Amendments refer to materials that can be added to natural capping materials (e.g., sand or soils) or can be used on their own without the addition of other materials. Amendments are intended to enhance the chemical isolation properties of the cap. The 2014 Contaminated Sediments Remediation guidance document (ITRC 2014) included a list of amendments that is expanded in this appendix based on new information that has become available since that guidance was published.

The use of amendments can reduce the thickness and increase the chemical isolation performance of a cap. Typical objectives when using amendments are listed below (ITRC 2014):

- reduction of permeability at the sediment–water interface to limit contaminant transport through interstitial water exchange processes, such as groundwater upwelling or tidal pumping
- optimization of the sorption capacity of the cap layer, which reduces contaminant flux while also reducing the thickness of the cap
- enhancement of contaminant transformation and degradation processes to reduce or eliminate contaminant release into the overlying water

Determination of the quantity of amendments applied and the relative thickness of the layer is determined during the design and modeling stages (see Sections 3 and 5). Often, the dose or quantity of raw amendment is blended or added to a bulking material (i.e., sand or aggregate), but many can be pre-blended and placed directly depending on the selected construction method.

Amendments commonly used to enhance cap chemical isolation are described below. This list identifies the most commonly applied and regulatorily accepted amendments, and also includes some of the less common (or newer and more innovative) potential amendments.

A. Low-Permeability Clays

A cap or cap layer constructed using bentonite clays or other fine-grain materials is generally intended to minimize contaminant transport from sediments at the sediment–water interface or from within the overlying cap to the surface water. Low-permeability clay caps/cap layers provide effective chemical isolation and limit interstitial water exchange processes, such as groundwater upwelling or tidal pumping. Bentonite-based low-permeability materials have been used in a wide range of environmental applications for decades. As an alternative to, or addition to, other adsorptive capping amendments, low-permeability clay amendments have been installed at full scale to enhance cap performance and design life by decreasing porewater advection. The raw bentonite clays or mat-based products (i.e., geosynthetic clay liners) can be used to effectively divert upwelling groundwater away from a contaminated sediment area. Commercial products are available that can place clays directly through the water column. AquaBlok®, a bentonite clay and polymer-based mineral formed around an aggregate core, is one effective capping material (John H Hull, Jersak, and McDonald 1998). AquaBlok® can settle to the bottom of the water column and form a cohesive boundary with minimal intermixing with the underlying contaminated sediment and provide hydraulic conductivity on the order of 10^{-9} cm per second. Geosynthetic clay liner mats have been used as a low-permeability cap at several sediment projects, including the Galaxy/Spectron, Marathon Battery, and Lower Duwamish sites. Placement and incorporation of clay materials into amended caps has been performed at dozens of full-scale installations throughout the United States, and success of the approach has been documented in five-year monitoring events at Superfund sites such as the Tennessee Wood Products site on Chattanooga Creek (USEPA 2011b). Permeability control with clay materials can be used in effective cap designs provided gas or water upwelling is negligible or managed by the design. Natural sodium bentonite clay can become several orders of magnitude more permeable in brackish water and saltwater (Shackelford et al. 2000); however, clay blends exist that can provide low permeability in marine environments. It is important to understand the level of salinity and mineral composition of clays being applied for this purpose.

B. Activated Carbon

Activated carbon is known to strongly adsorb hydrophobic organic contaminants that are commonly associated with sediments (e.g., PCBs and petroleum compounds at MGP sites) and thus has become one of the most widely studied and accepted treatment amendments. Activated carbon has been used in a raw granular form (GAC) mixed with sand, in a powdered form (PAC) with the use of weighting agents, and in the form of a geotextile mat containing GAC. Placement of activated carbon for capping is difficult due to the nearly neutral buoyancy of this material. Placement methods have been developed that seek to overcome this fundamental issue. Examples of weighting systems for delivery of PAC include both

AquaGate+®PAC (a PAC delivery system that uses the AquaBlok® technology) and SediMite™ (Ghosh et al. 2011; C.A. Menzie 2012). Examples of the geotextile approach use a Reactive Core Mat® (McDonough et al. 2007) or Tektoseal® Active (Australasian Chapter of the International Geosynthetics Society 2023). In addition to the above placement approaches, a pre-hydrated GAC mixed with sand has been applied at multiple sites over the last decade, including at Lake Onondaga (Patmont et al. 2015), which was one of the largest single applications of activated carbon at a contaminated sediment site.

Care must be taken when placing a GAC/sand mixture to ensure, confirm, and document a uniform as-constructed mixture of GAC within the capping layer. Activated carbon has also been modified or impregnated with amendments (i.e., sulfur, microbes) to enhance performance under specific conditions. Multiple successful applications of each of these placement approaches has demonstrated that placing a high-cost, difficult-to-handle material such as activated carbon in a controlled manner is feasible and that typical design objectives can be achieved.

C. Organophilic Clays

Organophilic clays, also known generically as organoclay, are created by introducing a cationic surfactant onto the surface of clays. Unlike low-permeability clay, virgin granular organophilic clay has a permeability similar to sand in “clean” water. Once exposed to hydrocarbon-based contaminants, the clays swell and permeability is reduced. Organophilic clay is not affected by brackish water or saltwater. These clays can be used in caps to create a hydrophobic, adsorbing functional layer for nonpolar organics, which is effective for control of NAPLs in particular (D Reible et al. 2007), such as fuels and heavy oils, dissolved PAHs, and NAPL present at MGP sites. Organophilic clays have also been evaluated for sorption of heavy metals and methylated mercury (Knox et al. 2016; Gilmour et al. 2013). An organophilic clay cap has been used for sediment remediation at the McCormick and Baxter site (Parrett and Blishke 2005; Danny Reible, Lu, and Blishke 2005) and several other sites, including multiple sites on the Grand Calumet River (e.g., East Branch Grand Calumet River 2015 [Case Study No. 4 in Appendix A]). Placement of granular organophilic clay can be challenging for reasons similar to those for activated carbon (i.e., lower relative bulk density than sand or other bulking materials), but placement systems have been developed by contractors that are intended to overcome these challenges. Weighting agents can also be applied to organophilic clay placement (e.g., AquaGate+®Organoclay); these agents have been demonstrated to be effective at numerous full-scale installations (Case Study No. 4 in Appendix A). In addition, granular organophilic clay has been placed in the form of a geocomposite where the material is contained between two geotextile layers (e.g., Reactive Core Mat®, Tektoseal® Active).

D. Zeolites

Zeolites are microporous aluminosilicate minerals with a high cationic exchange capacity. Theoretically, zeolites should be effective in an active barrier system or functional layer intended for containment of metals (Patrick H. Jacobs and Förstner 1999). One study found that zinc and iron were effectively demobilized using a zeolite-based amended capping system (P.H. Jacobs and Waite 2004). Knox, Paller, and Dixon (2014) demonstrated that a thin cap of zeolite over Anacostia River sediments effectively reduced heavy metal concentrations in lab mesocosms.

E. Apatites

Apatites are a class of naturally occurring minerals that have been investigated as a sorbent for metals in soils and sediments (Conca and Wright 2006; Chen et al. 1997; Peld, Tõnsuaadu, and Bender 2004). Apatites consist of a matrix of calcium phosphate and various other common anions, including fluoride, chloride, hydroxide, and occasionally carbonate. These minerals sequester metals either through direct ion exchange with the calcium atom (Miyake, Ishigaki, and Suzuki 1986; Takeuchi and Arai 1990) or dissolution of hydroxyapatite followed by precipitation of the metal phosphate mineral (Ma et al. 1993; Xu, Schwartz, and Traina 1994). Commonly used sources for apatite are processed animal bones and mined fossilized bones, such as from fish. Pilot-scale apatite caps have shown reductions in lead, cadmium, and zinc porewater concentrations and reduced bioaccumulation of cadmium compared to control (sand) caps (Crannell et al. 2004). One successful implementation of an apatite cap for control of metals was conducted in the Anacostia River in Washington DC (Danny Reible et al. 2006). Solid-phase concentration profiles suggested effective containment of the underlying contaminated metals six months after cap installation.

F. Microorganism Bioaugmentation/Nutrient Addition/Siderite

Laboratory and pilot-scale field studies have demonstrated that an activated carbon amendment can be used to deliver microorganisms that have the potential to perform dechlorination of PCBs (Sowers 2019). Bioamended activated carbon has been reported to reduce both the total mass and soluble/bioavailable fractions of PCBs with reduction in toxic equivalency of coplanar PCBs.

Two other novel amendments were used at Onondaga Lake, New York. The first was a nutrient-based amendment that involved the addition of a nitrate to sediments to control the formation of methylmercury. This large-scale nutrient addition successfully reduced the formation of methylmercury that had been impacting aquatic life (Matthews et al. 2013). The second amendment used was Siderite (a ferrous carbonate mineral). This was used within the capping layer to provide for pH adjustment to the porewater moving up through the capping layer. The purpose was to provide pH adjustment and enhance mineralization of dissolved metals.

G. Lab-Scale Amendments

A number of materials have been evaluated at a lab scale for their potential to sequester various metals from sediments, sometimes in combination with other hydrophobic contaminants. Various amendments studied for this purpose are listed below:

- Zero-valent iron (ZVI) is an amendment used for soil and sediment remediation that provides a reactive surface that can chemically reduce and subsequently immobilize a variety of compounds (Li, Elliott, and Zhang 2006). Degradation of mixtures of PCBs and other chlorinated compounds have been reported through reactions with ZVI (Wang and Zhang 1997). Other laboratory-scale feasibility assessments have shown the potential for use of ZVI to treat nitroaromatic compounds (Agrawal and Tratnyek 1996), arsenic (Kanel et al. 2005), chromium (VI), and lead (II) in aqueous solutions (Ponder, Darab, and Mallouk 2000) and dichlorodiphenyltrichloroethane and related compounds (Sayles et al. 1997). More pilot and field-scale demonstrations are needed, however, to assess the long-term feasibility of ZVI as a capping amendment.
- activated alumina/aluminum and iron oxide—Sorbster® (Sorbster, Inc.), bauxite / bauxite residue / red mud (Alcoa)
- manganese oxides—amorphous manganese oxide (Carus, Inc.)
- ion exchange resins—SIR-300, Amberlite IX resin (Rohm & Haas)
- engineered materials—ATS (cation exchange ceramic, Engelhard), Thiol functionalized mesoporous silica (Th-SAMMS, Steward Environmental Solution Inc.)
- sulfide minerals—Mackinawite structure iron sulfide, Redox Solutions
- other carbonate minerals—Sidco Minerals
- biomaterial byproducts—oyster shell powder, Chitosan (crab-shell-product polysaccharide)
- PFAS targeted amendments—activated carbon-based materials, RemBind®, and Fluoro-Sorb®