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Polymeric Adsorbent for Radium Removal from Groundwater

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Abstract. Radium removal from groundwater by adsorption on polymeric adsorbent represents the latest application of adsorption process in water treatment. A three-month pilot study was carried out in the customer site to collect process performance data on Dowex RSC (radium selective complexer) for a large scale plant design. It was observed from the pilot test that the RSC resin has exceptionally high adsorption capacity for radium, no radium breakthrough from 38″ RSC bed during the entire pilot test; however the adsorbent mass transfer zone extended with the progress of pilot test. The increasing mass transfer zone was probably caused by the changing adsorbent properties. This interesting phenomenon presents a very tough challenge to both adsorption process design and simulation. Another very unique aspect of this process is that the adsorbent with the exceptionally high adsorption capacity may not be suitable for this process due to radiation safety concern and waste disposal limit.

Keywords: polymeric, adsorbent, radium, water treatment, complexation, MTZ

1. Introduction

Radionuclide contamination of drinking water is a significant, emerging issue. Because of their potential health effects and widespread occurrence, natural radionuclides—including radon, radium, and uranium—cause much concern. As listed in Table 1 the existing treatment technologies for removing radionuclides from the contaminated water include ion-exchange, reverse osmosis, lime softening, green sand filtration and preformed hydrous manganese oxides processes (Letterman, 1999; Melis, 1985). These processes are either complicated, expensive or have serious waste disposal issues. Many of the processes simply remove the radionuclides from the contaminated water, and create another liquid and/or solid wastes that are released right back into the community.

The new EPA regulation on safe drinking water (US EPA, 2000), which was effective on Dec. 8, 2003, requires all the drinking water has to met combined Ra226 and Ra228 to less than 5 pCi/L. This new regulation has spurred significant research efforts for developing better technology for radium removal from groundwater. A direct RSC (Radium Selective Complexer) radium removal process was commercialized at Layne Christensen Company, New Jersey, USA. The commercial plant was designed based on three-month pilot study results. The design basis and challenges for this process will be discussed in the following sections.

2. Radium Removal Adsorbents and Process Design

Radium selective complexer (RSC) resin is a polymeric adsorbent that was originally developed by DOW Chemicals Company for uranium containing waste water treatment in the mining industry. The basic matrix is Styrene-DVB gel. This adsorbent can selectively adsorb radium and other radionuclides from water through chemical complexation with BaSO4 on the polymer adsorbent support. The highest radium capacity on this adsorbent is 170 nCi/g at radium

*The Pilot Study Reported in This Paper was Carried Out in Layne Christensen Company, New Jersey, USA.

Table 1. Summary of radium removal technologies and waste disposal (Melis, 1985).

Treatment process	Ra removal efficiency (%)	Type(s) of waste	Radium loaded waste	Appropriate waste disposal
Na-cation exchange	95	Backwash & rinse brine	Brine	To sewer sanitary
Lime-soda softening	80–90	Lime sludge and backwash water	Lime sludge	Landfill of sludge
Reverse osmosis	95	Continuous brine wastewater	Continuously rejected wastewater	Rejected wastewater to sewer sanitary
Low pressure membrane filter	>93	Continuous brine wastewater	Continuously rejected wastewater	Rejected wastewater to sewer sanitary
Manganese greensand	50	Backwash water	Solid waste of used media	Solid waste to landfill
Manganese dioxide impregnated resin	90	No regeneration	Used resin	Used resin to specific landfill site
Acid-washed sand filter	80–90	Acid rinse wastewater	Rinse water	Wastewater to sewer sanitary
Radium Selective Complexer Resin	98	May need periodical backwashing	Used resin	Used resin to specific landfill site

Table 2. Physical properties of DOWEX RSC resin.

Physical form	Spheres
Total exchange capacity	0.65 meq/ml (min.)
Water retention capacity	65 – 75%
Packing density	49 lb/ft^3 or 780 g/l
True density	1.18 – 1.25 g/cc
Estimated radium capacity	10–20 nC$_i$/g for raw water contains less than 10 pCi/L of radium.
Particle size analysis	
On 16 mesh, max.	5%
Through 40 mesh, max.	8%
Through 50 mesh, max.	1%

concentration of 1621 pCi/L (Melis, 1985). The physical properties of Dowex RSC is given in Table 2. The estimated radium given by the vendor is only an educated guess from Melis's previous test results (Melis, 1985).

The RSC resin is effective at removing radium from water because the water soluble radium precipitates around barium sites on the RSC resin forming an insoluble complex. This is an irreversible chemical adsorption process. The adsorbed radium will decay and give out radon gas. Spent adsorbents need to be disposed as low radioactive solid wastes in specific sites. Several other radium removal adsorbents were investigated by a few research groups in USA (Clifford et al., 1988; Clifford and Zhang, 1994; Zhang and Clifford, 1994; Komarneni et al., 2001).

There have been several other pilot and or full scale tests using the RSC in mining operations, and for brine waste treatment associated with potable water production. Several tests were performed using Dowex RSC for radium removal in the past 20 years (Myers et al., 1985; Mangelson, 1988; Melis, 1985; Rozelle, 1983). Most notable is the study conducted in 1984 in the small community of Redhill Forest, Colorado (Myers et al., 1985). This study used the RSC resin to treat the radioactive brine produced from using an ion exchange softener to remove the radium from the water supply. The published data showed that the RSC system removed 99% of the radium from the brine wastewater. However, no detail adsorption equilibrium, kinetics and process data were reported in any of these tests. The lack of fundamental data makes it very challenging to design a large scale radium treatment plant even with comprehensive pilot study results.

The design for this type of adsorption filtration system should consider the following unique characteristics of this process: (1) Adsorbent has exceptionally high adsorption capacity; (2) There is no desorption step; (3) The mass transfer zone could be significant as compared with the adsorption equilibrium length. The key to the successful design of this type of adsorption filtration system is to quantify the adsorbent bed length requirement, and use of double-pass adsorbent bed configuration, as shown in Fig. 1. This configuration allows the first bed to be fully saturated while the second one partially saturated for the purpose of containing the mass transfer zone inside the second bed. So the first bed (adsorption equilibrium length) is basically determined by the adsorption time and the second bed by the mass transfer zone length. For radium removal the adsorbent bed can not be loaded to more than

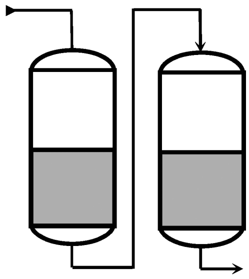

Figure 1. Double-pass bed configuration.

10 nCi/g due to radiation safety concern; so any adsorbents with capacity higher than 10 nCi/g has no use, instead it produces radiation hazard if the adsorbent loading exceeds the EPA limits. This creates a very interesting and peculiar situation for adsorbent selection that is in favor of adsorbents with radium capacity less than 10 nCi/g, but close to 10 nCi/g.

3. Pilot Plant Study

A pilot study of direct RSC process was carried out in a customer site (Well #28, Washington Township MUA, Gloucester County, New Jersey, USA) for over three months to collect sufficient performance for process design and to validate the design concept described above. The process flow diagram for the pilot test is shown in Fig. 2. The raw water was pumped from a well, followed with air stripping column to remove the dissolved gases including carbon dioxide and radon from the water; and to oxidize the dissolved iron ions. The settling tank was used to remove the resulting iron oxide after air stripping column. The clear water then to a buffer tank before fed into RSC column GWTS-1.

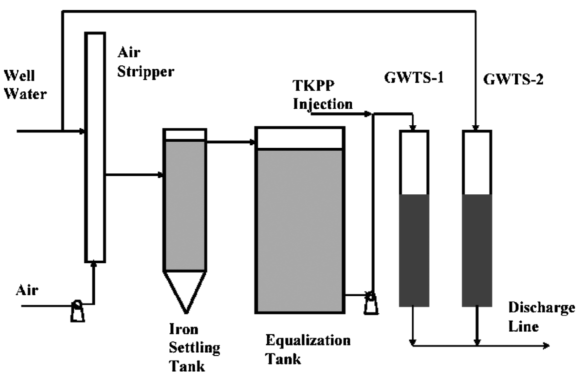

Figure 2. Flow diagram of direct RSC radium removal process.

The feed to RSC column GWTS-2 was raw well water.

The water quality data was obtained on both raw water and RSC treated water. The radium concentration in water was measured by EPA approved method (SM 7110B, SM 7500-Ra B, EPA 904.0, SM 7500-RN/EPA 913) in a certified analytical laboratory (Waste Stream Technology in Buffalo, New York, USA). Sometimes gross-alpha was measured in place of radium because it is much easier and faster to get gross-alpha data than radium data. The key objective of this pilot test was to measure the radium (gross-alpha) breakthrough curve and radium (gross-alpha) concentration profiles inside RSC bed. These data would allow us to determine the adsorption equilibrium capacity and mass transfer zone length under the experimental conditions. Theoretical speaking the radium breakthrough curve and radium concentration profile are symmetric S-Shape curves. The other objective of this pilot test is to elucidate the iron effect on RSC performance and to address the radiation safety issues associated with this project.

4. Results and Discussion

The radium adsorption breakthrough curves from two RSC columns and radium concentration profiles inside the first RSC column GWTS-1 were measured and plotted in Figs. 1 and 2 respectively. Due to the exceptionally high adsorption capacity on RSC adsorbent there was no radium breakthrough detected during the 3-month pilot test period as shown in Fig. 3. Although this result was expected from the estimated radium capacity provided by the vendor, it makes it very difficult to estimate the working capacity of the adsorbent under a given operation conditions.

In order to estimate the adsorption capacity of radium on RSC adsorbent, RSC adsorbent samples were taken from the RSC columns after the pilot study. Table 3 lists the analytical results of fresh and used RSC resins from this pilot test. The radium content was determined by measuring their daughter products Ac228 and Pb214 on the RSC adsorbents. It was found

Table 3. RSC resin analysis results.

RSC resin	Ac228 (μCi/kg)	Pb214 (μCi/kg)	Total radium (μCi/kg)
Fresh RSC resin	0.00183	0.000	0.00183
Top 1″ of GWTS-1	0.304	0.779	1.083
Top 1″ of GWTS-2	0.353	0.781	1.134

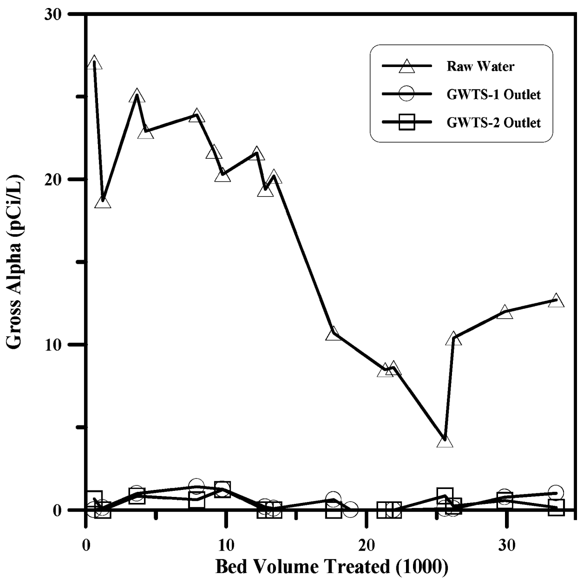

Figure 3. Radium (Gross-alpha) concentration in raw water and treated water streams.

that the top 1″ of the RSC has adsorbed more than 65% of the radium from the feed water. The radium loading on the top 1″ RSC reached about 1 nCi/g after treating well water with an average radium concentration of 10 pCi/L for about 3 months. Although the radium loading of 1 nCi/g is still way below the EPA waste disposal limit of 10 nCi/g and also lower than the estimated radium capacity provided by the vendor, it gave us the best indication about the RSC capacity consumption rate. We probably have to rely on the vendor data and EPA disposal limit (10 nCi/g) to size the lead RSC bed in Fig. 1. The estimated bed replacement time for one bed is about 5 years based on feed water of 10 pCi/L and RSC capacity of 10 nCi/g if the commercial plant is strictly scaled up from the pilot test column size.

If the lead RSC bed in the double-pass configuration is fully saturated, will the second bed have a radium breakthrough? This question can only be answered by the mass transfer zone length calculation. The radium concentration profiles inside the RSC columns were measured during the pilot test by analyzing water samples from different locations of RSC columns. As shown in Fig. 4, majority of radium were removed by the first 4″ of RSC, radium was detected in all locations except the exit, which suggests a very broad mass transfer zone. It can be found from Fig. 4 that the mass transfer zone did expand with the progress of pilot test. This is a very complicate issue; the most likely cause for this mass transfer zone expansion is the changing adsorbent properties by other ions including iron, sulfate concentration and pH changes. It was observed in the pilot test the barium loading in RSC decreased significantly after the 3-month pilot test, this could have caused the mass transfer zone expansion.

5. Conclusions and Recommendations for Future Work

Dowex RSC polymeric resin is an effective adsorbent for radium removal from well water; it has high

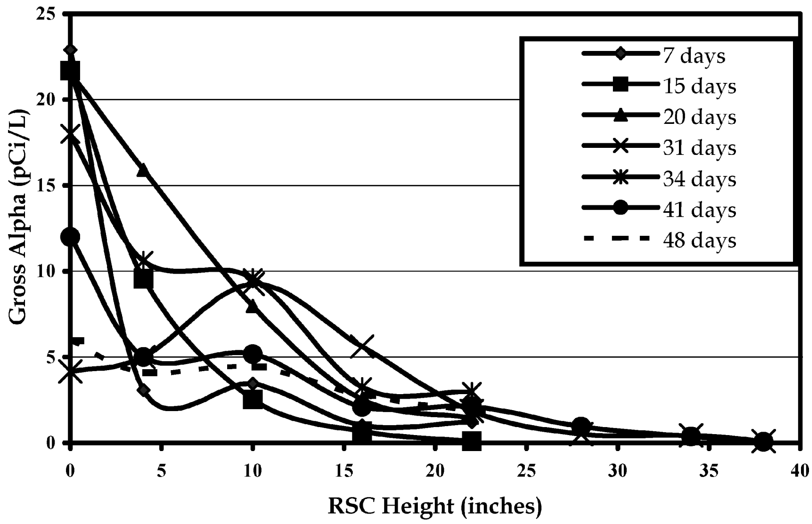

Figure 4. Radium (gross-alpha) concentration profiles inside the RSC bed (GWTS-1) during the pilot test.

capacity for radium. However the lack of fundamental adsorption equilibrium and kinetics data makes it very challenging to design the direct RSC process for radium treatment. The expanding mass transfer zone is an alarm signal of early radium breakthrough even if the adsorbent has sufficient adsorption capacity, the extended mass transfer zone could create instant radium breakthrough.

There is an urgent need in the water treatment industry to develop novel adsorbent materials for radium removal. This new adsorbent should have about 10 nCi/g of radium adsorption capacity that is specified by the current EPA waste disposal limit, and the adsorbent is less susceptible to other ions in the water. There is also a need for an accelerated evaluation of adsorbent with exceptionally high capacity and very long breakthrough time. Adsorption process simulation could help but needs more fundamental data of adsorption equilibrium and kinetics at very low concentrations of adsorbate molecules.

References

Clifford, D., W. Vijjeswarapu, and S. Subramonian, "Evaluating Various Adsorbents and Membranes for Removing Radium from Groundwater," *Journal of the American Water Works Association*, **80**(7), 94 (1988).

Clifford, D. and Z. Zhang, "Modifying Ion Exchanging for Combined Removal of Uranium and Radium," *Journal of the American Water Works Association*, **86**(4), 214–227 (1994).

Cole, L. and J. Cirrinclone, Radium Removal from Groundwater by Ion Exchange Resin, Technical Paper, Water Quality Association, Lisle, 1987.

Hahn, N.A. Jr., "Disposal of Radium Removed from Drinking Water," *Journal of the American Water Works Association*, **80**(7), 71–78 (1987).

Komarneni, S., N. Kozai, and W. Paulus, "Superselective Clay for Radium Uptake", *Nature*, **410**, 771–771 (2001).

Letterman, R.D. "Water Quality and Treatment," *A Handbook of Community Water Supplies*, 5th edn., American Water Works Association, New York, 1999.

Mangelson, K.A., Radium Removal for a Small Community Water Supply System, *EPA Project Summary* EPA/600/S2-88/039 (Sept., 1988).

Mangelson, K.A. and R.P. Lauch, "Removing and Disposing Radium from Well Water," *Journal of the American Water Works Association*, **82**(6), 72–76 (1990).

Melis, L.A., "Radium Removal from Canadian Uranium Mining Effluent by a Radium-Selective Ion Exchange Complexer," *Metallurgical Society of CIM Bulletin*, **78**(883), 82–90 (1985).

Myers, A.G., V.L. Snoeyink, and D.W. Snyder, "Removing Barium and Radium Through Calcium Cation Exchange," *Journal of the American Water Works Association*, **77**(5), 60–66 (1985).

Rozelle, R.E., "A New Potable Water Radium/Radon Removal System," *in Presented in 44th International Water Conference Annual Meeting*, Pittsburgh, PA, Oct. 1983.

Snoeyink, V.L., C. Cairns-Chambers, and J.L. Pfeffer, "Strong-Acid Ion Exchange for Removing Barium, Radium and Hardness," *Journal of the American Water Works Association*, **79**(8), 66–72 (1987).

Surbramonian, S., D. Clifford, and W. Vijjeswarapu, "Evaluating Ion Exchange for Removing Radium from Groundwater" *Journal of the American Water Works Association*, 82(5), 61–70 (1990).

United States Environmental Protection Agency, "National Primary Drinking Water Regulations, Radionuclides, Final Rules," *Federal Register*, **65**, (236), P. 76708–76753 (2000).

United States Environmental Protection Agency, Technical Fact Sheet: Final Rule for (Non-Radon) Radionuclides in Drinking Water, EPA 815-F-00-013 (2000).

United States Environmental Protection Agency, Office of Groundwater and Dinking Water and Office of Indoor Air and Radiation, United States Geological Survey, Radionuclides: Notice of Data Availability—Technical Support Document, (2000).

Zhang, Z. and D. Clifford, "Exhausting and Regenerating Resin for Uranium Removal," *Journal of the American Water Works Association*, **86**(4), 228–241 (1994).