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# Ask Tom! Column

## Low Cost Solution for Heavy Metals Contamination Removal

Guest article by Doug Austin PE, ADT Environmental Solutions

**The 'Blackhawk Site'**

"Battery breaking" plants were once common in the U.S. Operators took in spent batteries from cars and other vehicles and literally smashed them to facilitate the recovery and recycling of lead and other materials. Such low technology operations often produced sites contaminated by high concentrations of lead. Making things worse, the battery (sulfuric) acid that often spilled during operations tended to accelerate the migration of lead toward groundwater.

Dozens of such plants in the U.S. were closed and abandoned by their owners during the 4-5 years following 11/84, when the U.S. Congress passed tough, enforceable environmental protection laws (HSWA Amendments to the Resources Conservation and Recovery Act). Many of these properties subsequently became Superfund sites.

The 'Blackhawk site' was located in a remote area outside of Des Moines, Iowa. It operated profitably until early 1985 then sold the property to real estate speculators. During the early 1990s the City of Des Moines was expanding toward the site and the city's boundaries were extended to include the region around it. Developers began construction of a large housing development with a 10-acre central area that would become a park, complete with community center, swimming pool, children's play area, picnic benches, barbeques, etc.

Development of the park was scheduled to take place after most of the homes were constructed and sold. When contractors and heavy equipment moved in to begin excavation of the swimming pool, they immediately uncovered substantial volumes of battery debris. Lead concentrations ranged upwards of 50,000 ppm in some areas, with TCLP leachability of lead as high as 750 mg/L. The total volume of soil with leachable lead exceeding the regulatory maximum of 5 mg/L TCLP was estimated at 35,000 $yd^3$. Construction operations were halted as the worried developer considered his options, and as surrounding residents became increasingly aware and concerned.

The chosen solution centered on implementation of a process of 'mineral synthesis'. That is, chemical reagents introduced to affected media initiate the formation of stable, lead bearing mineral forms. Candidate minerals included species such as anglesite (lead sulfate, $Pb(SO_4)_2$ and galena (lead sulfide, $PbS$ – the most common lead ore).

However, the preferred mineral option, from the standpoints of minimum cost, ease of implementation, best overall results, and longevity was 'lead substituted, calcium hydroxyapatite. This mineral has the following generic chemical formula: $Ca_{5-n}Pb_n(PO_4)_3OH$ (where n=5) This solution has several advantages, including the following:

- Treated media is very stable and secure over a wide range of environmental conditions (2.5=pH=13
- Lead bearing mineral forms have low solubility in water (<5 parts per billion).
- Apatite mineral forms are hard (Mhos hardness = 5.0) and resist physical degradation.

- Treatment results are effectively permanent (stable over a wide range of environmental conditions).
- In-situ application. Site operations involve minimal noise and there is no dust generation. Typically, mineral forming reagents are liquids or slurries applied directly to impacted media and permitted to soak in (typically 0.5 to 0.7 meters). ‘In-situ’ operations are inherently less noisy than ex-situ treatment systems involving pugmills or similar mixing systems and there is significantly less likelihood of transient dust generation.
- Speed. 50,000 cubic meters of impacted media could be treated in less than two months.
- Low Cost. Significantly less than US$50 per cubic meter, inclusive of all site operations and subsequent disposition of treated media.
- Regulatory acceptance. USEPA and State of Iowa regulators were familiar with results from a difficult site in neighboring Missouri and were very supportive.

**The Process**

Minerals of the apatite group are characterized by a phenomenon known as isomorphic substitution. For example, hydroxyapatite has the following chemical formula: $Ca_{10}(PO_4)_6(OH)_2$

This common mineral will “scavenge” heavy metals (incl. some radionuclides) into positions within its crystalline structure that might normally be occupied by other ions. This ‘substitution’ results in little or no change to the crystalline structure and physical properties of the mineral. For example, under the right conditions lead, nickel, strontium, and several other ionic metals will preferentially replace calcium, taking up that ion’s position in the apatite crystal structure. Similarly, arsenic, chromium and other anionic species can substitute for phosphate ($PO_4$).

In some cases, a heavy metal ion species will not combine into an apatite mineral form. Examples include cadmium, selenium, antimony, etc. For these heavy metal species mineral forms such as sulfides and sulfates are preferred for the purpose of leachability reduction.

The process of isomorphic substitution is essentially irreversible. The substituting metallic ion becomes an integral part of a mineral crystal structure which is physically durable (Mohs>5), chemically stable ($2.0<pH<13$), and from which the metal will not leach into the environment. A key aspect of this phenomenon, for the purposes of use during clean up projects, is that appropriate minerals are easily synthesized at ambient conditions in a wide range of solid and liquid media. Even more important for the owners of contaminated sites, such methods are readily implemented in the field for significantly lower cost than all other known methods.

**Mineral Synthesis at Blackhawk**

The Blackhawk Site was a moderately level property covering roughly 60,000 $m^2$. Roughly 2/3 of the property was contaminated by lead at levels exceeding regulatory standards. However, in no case was contamination found at depths below 2 meters. Soil on the site was a moderately permeable glacial till. This suggested a strategy involving direct application to the soil surface of a liquid phosphate reagent. The chosen reagent is aggressively hygroscopic and rapidly distributes itself through the top 0.7 meters of the soil. The reagent soaks into soil very quickly, and there was no concern about runoff.

In areas where contamination was found at depths greater than 0.7 meters (roughly 70% of the site), a treated layer or ‘lift’ is removed and staged elsewhere on the site in order to provide access to lower layers requiring treatment.

Note – Depending upon media characteristics more than one reagent type may be required to insure all of the materials necessary to form a target mineral species are present. At Blackhawk, all requirements were met with a single, low cost reagent.

The strategy was to remove all vegetation and debris from the site surface and to stake out plots measuring roughly 10 meters square. A tank truck carrying the chosen reagent was connected to a chemical pump with a timer. The pump flow rate and timer were set to provide the quantity of reagent for a 900 m2 area and 0.7-meter penetration. A site worker wearing appropriate protective clothing distributes the reagent as uniformly as possible over the soil surface within the staked area until the pump timed out (typically 2-3 minutes).

The apatite forming reaction is complete within seconds. Immediately following reagent application, excavators remove the top 0.7 meters of treated soil and the operation is repeated for the next ‘lift’, if required. Treated materials were staged elsewhere on the site pending confirmation testing. Testing samples were collected immediately following treatment. If necessary, staged materials may receive additional applications using ‘land row’ methods (linear piles measuring 1 meter high and 2-3 meters wide. At Blackhawk, however, none of the 41,700 m3 of treated material required a second treatment application.

At the Blackhawk Site no more than three lifts were required. At other sites where similar strategies have been employed there have been as many as 12 lifts required to pursue contamination to its ultimate depth. At sites where contamination is found at depths greater than 10 meters, or where excavation in lifts is impractical for some reason, there are pressure injection techniques for reagents that may be more costly (50% higher, or less), but are equally effective.

Under U.S. environmental regulations it is possible to leave previously contaminated materials in place following treatment. A cosmetic soil cap may assuage individuals who have residual concerns. At the Blackhawk Site the conservative developer elected to have treated media hauled to a nearby construction debris landfill for use as ‘daily cover’, at a cost less than 10% of disposal at a hazardous waste facility.

The table below randomly lists typical confirmation test results from treated soil at the Blackhawk Site.

| **Grid Location** | **a-3** | **d-12** | **e-1** | **f-15** | **m-6** | **q-2** | **t-11** | **aa-9** | **ad-3** |
|---|---|---|---|---|---|---|---|---|---|
| Total Lead (ppm) | 8,340 | 42,120 | 3,860 | 1,510 | 11,870 | 4,360 | 13,880 | 2,510 | 7,970 |
| Pre-treatment TCLP (mg/l) | 122 | 795 | 87 | 31 | 156 | 93 | 225 | 42 | 227 |
| Post-treatment TCLP (mg/l) | 0.38 | 1.56 | ND* | ND* | 0.42 | ND* | 0.49 | ND* | 0.29 |

*Where ND < 0.12 mg/l

**Summary**

ADT has hundreds of formulations for treating toxic heavy metals in a wide variety of media. This approach to resolving heavy metal contamination is exceptionally flexible and cost effective and can be adapted to most site remediation tasks.

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**Welcome to Ask Tom!**, a monthly column by our resident water treatment guru, Tom Keenan of National Environmental Services Agency (NESA). Tom addresses the issues that bug you the most. And Tom knows!! With 35 years experience in providing environmental support services to public and private sector clients on a wide range of environmental issues.

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