination as well as removal of natural radionuclides from drinking water has become increasingly important during the past few years. This is mainly attributed to possible health impacts and new regulations in the European Union and in the USA [2]. The EU Drinking Water Directive (DWD) 98/83/EC lays down a reference effective dose of 0.1 mSv/yr for public waterworks. The effective dose should be calculated for all radionuclides, but in practice only isotopes of uranium and radium are included in this dose. The World Health Organization (WHO) has set the following conditions to guarantee that the effective dose will remain <0.1 mSv/yr: gross-alpha <0.5 Bq/L, gross-beta <1.0 Bq/L, and gross-gamma <100 Bq/L [9]. However, this approach is not valid in the case of radium isotopes, as the ^{226}Ra content of 0.5 Bq/L already corresponds to the effective dose of 0.1 mSv/yr, and 1.0 Bq/L of ^{228}Ra means even a higher effective dose.

As to the long-lived radionuclides (^{234}U, ^{238}U, ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{210}Po), no exact recommendations have been issued by the Commission of the European Communities yet. According to the DWD the guideline for ^{238}U is approximately 100 μg/L, for ^{210}Po 0.1 Bq/L was suggested, and for ^{210}Pb 0.2 Bq/L. In the USA the Environmental Protection Agency (EPA) has set the following maximum concentrations: for uranium 30 μg/L, for ^{226}Ra and ^{228}Ra 5 pCi/L (1 pCi/L = 0.037 Bq/L), for radon 300 pCi/L, and for gross-alfa particles 15 pCi/L [10].

At the present time, data concerning natural radionuclides in potable waters are available from all over the world. The highest concentrations of radon in potable waters have been reported from Finland (77.5 kBq/L) and Sweden (55 kBq/L). High levels of natural uranium have been determined in tap waters from Canada, Greece, India, and Marocco. Elevated ^{226}Ra and ^{228}Ra concentrations have also been found in potable waters from Scandinavia, Hungary, and Spain. Radioactivity of natural water is a serious problem in 18 EU countries: Austria, Belgium, Bulgaria, Czech Republic, Germany, Spain, France, Finland, Greece, Ireland, Italy, Hungary, Luxembourg, Portugal, Romania, Sweden, Slovak Republic, and Estonia [11]. According to the recent analyses of ^{226}Ra, ^{228}Ra, and ^{40}K in Estonian groundwater, the concentration of ^{226}Ra was in the range of 0.024–0.588 Bq/L, ^{228}Ra in the range of 0.035–0.707 Bq/L, and ^{40}K in the range of 0.2–0.4 Bq/L [12]. The concentration of uranium isotopes in Estonian groundwater is negligible, but the concentrations of ^{210}Po and ^{210}Pb definitely need further studies.

Elevated levels of radionuclides in ground- and surface water are also a problem in several areas and states in the USA [13]. Radium levels are typically higher in groundwater than in surface water (0.5–50 and 0.01–1.0 pCi/L, respectively). The average concentration of ^{226}Ra in community drinking water supplies is estimated to range from 0.3 to 0.8 pCi/L. Five states – Georgia, Illinois, Minnesota, Missouri, and Wisconsin – have been noted to have still higher average concentrations, ranging from 1.27 to 5.29 pCi/L. Uranium activity as high as 652 pCi/L has been observed in both surface and groundwater samples. The average uranium concentrations in surface and groundwater are believed to be about 1 and 3 pCi/L, respectively. Average uranium concentrations in community drinking water supplies are estimated to range from 0.3 to 2.0 pCi/L.

The technology for the removal of radium and uranium isotopes has developed in time from lime softening and enhanced coagulation together with filtration to more sophisticated processes: ion exchange, electrodialysis, and reverse osmosis (RO). These technologies have been described in several research papers; however, their feasibility and costs have very rarely been evaluated and options of radioactive wastes management and disposal have been almost neglected.

This paper focuses on comparison of different technologies for radioactivity removal from water, their advantages, disadvantages, and efficiency as well as possible options for the treatment and disposal of liquid and solid radioactive wastes.

TECHNOLOGIES FOR RADON, RADIUM, AND URANIUM REMOVAL FROM WATER

Aeration for radon removal

Radon is a noble, heavy gas, which tends to collect in basements or other low places in housing. It has no colour, odour, or taste. ^{222}Rn is produced by the decay of radium, its half-life is 3.8 days and it emits an alpha particle as it decays to ^{218}Po and eventually to stable lead. Radon easily dissolves in water and also easily escapes from water under pressure when exposed to the atmosphere, especially if water is stirred or agitated [14]. Small concentrations of radon can also be adsorbed onto granulated activated carbon.

Aeration is capable of removing of the radionuclides only radon from water. This option is briefly mentioned in several papers [15–19]. However, only one paper [5] is dedicated to comparison of the construction and efficiency of different aeration columns for radon removal. That paper discusses radon removal efficiencies of different aeration methods (diffused bubble, packed tower, Venturi aerator, spray nozzle aeration) and commercial aerators in a number of Finnish, Swedish, and German waterworks. Their radon concentrations in raw waters varied between 8 and 5800 Bq/L, but aeration removed radon and carbon dioxide quite similarly. The results are summarized in Table 4. In conclusion, the highest radon removal degree (98–100%) can be achieved by optimizing the aeration processes that use spray nozzle and packed tower, aerators, and gas–degas technology (GDT).

Lime softening, coagulation, and co-precipitation with filtration for radionuclides removal

Radium is an alkaline earth element with chemical properties very similar to barium, calcium, and magnesium. The element exhibits only one oxidation state (+2) in solution. Radium cations are mobile in water and because of the highly basic character of Ra, are not easily complexed and are even called "hydrophobic" by some authors [20–22].

The state of uranium in water depends significantly on the pH of the water. In natural waters with pH values ranging from 7 to 10, the soluble carbonate complexes of UO_2^{+2}–$UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$ are the predominant anion species. These two complexes exist in various ratios depending on the pH of the water [22].

Under reductive conditions radium cations remain soluble in water, differently from uranium, which tends to precipitate. Under oxidative conditions, on the contrary, iron and manganese hydroxides are formed and co-precipitation of radium occurs, but uranium remains in the solution [12].

Non-sophisticated technologies for radium and uranium removal involve [20,21]:
- lime softening–filtration (Ra and U are removed)
- co-precipitation with barium sulphate (Ra is removed)
- enhanced coagulation–filtration (uranium is removed).

In lime softening lime or soda ash is added to precipitate ions, followed by sedimentation and filtration. Lime softening can remove 85–95% of uranium. The presence of Mg^{2+} and the pH of 10.6 or higher are essential for good uranium removal as the magnesium hydroxide precipitate plays a major role in uranium removal. Unless softening is also a treatment goal for the water utility, lime softening process can be costly [22].
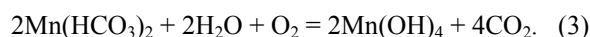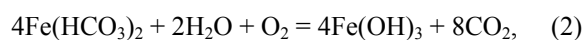
In co-precipitation with barium sulphate barium chloride is added to co-precipitate a radium-containing highly insoluble barium sulphate sludge, followed by sedimentation and filtration:

$$Trace(Ra^{2+}) + Excess(Ba^{2+}) + 2SO_4^{2-} = Ba(Ra)SO_4. \quad (1)$$
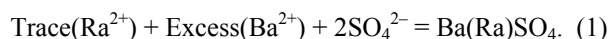
This process is capable of removing 50–95% of radium. Coagulation–filtration processes with iron or aluminium coagulants followed by filtration can remove 25–30% of radium and 50–90% of uranium at pH 6 and 10 [20].

## Radionuclides removal with optimized iron and manganese filtration

This is the most natural and probably also the most economical way to get rid of ^{226}Ra, ^{228}Ra, and ^{238}U in water. During the aeration of groundwater ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}), which readily forms the insoluble iron hydroxide complex $Fe(OH)_3$. Manganese (Mn^{2+}) is oxidized to $Mn(OH)_4$, which further forms insoluble MnO_2:

$$4Fe(HCO_3)_2 + 2H_2O + O_2 = 4Fe(OH)_3 + 8CO_2, \quad (2)$$

$$2Mn(HCO_3)_2 + 2H_2O + O_2 = 2Mn(OH)_4 + 4CO_2. \quad (3)$$

Table 4. Efficiency of different aerators for radon removal

| Aerator	Operation conditions	Efficiency, %	Reference
Diffused bubble aerator	Combined with spray aeration	98	[5,14,15,17]
Spray nozzle aerator		67–98	[5,18]
Packed tower aerator	Norpac rings, air/water ratio 20 m^3/m^3	80–99	[5,18]
Venturi aerator		70–80	[5,18]
GDT aerator	Air/water ratio ≥ 2 m^3/m^3	98–100	[19]
Domestic aerators		13–98	[5,14,17]

The chemistry of radium is controlled by co-precipitation with other elements or by other similar processes, such as adsorption. Hydrous oxides of Fe(III) and Mn(IV) have high sorption capacities for divalent metal ions. It is believed [23] that hydrous manganese oxide is a better adsorbent for divalent metal cations (Ra^{2+}, Ba^{2+}, Mg^{2+}, Ca^{2+}) due to the fact that differently from hydrous iron oxide particles, which are positively charged, the hydrous manganese particles have a negative charge. The general mechanism of sorption of metal ions on oxides and hydrous oxides and the exchange of bound H ion on the oxide surface with cations is decribed by the following scheme [24]:

$$M^{n+} + x[=R - OH] = M[=R - O]_x^{(n-x)+} + xH^+, \quad (4)$$
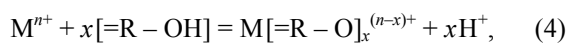
where M is the metal ion to be sorbed, x is the number of moles in oxide or hyroxide, and [=R – OH] and [=R – O] are the oxide surface sites. These findings also apply to the special case of radium.

The efficiency of iron and manganese removal was examined in 12 households in Finland whose water supply was known to contain some amounts of natural radionuclides [25]. The equipment (typically aerator + filter (anthracite–sand or anthracite–greensand media)) to remove only iron and manganese from household water had been installed at these homes before the radionuclide removal studies began.

Contemporary methods for the removal of iron, manganese, and hydrogen sulphides are mainly based on catalytic filter materials containing MnO_2 (Birm, manganese greensand, Filox, Pyrolox, Everzit Mn, and others). In the oxidation–reduction reaction MnO_2 is reduced to MnO, and ferrous iron is oxidized to ferric iron forming ferric hydroxide, which is precipitated:

$$2Fe(HCO_3)_2 + MnO_2 + H_2O = 2Fe(OH)_3 + MnO$$
$$+ 4CO_2 + H_2O. \quad (5)$$
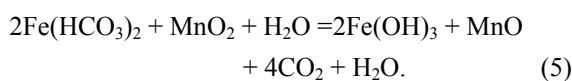
Manganese dioxide works most efficiently at a pH of 6.5 to 9.0. It should not be used on waters that have bacterial or organic iron.

Moon et al. [26] studied radium adsorption onto MnO_2 containing materials (using ^{133}Ba as a proxy for Ra) over wide ranges of pH, reaction times, and salt concentrations. They found the sorption characteristics to be especially favourable for low salinity waters, i.e. for typical drinking waters. According to their study, sorption rates decrease as the salt concentrations in solution increase. The sorption of radium is highly dependant on the pH with its most useful range from 4 to 8.

Baeza et al. [27] studied the typical procedure for iron and manganese removal (coagulation with iron sulphate, flocculation, settling, filtration) and specifically designed this flow sheet to maximize the elimination of natural radionuclides. The results showed the radium and

uranium elimination efficiencies to depend strongly on the water alkalinity (bicarbonate ions) and concentrations of calcium and magnesium ions. The authors proposed different mechanisms of radium and uranium removal. For radium it is mostly adsorption of radium cations onto $Fe(OH)_3$ flocs and especially onto the negatively charged hydrated particles of $Mn(OH)_4$, but for uranium it is mostly a complex, non-specific co-precipitation process that includes adsorption, inclusion, occlusion, and the formation of a solid solution.

The company Water Technology Partners Ltd. in Estonia [28] has applied for the patent on a combined treatment technology of groundwater consisting of intensive aeration, oxidation, and catalytic filtration (filtermedia FMH, Everzit Mn) stages for radon and ^{226}Ra and ^{228}Ra removal. For aeration a very efficient GDT (Mazzei Corp., Bakersfield, CA) is applied followed by the gases liberation reactions in an oxidation tank. The next filtration stage proceeds in a multilayer catalytic filter where the MnO_2 content in filter materials is growing with the downflow of water through the filter.

Table 5 summarizes the main results of the removal of radionuclides together with iron and manganese. It can be seen that radium is in general better removable than uranium, and the highest degree of ^{226}Ra removal (91–94%) can be achieved by the optimized iron–manganese removal process using intensive aeration in the GDT unit (Water Technology Partners Ltd., Estonia) [28].

Table 5. Efficiency of radionuclides removal together with iron and manganese

Process	Removal, %			Reference
	Rn	^{226}Ra and ^{228}Ra	^{238}U	
Domestic aeration + catalytic filtration	90–100	>95	>95	[25,29]
Industrial scale aeration + catalytic filtration		19–63/23–82	10–60	[30]
Coagulation–flocculation–settling–filtration		50–90	60–90	[27,29]
Aeration in GDT– oxidation–catalytic filtration	95–98	91–94/70–75		[28]

Radium removal through co-precipitation with hydrous manganese oxide (HMO)

Processes using manganese greensand or manganese oxide coated media are relatively inexpensive techniques for radium removal [29]. Efficiencies of up to 80% may be achieved using this technology. There are basically two mechanisms to remove radium in these processes: (a) co-precipitation and (b) contact oxidation. The following reaction summarizes the formation of HMO slurry:

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + 4H^+$$
$$+ 2K^+ + 3SO_4^{2-}. \quad (6)$$
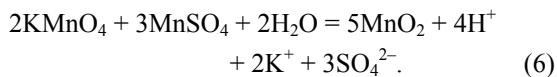
In the co-precipitation process, the water supply either has sufficient naturally occurring manganese or additional dissolved manganese is added. Potassium permanganate is then applied to convert the manganese to manganese dioxide prior to filtration. The manganese oxide–radium complex forms a precipitate and is then filtered. The accumulated precipitate is periodically backwashed off the media during the normal filter back-washing. When there is insufficient manganese in the feed stream, dissolved radium will adsorb onto manganese dioxide media coating. Under this scenario, radium is not backwashed off and may accumulate in the bed. This contact oxidation technique, although effective, is generally not recommended by the Tonka Equipment Company [31] because it carries a high potential for radium accumulation in the filter media. As radium degenerates, radioactive radon is emitted, so radium accumulation technologies should be generally avoided or carefully controlled [29,32].

Valentine et al. [33] carried out laboratory studies and pilot plant tests according to the following treatment scheme: raw water aeration $\rightarrow$ contacting with HMO precipitate $\rightarrow$ filtration through a sand filter. Removals obtained by freshly precipitated HMOs were much greater (80–90%) than those obtained in systems con-taining only iron oxides or mixtures of iron and manganese oxides produced by the aeration and oxida-tion of ferrous iron and divalent manganese. The main conclusion was that the precipitation of iron oxides onto manganese oxides can interfere with radium adsorption (both Fe^{3+} and Ra^{2+} have a positive charge), and a two-stage oxidation process may be warranted when both iron and manganese are present.

A technology for ^{226}Ra and ^{228}Ra removal is also studied in [34]. Greensand filtration is designated as an applicable technology for achieving combined radium maximum permissible concentrations. The average removals observed were 83–85%. Permanganate was used in the regeneration of manganese oxide activated greensand. Radium removal occurred as a result of adsorption to the manganese dioxide (hydrous) present

in the filter. The adsorption of radium by MnO_2 was dependent on the pH. A general improvement was observed as the pH increased from approximately 5 to 9.

Radionuclides removal using ion exchange processes

Of the numerous alternatives for radium removal (cation exchange softening, lime softening, RO, hyperfiltration, electrodialysis, sorption onto HMO, and sorption onto barium sulphate-impregnated resins and alumina) sodium cation exchange softening has received the most attention for application to small and medium-sized water systems because of its relative simplicity and economy [35]. In this process, contaminated water is passed through a bed of strong acid cation (SAC) resin in the sodium form, which, when exhausted, is regenerated with 1–2 N NaCl or KCl. The exchange reaction is:

$$2R[Na] + Ra^{2+} = R_2Ra + 2Na. \quad (7)$$
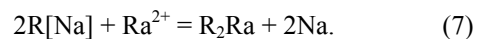
Clifford and Zhang [35] concluded that adding a small amount (~10%) of a strong base anion (SBA) resin to the SAC resin (~90%) in a conventional water softener provides good radium and uranium removal during cyclic operation with sodium chloride or potassium chloride regeneration.

At exhaustion, which occurs at hardness or radium breakthrough depending on how the process is operated, most of the exchange sites are occupied by calcium or magnesium because these are the predominant cations and also competitors to radium in feedwater. Ion exchange softening has two significant disadvantages: it adds sodium to the product water in exchange for calcium, magnesium, and radium, and it produces a regenerant wastewater typically having about 100 times the radioactivity level of the raw water. The first disadvantage can be overcome by regeneration with KCl rather than NaCl. Potassium chloride has proved to be a much better regenerant for radium than sodium.

As to uranium, conventional alum and iron coagula-tion, lime softening, RO, and anion exchange have proved effective for its removal from drinking water and are considered the best available technologies (BATs) by the US EPA for drinking water treatment [36]. Dur-ing pilot scale tests it was found that the SBA resin exhibited an enormous capacity for the uranyl carbonate complexes ($UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) prevailing in water in the pH range from 5.5 to 10. The exchange reaction with a chloride-form anion resin (R[Cl]) is:

$$4R[Cl] + UO_2(CO_3)_3^{4-} = R_4UO_2(CO_3)_3 + 4Cl^-. \quad (8)$$
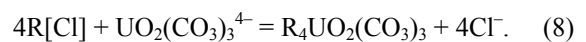
Elution of adsorbed uranium is easily accomplished with 3–5 bed volumes of 1 N sodium chloride (NaCl),

sodium nitrate ($NaNO_3$), or ammonium carbonate [$(NH_4)_2CO_3$]:

$$R_4UO_2(CO_3)_3 + 4NaCl = 4R[Cl] + UO_2(CO_3)_3^{4-} + 4Na^+. \qquad (9)$$
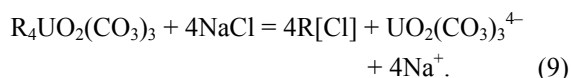
Radionuclides removal using membrane technology

Information about radionuclides removal by membrane technology (high pressure RO–nanofiltration (NF) membranes) is very limited. It is usually mentioned in the literature that RO/NF membranes remove at least 95% of radionuclides, in addition to improving other water quality parameters that may be a concern. Salts are concentrated in brine and the overall efficiency of their removal is over 99% [37].

In [36] three different RO modules (thin-film polyamide hollow-fibre, low-pressure composite spiral-wound, and thin-film composite) were tested. For the standard pressure modules (the first and the third module) ^{226}Ra rejection exceeded 99%, whereas for the low-pressure module it was 91%. In all three cases, radium rejection slightly exceeded hardness rejection, suggesting that hardness monitoring might be used as a surrogate for radium.

According to Havener [23], RO systems have demonstrated an ability to remove 87–98% of the radium present in drinking water. Similar elimination can be achieved for alpha particle activity and total beta and photon emitter activity.

A disadvantage of the membrane technology is generation of 15–25% of highly concentrated (by a factor of four, if the RO system design value is 75% of recovery) radioactive wastewater (retentate) flow, which as a low-level radioactive waste will have to be disposed of in accordance with local regulations. Other factors to consider in RO-based radium removal systems are the possible need for pretreatment and the possibility of high capital and operating costs [38]. However, continuing advances in membrane technology are bringing RO for radionuclides removal into a more competitive position.

Comparison of the preliminary costs of different processes

Economy or costs of water treatment are always a crucial point in the selection of an adequate technology, in this case the process of radionuclides removal. Some cost data, referred to Milano aqueduct in Italy [37], are reported in Table 6. Among the three treatment processes (aeration for radon removal; activated carbon adsorption for radon, radium, and uranium removal; and RO for radium and uranium removal) RO, as expected, has the highest costs.

Table 6. Radionuclides removal costs, referred to Milano aqueduct, Italy [37]

Treatment process	Total costs, eur/m³
Aeration for Rn removal	0.009–0.018
Activated carbon adsorption (incl. annual regeneration)	0.007–0.008
Reverse osmosis	0.092–0.11

Table 7. Radionuclides removal costs, referred to the American situation [39]

Treatment process	Total costs, eur/m³
Ion exchange	0.07–0.19
Lime softening	0.07–0.19
MnO₂-based methods	0.07–0.19
Ra selective adsorption	0.04–0.09

Some more data, referred to the USA [39], are reported in Table 7. The total costs of ion exchange, lime softening, and MnO_2-based methods are in the same range, 0.07–0.19 eur/m³, while use of radium selective adsorbents should be an about twice cheaper option.

According to preliminary estimations, the process of radium removal by optimized iron–manganese filtration, patented by the Estonian company Water Technology Partners Ltd. [28], seems to be one of the cheapest options. The preliminary total costs of this process are about 0.02 eur/m³.

Radioactive waste management

Removal of radionuclides from water creates gaseous (desorbed radon), liquid (backwash water from filters, ionites regeneration solutions, brine from RO systems), and solid (spent filter materials or resins, spent membranes) radioactive wastes. The characteristics of the residuals can be affected by the initial concentration of radionuclides in the source water, frequency of filters backwash and resin/filter media/membrane replacement, efficiency of the treatment process, loading to the treatment system, etc.

According to the Finnish Centre of Radiation Safety (STUK), radon- or carbon dioxide-rich air can be diverted from a packed tower column or any other aerator directly out of the waterworks building [5,32]. However, the US EPA Regulations require a 3 pCi/L concentration limit for radon "at the boundary of the controlled area", and accounting for "dilution, dispersion or decay" from the source to the boundary. The calculations using US EPA's "SCREEN" model have proved that the 1.5 m tall stack discharge of 17.5 pCi/L is diluted to less than 0.01 pCi/L. Thus, the 3 pCi/L limit is easily met [20].

If radon is adsorbed in a granular activated carbon (GAC) filter, then close to the filter without shielding the external dose rate may be of the order of 100 μSv/h. However, it is recommended that the dose rate at a distance of 1 m from the filter should not exceed 1 μSv/h. When the GAC filter is no longer used, the amount of radon in the filter decreases rapidly and it is close to zero after four weeks [21].

Each coagulation–co-precipitation–settling technology will produce solid–liquid residuals (sludges), whose radioactivity level is the higher the more efficient is the radionuclides removal from water. Clifford [40] characterized the radioactivity of wastes depending on the initial concentration of radionuclides in water and on the lime or coagulant dose applied. For example, for 90% removal of 40 μg/L of uranium with lime at pH 10.6, the dry sludge has to contain 135 pCi/g (5 Bq/g) of $CaCO_3$. And for 50% removal of 40 μg/L of uranium with 25 mg/L of ferric sulphate the dry sludge has to contain 800 pCi/g (30 Bq/g) of $Fe(OH)_3$.

^{226}Ra presents the greatest long-term health risk due to the subsequent production of radon gas, which may enter households through the soil. Health risks associated with uranium in solid waste are approximately 10 times less than those of radium. According to the US EPA regulations [38], if radium and ^{210}Pb activity is <3 pCi/g (<0.11 Bq/g) and uranium activity is <30 pCi/g (<1.1 Bq/g), the waste can be disposed after dewatering on municipal landfills. Higher radioactivities require special non-radioactive cover installation or disposal of the waste on hazardous wastes landfills.

The primary liquid wastes from the process of radionuclides removal together with iron and manganese are the backwash waters of filters. Solid wastes are created in case the filter materials or zeolites that accumulated the radioactivity are removed from use.

According to Shabana and Al-Jaseem [24], the conventional sand bed may be regenerated with HCl acid (~4 M), which is more efficient than HNO_3 and H_2SO_4 acids for the removal of radium from the filter sands. Organic ion exchangers can usually also be regenerated. The properties of many inorganic (natural or mineral based) exchangers cannot be restored by regeneration and therefore they must be discarded after exhaustion and, as a rule, are disposed on common municipal landfills [41].

It is recommended that iron and manganese removal filters should be backwashed about once a week to allow the backwash water to discharge into the sewer. The same is valid for the regeneration liquids of anion and cation exchange resins if the filters are regenerated about once a week [25,31].

Over 95% of the radioactivity of Estonian groundwater is caused by two radium isotopes: ^{226}Ra and ^{228}Ra. Concentrations of uranium isotopes are negligible. According to the EU Regulation Radiation Protection 122, Part II, 2001 [42], the rounded general clearance level to discharge different radioactive wastes to nature for ^{226}Ra is 500 Bq/kg and for ^{228}Ra 1000 Bq/kg. The Estonian Regulations [26] have set for ^{226}Ra, ^{228}Ra, Pb^{210}, and Po^{210} the same clearance level – 10 Bq/kg.

Some of the above-given suggestions were checked in practice on the Viimsi Water Ltd. pilot plant where the iron and manganese removal filters were backwashed 1–2 times a week [28]. The average gross-alpha (~^{226}Ra) activity of the filters backwash water with suspended solids was 3.85 Bq/L and the average gross-beta (~^{228}Ra) activity was 7.6 Bq/L. Both remained below the Estonian clearance levels of 10 Bq/L, which allowed the discharge of the backwash water directly to the sewerage.

The common practice in water and wastewater treatment is to settle the filters backwash water that contains suspended solids in sedimentation basins. The sludge from the process of radionuclides removal is radioactive and needs analysis, dewatering with filter presses or centrifuges, and adequate disposal. According to the contemporary EU regulations [37], the clearance levels for some natural radionuclides in all residues and wastes are the following: ^{238}U and ^{235}U 1000 Bq/kg and ^{226}Ra, ^{228}Ra, ^{210}Pb, and ^{210}Po 10 Bq/kg (all rounded general levels).

In the USA (states of Wisconsin and Illinois) one of the first options for the disposal of radium-containing solid and liquid wastes has been their spreading on land, which appeared to be more cost-effective and practical than landfills [43].

In the framework of Estonian–Italian cooperation [37] the situation with liquid and solid wastes from iron and manganese removal in several Estonian waterworks (Tallinn, Keila, Rakvere, Viimsi, etc.) was analysed. It was concluded that the backwash waters of treatment systems generally complied with reference levels, apart from Rakvere where sewer sludges are used in agriculture. However, the solid residues from filters exceeded the general clearance levels. As no ionite or membrane filters are now in use in Estonia for special radionuclides removal, there are no data on the radioactivity of used resins or membranes yet, but it is very likely that these solid residues will also exceed the EU clearance levels. Corresponding measurements are one of the tasks of the planned cooperation between Tallinn Technical University and the University of Tartu at Viimsi Water Ltd. in the coming years.

On this background information, spent filter and ion exchange materials represent a special type of radioactive waste and pose unique problems in the selection of their treatment options [44]. The best solution here is probably incorporating solid waste into a matrix material (cement, bitumen, polymer, etc.) for solidification or directly into a storage and/or final disposal container.

CONCLUSIONS

Contamination of drinking water with radionuclides has become a significant, emerging issue today. There are 10 natural radionuclides (^{238}U, ^{234}U, ^{235}U, ^{226}Ra, ^{222}Rn, ^{210}Po, ^{210}Pb, ^{228}Ra, ^{224}Ra, and ^{231}Pa) that may occur in potable waters in harmful concentrations.

Radon is a naturally occurring radioactive gas, which emits ionizing radiation. Radon in drinking water does not present a major health concern compared to radium and uranium.

^{226}Ra and ^{228}Ra are natural groundwater contaminants, which usually occur at trace levels. Radium is one of the most hazardous elements with respect to internal radiation exposure. At high exposure levels both radium isotopes can cause osteoporosis, anemia, kidney and liver disease, and bone cancer in humans, and are believed to cause stomach, lung, and other cancers as well.

Uranium is a naturally occurring radioactive contaminant, which is found not only in groundwater but also in surface waters. Uranium has no known metabolic function in the human body and is considered to be relatively non-essential. However, US EPA believes that uranium can be toxic to the kidneys.

The determination as well as removal of natural radionuclides from drinking water have become increasingly important during the past few years. This is mainly attributed to possible health impacts and new regulations in the European Union and in the USA. The EU Drinking Water Directive (DWD) 98/83/EC lays down a reference effective dose of 0.1 mSv/yr for public waterworks. The effective dose should be calculated for all radionuclides, but in practice only isotopes of uranium and radium are included in this dose.

Several processes can be applied for radionuclides removal. Aeration is capable of removing only radon from radionuclides. Contemporary intensive aeration systems of water (fine-bubble and Venturi-type GDT aerators) can remove 98–100% of radon. To get rid of radium and uranium isotopes is more complicated. Removal of radium and uranium by lime softening–filtration, co-precipitation with barium sulphate, and enhanced coagulation–filtration have been historically the first technological options, but have lost their practical significance nowadays.

Radionuclides removal with optimized iron and manganese filtration is the most natural and economical way for radium and partially also for uranium removal. The process is based on one hand on the phenomenon of co-precipitation of radium cations together with Fe(OH)$_3$ sludge, and on the other, on the sorption of radium cations onto hydrous manganese oxide particles. In the case of relatively low manganese concentrations in raw water, filtration through a catalytic (MnO$_2$ containing) material (manganese greensand, FHM, Everzit Mn, Pyrolox, etc.) can be suggested. A combined and chemicals-free treatment technology (aeration, oxidation, catalytic filtration, ion exchange) has been elaborated by Tallinn University of Technology and by the companies Water Technology Partners Ltd. and Viimsi Water Ltd. in Estonia. The Viimsi WTP (2500 m^3/d) was put into operation in January 2012.

In the USA the hydrous manganese oxide technology for radionuclides removal has been proposed. It is based on continuous injection of two chemicals (KMnO$_4$ and MnSO$_4$ solutions) into the raw water to form a hydrous MnO$_2$ precipitate in situ. Compared to the technology of optimized iron and manganese removal, the HMO technology has obviously higher operation costs.

As to the application of ion exchange and modern membrane processes for radionuclides removal, further studies on waste solutions from the regeneration of resins and radioactive saline retentate from the RO unit disposal are needed. However, continuing advances in membrane technology and reduction of membrane prices will certainly bring RO for radionuclides removal into a much more competitive position in the near future.

Management of radioactive liquid and solid wastes from the radionuclides removal processes is not totally elaborated yet, and there are different approaches to the solution of this problem. However, the scheme for the treatment of the most common iron and manganese filters backwash water is obviously the following: sedimentation, sludge removal, thickening, dewatering, encapsulation into matrix material, and ultimate deposition. Incorporation into a matrix material (cement, bitumen, polymer) will be an option also for other solid wastes (saturated filter materials and ion exchangers). In Estonia the solid waste (fly ash) from thermal power plants together with the cement from the Kunda Nordic Cement Ltd. are the potential materials for these purposes.

Successful solution of the problems linked to natural radionuclides analysis, technology of removal, and waste management in Estonia requires cooperation of the Ministry of Environment, Estonian Radiation Centre, Institute of Physics of the University of Tartu, and Tallinn University of Technology. The Institute of Physics of the University of Tartu is dealing with the elaboration of a methodology of natural radionuclides analysis [45], and will supervise the measurements of radiation levels in the air, water, and solid materials at the new Viimsi Water Treatment Plant, which was put into operation in January 2012.

pollutants with advanced oxidation technologies" is gratefully acknowledged.

Rein Munter was born in Tallinn on 23 December 1936. Graduated from Tallinn Technical University (presently Tallinn University of Technology, TUT) in 1960 as a Chemical Engineer. Defended his PhD on water ozonation in a downflow static mixer at TUT in 1968, and his DSc degree on water and wastewater ozonation theory and practice at the Institute of Colloidal and Water Chemistry in Kiev (Ukraine) in 1991. From 1991 to 2011 Professor of Environmental and Chemical Technology and Chair of Environmental and Chemical Technology at the Department of Chemical Engineering of TUT. In 2001 he and his co-workers M. Trapido, J. Kallas, and S. Preis were granted the Estonian National Science Award "Advanced Oxidation Processes for Water Recycling and Water Bodies Protection". Member of the European Board of the International Ozone Association (IOA), member of the International Water Association (IWA), and editorial boards of the journals Ozone: Science and Engineering *and* Water Chemistry and Technology. *Honorary Editor of Chapter 6.192 "Ozone Science and Technology" of the UNESCO* Life Systems Encyclopedia *(EOLSS). Fulbright scholarship "Kinetics of radical reactions and oxidation of ships ballast water" (March–May 2009, California University, Irvine, USA). Author of more than 180 papers on water and wastewater ozonation and advanced oxidation. Since 1 September 2011 Professor Emeritus and Senior Researcher at the Department of Chemical Engineering (TUT). Under his supervision five PhD theses have been defended.*

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Tehnoloogia radionukliidide eraldamiseks veest ja jäätmekäitlus

Rein Munter

Joogivee saastumine looduslike radionukliididega (^{238}U, ^{234}U, ^{235}U, ^{226}Ra, ^{222}Rn, ^{210}Po, ^{210}Pb, ^{40}K, ^{228}Ra, ^{224}Ra ja ^{231}Pa) on muutunud ülemaailmselt oluliseks, edasilükkamatuks probleemiks. Loodusvee kõrgendatud radioaktiivsus on tuntud 18 EL-i riigis (k.a Eesti): Austrias, Belgias, Bulgaarias, Tšehhis, Saksamaal, Hispaanias, Prantsusmaal, Soomes, Kreekas, Iirimaal, Itaalias, Ungaris, Luksemburgis, Portugalis, Rumeenias, Rootsis ja Slovakkias. Põhjavees domineerivad eelloetletud radionukliididest peamiselt ^{222}Rn, ^{226}Ra, ^{228}Ra ja ^{40}K ning vähemal määral ^{238}U, ^{234}U ja ^{235}U ning ^{210}Po ja ^{210}Pb.

Raadiumi isotoopidega võrreldes ei kujuta radoon (^{222}Rn) joogivees endast erilist ohtu. Põhjavee intensiivsel õhustamisel eraldub radoon peaaegu täielikult. Inimese sisemise ekspositsiooni seisukohalt on ^{226}Ra ja ^{228}Ra kõige ohtlikumad radionukliidid, kuna need võivad põhjustada osteoporoosi, aneemiat, maksa- ning neeruhaigusi ja mao- ning luuvähki. Uraani isotoope peetakse inimese ainevahetuses ebaolulisteks, kuid USA Keskkonnaagentuuri (US EPA) arvates on uraan toksiline eeskätt neerudele.

Viimaste aastate jooksul on radionukliidide analüüs loodusvees ja nende kõrvaldamise tehnoloogia valik üha olulisemaks muutunud. EL-i joogivee direktiiv (98/83/EC) nõuab, et joogiveest saadav kiirgusdoos täiskasvanutele aastas ei tohi ületada 0,1 mSv. Efektiivdoos arvutatakse tavaliselt raadiumi ja uraani isotoopidele.

Radionukliididest on kõige hõlpsam vabaneda radoonist. Intensiivne peenmulliline või injektsioon-õhustamine kõrvaldavad kergesti 98–100% radoonist. Keerulisem on vabaneda raadiumi ja uraani isotoopidest. Ajalooliselt on esimesteks uuritud protsessideks olnud lubjaga pehmendus, koossadestamine baariumsulfaadiga ja kiirendatud koagulatsioon koos filtrimisega, mida nüüd ei saa enam tänapäevasteks tehnoloogilisteks lahendusteks pidada.

Praegusaegseteks raadiumi ja uraani eraldusmeetoditeks on ioonvahetus ning membraaneraldus (pöördosmoos). USA-s on leitud, et kasutades veepehmendusfiltris ~10% tugevaaluselist anioniiti ja ~90% tugevahappelist kationiiti,

on võimalik edukalt vabaneda nii raadiumist kui uraanist. Tunduvalt vähem infot on pöördosmoosi kasutamise tulemuslikkuse ja selle rakendamisega kaasneva jäätmekäitluse kohta.

Kõige odavamaks ja lihtsamaks lahenduseks on tavalise raua/mangaani eraldusprotsessi optimeerimine, kasutades katalüütilisi (MnO_2 sisaldavaid) filtermaterjale (mangaanroheline liiv, FMH, Everzit Mn, Pyrolox jt). OÜ Water Technology Partners poolt on välja töötatud ja patenteeritud kombineeritud tehnoloogiline protsess (õhustamine, oksüdatsioon, katalüütiline filtrimine, ioonvahetus (II astme filtris).

Radionukliidide eraldustehnoloogiatega võrreldes on sealjuures tekkivate radioaktiivsete jäätmete käitlus tunduvalt vähem läbi töötatud. Lähenemisviisid jäätmekäitlusele selles osas on riigiti erinevad. Kõige selgem on raua/mangaani eraldusfiltrite pesuvee käitlus: vesi selitatakse, muda eraldatakse, paksendatakse, veetustatakse ja immobiliseeritakse, kasutades tsementi, bituumenit või polümeere. Ka teiste jäätmete (äratöötanud filtermaterjalid, ioniidid) käitlusel on immobiliseerimine ilmselt parim lahendus. Eestis saab selleks suurepäraselt ära kasutada põlevkivi-energeetika jääkprodukti, lendtuhka koos tsemendiga Kunda tehasest Nordic Cement.