Monitored Natural Attenuation for Coal Combustion Product Constituents in Groundwater
Jim Redwine¹, Bruce Hensel²

¹Anchor QEA, LLC, One Perimeter Park South, Suite 100N, Birmingham, AL 35243; ²Electric Power Research Institute, Inc., 3420 Hillview Ave, Palo Alto, CA 94304

Abstract

Monitored natural attenuation (MNA) can be a component of corrective action for impacted groundwater at coal combustion product (CCP) management facilities. The Electric Power Research Institute (EPRI) examined 24 inorganic constituents of interest with respect to CCP and determined how MNA could be used as a viable corrective measure for groundwater. Where site conditions are conducive to MNA, it has potential to provide a sustainable and cost-effective remedial alternative, either as a stand-alone remedy or as part of a remedy involving other remediation technologies. For example, MNA can provide a polishing step in corrective action where other technologies address areas with higher concentrations of constituents or greater risk.

In this study, constituents were carried through the U.S. Environmental Protection Agency’s (USEPA’s) four phases (tiers) of MNA: 1) area of groundwater impacts not expanding; 2) mechanisms and rates of attenuation; 3) aquifer capacity for attenuation and stability of attenuating mechanisms; and 4) monitoring program and contingency plans should MNA not perform as expected.

One key component of MNA is identifying MNA processes. Chemical attenuation processes for CCP constituents include 1) precipitation and coprecipitation, such as incorporation into sulfide minerals; 2) sorption to iron, manganese, aluminum, or other metal oxides or oxyhydroxides, or sorption to sulfide minerals or organic matter; and 3) ion exchange. Physical processes such as dilution, dispersion, and flushing can reduce concentrations of constituents and can be considered in MNA evaluations.

The EPRI study also evaluated tools and techniques to meet the requirements of each of USEPA’s four phases and typical time frames for natural attenuation to be effective.

Introduction

Monitored natural attenuation (MNA) has been an accepted corrective action alternative for inorganic and organic constituents since the 1990s. Several guidance documents are available for MNA, including Monitored Natural Attenuation of Inorganic Constituents in Ground Water, Volumes 1 and 2 (USEPA 2007a, 2007b); Use of Monitored Natural Attenuation for Inorganic Contaminants at Superfund Sites (USEPA 2015); and Monitored Natural Attenuation for Inorganic Constituents in Coal
Combustion Residuals (EPRI 2015). In this study, the Electric Power Research Institute (EPRI) evaluated MNA for 24 inorganic constituents, including most Appendix III and Appendix IV constituents (U.S. Environmental Protection Agency [USEPA] coal combustion residuals rule 40 Code of Federal Regulations Part 257 Subpart D). Though few case histories are available from the electric utility industry to date, MNA has been widely evaluated for inorganic constituents in other industries, particularly mining and minerals processing. Each inorganic constituent was examined in the context of USEPA’s four phases of MNA, as described in the next section.

USEPA Protocols for MNA

USEPA defines MNA as follows:

…the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The “natural remediation processes” that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater (USEPA 1999, 2015).

USEPA’s requirements for MNA, formerly known as tiers, are as follows (USEPA 1999, 2007a, and 2015):

1. Demonstrate that the area of groundwater impacts is not expanding.
2. Determine the mechanisms and rates of attenuation.
3. Determine that the capacity of the aquifer is sufficient to attenuate the mass of constituents in groundwater and that the immobilized constituents are stable and will not remobilize.
4. Design a performance monitoring program based on the mechanisms of attenuation and establish contingency remedies (tailored to site-specific conditions) should MNA not perform adequately.

Minimum requirements for MNA implementation will likely include demonstrating that the impacted area is stable or shrinking and identifying a stable mechanism or mechanisms of attenuation. The first requirement can be satisfied through ongoing groundwater monitoring. Identifying attenuating mechanisms is described in the next section. Assessments of corrective measures for CCP sites may include remedies other than MNA, in which case the contingency remedies in the fourth requirement above can be satisfied through the assessments of corrective measures.
Attenuation Mechanisms and Stability of Immobilized Constituents

EPRI (2015 and 2018) provide attenuation mechanisms for the 24 inorganic constituents studied. Physical mechanisms, such as dilution, dispersion, and flushing, are operative for all constituents and may be the primary attenuation mechanisms for those that are poorly chemically attenuated such as boron, chloride, and lithium.

Chemical attenuation mechanisms include precipitation and coprecipitation; ion exchange; and sorption to various materials, including iron, manganese, and aluminum oxides and hydroxides, sulfide or other minerals, or organic matter. Because of the abundance of iron in natural systems, sorption to iron compounds (e.g., ferrihydrite) and coprecipitation with and sorption to iron sulfides (e.g., pyrite or its precursors) are expected to be major attenuating mechanisms for several CCP constituents.

Analysis of groundwater and aquifer solids can be used to evaluate attenuation mechanisms, capacity of the aquifer for attenuation, and stability of the immobilized constituents. EPRI (2015 and 2018) describe several tools and techniques to achieve USEPA’s second and third requirements for MNA. These tools and techniques include X-ray diffraction, X-ray fluorescence, sequential chemical extraction, scanning electron microscopy, conventional wet chemical analysis, geochemical analysis such as Eh-pH (Pourbaix) diagrams, geochemical and groundwater modeling, and several others.

MNA Compared to Other Corrective Action Technologies

MNA is compatible with most (if not all) corrective action technologies at CCP sites, and can be a sole remedy or a component of corrective action at CCP sites. Because of slow desorption of some inorganic constituents from aquifer solids, more intensive technologies, such as pump-and-treat or permeable reactive barrier walls, may not offer a significant time advantage over MNA. Based on MNA case histories for inorganic constituents in other industries, proposed times for MNA to achieve groundwater protection standards range from 5 to 150 years, with 10 to 40 years being the most commonly proposed (EPRI 2015).

References


USEPA (U.S. Environmental Protection Agency), 1999. Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage

