Water Treatment for Uranium at the U.S. Department of Energy's Legacy Management Sites – 9438

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ABSTRACT

The U.S. Department of Energy's Legacy Management (LM) Program is responsible for 82 sites as of September 30, 2008, more than 30 of which contain uranium contamination in the ground water. The compliance strategy for some of the uranium-contaminated ground-water systems is monitored natural attenuation (MNA); however, five sites have active ground-water remediation systems for uranium. Active remediation methods, goals, and scales vary widely among sites. This paper discusses and contrasts methods used to treat ground water contaminated with uranium at LM sites.

At a former uranium milling site in Monticello, Utah, uranium-contaminated ground water is pumped through two reaction vessels containing a total of 7.6 cubic meters (m^3) of a mixture of gravel and zero-valent iron (ZVI). The flow rate is typically about 38 liters per minute (lpm), and the influent uranium concentration is about 300 micrograms per liter (µg/L). About 5.9 kilograms (kg) of uranium is removed from the aquifer per year. The system is monitored by a telemetry system and requires minimal maintenance; however, the reactive media requires replacement every 1 to 2 years. Some treated ground water is discharged back to the aquifer to enhance MNA, and some is discharged to a nearby creek.

At the Rocky Flats Site near Denver, Colorado, contaminated ground water is collected in subsurface drains and pumped through a reaction vessel containing 136 m^3 of a mixture of sawdust and ZVI, followed by a second reactor containing 40 m^3 of a mixture of gravel and ZVI. Microbial activity in the sawdust/ZVI reactor removes nitrate and some uranium, and the ZVI/gravel reactor removes the remainder of the uranium. The flow rate is typically about 1.9 lpm. The typical influent uranium concentration is about 40 µg/L, and the effluent concentration is less than 5 µg/L. Treated water is discharged to an infiltration gallery that feeds to a nearby creek. The system is removing approximately 0.05 kg of uranium per year from the aquifer. The system requires minimal operation and maintenance; however, the reactive media requires occasional replacement.

At a former uranium milling site in Shiprock, New Mexico, uranium-contaminated ground water is captured by pumping wells and subsurface collection drains. The captured water is conveyed to an 11-acre evaporation pond. The total flow rate of contaminated ground water to the evaporation pond is about 190 lpm. Influent uranium concentration is about 800 µg/L, and about 80 kg of uranium is removed from the subsurface annually. Because of the evaporation process, the ground-water resource is lost. Operation of the system is limited to occasional pump maintenance.

A pump-and-treat system is used at the Fernald Preserve in Ohio to lower uranium concentrations to less than 30 µg/L prior to discharge to the Great Miami River. The treatment system uses six flow-through vessels, each containing 8.9 m^3 of anion-exchange resin. The treatment flow rate is currently about 5,678 lpm, and the system is removing about 54 kg of uranium per year. Some ground water is blended with treated water such that about 300 kg of uranium is removed from the aquifer per year. The treatment process requires continuous operation and maintenance.

At a former uranium milling site near Tuba City, Arizona, uranium-contaminated ground water is pumped from extraction wells and treated by ion exchange followed by distillation. The average flow rate is about 340 lpm, and the influent uranium concentration is about 250 µg/L. About 40 kg of uranium is removed from the aquifer per year. The distillation treatment process is operated full time, with the treated water being injected back into the aquifer.

INTRODUCTION

The U.S. Department of Energy's Legacy Management (LM) Program is responsible for the surveillance and maintenance of 82 sites as of September 30, 2008, more than 30 of which contain uranium contamination in the ground water. The compliance strategy for some of the uranium-contaminated ground-water systems is monitored natural attenuation (MNA); however, five sites have active ground-water remediation systems for uranium. All five sites use pump-and-treat remediation, but methods, goals, and scales vary widely. This paper discusses and contrasts methods used to remediate uranium in ground water at the five LM sites.

LM sites utilizing pump-and-treat remediation for ground-water uranium contamination are (ordered in increasing complexity of their treatment systems) Monticello, Utah; Rocky Flats, Colorado; Shiprock, New Mexico; Fernald, Ohio; and Tuba City, Arizona (Fig. 1). A number of factors were considered in the designs of the ground-water remediation systems: desired cleanup timeframe, constituents (in addition to uranium) that require removal, radioactive disposal options, reactive media costs, and operation and maintenance costs. Physicochemical uranium-removal methods include reductive precipitation (Monticello, Rocky Flats), evaporation (Shiprock), ion exchange (Fernald), and distillation (Tuba City). At Monticello and Fernald, uranium is the primary target constituent. In contrast, nitrate is the primary target constituent at Rocky Flats, and sulfate, nitrate, and uranium are primary target constituents at Shiprock and Tuba City.

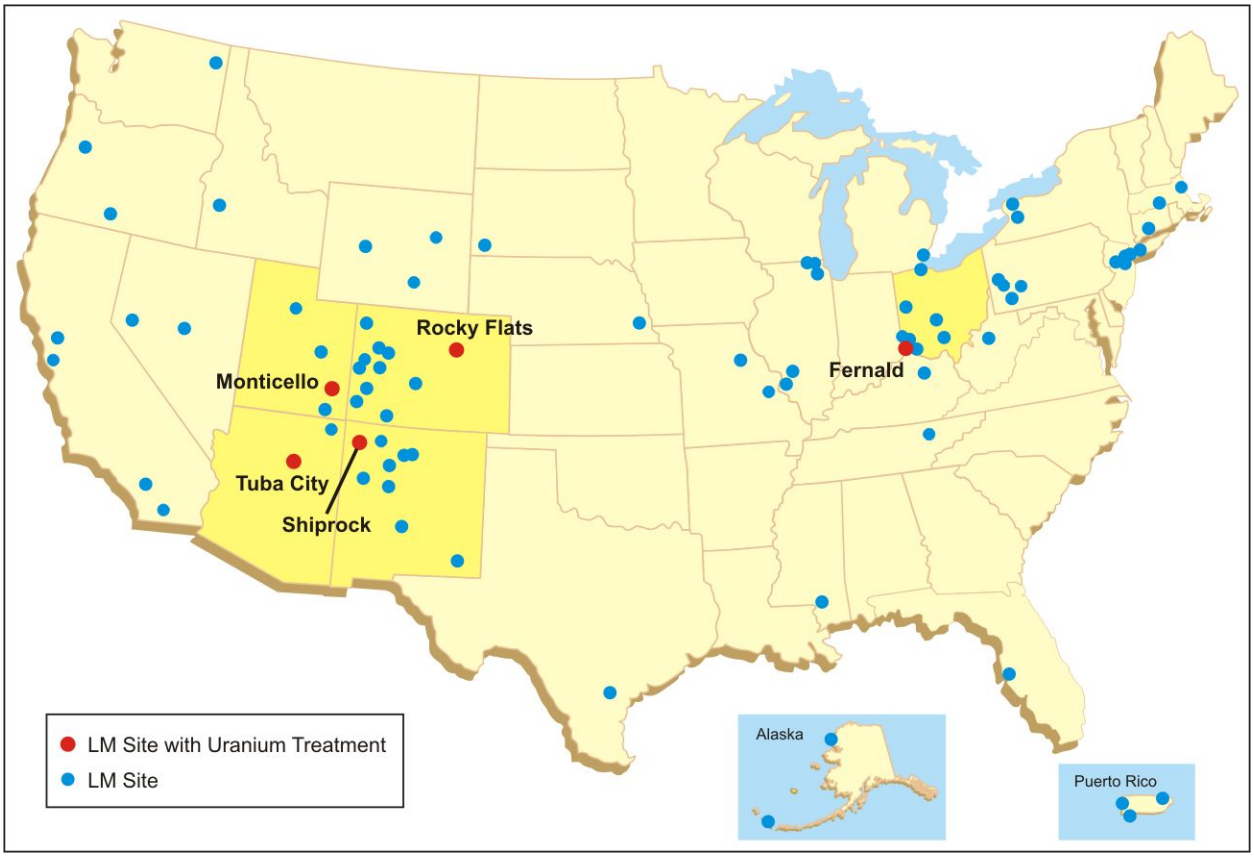

Fig. 1. Locations of the Five LM Sites with Uranium Treatment Systems.

Discussions of the treatment systems follow. Although cleanup goals vary, an effort was made to compare the efficiencies of the five systems by normalizing to the mass removal of uranium. Other considerations were important in selecting the treatment methods. For example, at some sites, contaminants other than uranium required treatment.

DISCUSSIONS OF URANIUM TREATMENT SYSTEMS AT LM SITES

The sites are discussed in order of increasing complexity of the treatment systems. For each site, the physical treatment system, physical-chemical removal mechanism, treatment efficiency, and advantages and disadvantages are discussed. Table I summarizes properties of the five treatment systems.

Table I. Properties of Systems Used to Treat Uranium at Five LM Sites

	Monticello	Rocky Flats	Shiprock	Fernald	Tuba City
System Type	Pump-and-Treat	Pump-and-Treat	Pump-and-Treat	Pump-and-Treat	Pump-and-Treat
Treatment Media (method)	Zero-Valent Iron	Zero-Valent Iron	Evaporation Pond	Dowex 21K	Distillation and Ion Exchange
Reaction Mechanism	Chemical Reduction	Chemical Reduction	Evaporation	Ion Exchange	Distillation and Ion Exchange
Average Flow Rate (lpm)	38	1.9	190	5678	340
Influent Uranium Concentration (µg/L)	300–400	40	500–1,000	50–60	250
Uranium Mass Removal (kg/yr)[a]	6	0.05	80	54	40
Reactive Media Volume (m^3)	7	180	None	54	10
Other Major Contaminants	Selenium	Nitrate	Sulfate, Nitrate	None	Sulfate, Nitrate
Fate of Treated Water	Injection[b] Discharge[c]	Injection[b]	Loss to Atmosphere	Discharge[c]	Injection[b]
Capital Cost	Low	Medium	Medium	High	High
Operation and Maintenance Cost	Low	Low	Low	High	High

[a]Mass removed by the treatment process.
[b]Injection back into aquifer.
[c]Discharge to stream or river.

Monticello

Ground water at the Monticello Site is contaminated with uranium from ore processing in the 1950s. A treatment system was installed in 2005 to supplement a subsurface permeable reactive barrier. The treatment system is nearly passive, requiring only occasional (approximately quarterly) minor maintenance of the extraction pump and treatment cells. Media change-out is required approximately every 1 to 2 years. The two treatment cells and a single extraction well are constructed in an agricultural field used for alfalfa production. A portion of the treated water is discharged to an infiltration gallery, and a portion is discharged to a nearby creek. The system is remotely monitored by LM personnel through a Web-based telemetry system. Telemetry data include flow rates and influent pipe pressure for each cell and water depths in the extraction well, the infiltration gallery, and each treatment cell. Data are automatically downloaded and graphed daily. If water levels rise too high in the treatment cells, the system shuts down automatically to avoid overflow.

Each of the two treatment cells is built from a cylindrical concrete culvert that is 1.8 meter (m) in diameter and 1.5 m high (Fig. 2). The cells contain a mixture of pea gravel that is 1 centimeter in diameter and zero-valent iron (ZVI). The ZVI is a granular, cast-iron (-8 +20 mesh) product generated by the automotive industry. We assume for the purpose of this paper that chemical reduction caused by the corrosion of ZVI results in uranium precipitation as a reduced uranium mineral such as uraninite (UO_2) (S.J. Morrison et al., 2002). The solid-phase uraninite remains in the treatment cell, and effluent

concentrations of dissolved uranium are less than the treatment goal of 44 micrograms per liter (µg/L). Influent uranium concentrations average about 300 to 400 µg/L.

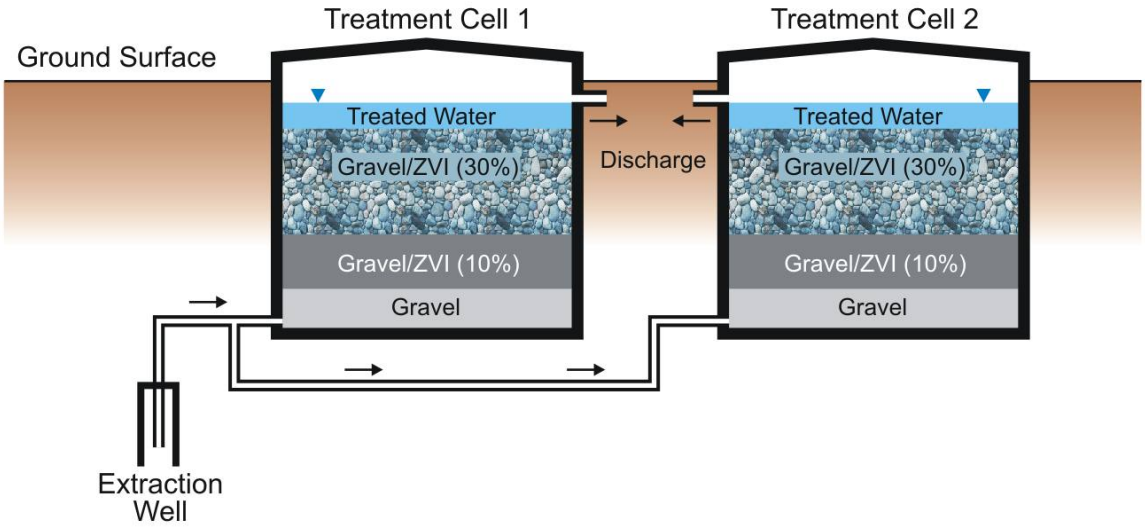

Fig. 2. Schematic of the Monticello Treatment System.

The volumetric ratio of ZVI to gravel varies from 10 to 30 percent; the ratio is lowest near the bottom of the cell and highest near the top (Fig. 2). Contaminated ground water is pumped from the extraction well and flows upwards through each cell in parallel. The system has successfully treated uranium for more than 3 years, but attempts to optimize it are ongoing in order to lower costs further. One improvement was to grade the media mixtures with a lower ZVI content near the bottom of the cell. Examination of the media during change-out indicated that abundant ZVI was still present even after the media was expended (based on effluent uranium concentrations exceeding the treatment goal). The bottom portion of the media had hardened, and the permeability was reduced. The hardening results from precipitation of ferric oxide and calcium carbonate minerals caused by ZVI corrosion (S.J. Morrison et al., 2002). Detailed tracer testing indicates that the dispersivity of the media increases as the cell ages. The increased dispersivity likely results from preferential flow around the hardened (lower-porosity) areas. Hydraulic conductivity, calculated from influent pressure and flow rate, is continuously monitored. The media's hydraulic conductivity decreases over time, an effect also likely related to mineralization of the media. Therefore, it appears that there is ample ZVI to treat water for longer periods and that preferential flow may be the main reason that the media's ability to treat uranium decreases over time. Engineered methods to limit preferential flow, such as optimizing the reactive media's hydraulic properties, may be the best approach to increasing the longevity of the media and, in turn, lowering costs.

This treatment method presents several problems. The ZVI/gravel mixture becomes contaminated during the operation of the treatment cells; thus, removal and disposal requires radiation-control measures. Iron dissolves in the ground water as it is treated. Upon exposure to air, this iron precipitates as ferric oxide (red rust) and colors the discharge area red. Although not detrimental to the environment, the coloration on the ground is aesthetically undesirable.

Rocky Flats

The uranium contamination in ground water at the Rocky Flats Site is a result of weapons-production operations from 1952 to 1994. A treatment system was installed in 1999 at the Rocky Flats Site to treat

nitrate and uranium ground-water contamination resulting from the leakage of a series of evaporation ponds (the former Solar Evaporation Ponds). The contaminated ground water is collected by a 335-m-long subsurface collection drain and is pumped by a solar pump through a treatment system. Flow rates and water levels are monitored through a Web-based telemetry system. Contaminants in the ground water are nitrate and uranium.

The treatment system consists of a concrete vault that is 12.8 m long, 5.2 m wide, and 7 m deep (Fig. 3). The vault is divided into 2 cells separated by a vertical concrete partition. Cell 1 contains 136 cubic meters (m^3) of a mixture of sawdust (which makes up 90 percent of the volume) and ZVI (which makes up 10 percent), while cell 2 contains 45.3 m^3 of a mixture of gravel (85 percent of the volume) and ZVI (15 percent of the volume). The upper 3.4 m of the vault is backfilled with woodchips for freeze protection. Contaminated ground water is pumped from the collection drain to distribution piping at the top of Cell 1. The water migrates through the sawdust/ZVI media and then through the gravel/ZVI media in Cell 2.

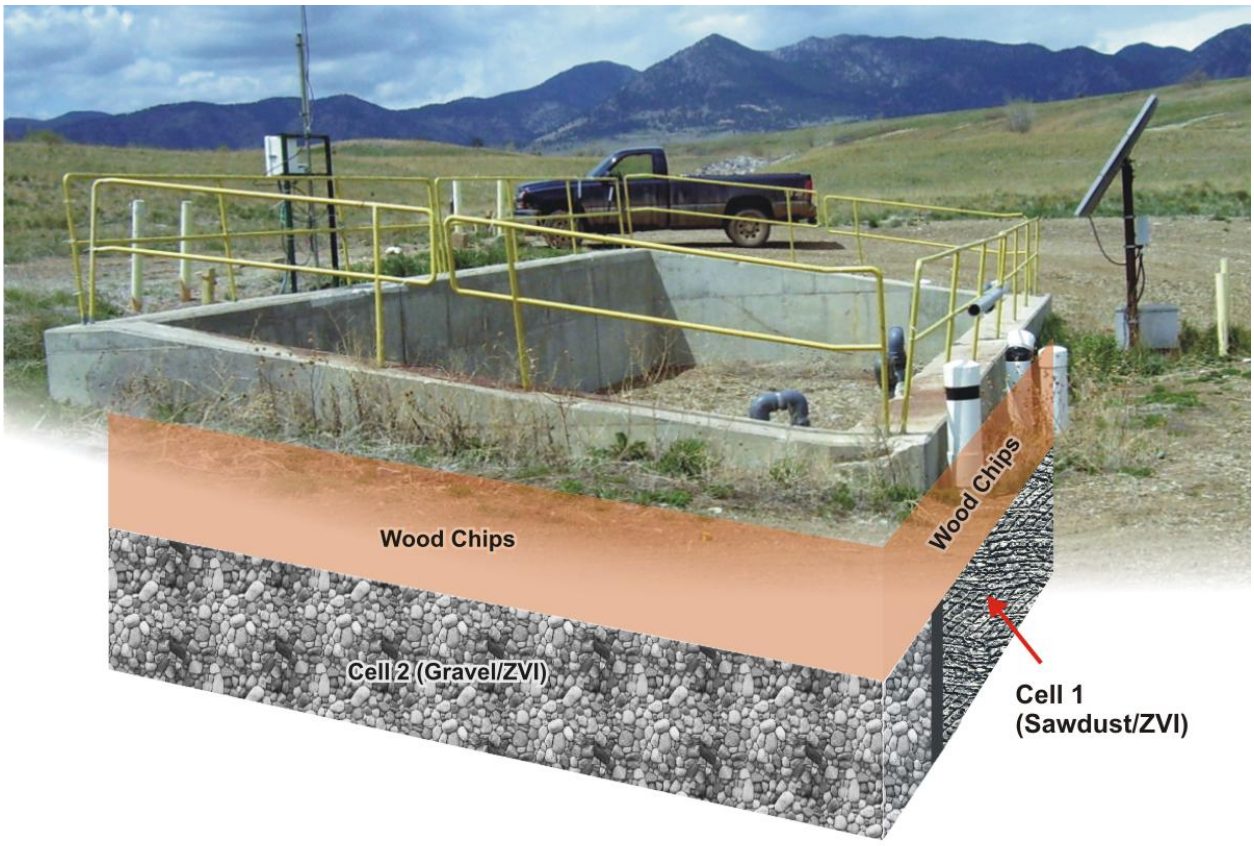

Fig. 3. Schematic of the Rocky Flats Solar Ponds Treatment System.

Nitrate and some uranium are removed in Cell 1. The remainder of the uranium is removed in Cell 2. Biologic denitrification is thought to occur in Cell 1, and abiotic reductive precipitation in Cell 2. The flow rate of contaminated water through the system varies greatly but averages about 1.9 liters per minute (lpm). Treated water is conveyed to a shallow infiltration gallery adjacent to a creek.

Nitrate concentrations in the influent to the treatment system average about 280 milligrams per liter (mg/L) (as N), and effluent concentrations are typically less than 0.5 mg/L (Table II). Influent uranium

concentrations average about 50 µg/L, and effluent concentrations are typically less than 1 µg/L. The results indicate that the treatment system is functioning as intended. Because of the relatively low flow rates and low influent uranium concentration, the system removes only about 0.05 kilograms (kg) of uranium annually.

Table II. Solar Ponds Treatment System – Recent Results

	5/18/07	7/16/07	11/07/07	5/19/08
NO_3 Influent	360	270	220	363
NO_3 Effluent	0.36	0.03	0.14	0.12
U Influent	51	62	53	44.6
U Effluent	1.2	0.36	0.49	0.69

NO_3 = nitrate + nitrite as N in mg/L; U = uranium in µg/L.

The treatment system is nearly passive, requiring only infrequent pump maintenance. The ZVI medium has been replaced only once since its installation in 1999, and the sawdust medium has never been replaced. Because of the media's large volume, it is expensive and labor intensive to replace them. Some of the valves have leaked, and because of their depth (valves are more than 3.7 m beneath the surface), plumbing repairs were costly. As with the Monticello system, iron dissolves from the ZVI and oxidizes at the discharge, coloring the surface environment red.

Another issue is the high disposal cost of the reactive media. The mass of uranium in the sawdust/ZVI media is relatively small; however, regulations require transport and disposal at a radioactive-waste repository. Disposing of this large volume of media is costly. Efforts are underway to modify the treatment train such that uranium is removed by a small quantity of ZVI prior to the sawdust/ZVI cell. If efforts are successful, the sawdust/ZVI could be disposed of at a municipal landfill, which would lower disposal costs.

Shiprock

A uranium mill that operated from 1954 to 1968 at the Shiprock Site resulted in the widespread uranium contamination of the ground-water system. A pump-and-treat system was constructed in 2003 to remediate the ground water. Ground water is currently pumped from 12 extraction wells and 5 collection drains to a lined 11-acre evaporation pond (Fig. 4). The system extracts contaminated ground water from a floodplain of the San Juan River as well as an alluvial terrace elevated about 15.2 m above the floodplain. Most of the extracted water comes from the floodplain.

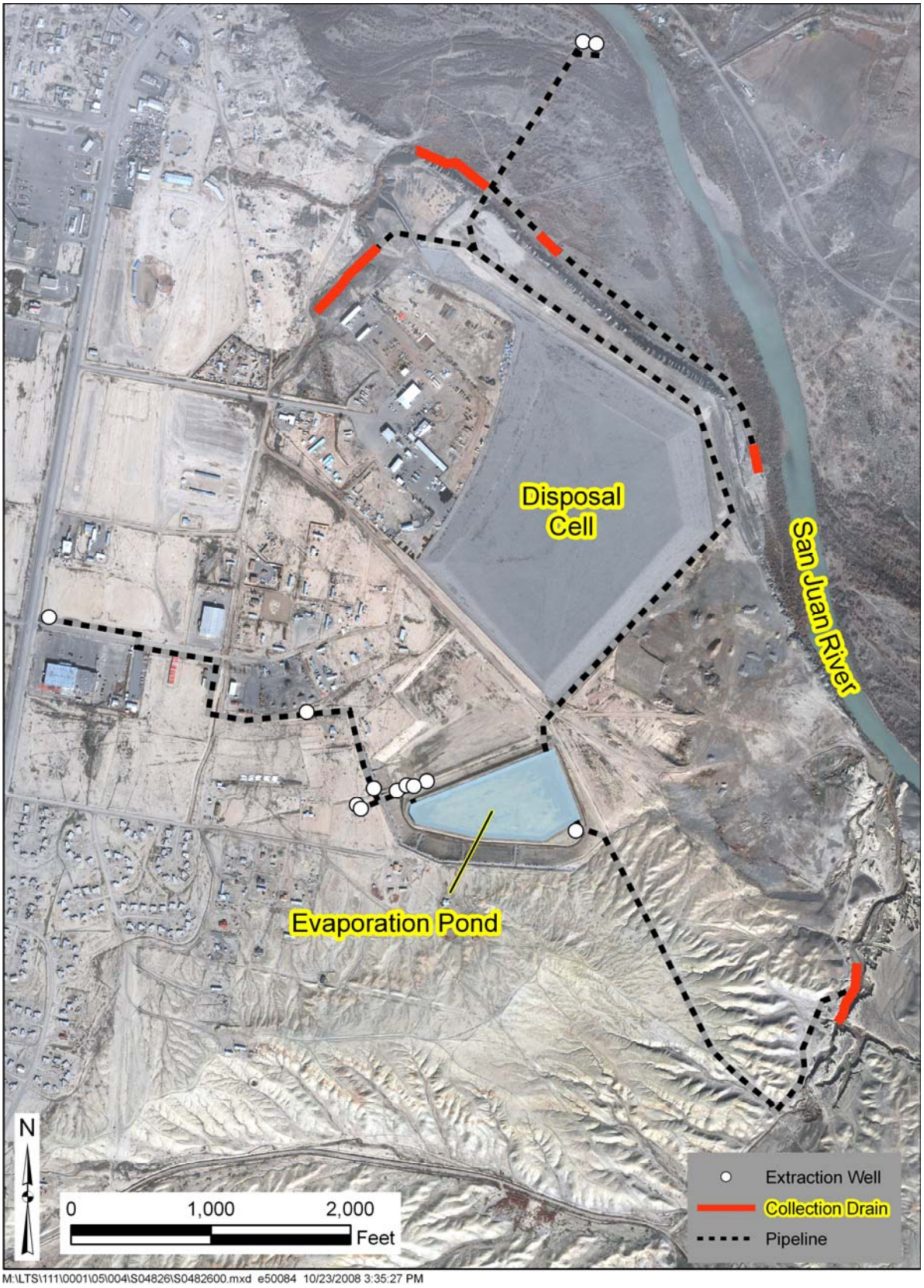

Fig. 4. Map of the Shiprock Extraction System and Evaporation Pond

Flow to the evaporation pond averages about 190 lpm. Flow rates, water levels, and electrical conductivity in the ground water are monitored remotely through a Web-based telemetry system. Electrical conductivity of the ground water correlates with ground-water contamination; thus, electrical conductivity is monitored at selected extraction and monitoring locations to provide data on ground-water cleanup rates.

Conventional extraction wells often produced relatively low flow rates, most less than 3.8 lpm and some less than 0.8 lpm. The extraction system was greatly enhanced by the addition of two large-diameter wells (installed using a backhoe) and five collection drains. The large-diameter wells produce 19 to 38 lpm each, whereas the collection drains produce up to about 76 lpm. Results from the two highest-producing collection drains on the floodplain exemplify uranium removal capacity (Table III).

Table III. Recent Uranium Concentrations (µg/L) and Flow Rates (lpm) for the Two Main Collection Drains on the Floodplain – Shiprock Site

Date	9/12/06		3/06/07		9/11/07		3/06/08	
	U	Flow	U	Flow	U	Flow	U	Flow
Drain 1	2,100	23	2,000	26	1,500	15	1,500	30
Drain 2	380	72	220	57	140	68	100	64

Since no treatment system is used at Shiprock, operation is largely limited to infrequent well maintenance and repair. Shortly after startup, evaporation in the pond exceeded the rate of inflow, and dried salts in the pond bottom were exposed to wind erosion. The installation of two floodplain collection drains in 2006 provided sufficient water to continually cover the bottom sediments, and windblown contamination is no longer a problem. In fact, at maximum pumping, the system is now capable of filling the pond, and strategies to cycle pumping are in place. Water levels in pumping wells and well cycling are controlled remotely through a Web-based telemetry system.

A disadvantage of the system is that the ground-water resource is lost to evaporation. The evaporation rate averaging about 190 lpm limits the amount of uranium that can be extracted to about 80 kg per year (Table I). Since water is not reinjected, extraction rates are limited by the rate of influx of ground water to the extraction sites.

Fernald

At the Fernald Site, high-purity uranium metal was produced for the U.S. Defense Program from 1951 to 1989. This processing resulted in uranium contamination in ground water of the Great Miami Aquifer. A pump-and-treat operation was initiated in 1993. Between 1993 and 2008, 83 billion liters of ground water were pumped, removing 4,000 kg of uranium from the aquifer. Of this, 35 billion liters were treated, and the rest was blended and discharged without treatment. Currently, 23 extraction wells are operating at a combined rate of about 18,000 lpm. Treated water is discharged to the Great Miami River.

The extracted water is treated with an anion-exchange resin (Dowex 21K) at a rate of about 5,678 lpm. The treatment plant uses six flow-through vessels, each containing 8.9 m^3 of resin (Fig. 5). The average influent uranium concentration is about 60 µg/L; the effluent uranium concentration is maintained at less than 30 µg/L. The system removes about 54 kg of uranium per year. Loading on the resin is about 3.2 kg/m^3. The spent resin is not regenerated but rather is disposed of at a radioactive-waste repository. Flow enters a “lead” vessel and then travels to a “lag” vessel. This configuration allows for maximum uptake of uranium on the resin prior to disposal. Approximately one-third of the resin is replaced every year.

Fig. 5. Photo of the Fernald Site Treatment Plant, Showing Resin Vessels

The treatment plant is relatively easy to operate, given the simplicity of the ion-exchange process. However, because of the high flow through, staffing for oversight, operation, and maintenance is required 365 days per year. Resin replacement and spent resin disposal costs are relatively high.

Tuba City

A uranium mill operated at the Tuba City Site from 1956 to 1966. Seepage from evaporation ponds and slurried mill tailings resulted in a ground-water uranium plume. A pump-and-treat system was constructed in 2002 to remediate the ground water. The tailings were stabilized in an on-site repository. The ground-water aquifer is in aeolian sandstones of the Navajo Formation.

The extraction system currently consists of 37 wells that supply contaminated ground water to a water treatment plant. The treatment consists of ion exchange followed by distillation (Fig. 6). The ion-exchange unit removes calcium and magnesium from the water and replaces it with sodium to minimize scale in the distillation unit. Distillation occurs at about 145 °C and at a pressure of 3.3 pounds per square inch. A vapor recompression evaporator, which incorporates a large heat-exchange area to maximize energy efficiency, is used. In addition, a parabolic trough solar water-heating system was just installed to further reduce the purchase of electricity. Treated water is injected back into the Navajo Aquifer via an infiltration trench located immediately upgradient of the tailings pile.

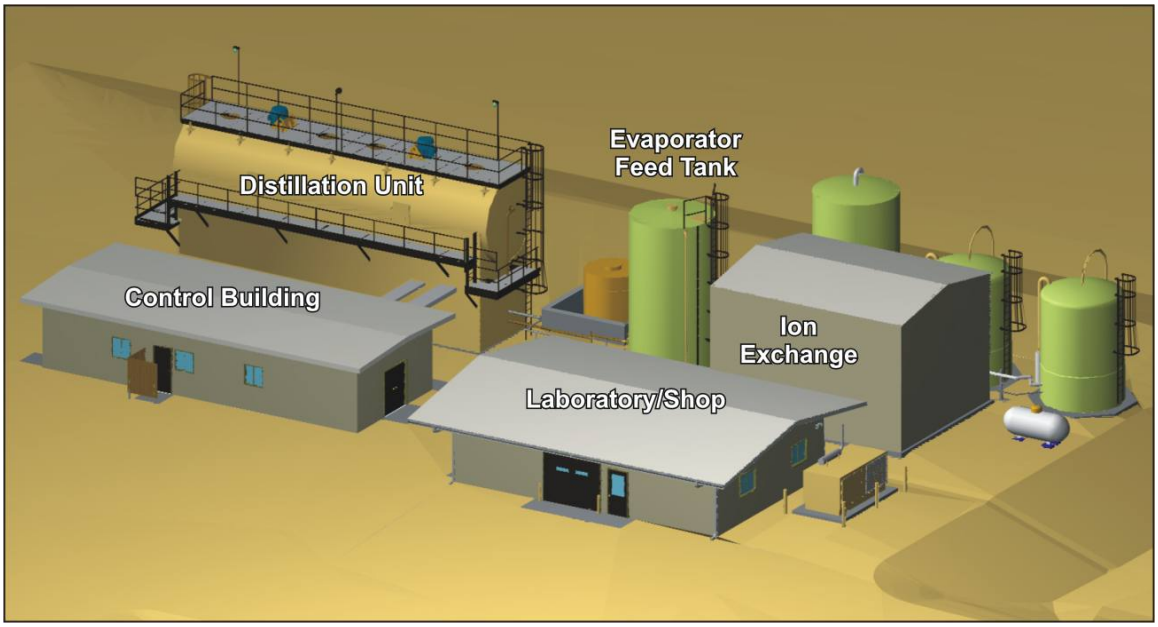

Fig. 6. Drawing of the Water Treatment Facility at the Tuba City Site

High concentrations of sulfate and nitrate contribute to the ground-water contamination. Concentrations of uranium, sulfate, and nitrate inflowing to the treatment plant average about 240 µg/L, 1,000 mg/L, and 350 mg/L, respectively. About 151 million liters of water are treated annually at an average flow rate of about 300 lpm. A total of 1 billion liters have been treated as of 2008. Average distillate contains 10 µg/L, 59 mg/L, and 17 mg/L of uranium, sulfate, and nitrate, respectively. The process removes about 40 kg of uranium per year.

About 9 percent of the influent water is discharged to an evaporation pond on site; the contaminants are contained in this 9 percent. The treatment plant is relatively complex and requires experienced operators. Maintenance includes removing radioactive scale from the distillation unit and backflushing the ion-exchange unit.

SUMMARY AND CONCLUSIONS

A wide variety of water treatments are used by the LM Program to remove uranium from contaminated ground water. If uranium is the only contaminant, it can be removed by simple flow-through columns containing an ion exchanger (Dowex) or a reductant (ZVI). Ion exchange with Dowex may be limited to ground water with relatively low levels of dissolved solids. ZVI can remove other trace contaminants, such as selenium, arsenic, and vanadium; however, the process yields high concentrations of dissolved iron in the effluent. The contaminated ground water at the Rocky Flats Site contains nitrate, which is successfully treated using biological methods, but biological treatment can require relatively large volumes of media. If the water contains a high concentration of sulfate, a more expensive method, such as distillation, is required. The water resource at Shiprock is expendable; thus, the lower-cost alternative of evaporation is used to treat this water, which is high in uranium, sulfate, and nitrate. Following is a list of the five LM sites arranged in order of mass removal of uranium by the treatment systems, with the mass-per-year removal in parentheses: Shiprock (80 kg), Fernald (54 kg), Tuba City (40 kg), Monticello (7 kg), Rocky Flats (0.05 kg).

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