

Ion Exchange Technology in the Remediation of Uranium
Contaminated Groundwater at Fernald

By

Chris Sutton, Cathy Glassmeyer, and Steve Bozich

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Fluor Fernald, Inc.
Fernald Environmental Management Project
P.O. Box 538704
Cincinnati, OH 45253-8704

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ION EXCHANGE TECHNOLOGY IN THE REMEDIATION OF URANIUM CONTAMINATED GROUNDWATER AT FERNALD

Chris Sutton, Fluor Fernald, Inc.; Cathy Glassmeyer, Fluor Fernald, Inc.; Steve Bozich
Fluor Fernald, Inc.: P.O. Box 538704, Cincinnati, OH 45238-8704

Abstract

Using pump and treat methodology, uranium contaminated groundwater is being removed from the Great Miami Aquifer at the Fernald Environmental Management Project (FEMP) per the FEMP Record of Decision (ROD) that defines groundwater cleanup. Standard extraction wells pump about 3900 gallons-per-minute (gpm) from the aquifer through five ion exchange treatment systems. The largest treatment system is the Advanced Wastewater Treatment (AWWT) Expansion System with a capacity of 1800 gpm, which consists of three trains of two vessels. The trains operate in parallel treating 600 gpm each. The two vessels in each train operate in series, one in lead and one in lag. Treated groundwater is either reinjected back into the aquifer to speed up the aquifer cleanup process or discharged to the Great Miami River. The uranium regulatory ROD limit for discharge to the river is 20 parts per billion (ppb), and the FEMP uranium administrative action level for reinjection is 10 ppb.

Spent (i.e., a resin that no longer adsorbs uranium) ion exchange resins must either be replaced or regenerated. The regeneration of spent ion exchange resins is considerably more cost-effective than their replacement. Therefore, a project was undertaken to learn how best to regenerate the resins in the groundwater vessels. At the outset of this project, considerable uncertainty existed as to whether a spent resin could be regenerated successfully enough so that it performed as well as new resin relative to achieving very low uranium concentrations in the effluent. A second major uncertainty was whether the operational lifetime of a regenerated resin would be similar to that of a new resin with respect to uranium loading capacity and effluent concentration behavior. The project was successful in that a method for regenerating resins has been developed that is operationally efficient, that results in regenerated resins yielding uranium concentrations much lower than regulatory limits, and that results in regenerated resins with operational lifetimes comparable to new resins.

Introduction

Using pump and treat methodology, uranium contaminated groundwater is being removed from the Great Miami Aquifer at DOE's Fernald, Ohio (FEMP, Fernald Environmental Management Project) site near Cincinnati per the FEMP Record of Decision that defines groundwater cleanup requirements. Standard extraction wells pump about 3900 gallons-per-minute (gpm) from the aquifer through five treatment systems. All of the treatment systems use Dowex 21K, 16 to 30 mesh, ion exchange resin for uranium removal. Dowex 21K is a macroporous, Type I, strongly basic, anion exchange resin in the chloride form. Anionic ion exchange resins are necessary because dissolved uranium in FEMP groundwaters exists as a negatively charged uranyl carbonate.

The largest FEMP treatment system is the Advanced Wastewater Treatment (AWWT) Expansion System with a capacity of 1800 gpm. The AWWT Expansion System consists of an aeration tank for iron oxidation, multimedia filtration to remove oxidized iron and other particles, followed by ion exchange for uranium removal. The AWWT expansion ion exchange system itself consists of three trains of two vessels. The trains operate in parallel treating 600 gpm each. The two vessels in each train operate in series, one in lead and one in lag. Treated groundwater is either reinjected back into the aquifer to speed up the aquifer cleanup process or discharged to the Great Miami River. The uranium regulatory limit for discharge to the river is 20 parts per billion (ppb), and the administrative action level for reinjection is 10 ppb.

Each groundwater ion exchange vessel contains about 314 cubic feet of ion exchange resin. In the interest of minimizing waste and costs it is desirable to regenerate the resin rather than dispose of it when it is exhausted.

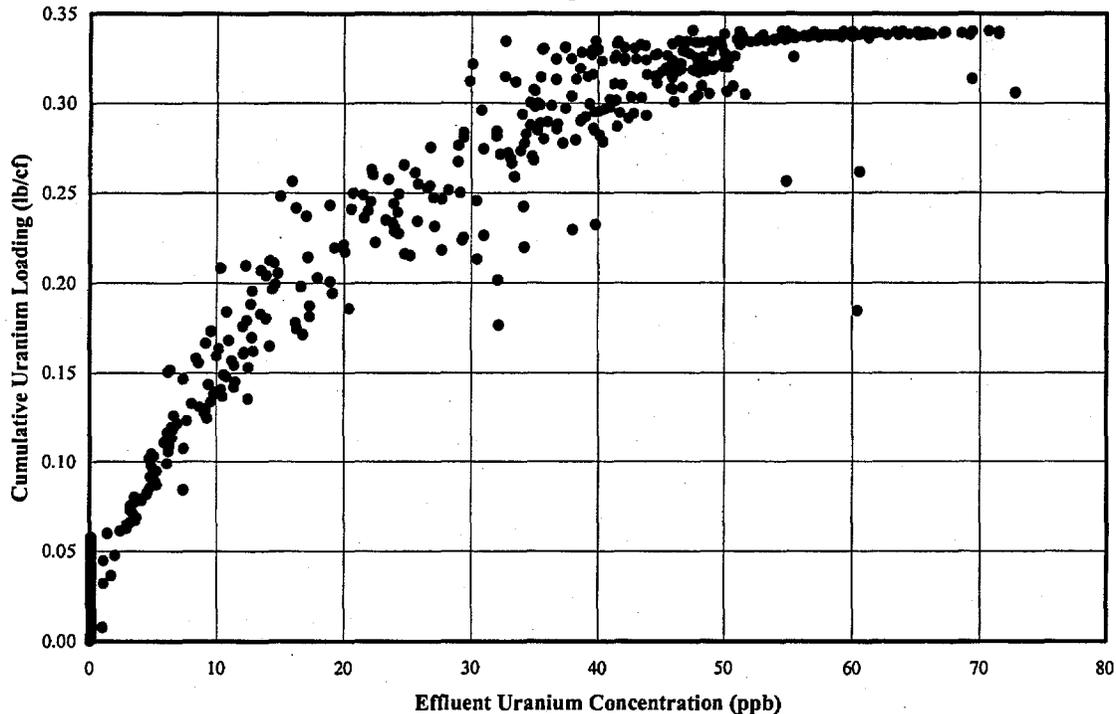
Ion Exchange Resin Behavior at Fernald

The ultimate drivers for the frequency of regeneration of groundwater ion exchange resins at Fernald are the FEMP administrative action level of 10 ppb and the regulatory ROD limit of 20 ppb uranium for reinjection and discharge waters, respectively. As an ion exchange resin becomes increasingly loaded with uranium, the concentration of uranium in the effluent from the vessel containing that resin also increases. When the resin is "spent" and can no longer adsorb uranium, the concentration of uranium in the effluent equals the concentration of uranium in the influent. Figure 1 shows a typical trend of resin loading in relation to effluent uranium concentration for a groundwater vessel in lead position. At the FEMP influent and effluent uranium concentrations for each vessel are monitored on a daily basis. Uranium in the influent groundwater averaged 50 to 60 ppb for the groundwater vessel in Figure 1. When the effluent from the groundwater ion exchange vessel in Figure 1 also reached 50 to 60 ppb, the resin had loaded 0.34 pounds of uranium per cubic foot (lb/cf) of resin, or about 105 lb of uranium per vessel. At a loading of 0.34 lb/cf, the resin in this vessel was spent per the definition above. However, effluent from the vessel reaches 20 ppb (20 ppb corresponds to approximately 0.23 lb/cf, or about 72 lb of uranium per vessel.) well before the loading limit of 0.34 lb/cf is reached. The practice at the FEMP is to switch a vessel from lag to lead position as its effluent approaches 20 ppb and to regenerate a lead vessel as its effluent approaches 50 ppb.

The Problem

Prior to August 1999, the FEMP had no experience with respect to regenerating resin in the groundwater ion exchange vessels. Therefore, considerable uncertainty existed as to whether a spent resin could be regenerated successfully enough so that it performed as well as new resin with respect to achieving very low uranium concentrations in the effluent. Another uncertainty was whether the operational lifetime of a regenerated resin would be similar to that of new resin with respect to uranium loading capacity. Although some information concerning uranium loading and regeneration practices was available from the uranium mining industry, its applicability to Fernald was uncertain because of the very low concentrations of uranium in discharge waters that must be met to comply with regulatory requirements.

Figure 1
Uranium Loading of Ion Exchange Resin of Groundwater Vessel in Lead Position
Prior to Regeneration



Approach

A two-phase approach was undertaken with respect to ion exchange regeneration at the FEMP. One phase involved an extensive series of laboratory studies to optimize regeneration parameters, such as the chemical composition of the regeneration solution, the amount of regeneration solution, and the length of contact time between the regeneration solution and the resin. The second phase involved actual regeneration attempts in the AWWT. Each such regeneration attempt was thoroughly documented so that lessons learned and experience gained from one regeneration could be successfully applied in subsequent regenerations. Starting points in the field trials were based upon common industrial ion exchange practices.

Ion Exchange Resin Regeneration Process

Using the approach outlined above, the following steps constitute the way in which groundwater vessels are now regenerated at the FEMP.

- Prior to regeneration, the resin bed is backwashed with city water until the backwash is clear. At a backwash flow rate of 350 gpm, this takes approximately 13-14 bed volumes of water over a 90 minute period.
- The vessel is then drained to avoid diluting the first bed volume of saturated sodium chloride solution (brine), which is used as the eluant in the FEMP process.
- One bed volume of brine is added to the tank. The brine solution is pumped into the vessel through a regeneration header that is just above the surface of the resin.

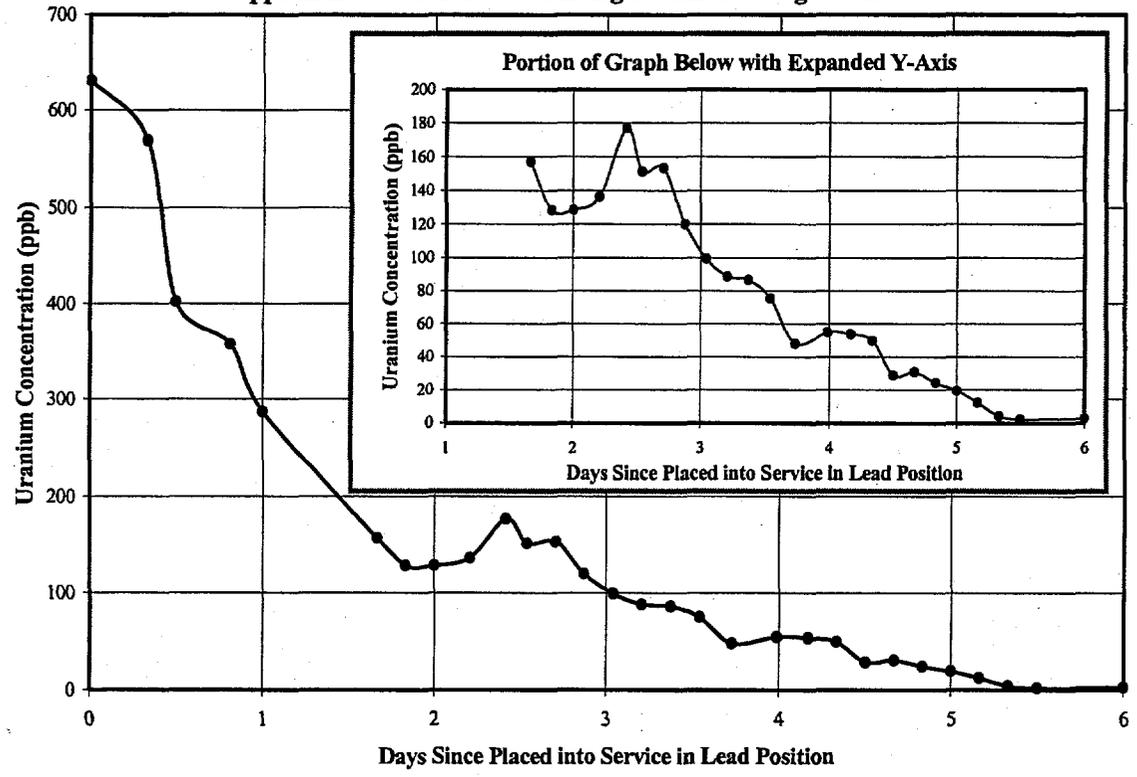
- An air hose is connected to the bottom of the tank and air is bubbled upward through the tank to promote mixing of brine and resin and to enhance contact time between the brine and the resin. The brine is allowed to remain in the tank overnight to allow additional contact time.
- Five additional bed volumes of brine are eluted through the resin at a flow rate of about 15 minutes per bed volume. A total of six bed volumes of brine are used. The brine solution exits the vessel via a process outlet line to a brine eluate storage tank. The sixth bed volume also is allowed to sit overnight to promote brine contact with resin. Laboratory studies and field trials demonstrated that six bed volumes of brine are sufficient to remove >98% of the uranium on the resin, and that four to six additional bed volumes of brine only remove an additional few tenths of a percent uranium.
- Eluate samples are collected for analysis of uranium and chloride ion periodically throughout the elution. If the sample representing the first bed volume contains on the order of 2000 or more ppm uranium in the eluate, experience has shown that the regeneration will be successful. The chloride concentration is useful as a tracer of both brine quality and certain hardware problems, such as leaking valves.
- The resin is next slow-rinsed with 10 bed volumes of city water at a rate of one bed volume every fifteen minutes. Samples are again collected for analysis of uranium and chloride ion. At the end of slow rinse, the concentration of uranium in the rinsate should be in the low ppm or high ppb range, and chloride ion should be less than 1000 ppm.
- The vessel is then fast-rinsed with five bed volumes of water at a rate of one bed volume every five minutes to settle the resin bed. One sample is collected of the fifth bed volume of fast rinse for analysis of total uranium and chloride ion concentrations.
- Following fast rinse the vessel is placed into service in lead position and groundwater is pumped through it at normal rates (approximately 500-600 gpm). Samples of the lead vessel effluent are collected every four hours for three to six days and analyzed for total uranium. When the concentration of uranium falls below 5 ppb for several consecutive samples, the performance of the vessel is judged to be good enough to greatly exceed the regulatory criteria for discharge or reinjection specified in the introduction, and the vessel is switched to lag position. Figure 2 shows an effluent uranium concentration profile for a newly regenerated vessel in lead position. The FEMP has found that it may take as long as five to six days in lead position before the effluent uranium remains consistently below 5 ppb for an extended period of time.

The brine eluate and slow rinse solutions must be treated to remove uranium before the solutions can be discharged. Uranium removal is by precipitation with lime, followed by filtration. Because there is limited storage capacity for brine/rinse solutions, practical considerations mandate a need to balance regeneration completeness with the volume of produced brine eluate and slow rinse water. In this regard laboratory studies showed that concentrated sodium chloride brine to be the most effective regenerant in the FEMP AWWT system relative to effecting complete regeneration with the least amount of brine. Laboratory studies and successful field trials indicated that only ten bed volumes of slow rinse water are required.

One operation was extremely helpful in the first two regeneration attempts of groundwater vessels in that it provided a measure of quality control relative to ascertaining the amount of uranium actually removed from the resin. A grain thief coring device was used to take resin core samples at six inch intervals throughout the resin bed, both before and after elution of the resin

with brine. The resin core samples were analyzed for total uranium, and the difference between pre- and post regeneration uranium concentrations provided a direct measure of the percentage of uranium removed by the brine. For the first two regenerations the results of uranium analyses of pre- and post regeneration core samples indicated that >98% of the uranium was removed during the regeneration. After the second regeneration the coring operation was discontinued in order to speed up the overall regeneration process. A second operation has proved less successful in providing reliable data that can be used to ascertain the amount of uranium actually removed from resin during regeneration. Knowing the uranium concentrations in brine samples taken during elution, and knowing the volume of brine represented by those samples, mass balance calculations were carried out. Results for the regeneration of the six groundwater vessels showed that the calculated masses of uranium in the eluate were 72, 72, 83, 102, 105, and 112% of the masses of uranium estimated to be loaded on the six resins, respectively. The large variability in the results of the mass balance calculations suggests that this method of calculation be used more for general guidance than for driving specific decisions pertaining to the success or failure of a regeneration. Instead, as noted above, experience has shown that a good measure of success is whether or not the first bed volume of eluate has a uranium concentration greater than 2000 ppm.

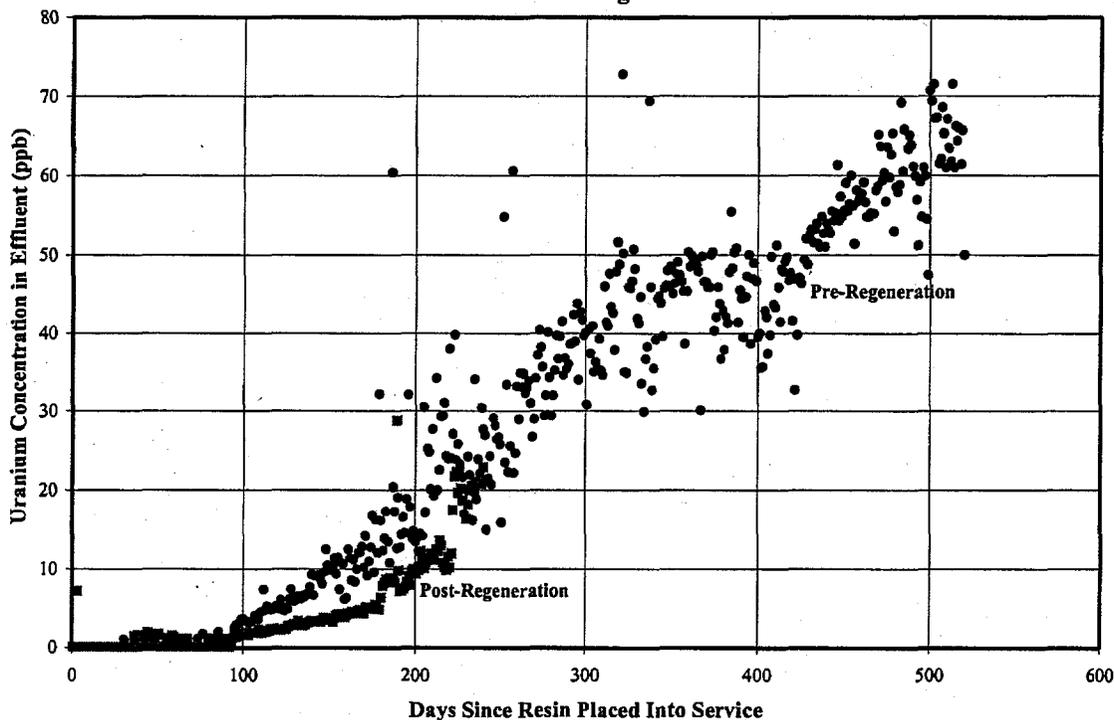
Figure 2
Effluent Uranium Concentration in Newly Regenerated Resin Must Reach <5.0
ppb in Lead Position Before Being Switched to Lag Position



From July, 1999 through August, 2000 all six groundwater ion exchange vessels were successfully regenerated at the FEMP. Success is defined as achieving very low ppb concentrations of uranium in the vessel effluent when a regenerated vessel is put into operation

in lag position. Operational behavior for vessels successfully regenerated shows that in the first 100 days of operation following regeneration, a large majority of the daily uranium analyses indicate uranium concentrations in the effluent of 2.0 ppb or less. A trend of increasing uranium concentration is observed after 100 days. However, even after 180 days, effluent concentrations generally have not reached 5.0 ppb. In this regard, regenerated resins behave similarly to new resin. Figures 3 and 4 compare the performance of resin in a groundwater vessel before and after regeneration. In figure 3, for the first 240 days of service after regeneration, the regenerated resin appears to have had a consistently lower effluent uranium concentration than the resin

Figure 3
Comparison of Effluent Uranium Concentrations For a Groundwater Vessel
Before and After Regeneration



(which was new) before regeneration. Similarly, in figure 4 the regenerated resin appears to be loading uranium at a slower rate than did the resin before its regeneration. However, caution must be taken in interpreting Figures 3 and 4, because the new resin, in lead position before regeneration, was exposed to influent water with higher uranium concentrations, than was the regenerated resin in lag position. Nonetheless, Figures 3 and 4 suggest that the performance of regenerated resins is comparable to that of new resins.

Operations Strategy

The success of the FEMP in regenerating ion exchange resins used for groundwater uranium removal has allowed a regular groundwater vessel regeneration schedule to be put into place. Each vessel is planned to be regenerated once per year with those regenerations staged throughout the year. This frequency of regeneration is sufficient to ensure that a daily composite of the three vessels in lag position does not exceed 10 ppb, that the effluent from individual

vessels does not exceed 20 ppb uranium concentration, and that vessels in lead position do not become spent. The staging of regenerations ensures a relatively constant, and low, uranium concentration in reinjection and discharge waters. Uranium influent and effluent concentrations for each groundwater ion exchange vessel continue to be monitored on a daily basis.

Figure 4
Comparison of Pre- and Post-Regeneration Loading Rate Curves for a Groundwater Vessel

