Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 144 (2007) 1–14
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Review

Phosphate application to firing range soils for Pb immobilization: The unclear role of phosphate

Maria Chrysochoou*, Dimitris Dermatas, Dennis G. Grubb

W.M. Keck Geoenvironmental Laboratory, Stevens Institute of Technology, Castle Point on Hudson, Hoboken, NJ 07030, USA

Received 22 March 2006; received in revised form 30 January 2007; accepted 5 February 2007
Available online 12 February 2007

Abstract

Phosphate treatment has emerged as a widely accepted approach to immobilize Pb in contaminated soils and waste media, relying on the formation of the highly insoluble mineral pyromorphite as solubility-controlling phase for Pb. As such, phosphate treatment has been proposed as a Best Management Practice (BMP) for firing ranges where Pb occurs in its metallic forms and several other phases (carbonates, oxides). While pyromorphite thermodynamically has the potential to control Pb solubility at low levels, its formation is kinetically controlled by pH, the solubility of the phosphate source, and the solubility of Pb species. Treatability studies have shown that excess quantities of soluble and acidic phosphate sources, such as phosphoric acid, are necessary for successful in situ treatment. Even under these conditions, Extended X-ray Absorption Fine Structure (EXAFS), the only reliable method to identify and quantify Pb speciation, showed that Pb conversion to pyromorphite in in situ treated soils was less than 45% after 32 months. Furthermore, the use of lime (CaO) to restore soil pH in acidified soil treatments inhibited further conversion. Additionally, phosphate treatment is known to reduce bioavailability through pyromorphite formation in the intestinal tract, and the phytoaccumulation of Pb; both desirable effects for Pb-impacted areas. Given the costs of phosphate treatment, the use of biogenic phosphate sources, such as bone meal, may be a more environmentally sustainable approach toward this end. In the many studies focusing on phosphate treatment, the attendant P leaching and eutrophication have been largely overlooked, along with other issues such as the enhanced leaching of oxyanionic contaminants, such as Se, As and W. The success and sustainability of applying phosphate as a BMP in firing range soils therefore remain questionable.

Keywords: Lead; Soil stabilization; Phosphate; Firing ranges; Eutrophication

Contents

---

* Corresponding author. Tel.: +1 201 216 8773; fax: +1 201 216 8212.
E-mail address: mchrysoc@stevens.edu (M. Chrysochoou).

0304-3894/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2007.02.008

1. Introduction

Lead (Pb) contamination in soils has received much attention in recent years and several remedial alternatives have been proposed and researched, such as physical and chemical extraction and stabilization/solidification (S/S). Among these, the use of phosphate as a stabilizing agent to remove soluble Pb from the aqueous phase was suggested as early as 1974 by Nriagu [1] in a comprehensive study on the formation and properties of lead orthophosphates. Since then, extensive research on phosphate treatment of Pb-contaminated soils and solid waste has lead to the broad acceptance of phosphate as a stabilizing agent for Pb-contaminated media.

Firing ranges are the second most important source of Pb contamination according to a study by the U.S. Geological Survey [2]. In 2001, the U.S. Environmental Protection Agency (USEPA) issued a manual on Best Management Practices (BMPs) for lead in outdoor shooting ranges, acknowledging the need to minimize Pb release in the environment through range maintenance activities [3]. Among the BMPs to prevent Pb migration in soils, the USEPA included phosphate application to bind Pb particles, alone or in conjunction with lime (the latter used for pH control of acidic soils). The USEPA recommendation was based (though not explicitly stated in the manual) on the results of a series of studies on Pb immobilization in phosphate-treated soils, including their own study. Although the number of studies on phosphate-based soil treatment is quite high, there are still many unresolved questions regarding its in situ viability and environmental sustainability.

A key question when considering remedial choices or BMPs is whether the proposed approach is economically and environmentally sustainable. In other words, an investment on studying the effectiveness and the engineering details of a treatability scheme is only worth undertaking when the treatment: (a) has a potential to be financially viable in field scale applications; and, (b) does not compromise the environment in other ways. A treatability study is then directed to assess the effectiveness of treatment in reducing the contaminant concentration below an acceptable (usually regulatory) level. Furthermore, the mechanisms and kinetics of contaminant removal/immobilization need to be established to reliably predict treatment in the short- and long-term under different conditions.

The authors of this paper participated in an extensive investigation on metal contamination in firing ranges operated by the U.S. Department of Defense (U.S. DoD); the results on Pb speciation and leaching behavior for several ranges are presented in Dermatas et al. [4–8] and Dermatas and Chrysochoou [9]. The characteristics of the examined sites varied greatly with respect to such factors as the magnitude of Pb concentration, Pb fragment particle size distribution, soil pH, particle size and the mineralogy of the soils. Consequently, the remedial investigation involved the screening of a number of available technologies, including phosphate. The current literature review was conducted to identify and verify Pb immobilization mechanisms under different conditions. Thus, the review broadly includes studies on Pb-contaminated media other than shooting ranges, but the conclusions are primarily drawn with regard to phosphate application in firing ranges, both as a preventive measure, remedial option and BMP, which introduces sustainability issues.

The review attempts to examine the following questions:

1. Which are the thermodynamic constraints for formation and stability of insoluble lead phosphates?
2. Which are the parameters that affect the kinetics of lead phosphate formation and how can they be optimized under field conditions?
3. Which criteria can be used to evaluate treatment success? Which are the most pertinent in the case of firing ranges?
4. Which are the environmental impacts of phosphate-based treatment and how do these vary under different conditions?
5. When is phosphate treatment necessary/appropriate?

2. Theoretical background

The principal mechanism of Pb stabilization by phosphate, as put forth by Nriagu [1], is the formation of the mineral pyromorphite ($Pb_5(PO_4)_3X$ where $X = Cl^-, OH^-, F^-$). Depending on the monovalent ion in the structure, pyromorphite may be encountered as chloropyromorphite (CP), hydroxypyromorphite (HP) or fluoropyromophite (FP), the chlorinated species being the most stable form, followed by the hydroxylated and fluorinated species [1,10]. The term pyromorphite in the text will generally refer to all three species unless otherwise noted. Nriagu [1] constructed the stability field diagrams for Pb considering the mutual presence of phosphate, sulfate, carbonate and chloride and found that CP was the most stable Pb species in the pH range 3–11. Cerussite ($PbCO_3$) was predicted as the dominant species at pH 11–13 and massicot (PbO) at $pH > 13$ with Eh values > -400 mV. The redox potential was predicted to be the controlling factor for the relative stability of galena (PbS) and pyromorphite at pH 3–11, with -270 mV being the lower threshold for CP stability at neutral pH. Nriagu [1] consequently suggested that the formation of the insoluble pyromorphite could be an effective mechanism to stabilize Pb in natural waters and sediments, and to remove both Pb and phosphate from wastewater. However, Nriagu [1] pointed out that this natural mechanism had previously escaped the attention of geochemists in diagenetic sediments, probably owing to the slow dissolution of phosphate, its low solubility with respect to natural apatites, and the potential co-precipitation of Pb with Ca in apatites. Pyromorphite also escaped identification in subsequent studies, as reported by Cotter-Howells et al. [11], due to the extensive Ca substitution that shifted pyromorphites' lattice constants and its peak positions in X-ray diffractograms. Cotter-Howells et al. [11] identified CP as the predominant Pb-bearing phase in mine-waste soils by means of analytical transmission electron microscopy (ATEM) and X-ray absorption spectroscopy (XAS). Analyses of the high-density soil fractions showed that Pb was almost exclusively associated with CP, with a phosphorus-to-lead ratio of approximately 0.6, based on the total concentrations provided by Cotter-Howells et al. [11]. Given the fact that Cotter-Howells et al. [11] studied lead mine wastes originating back to 1750, equilibrium of Pb with the available soil phosphorus was probably established and therefore was not a limiting fac-