



Understanding Apatite Crystallization

The unparalleled technical and economic performance of OxyTek™-ADT stabilization is the synthesis of a naturally occurring geologic phenomenon. Members of the apatite group of crystalline minerals exhibit the property of isomorphism, which may be defined as follows:

Isomorphism - *A condition present when an ion at high dilution is incorporated by mixed crystal formation into a precipitate, even though such formation would not be predicted on the basis of crystallographic and ionic radii; an example is the coprecipitation of lead with calcium chloride. Any two or more crystalline mineral compounds having different chemical composition, but identical structure, such as the garnet series or the apatite group, are known as isomorphs.*

In an isomorphous mineral certain ions or molecules will enter into the crystal-lattice of a mineral solid without causing any marked change in crystal morphology or other physical properties. For simplicity, this is accomplished by the two ions having similar but not equal radii and the same charge, with the smaller ion radii being preferentially concentrated in early formed specimens of a crystallizing mineral series. For example, a lead (Pb) ion commonly coprecipitates with a calcium (Ca) ion where Pb^{+2} substitutes for Ca^{+2} within a defined crystal lattice to form a common mineral solid. The Pb^{+2} substitution for Ca^{+2} usually occurs based on availability of the closest ion to a vacant crystal-lattice site and in the later stages of the crystallization event when available Ca^{+2} has been naturally depleted (or if the available Ca^{+2} can be manipulated out of the system).

The OxyTek™-ADT stabilization process initiates the formation of isomorphous minerals that are representative of the reaction-series association existing between a series of stable mineral solids with analogous chemical formulas and crystal forms. (Note – Analogous formulas possess an identical number of atoms and valences and analogous crystallographic forms are geometrically similar crystal-units in which an equal number of atoms are geometrically arranged in a similar manner). When the atoms have similar sizes and similar physical properties (e.g. specific gravity, optical properties, etc.) a stable isomorphous situation exists.

All precipitation/crystallization reactions tend to carry other constituents (ions) from the mother-solution. Actual precipitation/crystallization occurs in a succession of steps as the process seeks equilibrium. The driving force for precipitation/crystallization is coincident crystal nucleation and heat loss. Initial nucleation is characterized by expanded growth-rate, and greater opportunity for substitutions in the crystal's structure. This mechanism leads to the desired formation of coprecipitated isomorphous minerals in a reaction-series. As coprecipitation accelerates, the larger crystals grow at the expense of smaller crystals with the smaller crystals dissolving and reprecipitating on the surfaces of larger crystals.

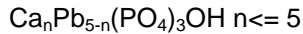
The process continues until equilibrium is reached and the mother-solution is depleted by initial nucleation, coprecipitation, and post-coprecipitation. Problematic heavy metal ions are effectively rendered stable, insoluble and non-hazardous within distinct new mineral species.

There are more than 300 apatite isomorphs. One of the most common is fluoroapatite, $Ca_5(PO_4)_3F$; the principal constituent of bone and teeth. Another form is hydroxyapatite, which has the following formula:





Lead, strontium, zinc, and other metal ions will preferentially substitute for calcium within the hydroxyapatite crystal structure, leading to a formula such as the following:



Other materials may substitute at other points in the crystal. F (fluorine) or Cl (chlorine) can substitute for OH (hydroxyl), SO₄ (sulfate) or AsO₄ (arsenate) may substitute for PO₄ (phosphate), etc. Substitutions do not change physical structure and have minimal effects on physical properties. Substituted apatites are durable (Mohs hardness is 5.0), resist pH transients (2-13), and will stand up under elevated temperatures (>1200°C). Exposed apatites exist largely unchanged in nature for millions of years.

Working at Contaminated Sites

During a site remediation the key question is whether or not apatite formation can be initiated synthetically, under field conditions. Fortunately, apatite synthesis at ambient conditions is simple and very rapid. Three things are required, as follows:

1. The appropriate reagent mixture.
2. Energy - to initiate and accelerate the formation reaction.
3. Nucleation points - to focus initial formation, and then be taken up in the new mineral.

In some instances, each of these requirements is met with a single reagent. In some cases, additional reagents will improve economic and technical performance.

Treatment involves distributing the required amount of reagent(s) within the contaminated media. The natural penetration characteristics of liquid/solid phosphatic reagents reduce the necessity for aggressive mixing. The reagent immediately initiates chemical reactions, which form microscopic apatite crystal forms, and the apatite crystals isomorphically substitute heavy metal contaminants within their structure, eliminating or reducing leachability drastically.

The Multiple Extraction Procedure (SW-846, Method 1320) is an excellent method to evaluate the longevity of the OxyTek™-ADT stabilization treatment process.

The Evolution from Ex-Situ to In-Situ OxyTek™-ADT Stabilization

Many remediation project managers who have dealt with the logistical challenges of excavating, staging, processing, storing, and disposing of materials during ex-situ treatment operations have wanted the potential simplicity of an in-situ treatment. Most remediation processes do not lend themselves to in-situ operations, but the OxyTek™-ADT stabilization process does.

The challenges of in-situ treatment include the following:

- Containment. We don't want the treatment agent getting away from us.
- Control. Process parameters must be maintained within limits.
- Access. How do you get treatment to contaminated media below the surface?

The OxyTek™-ADT stabilization process has solutions to all of these challenges. Containment is not a problem because the required amount of reagent addition is almost always less than 5% of treated media (by weight) and all reagents are consumed during initial reactions. Control is



enhanced by using reagents with excellent penetration and distribution properties and by the fact that precision is rarely critical. Penetration to depths vary with soil type with ranges of 12"-24" in soils, sediments, and sludges. If contamination goes to even greater depths, treatment is accomplished in lifts.

Reagent application during in-situ operations is simple. A laborer applies the reagent mixture directly to contaminated media, often from a simple hose and nozzle. A defined area is staked out, perhaps 25' square. The reagent mixture is applied evenly over the specified area using conventional excavators, backhoes and other soil moving equipment. The reagent initiates the formation of apatite mineral crystals and the crystals do the rest.

Excavation for off-site disposal, or to provide access to a new layer of contaminated soil, can be effected immediately following treatment. Or, since the soil was treated in-situ without being moved, and therefore never became a RCRA waste (assuming it is not a listed waste, or local state Totals values do not preclude), it could be possible to leave the soil in place.

Treatability Studies

Standard format, methodically conducted, laboratory glassware treatability studies are an important first step in the implementation of any remediation technology. No scale-up issues are associated with our treatment process, so laboratory test results are suitable for defining full scale processing parameters and for providing contractual performance guarantees. Steps include the following:

1. Contaminated media characterization. Total metals, metal valence state (where appropriate), TCLP leachable metals, pH, moisture content, soil classification (standard system), etc.
2. Selection of 2 or 3 preliminary treatment protocols, based upon prior experience.
3. Conduct selected treatment protocols on samples. Test for post-treatment TCLP leachable metals.
4. Select a cost effective treatment regime, which also meets other performance goals established for the site.