

REMEDICATION OF GROUNDWATER CONTAMINATED WITH RADIOACTIVE COMPOUNDS

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Summary

Both naturally radioactive isotopes and isotopes from man-made sources may appear in groundwater. Depending on the physical and chemical characteristics of the contaminant, different types of treatment methods must be applied to reduce the concentration. The following chapter discusses treatment options as well as the prominent contaminants found in groundwater. Uranium is the most common contaminant and several methods such as physical adsorption, reactive adsorption, precipitation, and reverse osmosis may be employed to treat the groundwater. Of the treatment methods, adsorption is the most common method used, thus more text is devoted to its description. Other radioactive contaminants include cesium, strontium, radium, radon, and technetium. Several different options for treatment exist for each of these contaminants. Some methods are applicable to *in situ* treatment while others are more suitable for *ex situ* approaches. Treatment cleanup criteria are site specific and there is no absolute concentration that must be achieved; however, safe drinking water standards for radioactive isotopes have been established by the World Health Organization. As a guideline, the gross alpha and gross beta activities in drinking water should be below 0.1 and 1 Bq L⁻¹, respectively. The recommended limit for human exposure from drinking water is 0.1 mSv per year.

1. Introduction

The presence of radioactive contaminants in groundwater may be caused by natural contaminants or could come from human activities. The natural occurring radioactive materials found in groundwater are mainly uranium, radium, and radon. Most of the sources for groundwater contaminated with higher levels of radionuclides are from the production of nuclear weapons or nuclear power plants. The materials from these activities are uranium, plutonium, thorium, cesium, strontium, technetium, and tritium (see *Radioactivity in Land, Water and Atmosphere*). Tritium is normally present as tritiated water (HTO), and there is currently no practical method to remove tritiated water from groundwater. All of the other radionuclides have multiple treatment options.

Treatment of radioactive contaminants in groundwater falls into a few broad categories:

- Adsorption or ion exchange. In this technology, the (water-soluble) contaminants are captured by sorption onto a solid support. The solid support can be a natural or synthetic material.
- Reactive adsorption. This technology is based on the reaction of the contaminants with a reactive solid substrate. It is often applied *in situ* as a barrier wall that the contaminant is forced through but becomes trapped.
- Precipitation. This approach is mainly practiced above ground and most precipitation involves the addition of alkali to raise the pH and precipitate the oxide or hydroxide. Often, benign metal ions are added to cause co-precipitation to occur.
- Reverse osmosis. In reverse osmosis, clean water is transported with the help of a high-pressure gradient through a membrane that is essentially non-permeable to the contaminants.
- Stripping. The stripping of contaminants is a technology only applicable for volatile contaminants such as radon. Clean air (or other gas) is contacted with the contaminated water, stripping out the volatiles.

Possible treatment technologies are described in this text from a theoretical standpoint and then the specific treatment technologies for each of the most common radionuclides, both natural and man-made, are explored. An overview of treatment technologies and their applicability may be seen in Table 1. Suggested limits for the concentrations of radionuclides in drinking water can be found in *Guidelines for Drinking Water Quality – Radiological Aspects*, World Health Organization (WHO). The recommended limit is based on a sustained effective dose of 0.1 mSv per year from drinking 2 liters of water per day. The corresponding concentrations, both activity and mass based are listed in the text, and can be used as a performance goal for water treatment. For comparison, the global average human exposure from all natural sources of radiation is 2.4 mSv per year. Table 2 shows the recommended limits published by WHO. As a practical guideline, the WHO suggests that the activity should be below 0.1 Bq L⁻¹ of gross alpha and that it should be below 1 Bq L⁻¹ of gross beta.

Treatment Process	Radionuclide					
	Cs	Sr	U	Ra	Rn	Tc
Adsorption and Ion Exchange	X	X	X	X	X	X
Reactive Sorption			X			X

Precipitation		X	X	X		
Reverse Osmosis	X	X	X	X	X	X
(Air) Stripping					X	

Table1. Cross-reference table for treatment technologies and radionuclides

Radionuclide	WHO Recommended Limit (Bq L ⁻¹)
³ H	7800
¹⁴ C	250
⁶⁰ Co	20
⁸⁹ Sr	37
⁹⁰ Sr	5
¹²⁹ I	1
¹³¹ I	6
¹³⁴ Cs	7
¹³⁷ Cs	10
²¹⁰ Pb	0.1
²¹⁰ Po	0.2
²²⁴ Ra	2
²²⁶ Ra	1
²²⁸ Ra	1
²³² Th	0.1
²³⁸ U	4
²³⁴ U	4
²³⁹ Pu	0.3

Table2. Recommended limits of individual radionuclides in drinking water based on an annual consumption of 2 liters per day

2. Adsorption and Ion Exchange Processes

Most of the processes for removal of radionuclides from groundwater are based on sorption phenomena. In adsorption processes, the contaminant is adsorbed on the surface of a solid particle or within the pores of the particles. In ion exchange, the radionuclide replaces another ion on the surface of a solid particle or within the pores of the particle. The difference is subtle and sometimes people use the theory that was developed for adsorption processes to model ion exchange. Reactive sorption is discussed in Section 3.

The performance and selectivity of adsorbents in applications are difficult to predict. These are affected by a variety of environmental factors, the most important being the composition of the groundwater. Thus, feasibility testing is usually part of the design process. Laboratory experiments are initially conducted to determine the equilibrium curves for the potential sorbent candidates. In these experiments known sorbent quantities are contacted with the contaminated water under controlled conditions and the amount of contaminant removed from the water by the adsorbent is recorded as well as the final liquid concentration of the contaminants. The data are then plotted in a graph

of the type shown in Figure 1. The data usually fall along a curve called an isotherm. Dependent on the shape, curve fitting is sometimes performed according to a predefined equation. The most common shapes and equations with one or two constants (a and b) are shown in Eqs. (1) to (3).

$$Q = aC \quad (\text{Linear isotherm}) \quad (1)$$

$$Q = \frac{aC}{1 + bC} \quad (\text{Langmuir isotherm}) \quad (2)$$

$$Q = aC^b \quad (\text{Freundlich isotherm}) \quad (3)$$

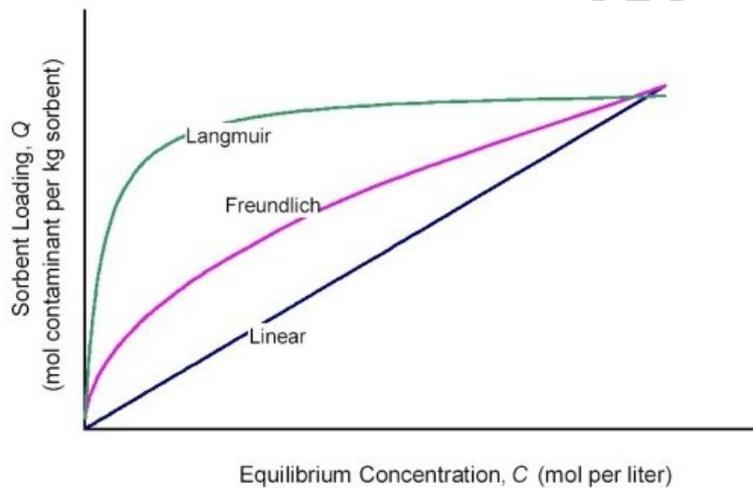


Figure1. Three typical isotherms- Linear, Langmuir, and Freundlich

The Langmuir and Freundlich isotherms are of the favorable type with a negative curvature and systems with favorable isotherms are especially suitable for water treatment processes; however, the systems with linear isotherms (no curvature) can also be suitable for water treatment processes. The terminology of adsorption isotherms was originally developed for adsorption of gases onto solids, but the terminology has carried over into the liquid-solid systems. Ion exchange equilibrium is fundamentally different than adsorption as the charged contaminant ion replaces a similarly charged ion within the sorbent. The same equations used in adsorption are often used to describe equilibrium data for ion exchange. From a theoretical standpoint, this is an incorrect approach but continues to be practiced.

The capacity of ion exchange materials is directly related to the available exchange sites. This theoretical capacity is often expressed in equivalents per unit volume or in equivalents per unit weight.

Both the adsorption and ion exchange processes use a bed of sorbent materials through which the contaminated water flows, and the radionuclide is selectively sorbed onto the material. The bed can be housed in a column above ground, a column below ground, or

can be part of a subsurface barrier that the water flows through. The water can be pumped through the columns with mechanical pumps or flow through the bed via natural hydraulic head. In either case, the concentration of the radionuclide within the bed gradually changes, according to more or less a sigmoidal curve. This concentration profile moves through the column, from the inlet to the outlet, with time.

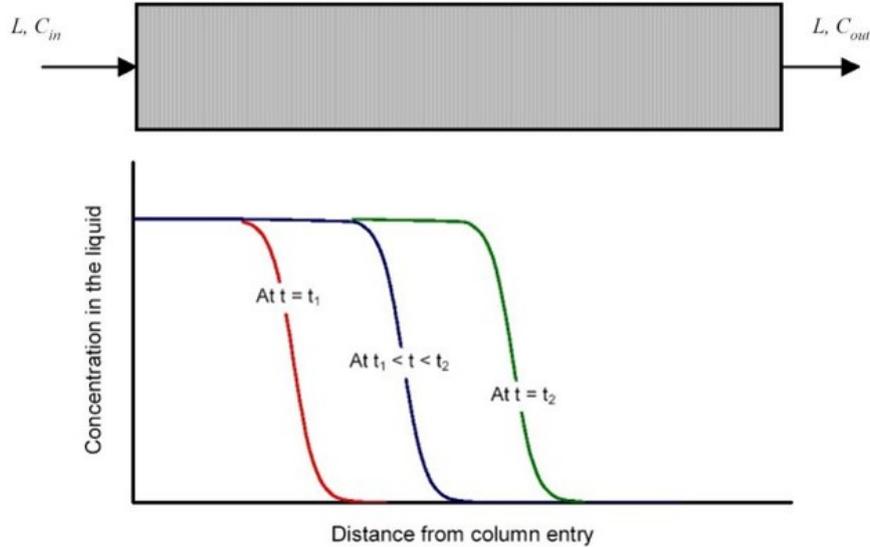


Figure2. Concentration profile of the contaminant in the column

A preliminary estimate of the capacity of a packed bed section in a column or horizontal underground barrier can be obtained from equilibrium loading capacity and the following expressions:

$$\text{Volume of groundwater that can be processed with } m \text{ kg sorbent} = \frac{m Q_{in}}{1000 C_{in}} \quad (4)$$

$$\begin{aligned} \text{Time to completely load a bed with } m \text{ kg sorbent at a flow of } L \text{ m}^3 \text{ s}^{-1} \\ = \frac{m Q_{in}}{1000 L C_{in}} \end{aligned} \quad (5)$$

The ratio of Q/C is often referred to as the equilibrium distribution coefficient, K_d . This simple approach of predicting the life expectancy of a sorption bed before replacement or regeneration is only true for an ideal system with a sharp breakthrough profile (Figure 3). The actual breakthrough is likely to be more gradual.

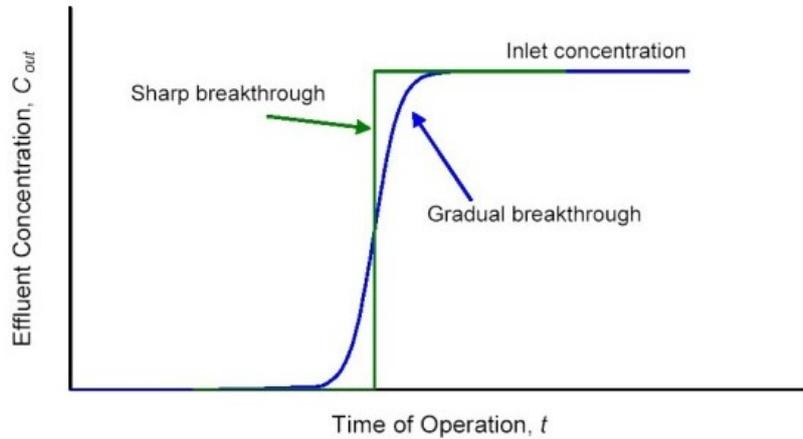


Figure 3. Breakthrough curve for adsorption and ion exchange bed operations
 To get information about the gradual breakthrough curve and to design a packed bed sorption system it is often advantageous to run preliminary experiments with a small test column and the contaminated groundwater. These experiments are usually performed at higher flow velocity than is anticipated in the full-scale implementation in order to accumulate data more quickly. The results for the small test columns can be used to predict the performance at other operating conditions, providing that we use normalized values in the comparisons. A typical breakthrough profile may look like the one presented in Figure 4 for the small test scale.

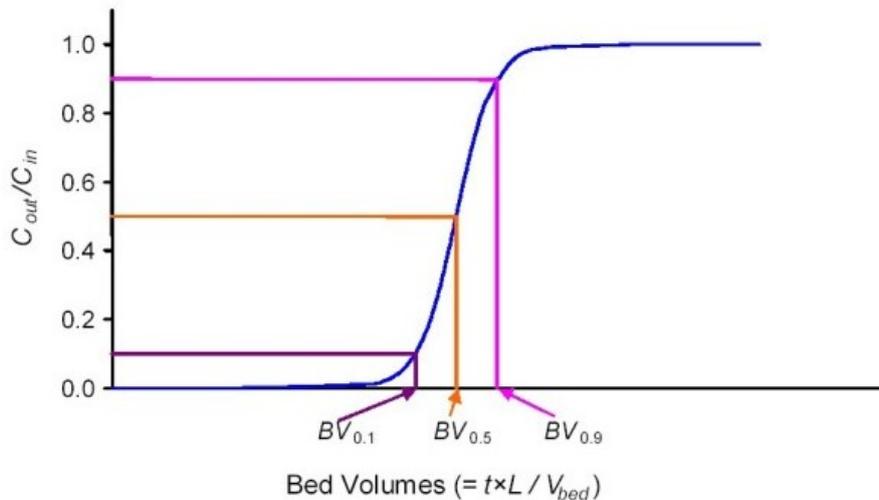


Figure 4. Breakthrough curve with normalized axis, here the points corresponding to 10, 50, and 90 percent breakthrough are highlighted

To reconstruct another breakthrough curve for a different bed size or for a different flow rate, we can use the following expressions providing that the inlet concentrations are the same for both cases.

$$BV_{0.5}|_{\text{case 1}} = BV_{0.5}|_{\text{case 2}} \quad (6)$$

and

$$\left. \frac{BV_X - BV_{0.5}}{L/A} \right|_{\text{case 1}} = \left. \frac{BV_X - BV_{0.5}}{L/A} \right|_{\text{case 2}} \quad (7)$$

if the sorption is solid phase mass transfer limited, or

$$\left. \frac{BV_X - BV_{0.5}}{(L/A)^{0.4}} \right|_{\text{case 1}} \approx \left. \frac{BV_X - BV_{0.5}}{(L/A)^{0.4}} \right|_{\text{case 2}} \quad (8)$$

if the sorption is fluid phase mass transfer limited. The pressure drop in packed beds may be estimated via a pressure drop equation,

$$\Delta p = 805 \frac{LZ \mu}{Ad_p^2} \quad (9)$$

for laminar flows and spherical particles.

A picture of a below surface treatment system for treatment of ^{90}Sr is shown in Figures 5 and 6. Here the groundwater is intercepted by a porous trench (French drain) and directed to flow through drums packed with zeolite.



Figure5: French drain to collect the groundwater is under the grass in the foreground. Drums of zeolite are located in the concrete vault. Treated water discharges to the creek in the background.



Figure 6: Drums of zeolite positioned in the underground vault. Flexible lines will connect the drums to the header pipe on the right and discharge pipe on the left.

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Biographical Sketches

Dr. Thomas Klasson is a Chemical Engineer and received his M.S. degree from the Royal Institute of Technology in Stockholm, Sweden in 1984 and his Ph.D. from University of Arkansas in 1988. Dr. Klasson joined Oak Ridge National Laboratory in 1992 as a Research and Development Engineer and was later the Group Leader of the Remediation Technology Group and the Biochemical Engineering Research Group. He left the Oak Ridge National Laboratory in 2004 and is currently working as a Research Leader with U.S. Department of Agriculture. As a staff member of Oak Ridge National Laboratory, Dr. Klasson has been the principal investigator for research and development activities for biological, chemical, and physical remediation of wastes contaminated with radionuclides, volatile organic compounds, polychlorinated biphenyls, and mercury. He has over 150 publications and presentations in the areas of waste treatment and conversion of wastes to fuels and chemicals. He is a member of the American Institute of Chemical Engineers and the American Chemical Society.

Paul Taylor received a B.S. degree in Chemical Engineering from Brigham Young University in 1974, and is currently a senior development engineer at Oak Ridge National Laboratory in Oak Ridge, Tennessee. He has 32 years experience in developing new waste treatment processes and in applying existing treatment technologies to new waste streams. Areas of interest include chemical and biological treatment of wastewater for removing metals, organics and radionuclides, and reducing the biotoxicity of effluents, with numerous publications and presentations in each of these areas. He is a registered professional engineer in the state of Tennessee, and is a member of the National Society of Professional Engineers, the American Institute of Chemical Engineers, and the Water Environment Federation.