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ABSTRACT

TENAWA project (Treatment Techniques for Removing Natural Radionuclides from Drinking Water) was carried out on a cost-shared basis with the European Commission (CEC) under the supervision of Directorate-General XII, Radiation Protection Unit. TENAWA project was started because in several European countries ground water supplies may contain high amounts of natural radionuclides. During the project both laboratory and field research was performed in order to test the applicability of different equipment and techniques for removing natural radionuclides from drinking water. The measurable objectives of the project were:

- to give recommendations on the most suitable methods for removing radon (^{222}Rn), uranium ($^{238, 234}$U), radium ($^{226, 228}$Ra), lead (^{210}Pb) and polonium (^{210}Po) from drinking water of different qualities (i.e. soft, hard, iron-, manganese- and humus-rich, acidic)

- to test commercially available equipment for its ability to remove radionuclides
- to find new materials, adsorbents and membranes effective in the removal of radionuclides
- to issue guidelines for the treatment and disposal of radioactive wastes produced in water treatment.

Radon could be removed efficiently (>95%) from domestic water supplies by both aeration and granular activated carbon (GAC) filtration. Defects in technical reliability or radon removal efficiency were observed in some aerators. The significant drawback of GAC filtration was the elevated gamma dose rates (up to 120 µSv/h) near the filter and the radioactivity of spent GAC. Aeration was found to be a suitable method for removing radon at waterworks, too. The removal efficiencies at waterworks where the aeration process was designed to remove radon or carbon dioxide were 67–99%. If the aeration process was properly designed, removal efficiencies higher than 95% could be attained.

Uranium could best be removed (>95%) with strong basic anion exchange resins and radium by applying strong acidic cation exchange resins. Also, weak acidic cation resin, zeolite A, sodium titanate and manganese dioxide were found efficient in radium removal. Hydroxyapatite removed both uranium and radium. Simultaneous removal (>95%) of uranium, radium, lead and polonium could be carried out by nanofiltration and reverse osmosis. The side-effect of RO-technique was the quality of the effluent; the water becomes almost totally demineralized and therefore corrosive. Commercially available iron and manganese removal equipment removed variable amounts of radon (0–90%), uranium, radium, lead and polonium (0–100%) depending on the operation principle.

Lead and polonium could be removed only fairly well by ion exchange and GAC filtration (35–100%). The presence of lead and polonium in particles of different sizes in groundwater was determined in the laboratory. Only in one type of water, with relatively high NaCl concentration and rich in humus material, was a considerable fraction, about 20%, of both radionuclides found to be present in the soluble form. In the other types of water only from 1 to 2% of lead and polonium was soluble. It is expected that neither lead nor, especially polonium would form intrinsic precipitates but they would be adsorbed on colloidal minerals and organics.

When different kinds of treatment methods are used to remove natural radioactivity from drinking water, wastes containing natural radioactivity will be produced. It is recommended that the annual dose to inhabitants from external gamma radiation of a GAC filter should not exceed 0.1 mSv. It is also recommended that the dose rate at a distance of 1m from the GAC filter should not exceed 1 μSv/h. To achieve these aims the GAC filter should be equipped with special shielding to attenuate gamma radiation. It is also recommended that the wastes containing natural radioactivity in solid form be discharged into communal dumps, and wastes containing natural radioactivity in liquid form be discharged into the sewer.

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TIIVISTELMÄ

TENAWA-projekti (Treatment Techniques for Removing Natural Radionuclides from Drinking Water) toteutettiin yhteisrahoitteisesti Euroopan komission (CEC) kanssa, sen kahdennentoista pääosaston (DGXII) Säteilysuojeluyksikön valvonnassa. TENAWA-projekti käynnistettiin, koska useiden Euroopan maiden pohjavesissä on havaittu esiintyvän korkeita määriä luonnon radionuklideja. Projektin aikana tehtiin laboratorio ja –kenttäkokeita, joilla testattiin eri laitteiden ja tekniikoiden soveltuvuutta luonnon radionuklidien poistamiseen juomavedestä. Projektilla oli seuraavat päätavoitteet:

- antaa suosituksia menetelmistä, joilla voidaan poistaa radon 222 , uraani 238, uraani 234, radium 226, radium 228, lyijy 210 ja polonium 210 erilaatuisista juomavesistä (esim. pehmeä vesi, kova vesi, rauta-, mangaani-, humus- tai hiilidioksidipitoinen vesi)
- testata kaupallisten laitteiden toimivuutta radionuklidien poistossa
- löytää uusia materiaaleja, adsorbantteja ja kalvoja, jotka tehokkaasti poistavat radionuklideja

- antaa suosituksia vedenkäsittelyssä syntyneiden jätteiden käsittelyyn ja hävittämiseen.

Radon voitiin poistaa tehokkaasti (>95 %) kotitalouksien vedestä sekä ilmastamalla että aktiivihiilisuodatuksella. Jotkin ilmastimet eivät kuitenkaan toimineet teknisesti odotetulla tavalla. Puutteita havaittiin myös radonin poistotehokkuudessa. Aktiivihiilisuodatuksen haittapuolena oli korkea gammasäteilyn annosnopeus (jopa 120 µSv/h) suodattimien pinnalla ja käytetyn hiilen radioaktiivisuus. Ilmastuksen todettiin soveltuvan hyvin radoninpoistoon myös vesilaitoksilla. Mikäli ilmastusprosessi oli suunniteltu radonin tai hiilidioksidin poistoon, radonin poistumat olivat 67–99 %. Kun ilmastusprosessi on oikein suunnitteltu, voidaan yli 95 prosenttia radonista poistaa.

Vahva anioninvaihtohartsi soveltui parhaiten uraanin poistoon ja vahva kationinvaihtohartsi radiumin poistoon. Radium poistui tehokkaasti myös heikolla kationinvaihtohartsilla, zeoliitti A:lla, natriumtitanaatilla ja mangaanidioksidilla. Hydroksiapatiitti adsorboi tehokkaasti sekä uraania että radiumia. Samanaikainen uraanin, radiumin, lyijyn ja poloniumin poisto (> 95 %) voitiin toteuttaa nanosuodatuksella ja käänteisosmoosilla. Käänteisosmoosin haittana on puhdistetun veden laatu. Demineralisoituna se ei sellaisenaan kelpaa talousvedeksi, vaan tarvitsee veden jälkikäsittelyn. Vesi on lähes täysin demineralisoitu ja siten syövyttävää. Kaupalliset raudan- ja mangaaninpoistolaitteet poistivat toimintaperiaatteesta riippuen vaihtelevia määriä radonia (0–90 %), uraania, radiumia, lyijyä ja poloniumia (0–100 %).

Lyijy ja polonium voitiin poistaa ioninvaihdolla ja aktiivihiilisuodatuksella vain osittain (35–100 %), koska näiden nuklidien kemialliset muodot pohjavesissä vaihtelevat. Lyijyn ja poloniumin sitoutuminen erisuuruisiin partikkeleihin tutkittiin laboratoriossa. Vain yhdessä tutkituista vesistä lyijyn ja poloniumin liukoisen muodon osuus oli merkittävä, noin 20 %. Tässä vedessä oli myös korkeahko NaCl-pitoisuus. Muissa vesissä liukoisen muodon osuus oli 1–2 %. Oletettavaa on, etteivät lyijy ja erityisesti polonium saostu puhtaina yhdisteinä, kuten esim. hydroksideina, vaan adsorboituvat mineraalisten ja orgaanisten kolloidien pinnoille.

Eri puhdistusmenetelmiä käytettäessä syntyy jätteitä, jotka sisältävät luonnon radioaktiivisia aineita. Suosittelemme, että aktiivihiilen lähettämän ulkoisen gammasäteilyn aiheuttama vuosiannos ei saa ylittää 0,1 mSv asukasta kohden. Suosittelemme myös, ettei annosekvivalenttinopeus ylitä arvoa 1 µSv/h yhden metrin päässä suodattimesta. Näiden tavoitteiden toteuttamiseksi suodattimet pitää varustaa gammasäteilyä vaimentavilla suojilla. Lisäksi suosittelemme, että käsittelyssä syntyvät kiinteät jätteet voidaan viedä kaatopaikalle ja nestemäiset jätteet laskea viemäriin.

CONTENTS

PREFACE

The shared-cost research project “Treatment Techniques for Removing Natural Radionuclides from Drinking Water” (TENAWA) was carried out in the fourth Framework Programme 1994–98 of research and training funded by the European Commission in the sector of Nuclear Fission Safety. The aim of the TENAWA project was the evaluation of treatment techniques for removing natural radionuclides from drinking water. It was carried out by the following partners, who were responsible for the scientific work and for writing this report:

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The TENAWA project was divided into 13 work packages:

WP 1.1: General Considerations: Literature Survey on Natural Radioactivity in Drinking Water and Treatment Methods in European Countries

WP 1.2: General Considerations: Intercomparison of Analysis Methods

WP 1.3: General Considerations: Definition and Classification of Different Water Types and Experimental Conditions

WP 2.1: Removal of Radon by Aeration: Testing of Commercially Available Equipment for Domestic Use

WP 2.2: Removal of Radon by Aeration: Testing of Various Aeration Techniques for Small Waterworks

WP 3.1: Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of Radon

WP 3.2: Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of U, Ra, Pb and Po

WP 4: Removal of Radioactivity by Methods Used for Fe- and Mn-removal from Private Wells

WP 5.1: Removal of U, Ra, Pb and Po by Ion Exchange Methods. Removal of U and Po from Private Ground Water Wells using Anion Exchange Resins

WP 5.2: Removal of U, Ra, Pb and Po by Ion Exchange Methods. Removal of Ra and Pb from Private Ground Water Wells using Cation Exchange Resins

WP 6: Removal of U, Ra, Pb, and Po with Adsorptive or Membrane Filters

WP 7: Speciation of U, Ra, Pb and Po in Water

WP 8: Disposal of Radioactive Wastes from Water Treatment Methods: Recommendations for EC.

1 INTRODUCTION

The reason for the TENAWA project was the fact that in several European countries ground water, especially bedrock water, may contain high amounts of natural radioactivity. Elevated levels of natural radionuclides in ground waters are mainly associated with uranium- and thorium-rich soil and rock minerals, or with uranium, thorium or radium deposits in soil or bedrock.

Nation-wide surveys of natural radioactivity in drinking water have been conducted in several European countries. The surveys made, e.g., in the Nordic countries, in Finland, Sweden and Norway, indicate that high concentrations of ^{222}Rn and other radionuclides usually occur in water from wells drilled in bedrock. In surface waters the concentrations are usually low, as well as in ground waters occurring in soil. Data on natural radioactivity in drinking and mineral waters have also been published, e.g., for Austria, Denmark, France, Germany, the United Kingdom, Ireland, Italy, Portugal, and Spain. High concentrations of natural radionuclides have been reported in some areas.

In most European countries ground water is used as drinking water. There is also an increasing tendency to replace surface water with water originating from various types of ground water aquifers. However, this involves an increased risk of finding natural radionuclides in the water.

Elevated levels of natural radionuclides in drinking water accompany potential health risks for the population because of the increase in the radiation dose. Therefore, the waters should be purified before use. Various processes based on different principles can be applied to removing radionuclides from water. Aeration is a method that can be applied to removing high levels of radon (^{222}Rn) from drinking water. GAC filtration can be used when the radon concentration of water is not exceptionally high. Ion exchangers are applied to removing uranium (^{238}U, ^{234}U) and radium (^{226}Ra). Lead (^{210}Pb) and polonium (^{210}Po) may sometimes be removed by ion exchange techniques as well. Membrane techniques, such as reverse osmosis (RO) or nanofiltration (NF), are used to remove uranium, radium, lead and polonium. Fe- and Mn-removal equipment also removes natural radionuclides from water.

When different kinds of treatment methods are used to remove natural radioactivity from drinking water, wastes containing natural radioactivity will be produced. The wastes are in liquid or solid form. Liquid wastes are produced when materials used to accumulate radioactivity are regenerated or backwashed. Solid wastes are formed in cases where regeneration or backwashing are not used or cannot be used.

2 OBJECTIVES

The overall objective of the TENAWA project was to study equipment currently available for removing natural radionuclides from drinking water. There is a definite need for well-tested methods and equipment both in small and large waterworks and in private dwellings. The measurable objectives of the TENAWA project were as follows:

- to make recommendations on the most suitable methods for removing ^{222}Rn, ^{238}U, ^{234}U, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po from drinking water of different qualities (soft, hard, Fe-, Mn- and humus-rich, acidic, etc.)
- to test commercially available equipment for its ability to remove radionuclides
- to find new materials, absorbers and membranes effective in the removal of radionuclides
- to issue guidelines for the treatment and disposal of radioactive wastes produced in water treatment.

The aims of the different WPs of the TENAWA project were as follows:

- to gain a European perspective for the TENAWA project as well as to find the potential risk areas for further studies and to point out areas where radionuclide removal techniques are most needed
- to ensure that the analysis methods used in the laboratories owned by the partners produce reliable and comparable results
- to make sure that different research groups produce results under comparable and pertinent experimental conditions
- to provide data which can be used when choosing an aerator capable of removing radon and of producing sufficient amounts of water from ground water wells
- to implement a cheap, easy-to-use aeration technique (e.g. spray aeration, diffused bubble method or packed column aeration) for various types of small water works and to write guidelines on how to build aeration systems
- to provide information and recommendations as to which types of waters GAC filtration can be safely used with
- to find out the usability of GAC filtration for removing uranium, radium, lead and polonium from various types of waters

- to test the removal efficiency of Fe- and Mn-removal equipment for different radionuclides
- to test the removal efficiency of anion exchange resins for uranium and polonium, to study the capacity and regeneration of the resins and necessary prefilters and to study cation exchange resins for radium and lead removal
- to study adsorbents for their efficiency in removing uranium and radium and reverse osmosis (RO) for its efficiency in removing uranium, radium, lead and polonium
- to make a literature survey of speciation of uranium, radium, lead and polonium in ground waters and to determine the oxidation states (IV, VI) and chemical forms of uranium in different groundwaters
- to estimate the effect of oxidation states and chemical form on the removal of these radioelements from ground waters
- to recommend guidelines for treatment and disposal of radioactive wastes produced by various water treatment methods.

3 PROGRESS AND RESULTS

3.1 Survey of Literature on Natural Radioactivity in Drinking Water and Treatment Methods in European Countries

A literature review was prepared with the title: "Natural radionuclides in drinking water in Europe and treatment methods for their removal". The review presents the fundamental hydrochemical processes which are responsible for the mobility of natural radionuclides in water. The main potential risk areas for the occurrence of high contents of natural radionuclides in ground and surface water in Europe are pointed out and data concerning contents in drinking, mineral, ground and surface water from 17 European countries are presented. An overview of treatment methods to remove natural radionuclides from drinking water is given, and human health aspects and regulations regarding natural radionuclides in drinking water are summarised.

3.2 Intercomparison of Analysis Methods

Six intercomparison runs were performed for quality assurance of the analytical results produced in the TENAWA project. Both natural water samples and spiked samples were distributed among the partners in the project for analysis of radon (^{222}Rn), radium (^{226}Ra), uranium-isotopes and -total content and in one intercomparison, thorium-isotopes and -total content, lead (^{210}Pb) and polonium (^{210}Po).

3.3 Definition and Classification of Different Water Types and Experimental Conditions

Experimental conditions, including the way of planning experiments, the type and frequency of the analysis to be made, documentation of results and the interchange of information between the project partners were defined regarding the different treatment technologies to be tested and the type of experiments.

Water types to be selected for the experiments were fixed for each treatment technology. The selection was based on the water quality parameters which were assumed to have relevant influence on the treatment technologies, and on surveys regarding water quality in the areas with elevated natural radionuclides in water.

The ftp-server, the communication platform and database for the whole TENAWA project was established at IWGA and was continuously serviced. A WWW page on the TENAWA project was implemented on the IWGA server and regularly up-dated (`http://iwga-sig.boku.ac.at/tenawa1_e.htm`).

3.4 Removal of Radon by Aeration: Testing of Commercially Available Equipment for Domestic Use

There are three basic water treatment methods that can be used to remove radon from water supplies, namely decay storage, aeration and granular activated carbon (GAC) filtration. In this study different types of aerators were tested for their performance in radon removal.

Because of its relatively high Henry's law constant, radon can be removed from water by aeration. Basically two different principles can be applied: water can be released into air or air can be released into the water. A common way to release water into air is to spray untreated water into a tank with a fine mist spray nozzle. To reach a radon reduction of 70%, theoretically one litre of air is mixed with one litre of atomised water. With diffused bubble aeration a high pressure blower forces air through a fine bubble diffuser located at the bottom of the tank. Commercial aeration systems usually use combinations of both principles.

Radon is released from the water at an increasing rate as the air to water ratio is increased. The radon diffuses from the water into the air and the air is then ventilated into the outdoor air. Most commercial systems work under atmospheric pressure and a re-pressurisation pump is therefore needed after the aeration tank. Further radon reduction can be achieved by