A HIGHLY SELECTIVE METHOD FOR REMOVING NATURAL RADIOACTIVITY FROM DRINKING WATER

M. GASCOYNE

Applied Geoscience Branch
Whiteshell Nuclear Research Establishment
Pinawa, Manitoba R0E 1L0

ABSTRACT

High natural concentrations of uranium and radium have been found in well waters in the Lac du Bonnet area, Southeastern Manitoba. A filter system has been developed at the Whiteshell Nuclear Research Establishment (WNRE) that removes > 90% uranium and > 70% radium and may be installed in-line with any household water supply. This system will be available soon through selected distributors.

INTRODUCTION

In 1983 May, high levels of alpha and beta radioactivity were discovered in private well waters in the Regional Municipality of Lac du Bonnet in Southeastern Manitoba. Many of the waters were considered unsafe for long-term, continuous human ingestion because gross alpha activities exceeded 1 Bq/L. It was subsequently determined that this radioactivity was caused almost entirely by isotopes of uranium and radium. Using the research and design expertise at the Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, a technique was developed to remove uranium and radium selectively from the drinking waters.

This paper briefly examines the causes of radioactivity in drinking water and existing methods of removal, and then describes the development and testing of a two-component system for the selective removal of uranium and radium from household water supplies.

RADIOACTIVITY IN GROUNDWATER

Radioactivity in groundwater may be either man-made, from waste discharges and atomic bomb fallout, or produced naturally, from the dissolution of gases and rock minerals. In the latter category, for most groundwaters, the radionuclides of concern are isotopes of uranium and thorium, and their daughter products (mainly ^{226}Ra, ^{222}Rn, ^{210}Pb and ^{210}Po). Some typical levels of uranium and radium in natural water are shown in Table 1.

TABLE 1. TYPICAL CONCENTRATIONS OF URANIUM AND RADIUM IN GROUNDWATERS (1)

Location	Rock	U(μg/L)	^{226}Ra(Bq/L)
Eastern UK	sandstone	5	-
Bath, UK	limestone	0.05	0.4
Central USA	dolomite/sdst.	0.6	0.3
USA regions	various	120	1.1
S. Carolina	sedimentary	-	1.0
S.W. Sask.	sediments	240	-
E. Germany	sandstone	17	-
Okanagan, B.C.	sedimentary	8000	-
Nevada	tuff	21	0.1
Minnesota	granite/gneiss	20	-
Helsinki	granite	14870	1.0
Japan	granite	23	-
Scotland	granite	15	-
Stripa, Sweden	granite	90	1.3
Atikokan, Ont.	granite	10	<0.1
Lac du Bonnet Manitoba	granite	840	16

Uranium occurs in groundwater mainly as the two isotopes in the ^{238}U decay series, ^{238}U and ^{234}U, with small amounts of the isotope ^{235}U, from the ^{235}U decay series (see Figure 1). The amount of ^{234}U relative to ^{238}U varies, especially in groundwaters, and its radioactivity level often exceeds that of ^{238}U because ^{234}U, the decay product, is more easily leached from mineral surfaces. Although radioactivity ratios of ^{234}U to ^{238}U in natural waters are generally between one and three, values of up to twenty have been observed.(2)

Uranium is slightly soluble in natural waters, occurring mainly as the carbonate ion complexes $UO_2(CO_2)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$, between pH 7 and 10.(3) For a typical groundwater under CO_2-rich, oxidizing conditions, the maximum solubility of uranium is about 1 g/L (4), although natural groundwaters seldom attain this value.

Although four radium isotopes occur naturally in groundwaters, only ^{226}Ra, and ^{228}Ra have sufficiently long half-lives to permit appreciable concentrations to occur (Figure 1). The isotope ^{228}Ra occurs in the ^{232}Th decay series and has a relatively insoluble parent (^{232}Th) and a moderate half-life (5.8 years). It is, therefore, less mobile than ^{226}Ra, which has a more mobile parent (^{230}Th) and a longer half-life (1600 years).

Radium concentrations (expressed as radioactivity levels of ^{226}Ra) are generally quite low (<1 Bq/L). Higher levels sometimes occur in brines and some near-surface fresh waters. In natural waters, radium exists mainly as the free ion, Ra^{2+}, or the uncharged complex, $RaSO_4^0$. Radium is readily absorbed from solution by clays and rock silicates but is stabilized by high concentrations of Ca^{2+}, Mg^{2+} and Cl^-.(5)

EXISTING REMOVAL METHODS

Various techniques to remove uranium and radium from water have been developed and tested on a laboratory scale or on actual drinking water supplies. Table 2 summarizes these techniques and their

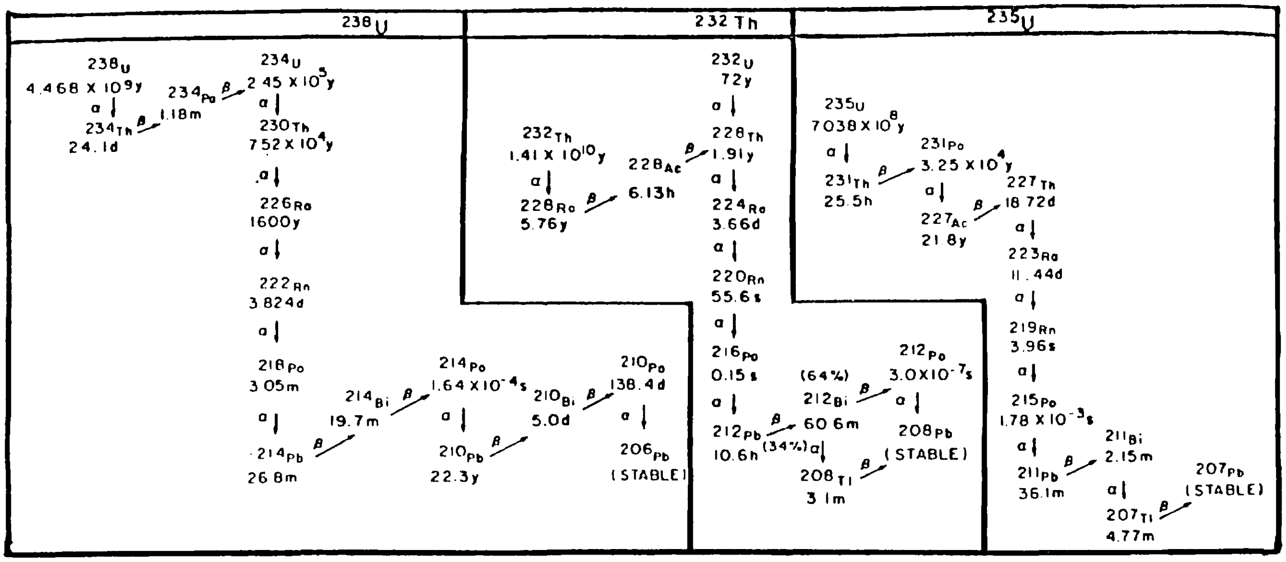

FIGURE 1. THE URANIUM AND THORIUM DECAY SERIES SHOWING DECAY MODES AND HALF-LIVES

advantages and disadvantages. A detailed review of the methods is given by Drury et al. (6), Lee et al. (7), and Reid et al. (8) Unfortunately, some of the techniques have not had enough testing to identify all their characteristics.

TABLE 2. EXISTING METHODS OF REMOVAL OF URANIUM AND RADIUM FROM DRINKING WATER

Method	Mechanism	Comments
Distillation	vapour condensation	efficient, unselective, low production
Reverse osmosis	membrane filtration	- as above -
Lime softening	coprecipitation	efficient, unselective, large scale, expensive, requires pretreatment
Coagulation	floc formation	removes U only, large scale, requires pretreatment
Adsorbents	sorption on peat, charcoal, Al_2O_3 etc.	removes U only, may add colour, needs low pH & HCO_3
Cation resins	ion exchange for Na	removes Ra only (U at low pH), adds Na to water, inexpensive & compact
Fe & Mn removal	coprecipitation	removes Ra only, low efficiency, requires pretreatment

None of these techniques is ideally suited to uranium and radium removal from waters in the Lac du Bonnet region. No system will selectively remove uranium and radium simultaneously, yet be inexpensive, require no preconditioning of the water, and be practical for point-of-use installation.

An alternative technique, which does satisfy the above criteria, is described in this paper.

SELECTIVE REMOVAL OF URANIUM AND RADIUM

Gascoyne (9) showed that uranium could be extracted from limestone groundwaters using anion exchange resin, with no preconditioning of the groundwater. In situ tests showed that extraction efficiencies for eight sites were high (mostly > 70%). Jasper and Oldham (10) and Lee and Bondietti (11) subsequently demonstrated the efficient and selective uptake of uranium using anion resin, from well water in British Columbia and from low-level radioactive waste pond water in Tennessee, respectively.

Moore and Reid (12) and Moore and Cook (13) removed radium from seawater and fresh water, respectively, using a man-made fibre impregnated with manganese dioxide. The removal efficiency was 90% in several tests.

These two methods form the basis of the selective removal system described here. It was devised and tested in a series of experiments using groundwaters in the Lac du Bonnet area, Manitoba. A summary of the tests is described below.

METHOD

The radium filter was made by treating loose acrylic fibres with potassium permanganate to impregnate them with manganese dioxide. The uranium filter was prepared by pre-rinsing an anion exchange resin to remove excess amine, followed by conditioning with a brine solution. Each material was packed into a ~ 1-L polycarbonate, water-filter housing, modified with a central riser pipe and steel mesh for flow distribution and material retention. The units were interconnected in series and installed in the cold-water line of the kitchen sink tap of a household in the Lac du Bonnet area, in 1984 March. Over 5000 L of water were passed through the system at a rate of 2 L/min, over the following two months before materials were renewed. Samples were taken frequently during this period to measure uranium, ^{226}Ra and major and minor elements. The radiation field arising from radionuclides trapped on the filters was measured in situ with a hand-held gamma monitor.

RESULTS

Variations in the radium and uranium concentrations over the duration of the test are shown in Figure 2. For the first 4000 L of water, removal efficiencies of radium and uranium were > 70% and > 90%, respectively. Radium removal was less consistent than uranium removal, possibly because of compacting of the fibre and channelling of flow during the test.

After ~ 4000 L of water had been passed through the filter, radiation fields on contact with the radium filter container were 0.018 mR/h, compared with 0.011 mR/h 30 cm away from the filter. Room background radiation was also about 0.011 mR/h. No radiation above background could be detected on the uranium filter. At this time, the filters had reached 60%, or more, of their final capacities.

Analyses of the filtered water to determine the effects on water quality showed that cation concentrations remained unchanged by filtration, throughout the experiment (see Figure 3). Anion concentrations varied only in the first ~ 200 L of water treated; after this, they were equal to raw water concentrations (Figure 3b). The main change$_2$initially in water quality was the removal of SO_4 from the water and release of Cl^- from the resin. Iron, well water colour and turbidity were also removed, resulting in a much clearer drinking water. Tests showed that the iron was replaced by manganese, derived presumably by a redox reaction occurring in the radium removal fibre. Although dissolved manganese does not constitute a health problem, it may affect aesthetic quality by producing black deposits on fixtures over time. To some extent, this is countered by the prevention of iron staining. Several other trace metals were also removed by the system, including copper, zinc, barium and lead.

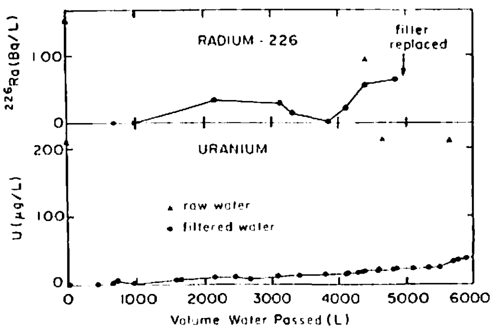

FIGURE 2. REMOVAL CHARACTERISTICS FOR URANIUM AND RADIUM FROM DRINKING WATER

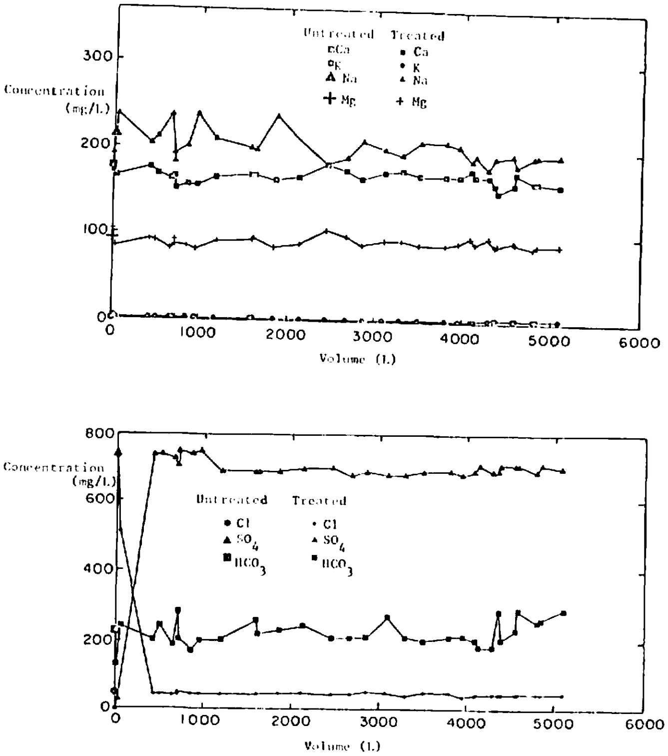

FIGURE 3. VARIATIONS OF (A) CATION AND (B) ANION CONCENTRATION IN WELL WATER TREATED BY THE URANIUM/RADIUM REMOVAL SYSTEM

Results of continuing tests of the household system, at lower water demand rates, over the period 1984 May to 1985 November confirmed the results described above and demonstrated the suitability of the system for long-term use.

A commercial version is now available, developed by the Whiteshell Nuclear Research Establishment in conjunction with Water Conditioning of Canada Limited, Regina. This version features sealed, disposable filter cartridges containing the sorbing materials. The cartridges are designed for about one year of use in a household with normal drinking water demand (~ 2 L per person per day). The cost of the complete system should be significantly less than that for a distillation or reverse osmosis unit. Although radiation fields were not significant during operation, used filter materials should be disposed of properly, preferably in a municipal landfill site.

SUMMARY AND CONCLUSIONS

The uranium and radium removal system has been found to reduce uranium and radium in drinking water to well within Provincial and Federal guidelines. General water quality and mineral content of the water are not affected, and radiation fields associated with the system are negligible.

A commercial version has been developed by the Whiteshell Nuclear Research Establishment in conjunction with a water treatment company. It uses sealed, disposable cartridges containing the filter materials, and the entire unit costs less than a reverse osmosis or distillation system.

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