A Simple Solution to a Complex Problem: Hexavalent Chromium in Landfill Stormwater – 16129

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ABSTRACT

Management of hexavalent chromium (Cr+6)-contaminated water at the Environmental Management Waste Management Facility (EMWMF) is a significant operational challenge, in addition to the challenges already posed by water management. The Cr+6 discharge criterion of 16 micrograms per liter (μg/L) is typically met; however, when demolition debris containing Cr+6 is received for disposal, concentrations up to 280 μg/L have been seen. The large volume of water generated at EMWMF from the 130-cm (51-in.) annual precipitation creates a complex water management problem that must be quickly addressed to maintain compliant landfill operations.

The EMWMF Operations Team devised and implemented a simple, low-cost method to rapidly reduce the Cr+6 from the landfill stormwater. The Cr+6 reduction system uses inexpensive, commercially available components of which the key is conventional steel wool in 760-L (200-gal) plastic bins. The Cr+6-impacted stormwater is pumped through the bins, where the Cr+6 reacts with the elemental iron of the steel wool and reduces to trivalent chromium. The water then spills back into the ponds. Water is continuously recirculated through the bins until the release criterion is verified to be achieved, allowing the stormwater to be discharged into the adjacent receiving stream.

This cost-effective system is operated with in-house craft personnel, requiring only minimal additional training and hazard controls. The system can operate continuously with minimal intervention and has successfully processed millions of liters of stormwater. The success of the initial installation has been refined over time, allowing Cr+6 reduction to proceed 24 hours a day and 7 days a week, with a Cr+6 reduction rate of about 20 μg/L per day. The system is scalable to achieve even higher reduction rates and adaptable to other metals.

Through October 2015, over 65.1E6 L (17.2E6 gal) of contact water with Cr+6 above the release criterion was managed using the EMWMF system. This simple solution to a complex water management problem provides significant cost savings and operational efficiencies over traditional transportation and treatment at a water treatment facility.

INTRODUCTION

The Environmental Management Waste Management Facility (EMWMF) (Fig. 1) in eastern Tennessee is a repository for selected waste generated on the Oak Ridge Reservation (ORR) and at ORR-associated sites. The EMWMF is authorized through the Record of Decision [1] to accept and dispose of LLW, RCRA hazardous waste, Toxic Substances Control Act waste, classified waste, and mixed waste generated from CERCLA response actions at the ORR. No RCRA-listed hazardous waste or TRU waste is accepted for disposal at EMWMF. The 1.68E6-m^3 (2.2E6-yd^3) facility began operations in May 2002.

Fig. 1. EMWMF Aerial View.

Water management is a top priority for EMWMF Operations. With the currently active disposal cells totaling 11.3 hectares (28 acres) and rainfall averaging 130 cm/yr (51 in./yr), the annual water budget for the landfill area is over 144E6 L/yr (38E6 gal/yr). Water that enters the leachate collection system is trucked via tanker for treatment at an ORR facility. Water that contacts the waste, but does not enter the leachate collection system (i.e., contact water), is pumped to lined impoundments, sampled, and then batch-released, if it meets the release criteria. Water that does not meet the release criteria is trucked for treatment at an ORR water treatment facility.

From March 2011 through October 2015, EMWMF successfully managed over 30E6 L (8E6 gal) of contact water that contained hexavalent chromium (Cr+6) above the established release criterion. This paper describes the simple, low-cost approach developed and implemented by EMWMF to safely manage this water.

Brief History of Cr+6 Issue at EMWMF

In November and December 2009, EMWMF Operations noted an increasing trend of Cr+6 in routine contact water results. Although the values were below the release criterion, an investigation was launched to identify the possible sources, as well as possible mitigative measures. While the Cr+6 levels returned to normal before the cause could be identified, the investigation did identify steel wool as a conditioning (i.e., reducing) medium that would likely be appropriate should this situation arise again. This knowledge and awareness allowed EMWMF Operations to respond quickly just one year later.

In March 2011, routine pre-discharge sampling again identified elevated levels of Cr+6 in contact water—this time in excess of the release criterion.

Drawing from the 2009 investigation, EMWMF Operations immediately deployed steel wool into the contact water as part of some pond-sized tests. Concurrent and complementary to the pond-sized tests, a treatability study with bench-scale tests was also initiated. These tests (described later) demonstrated that passing the impacted water through conventional steel wool would reduce the Cr+6 levels in the water to below the release criterion.

EMWMF Operations began improving and expanding the reduction systems, including the use of large containers filled with steel wool that were set up at the impoundments.

The source was subsequently determined to be pulverized concrete rubble (Fig. 2) from the second floor slab of the K-33 Building, primarily from the vicinity of the coolant coolers. The Cr+6 is believed to have resulted from spills of recirculating cooling water, which contained chromic acid as a corrosion inhibitor. Elevated Cr+6 in contact water continued throughout the K-33 waste disposal campaign, returning to pre-disposal levels by early 2012.

Fig. 2. Placement of Pulverized Concrete Rubble from K-33.

In November 2014, waste was received from Building K-31, which had a similar cooling water system as K-33. The EMWMF Operations staff were prepared for elevated Cr+6, which appeared soon after this waste stream began to be received. Additional bins of steel wool had been prepared and improved pumping systems installed, expanding the treatment capability by a factor of approximately 20.

As of November 2015, the reduction effort continues, but with minimal impact to routine operations.

Figures 3 and 4 illustrate the two significant episodes of managing Cr+6.

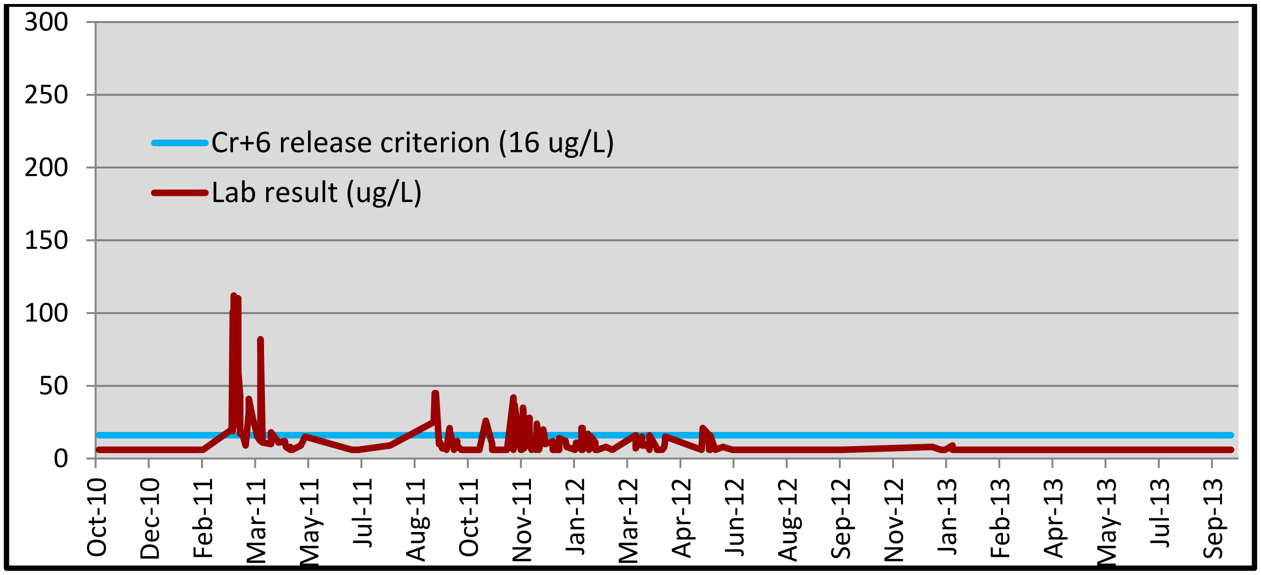

Fig. 3. Cr+6 Concentrations in Contact Water Associated with K-33 Waste Disposal.

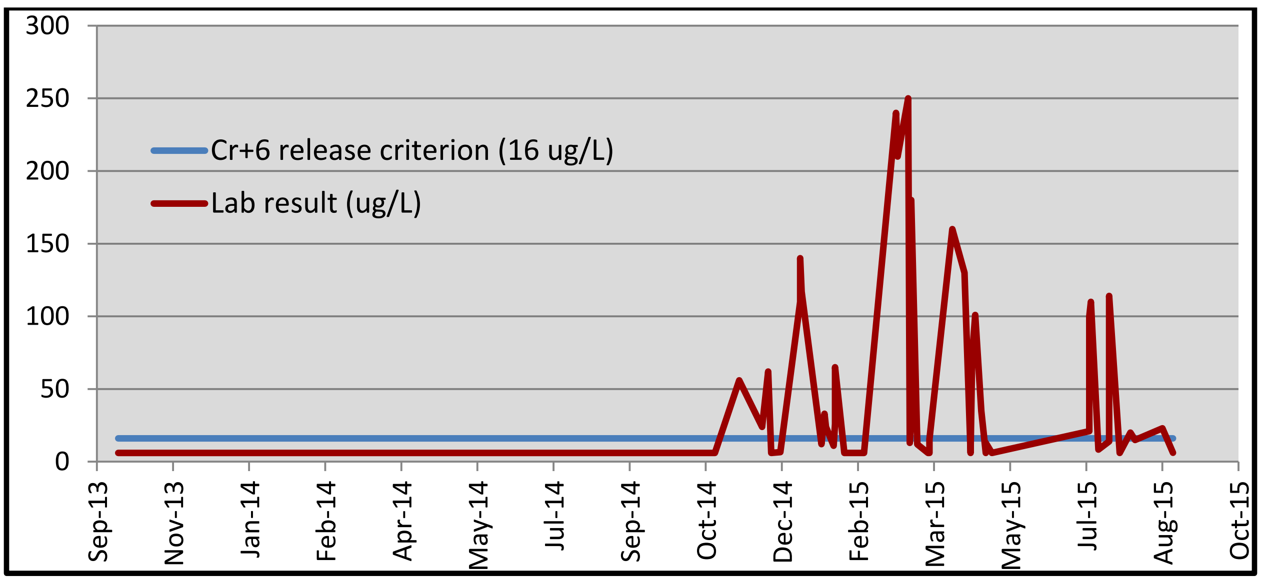

Fig. 4. Cr+6 Concentrations in Contact Water Associated with K-31 Waste Disposal.

When elevated Cr+6 in contact water was first identified at EMWMF, the site was faced with significant challenges. At that time, on-site water storage was nearing capacity, more rain was in the forecast, around 1.9E6 L (0.5E6 gal) of contact water was being collected per 2.54 cm (1 in.) of rainfall, and the 7.6E6-L (2E6-gal) Contact Water Ponds could not be released because the Cr+6 exceeded the release criterion. Consequently, EMWMF was faced with potentially trucking all impounded contact water, as well as the usual leachate, to a treatment facility. However, the water generation rate during prolonged storm events sometimes exceeded the ability of the site to ship the water, as well as the ability of the treatment facility to receive the water.

An alternative to transporting the impacted contact water to a treatment facility was needed immediately.

DESCRIPTION AND DISCUSSION

Reduction Chemistry and Analysis

Cr+6 is listed as a Contaminant of Concern (COC) for contact water monitoring at EMWMF. The EMWMF contact water release criterion for discharge of Cr+6 is 16 μg/L based on the Ambient Water Quality Criterion Maximum Concentration for Fish and Aquatic Life [2].

The science for using iron to reduce Cr+6 in water is well established [3], [4], [5], [6], [7], [8]. Iron is known to be an effective reducing agent for Cr+6 in solution and is often used as a conditioning medium for these processes.

Cr+6, as chromate, has been shown to be reduced by zero-valent reactive iron (Fe°). The Fe° donates the electrons necessary to reduce the chromate and becomes oxidized to divalent iron (Fe+2) or trivalent iron (Fe+3). When iron is present, the Cr+3 can precipitate as a mixed chromium-iron hydroxide solid solution, which has a lower solution equilibrium activity than pure solid-phase hydroxide. Therefore, both the toxicity and mobility of chromium are greatly decreased when it is reduced from Cr+6 to Cr+3. This reduction can be described by the overall reaction as follows:

$$\mathbf{Fe^0 + CrO_4^{2-} + 2H_2O \Rightarrow Cr(OH)_3 + Fe(OH)_3 + 2OH^-}$$

In the above reaction, Cr+6 (as chromate ion) is chemically reduced to the non-toxic, stable, highly insoluble, and biodegradable Cr+3 species [9].

EMWMF project personnel used a portable HACH®[a] Colorimeter to measure field Cr+6 in solution. The HACH® meter was used during the reducing process to monitor progress, ensure that the systems were performing at peak levels, and provide guidance for the reduction efforts. When the HACH® meter indicated that the Cr+6 level in a field sample met the release criterion, then an analytical sample was collected for laboratory analysis to verify that the individual batch met the

[a] HACH *is a trademark registered by the Hach Company in the U.S. Patent and Trademark Office.*

Cr+6 release criteria of 16 μg/L. The HACH® meter was used only for field screening, not to demonstrate compliance. Use of the HACH® meter saved significant time and analytical costs.

For Cr+6 compliance verification sampling, the field samples of contact water are filtered and the pH adjusted immediately with a buffer solution by lab personnel [10]. The samples are then analyzed by ion chromatography with post-column derivatization as defined in standard operating procedures for the analytical lab. Quality control includes blanks, continuing calibration verification samples, laboratory control samples, and matrix spikes. The local analytical laboratory (MCLinc) provided results within 24 hours of collection.

EMWMF contact water is also analyzed for total metals prior to discharge to ensure the reduction effort does not elevate other COCs. Any analytes resulting from this reduction process and any remaining Cr+6 is measured and reported.

The reduction reaction with Fe^0 produced no unwanted side effects. Although the process tends to increase pH, it does not exceed the EMWMF release criteria.

Pond-Sized Tests and Treatability Study

EMWMF Operations conducted pond-sized tests and a bench-scale treatability study to optimize the approach for deployment of steel wool into the contact water.

The treatability study [9] was performed to (1) determine application parameters (flow rate and contact time) for the batch-process Cr+6 reduction system already underway at EMWMF, (2) evaluate a batch process using sodium sulfide, and (3) evaluate other commercially available solid media for achieving batch reduction.

The treatability study demonstrated that:

- Passing the impacted water through conventional steel wool reduces the Cr+6 levels to levels below the release criterion.
- Cr+6 reductions of approximately 100% are readily attainable.
- The reaction rate is largely a function of the iron surface area.
- Steel wool with some rust out performs new steel wool because the corrosion etching increases the effective surface area available for the reaction.
- All steel wool grades of fineness were successful. Finer grades react more quickly, while the coarser grades tend to last longer. Finer grades also clog more quickly if a sediment-laden water is flowed through the medium.
- There was no appreciable difference in performance between the unwashed and the detergent-washed steel wools.

Initial Cr+6 Reduction Methods at EMWMF

When elevated Cr+6 in contact water was identified at EMWMF in March 2011, the site took aggressive measures to reduce the Cr+6. Steel wool was deployed in various configurations and locations, both in the disposal cells and in the contact water impoundments, as described below.

After evaluation of the tests and treatability study, the selected option was to deploy containers filled with steel wool to the in-cell catchments and the Contact Water Ponds, with pumps to circulate the impacted water through the containers (Fig. 5). These arrangements proved very efficient in reducing the Cr+6 to acceptable levels and provided the basis for the expanded reduction effort that would come later.

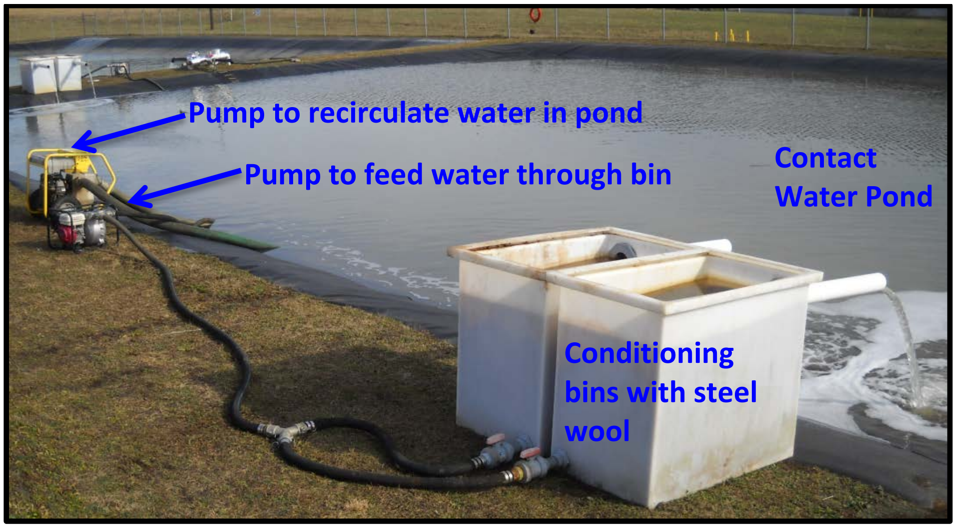

Fig. 5. Conditioning Bins Filled with Steel Wool During Early Reduction Effort.

EMWMF Expanded Systems for Cr+6 Reduction

When planning for receipt of the Building K-31 demolition debris, EMWMF Operations prepared for the possibility of Cr+6 in the concrete rubble. Drawing from the lessons learned during the K-33 campaign, the team developed a comprehensive strategy for dealing with Cr+6:

- Mitigate the impact from the source term
- Maximize the reaction opportunity (i.e., contact time between Cr+6 and Fe^0)
- Maximize the margin of safety for water management
- Observe and optimize the system

<u>Minimize the impact from the source term</u>

The source term was daunting. The K-31 and K-33 Buildings were massive structures. With a combined footprint of 20 hectares (50 acres), these multi-story buildings contained over 294E6 kg (648E6 lb or 324,000 tons) of building materials, primarily steel and concrete, that were disposed at the EMWMF.

EMWMF Operations implemented several measures to mitigate the source term.

- Coordinate with the demolition projects to:
  - Hold the concrete rubble, when practicable, until it could be campaigned during favorable weather windows.
  - Minimize the pulverization of the concrete rubble and thus minimize the surface area exposed to water.
  - Separate the concrete rubble from the steel and other debris during waste loading, allowing the source term to be campaigned and disposed over a smaller footprint.
- Minimize interaction between concrete rubble and water at the landfill:
  - Keep concrete rubble out of drainage paths in the landfill and out of areas where water might pool.
  - Place concrete rubble in the higher portions of the landfill.
  - Avoid receipt and placement of concrete rubble when rain is imminent.
  - Cover the concrete rubble with clay, optimally before its initial exposure to precipitation. (The “first flush” liberates significantly more Cr+6 than subsequent rainfalls [11])
  - Reduce the total quantity of water to be managed. (A temporary cover was placed over portions of the landfill to divert clean stormwater runoff out of the landfill. Although it reduced the volume of water to be managed, it also increased the Cr+6 concentration in the impacted water.)

<u>Maximize the reaction opportunity</u>

For the situation at EMWMF, the reaction rate is largely a linear function of the iron surface area and the time in which the impacted water interacts with the iron.

- Maximize the number of conditioning bins. (EMWMF was limited by the electrical power available for the pumps in the Contact Water Pond area.)
- Operate conditioning bins both at the in-cell catchments and the Contact Water Ponds. (The Contact Water Tanks were not used for Cr+6 reduction after the 2011–12 episode.)
- Operate reduction systems without interruption.
- Minimize short-circuiting and stagnation within the impoundments. (This was accomplished by continuously pumping the water in a circular motion within the impoundment.)
- Minimize short-circuiting in the bins. (This was accomplished by using a vertical upflow design [Fig. 9] and uniformly distributed steel wool.)
- Maximize the effective surface area of the steel wool.
- Monitor and recharge the bins with steel wool as needed.

Maximize the margin of safety for water management

- Develop effective contingencies, and be prepared to implement those contingencies immediately, if needed:
  - Be prepared to pump contact water to an inactive disposal cell for temporary storage should multiple storm events exceed the site's capacity to process the water.
  - Be prepared to transport impacted water to a treatment facility.
- Develop and implement effective preventative maintenance and corrective maintenance programs to ensure reliability of the pumps and other reduction process equipment.

Observe and optimize the system

Management of the Cr+6 issue is of the highest priority, even above the landfill's primary mission of receiving and disposing of waste. Although the Cr+6 issue crossed multiple job descriptions, a single point of responsibility was designated for keeping the reduction systems running at maximum efficiency, knowing the status of ponds and analytical results, tracking metrics, disseminating information, planning ahead, and staying prepared.

Current configuration

Building on the knowledge gained from the Cr+6 reduction efforts in 2011–12 and in accordance with the above strategy, EMWMF Operations refined and expanded the Cr+6 reduction system and process, which proved highly successful for the K-31 campaign.

The expanded system is far superior to the initial systems. The Cr+6 reduction rate was 1.9 μg/L per day for the initial batch of 1.63E6 L (431,300 gal) and 1.5 μg/L per day for the second batch of 1.44E6 L (380,000 gal). The current system achieves reduction rates of approximately 20 μg/L per day and can do so in each of the four Contact Water Ponds simultaneously. The expanded system also can operate continuously with minimal human intervention.

The current infrastructure and materials consist of containers filled with steel wool through which the impacted water is pumped at the Contact Water Ponds and the in-cell catchments.

Steel wool provides the key component of the Cr+6 reduction systems. This reaction medium is standard industrial grade steel wool, which is widely available in a variety of wire thicknesses and configurations. EMWMF Operations tried several different products, but ultimately selected Grade 2 (medium-coarse, 0.075-mm, 3-mil), unpolished, low-carbon, steel wool on 2.3-kg (5-lb) reels (Fig. 6). The steel wool on each reel was approximately 1.3-cm (0.5-in.) thick and 10-cm (4-in.) wide, wound onto a cardboard core.

Fig. 6. 2.3-kg (5-lb) Reel of Steel Wool.

The Contact Water Ponds is where most of the Cr+6 reduction occurs. The four ponds have a combined working capacity of 6.8E6 L (1.80E6 gal). The reduction system consists of six bins per pond, for a total of 24 bins. Electric pumps (Pacer model SE2ELC2) drive the water through the bins at approximately 190 L/min (50 gal/min) per bin. Wacker PTS4V trash pumps running at 1900 L/min (500 gal/min) recirculate water within the ponds (Fig. 7).

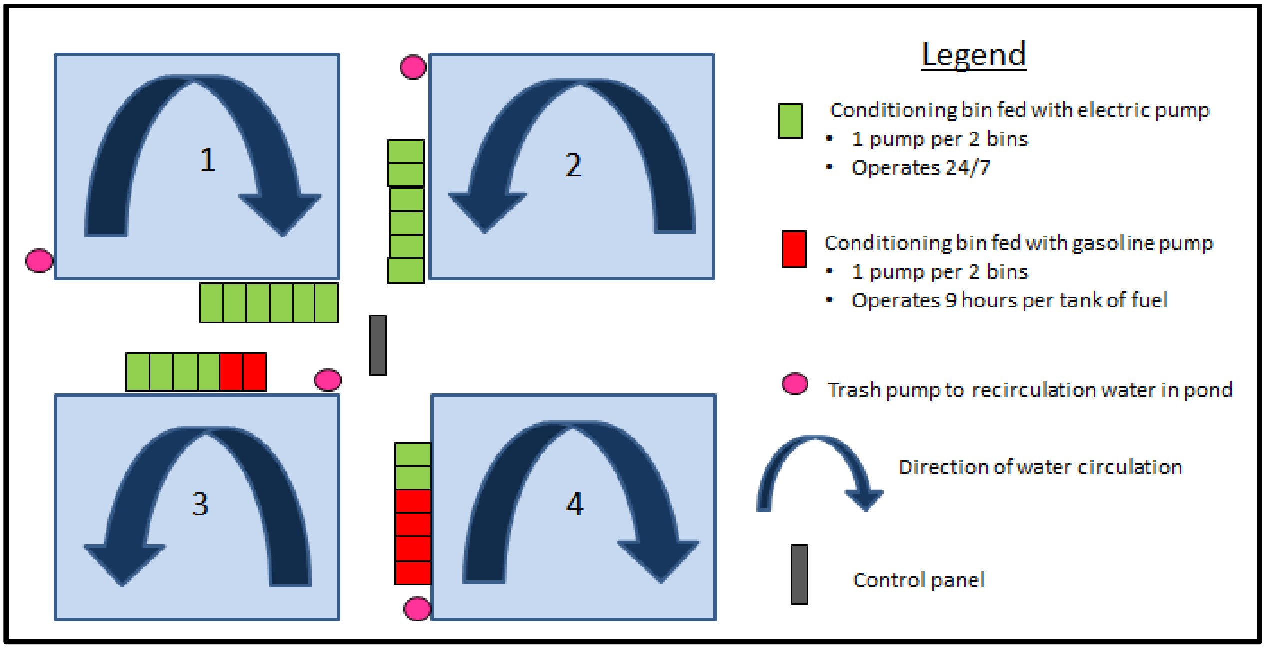

Fig. 7. Schematic of EMWMF Expanded System for Cr+6 Reduction in Contact Water Ponds.

The conditioning bins were fabricated on-site by craft personnel.

The bins are high-density polyethylene containers measuring about 120 cm x 71 cm x 100-cm tall (48 in. x 28 in. x 40-in. tall). Each bin has a working capacity of 760 L (200 gal) (Fig. 8).

Fig. 8. Cr+6 Conditioning Bins at a Contact Water Pond.

The bins feature an upflow design. Water enters the bins near the base, flows up through the steel wool, and spills back into the pond from the top. Fiberglass grating atop concrete blocks keeps the steel wool elevated and promotes a uniform upward flow. A top layer of fiberglass grating keeps the steel wool inside the bin (Figs. 9 and 10).

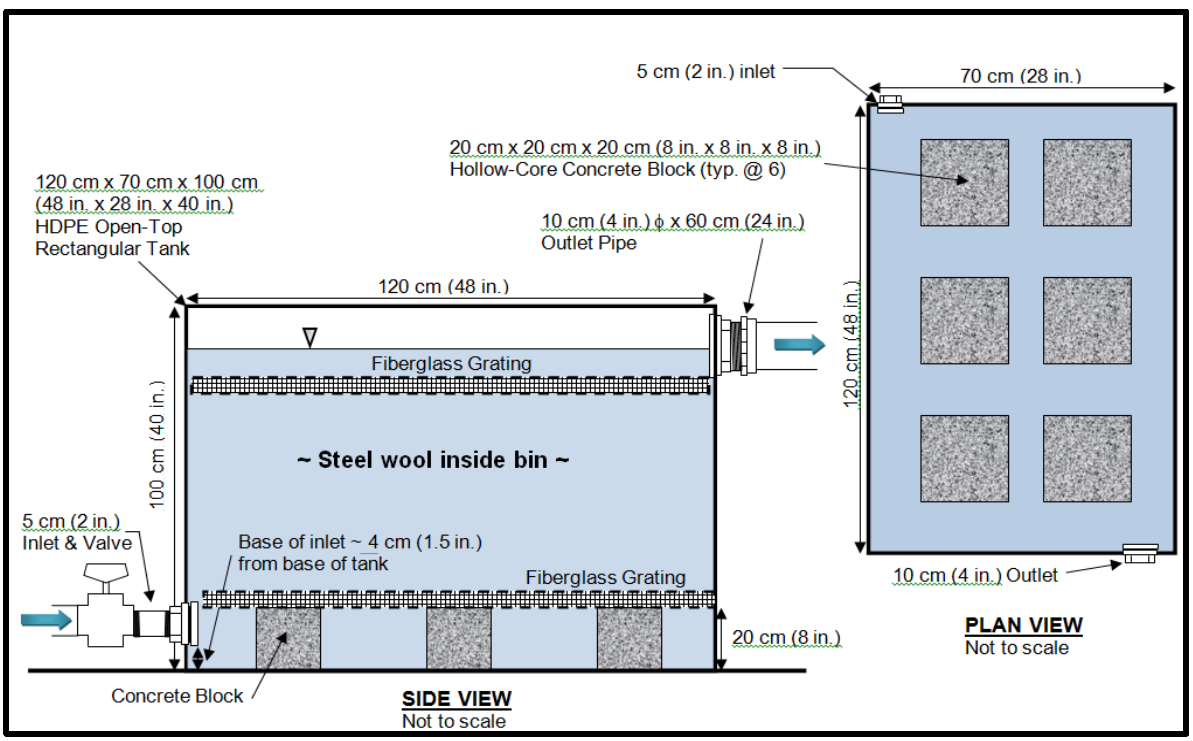

Fig. 9. Conditioning Bin for Reduction of Cr+6 in Water.

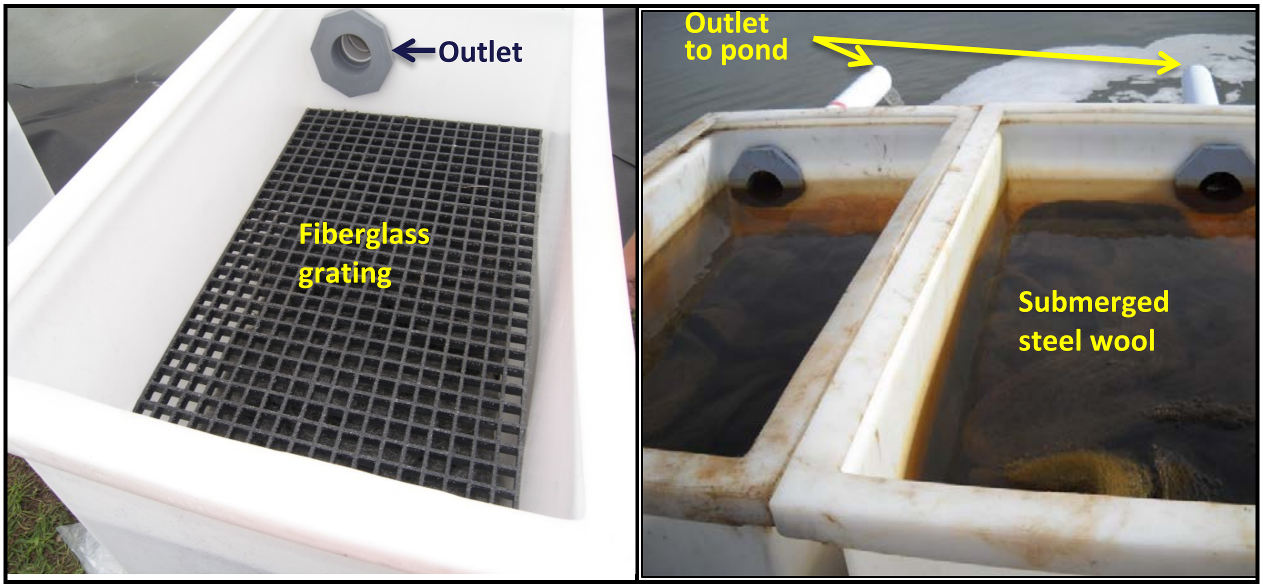

Fig. 10. Interior of Conditioning Bin Before and During Use.

Steel wool is placed into the bin, fluffed up, and uniformly distributed, taking care to avoid creating any short-circuiting flow paths. The objective is to maximize the amount of steel wool (to provide the greatest reaction opportunity for the Cr+6) without overly restricting the flow. EMWMF Operations currently uses a packing density of 14 kg (30 lb) of steel wool per 760-L (200-gal) bin.

The in-cell catchments include a reduction system similar to the bins used at the ponds. Each catchment has a working capacity of roughly 7.6E6 L (2E6 gal), although operational requirements include minimizing the water retained in the catchments to the extent practicable. The reduction system for the catchments consists of two 2300-L (600-gal) hoppers similar in setup to the aforementioned bins. Wacker PTS4V trash pumps drive the water through the hoppers at approximately 190 L/min (200 gal/min) per hopper, with the pump intake and the bin overflow configured to recirculate water within catchments (Fig. 11).

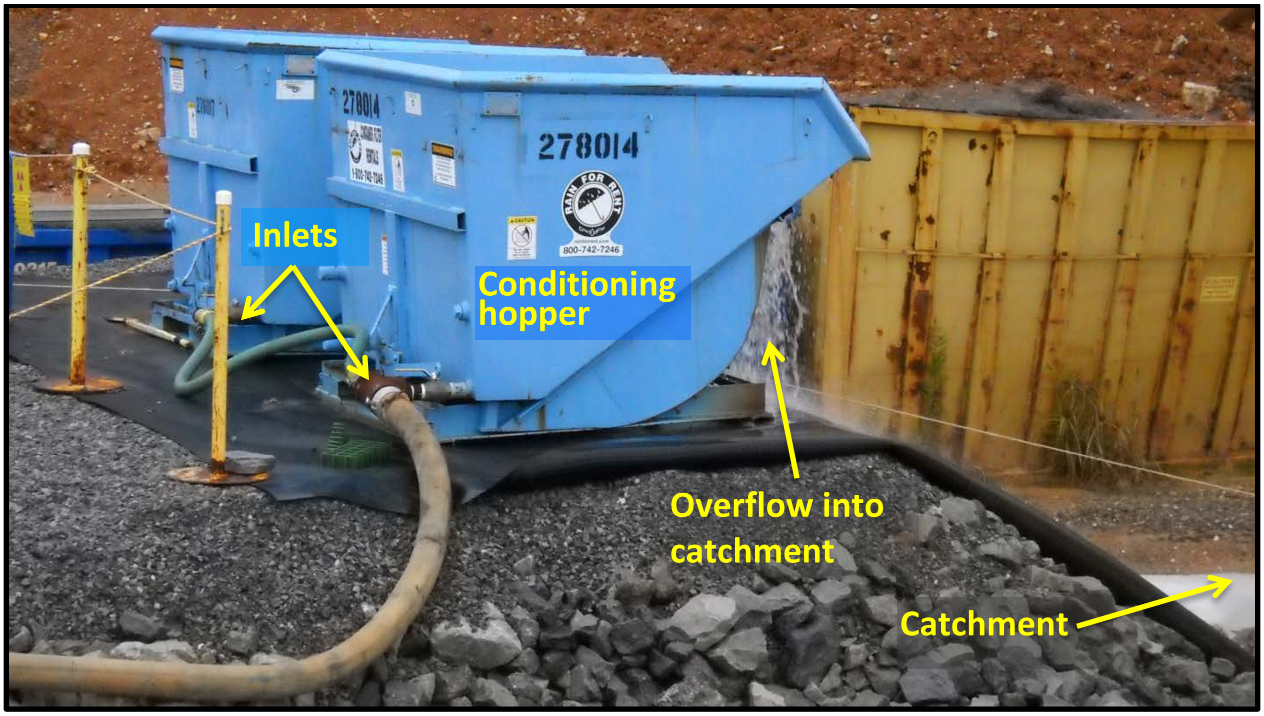

Fig. 11. Conditioning Hoppers at the Cell 5 Catchment.

CONCLUSIONS

The EMWMF system is a cost-effective, regulatory compliant, and safe way to quickly reduce the Cr+6 concentrations in water to meet the release criterion. The system is environmentally friendly, reliable, simple to operate and maintain, and does not degrade other water quality parameters, such as pH.

The EMWMF system is easily implemented using in-house craft and commercially available materials, and requires only minimal operations support and maintenance.

From March 2011 through October 2015, EMWMF successfully managed over 65.1E6 L (17.2E6 gal) of contact water that initially contained Cr+6 above the release criterion. In addition to the cost and risk avoidance from not transporting and treating this water, the water was returned to the local watershed and benefited the local ecosystem.

A cost-effective EMWMF-type system is readily implemented at other sites with similar water management challenges. The system is scalable and can be used as an active system (e.g., pumping water through bins filled with steel wool) and/or as a passive system (e.g., teabags of steel wool suspended from ropes in the contaminated water). The system is also adaptable to a broad spectrum of situations, including other metals. This type of system effectively maintains compliance with Cr+6 release criterion, while minimizing impacts.

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