

Mitigation of Hexavalent Chromium in Storm Water Resulting from Demolition of Large Concrete Structure at the East Tennessee Technology Park - 12286

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ABSTRACT

American Recovery and Reinvestment Act (ARRA) funding was provided to supplement the environmental management program at several DOE sites, including the East Tennessee Technology Park (ETTP) in Oak Ridge, Tennessee. Demolition of the ETTP K-33 Building, the largest building to be demolished to date in Oak Ridge, was awarded to LSRS in FY-2010 under the ARRA program. The K-33 building was an 82 foot tall 2-story structure covering approximately 32 acres. Once this massive building was brought down to the ground, the debris was segregated and consolidated into piles of concrete rubble and steel across the remaining pad. The process of demolishing the building, tracking across concrete debris with heavy equipment, and stockpiling the concrete rubble caused it to become pulverized. During and after storm events, hexavalent chromium leached from the residual cement present in the large quantities of concrete. Storm water control measures were present to preclude migration of contaminants off-site, but these control measures were not designed to control hexavalent chromium dissolved in storm water from reaching nearby receiving water.

The following was implemented to mitigate hexavalent chromium in storm water:

- Steel wool was distributed around K-33 site catch basins and in water pools as an initial step in addressing hexavalent chromium.
- Since the piles of concrete were too massive and unsafe to tarp, they were placed into windrows in an effort to reduce total surface area.
- A Hach colorimetric field meter was acquired by the K-33 project to provide real-time results of hexavalent chromium in site surface water.
- Three hexavalent chromium treatment systems were installed at three separate catch basins that receive integrated storm water flow from the K-33 site. Sodium bisulfite is being used as a reducing agent for the immobilization of hexavalent chromium while also assisting in lowering pH.

Concentrations initially were 310 – 474 ppb of hexavalent chromium in surface water at the outfalls that discharge to nearby receiving water. After implementation of the

actions described above, concentrations of hexavalent chromium have been effectively reduced to less than 25 ppb at the outfalls.

INTRODUCTION

Hexavalent chromium is highly toxic at low concentrations and is a contaminant of concern for sites requiring remedial action due to a variety of production and industrial activities. Hexavalent chromium is used for the production of stainless steel, textile dyes, wood preservation, leather tanning, anti-corrosion & conversion coatings, as well as a variety of niche uses. Industrial uses of hexavalent chromium compounds include chromate pigments in dyes, paints, inks, and plastics; chromates added as anticorrosive agents to paints, primers, and other surface coatings; and chromic acid electroplated onto metal parts to provide a decorative or protective coating. Hexavalent chromium can also be formed when performing "hot work" such as welding on stainless steel or melting chromium metal. In these situations, the chromium is not originally hexavalent, but the high temperatures involved in the process result in oxidation that converts the chromium to a hexavalent state.

There are substantive and a significant number of buildings that require demolition at facilities across the nation, including the DOE complex. Typically, environmental compliance associated with building demolition focus on contaminants such as mercury, lead, PCBs, dust/suspended solids, and asbestos. Hexavalent chromium has traditionally not been identified as a common contaminant of concern for demolition of concrete structures. The intent of this paper is to increase awareness of the presence of hexavalent chromium in concrete demolition debris and recognition that demolition of large structures can result in a significant source of a highly toxic contaminant. Increased awareness and recognition of the issue could lead to changes and improvements in initial characterization activities, demolition sequencing, site monitoring & controls, and storm water management & treatment. Alternatives considered and approaches implemented by the K-33 project for mitigating hexavalent chromium at low concentrations can be of benefit to remedial action and demolition projects associated with a wide range of production and industrial activities.

LSRS completed the largest demolition project to date for the U.S. Department of Energy's Oak Ridge Environmental Management (EM) program in September 2011. Constructed in 1954, the K-33 facility enriched uranium for defense and naval fleet purposes until 1985. A majority of the decontamination and decommissioning was performed in 1997, but the current project removed transite siding and universal waste, demolished the building to slab, and packaged and transported debris to the Environmental Management Waste Management Facility (EMWMF).

The source of hexavalent chromium at the K-33 site was massive amounts of concrete rubble. Approximately 118,000 tons of concrete were generated from the 2.8 million square foot floor space, two story building. According to *Hexavalent Chromium in Cement Manufacturing: Literature Review* sponsored by the Portland Cement

Association 2007, hexavalent chromium is common in cement. Chromium in cement can originate from 1) raw materials (e.g. , clay, sand, flyash) 2) magnesia-chrome kiln refractory brick, if used 3) wear metal from raw mill grinding process, if chromium alloys are used, and 4) additions such as gypsum, pozzolans, ground granulated blast furnace slag, mineral components, and cement kiln dust.

The cement process, specifically kiln conditions, can influence how much hexavalent chromium will form. In the kiln, oxidizing atmosphere will play the largest role, with more oxygen in the burning zone leading to increased hexavalent chromium formation. Alkali concentration is also of importance, since hexavalent chromium in clinker is primarily in the form of chromates. In the finish mill, thermodynamically favorable conditions for oxidation to hexavalent chromium exists, including high air sweep, moisture from gypsum dehydration, cooling water injection, and grinding aids, along with the high pH of cement. The use of additives such as ferrous sulfate to reduce the level of Cr (VI) formation in cement is a current practice. It is unlikely that such a practice occurred in the 1950s when the K-33 building was constructed.

METHOD – INITIAL SURFACE WATER CONTROL MEASURES

Surface water control measures at the K-33 site were established per the *LSRS Storm Water Pollution Prevention Plan (SWPPP) for the Building K-33 Demolition and Disposition/Removal Project*, K-33-PLA-ENV-005 Rev. 1, October 2010. These initial control measures were not designed to address soluble hexavalent chromium contamination, but primary controls included the following:

- About 40 -50 catch basins/storm drains that surround the K-33 pad are protected with a combination of crushed rock, concrete blocks and/or sand bags, and filter fabric to preclude suspended solids from exiting the site. The obstructed flow due to the storm drain protection also slows storm water flow which tends to pond surface water and settles out larger suspended solids.
- Surface water controls are inspected twice a week and after large rainfall events (greater than .5" of rain) and documented per *Storm Water Inspections for the Building K-33 Demolition and Disposition/Removal Project*, LSRS-K33-PRO-HS-050 Rev. 1, October 2010. Observations and required corrections from inspections are reported to the K-33 Project Field Manager to implement necessary repairs of surface water control features as required.
- Testing for pH is conducted during post rain event inspections for pooled water on the Building K-33 floor/pad that has a viable pathway for discharge to storm water basins. The intent is to test significant pools of water that are in contact with building debris piles.

INITIAL RESULTS

The K-33 debris disposal facility operations, Environmental Management Waste Management Facility (EMWMF), Oak Ridge, TN, were the first to suspect that K-33 concrete rubble was contaminated with hexavalent chromium. Elevated levels of hexavalent chromium were detected in surface water that discharged from the landfill cell containing primarily K-33 debris and collected in EMWMF contact water ponds. To verify the source, a sample was taken from each of six trucks loaded with K-33 debris that had arrived at the EMWMF site. Sample results were 282, 291, 347, 1908, 5299, 6561 ug/kg (ppb) of hexavalent chromium in the rubble.

Subsequent samples were then taken from the three primary outfalls that receive surface water from the K-33 site (See Figure 1). Analysis for hexavalent chromium yielded the following results:

- 474 ug/L (ppb) from Outfall 690, which receives runoff from the east/northeast side of the K-33 pad and discharges to Poplar Creek.
- 357 ug/L from Outfall 700, which receives runoff from the northwest side of the K-33 pad and discharges to the upper end of K-901-A pond
- 310 ug/L from Outfall 710, which receives runoff from the southwest side of the K-33 pad and discharges to the lower end of K-901-A pond

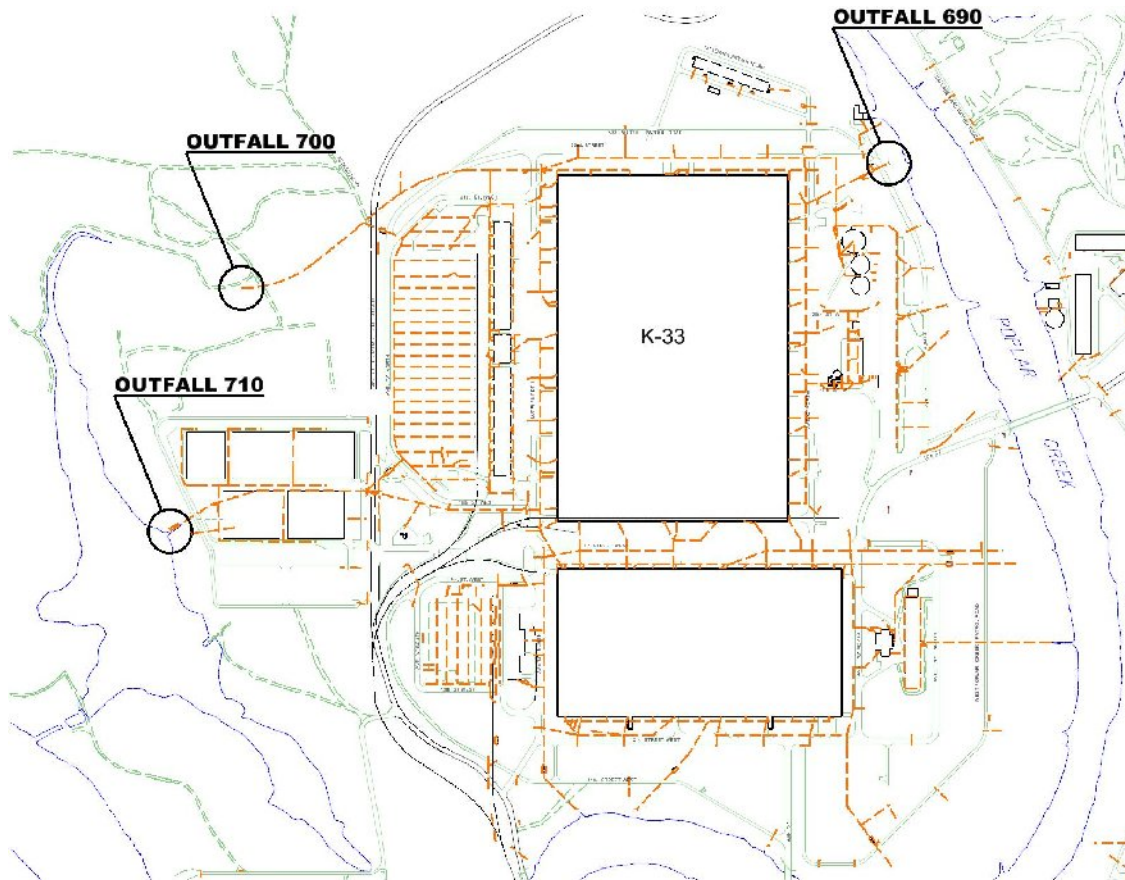


Fig 1. Site outfall locations

Additional samples were taken from surface waters that had contacted concrete rubble and pooled at the K-33 site. Sample results were 474, 996, 1536, 1553, and 15374 ug/L of hexavalent chromium. Sampling of on-site pools of water after storm events performed via a field Hach meter yielded hexavalent chromium results as shown on Figure 2. Real-time data indicating ppb levels of hexavalent chromium were beneficial in identifying initial site activities to mitigate hexavalent chromium in stormwater.

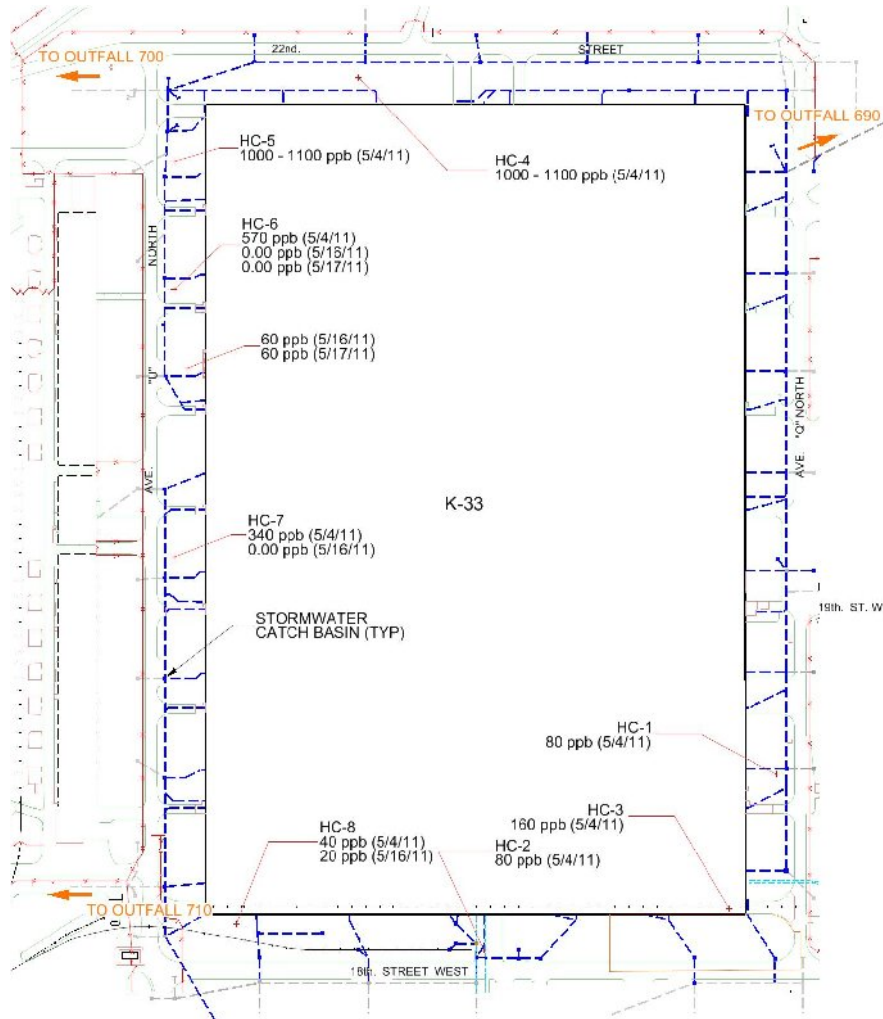


Fig 2. Hexavalent chromium concentrations in pooled water

DISCUSSION – ALTERNATIVE ANALYSIS

Alternatives were identified and evaluated to temporarily address the release of hexavalent chromium from K-33 concrete debris into nearby surface water. The approach was temporary in the sense that shipments of contaminated debris to EMWMF ultimately mitigated the source of hexavalent chromium. As such, structures, treatment facilities, and collection tanks/ponds constructed on-site were not considered as a part of the evaluation.

Primary alternatives considered were:

1. Place temporary covers over debris piles (e.g., tarps, encapsulation, and foam) or place debris piles in windrows;

2. Treat debris piles to remove or reduce hexavalent chromium with reducing agents such as ferrous sulfate;
3. Distribute steel wool near storm drains to reduce hexavalent chromium to less toxic/mobile trivalent chromium;
4. Route K-33 site storm water to K-901-A pond and reduce hexavalent chromium in the pond;
5. Treat storm water within K-33 site catch basins with sulfur-based reducing agents metered in via a control system.

Evaluation of alternatives was performed as follows:

- Alternative #1 (i.e. tarps, encapsulation, and foam) was deemed impractical due to the vast area over which the debris was spread (32 acres) and the non-homogeneous nature of the debris (steel, concrete debris, and crushed materials) that would create voids and preclude adequate coverage. However, windrowing of the piles was performed as an interim measure to reduce the exposure of the debris surface area to rainwater.
- Alternative #2 was determined to be ineffective due to the wide range of contamination levels and particulate sizes that would preclude adequate mixing. A reducing agent such as ferrous sulfate would be prematurely oxidized by inert solids further complicating stoichiometric balancing required for effective treatment.
- Alternative #3 would have limited effectiveness due to contact time required for producing ferrous iron to reduce hexavalent chromium and associated lack of controls. Steel wool is more effective by distributing in a recirculating pond, such as the approach used at the EMWMF contact ponds. Limited or temporary control of hexavalent chromium occurred by distributing steel wool near catch basins and in small on-site pools of water that collect after a rainfall event.
- Alternative #4 would be an effective way to treat hexavalent chromium, particularly since the K-901-A pond has a history of being used for chromium treatment until the 1990s. However, regulatory agencies deem the K-901-A pond as “waters of the state” and do not prefer using the pond for treatment. This option is further complicated by having to dike, pump water, or relocate waste from the east side (which naturally drains to Poplar Creek) to the west side which drains to the K-901-A pond.
- Alternative #5 was the primary alternative that was implemented. As shown in Figure 3, storm water from K-33 is collected in several collection systems, but each system exits the site through a single catch basin and outflow pipe (CB 1027 on the north east side, CB 1B002 on the north west side, and CB 6008 on the south west side). These three catch basins receive integrated flow, which

provides sufficient turbulence for mixing and contact time with the addition of sulfur-based reducing agents such as sodium bisulfite. This treatment approach is very similar to treatment used at the Y-12 National Security Complex for dechlorination of surface water. The treatment system had a short purchase/procurement time, since “off the shelf” equipment was used, and installation is straight forward.

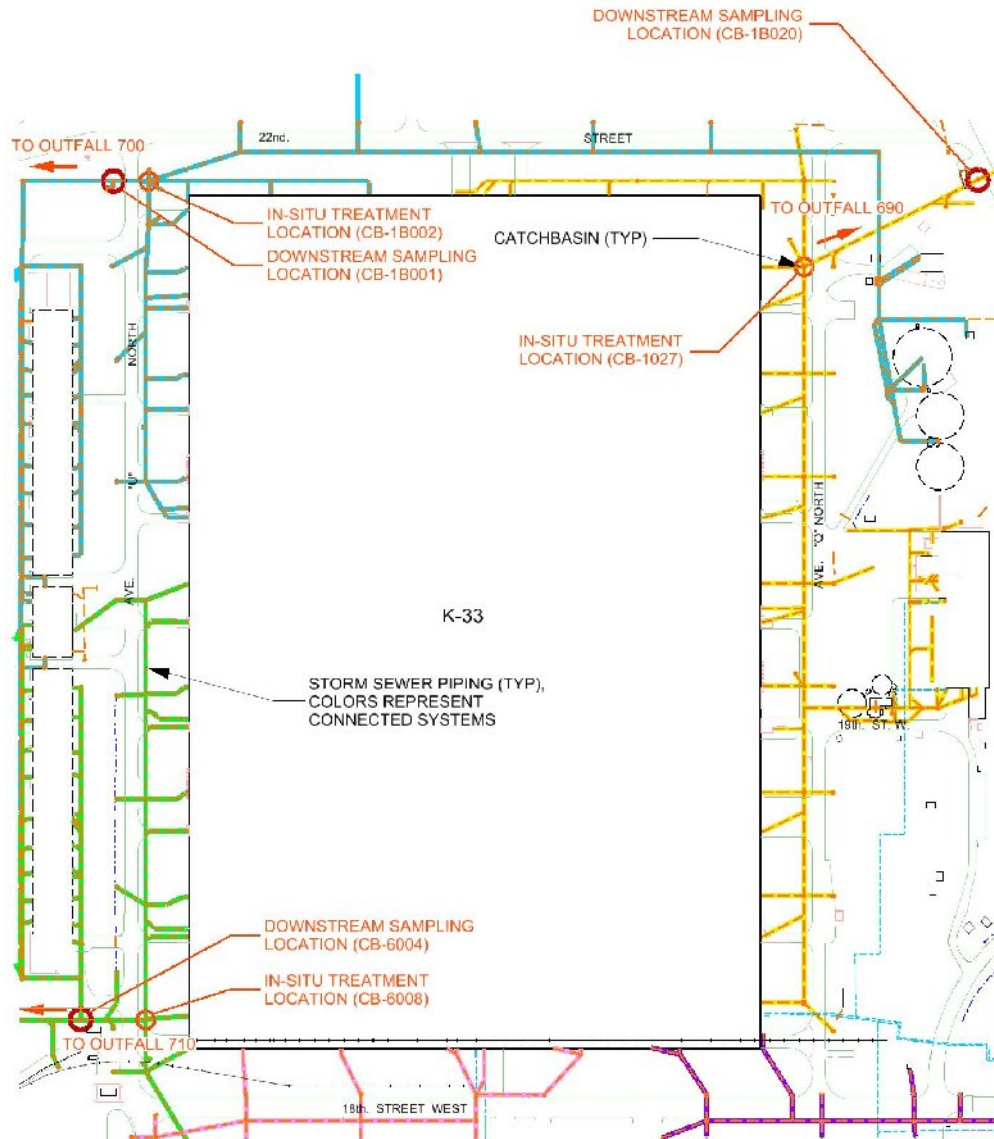
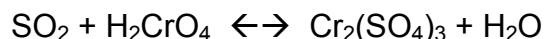


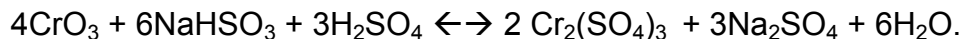
Fig 3. Storm water collection systems

The most common mechanism to treat hexavalent chromium in water is to convert it to the less soluble and less toxic trivalent chromium form. This is best accomplished via the addition of strong chemical reducing agents such as sulfur dioxide (SO₂), sodium

bisulfite (NaHSO_3), or sodium meta-bisulfate ($\text{Na}_2\text{S}_2\text{O}_5$), among a typical list of sulfur-reducing compounds. The crucial advantage of using sulfur-based versus iron-based reductants is the tremendous decrease in production of sludge. Depending on the specifics of treatment required, location of treatment, flow rates, and other field logistics, one of the above-listed, sulfur-based chemicals is generally selected. These compounds have been used for many decades in the industrial wastewater treatment industry where hexavalent chromium is often an issue - for example, in the plating industry. The reducing reaction proceeds quite rapidly upon contact of the contaminant and the selected chemical reducing agent. Stoichiometric quantities of the dosage can be calculated for a given hexavalent chromium stream that can be used for system sizing and chemical supply. For example, the following reaction takes place when sulfur dioxide, which is often employed in aboveground water treatment, reacts with hexavalent chromium:



The reaction will take place instantaneously at lower pH around 4 pH units. However, reduction with sodium bisulfite is also quite effective at neutral pH, or without supplementation with sulfuric acid, because sodium bisulfite alone is often sufficient to substantially lower the pH. The following reaction takes place when sodium bisulfite is used to reduce hexavalent chromium:



The final pH of the water can be adjusted, monitored, and automated with the use of pH controllers. Once the hexavalent chromium is reduced to the trivalent chromium form, it precipitates quite effectively at pH values greater than 6.0 units, which generally occur beyond the influence and point of chemical addition.

The schematic of the chromium treatment system is shown in Figure 4. The controls for the pH and ORP measurement are also illustrated in Figure 4. The controllers are the on/off type having a control relay switch with relays to indicate operation of conditions outside of the normal range. Initial efforts to control addition by ORP measurements were ineffective and impractical, so the system was modified to control addition of sodium bisulfite via the automated pH controller which is also an effective field indicator of treatment.

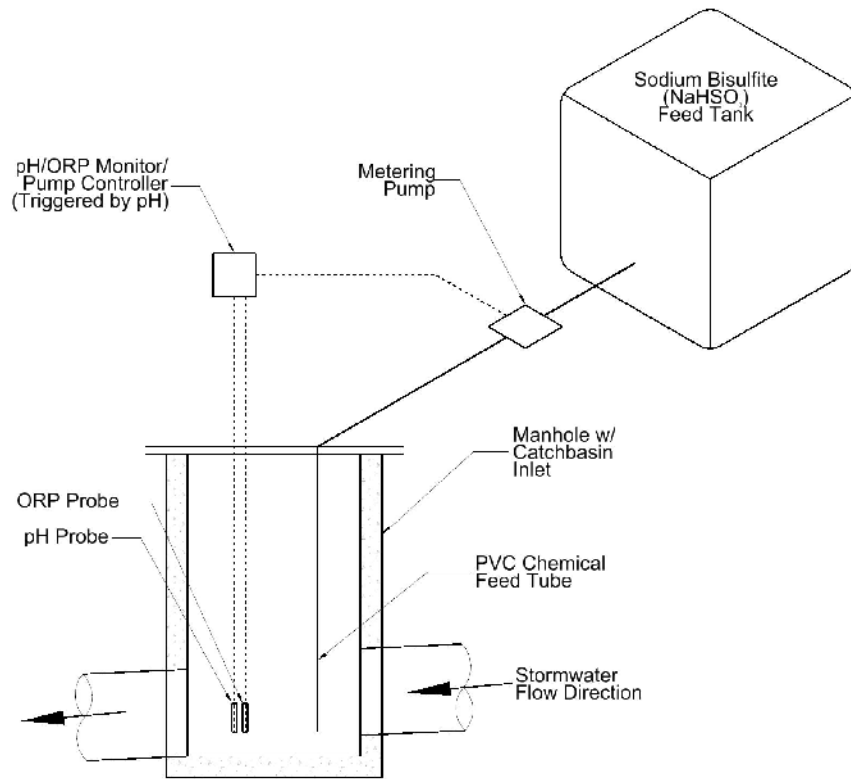


Fig 4. In-situ treatment system schematic

Finally, these reductants are also advantageous for pH reduction of the high-pH water (that is expected due to the contact with concrete rubble), thereby resulting in compliance with allowable discharge pH ranges at the outfall.

CONCLUSION

The LSRS team completed demolition of K-33 five months ahead of schedule, and debris removal was completed three months ahead of schedule. A total of 164,000 tons of steel and concrete from the building demolition, accounting for 13,000 shipments, were disposed to the EMWMF.

Because of the high toxicity of hexavalent chromium at low concentrations, hexavalent chromium had to be controlled at ppb levels. Hexavalent chromium contaminant concentrations were successfully reduced by over 90% in surface water discharged from the K-33 demolition site into nearby receiving water (See Figure 5). Initial efforts of windrowing debris piles and obtaining real-time hexavalent chromium measurements to focus initiatives coupled with placement of steel wool in pools or catch basins had some effectiveness. More significant reductions were obtained as the debris piles were

removed/disposed in EMWMF, and treatment of surface water with sodium bisulfite in integrated manholes occurred.

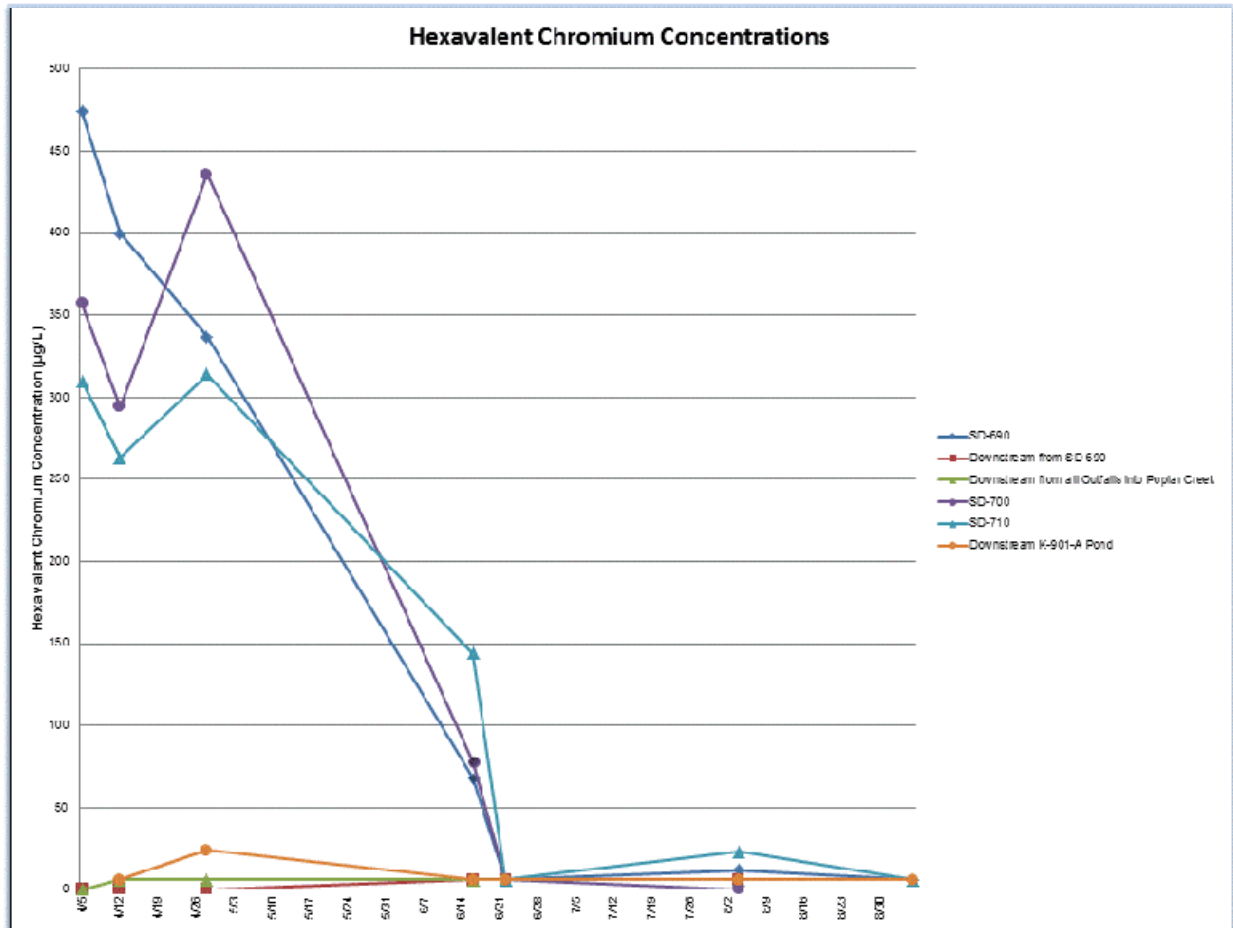


Fig 5. Hexavalent chromium concentration decreases at discharge locations

REFERENCES

1. *Hexavalent Chromium in Cement Manufacturing: Literature Review* sponsored by the Portland Cement Association 2007.
2. *LSRS Storm Water Pollution Prevention Plan (SWPPP) for the Building K-33 Demolition and Disposition/Removal Project*, K-33-PLA-ENV-005 Rev. 1, October 2010.
3. *Storm Water Inspections for the Building K-33 Demolition and Disposition/Removal Project*, LSRS-K33-PRO-HS-050 Rev. 1, October 2010.