ABSTRACT

PHOSPHATE AND THERMAL STABILIZATION OF HEAVY METALS IN DREDGED SEDIMENTS

by
Peter Kuria Ndiba

Treatment and reuse of dredged harbor sediments in construction as an alternative to disposal reduces costs and conserves resources. This research focused on leachability of metal contaminants subsequent to phosphate addition and thermal treatment at 700 °C. X-ray absorption spectroscopy (XAS) in combination with principal component analysis, target transformation, and linear combination revealed that in the untreated sediments Zn precipitated as the relatively soluble smithsonite ($ZnCO_3$) (67%) and adsorbed to hydrous iron oxides (15%) and hydrous manganese oxides (18%). Phosphate addition and calcination resulted in sparingly soluble phases, hopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$) (22%), and spinels, gahnite ($ZnAl_2O_4$) (44%) and franklinite ($ZnFe_2O_4$) (34%). Sequential extraction revealed similar shifts in metal forms from labile to recalcitrant residuals for Ni, Cu (spinels), Mn (crystalline oxides), Pb (phosphate mineral), Cd (alumino-silicate), and Co (adsorption to cryptomelane). The U.S. EPA toxicity characteristic leaching procedure (TCLP) confirmed both phosphate addition and calcination reduced leachability of metals with the combined treatment achieving up to an 89% reduction. In beneficial reuse, the synthetic precipitation leaching procedure (SPLP) revealed that impact to groundwater criteria can be achieved in the treated sediments but will be dependent on the applied dilution attenuation factor (DAF). This research demonstrates the importance of evaluating speciation alongside leaching behavior in developing accurate prediction and assessment of risks posed by waste materials.

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by

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This dissertation is dedicated to
my parents who set me on the path to education

and to

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CHAPTER 1

INTRODUCTION

Regular dredging of harbors and waterways is necessary for the maintenance and extension of water depths. The dredged materials (sediments) are often contaminated with heavy metals and organics and, therefore, their disposal is expensive and unsustainable. Treatment and reuse as construction material is highly desirable as it reduces costs and conserves resources. Many of the existing treatment technologies for reuse involve thermal application for production of cement, lightweight aggregate, bricks, and ceramic and glass tiles. However, few of these technologies are commercially used because of high costs and the large quantities of sediments involved (Mulligan et al., 2001; Burt and Fletcher, 1998); as such, there is need for further development.

In this research, the potential for phosphate addition followed by calcination at 700 °C to stabilize heavy metals and mineralize organics for beneficial reuse in construction was investigated. While phosphate minerals are used widely to stabilize metals in sparingly soluble phosphate minerals (Ma et al., 1995; Crannell, 1997; Chen et al., 1997), the role of the thermal treatment in metal sequestration is not well understood. Several studies (e.g., Nzihou and Sharrock, 2002; Sørensen et al., 2000; Wei et al., 2001; Shih et al., 2006) aimed at understanding behavior and form suggest formation of low solubility phases such as spinels. More specific to the issue of stabilization is an understanding of speciation to elucidate precipitation/sorption mechanisms. Heavy metals in sediments may exist as amorphous, poorly crystalline, or low-concentration crystalline phases. To study their speciation, a suite of analytical techniques including X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), and sequential extraction is employed. Additionally, thermodynamic analysis is used to evaluate stability of the observed species.

Beneficial reuse of treated sediments requires demonstration that contaminant leaching is within regulatory limits; as such, standard leaching procedures including the U.S. Environmental Protection Agency (EPA) toxicity characteristic leaching procedure (TCLP) (U.S. EPA, 1992) and synthetic precipitation leaching procedure (SPLP) (U.S. EPA, 1994) are conducted. Furthermore, understanding the impact of environmental variables such as pH, complexing ligands, and time is needed to address potential long-term beneficial use.

This dissertation includes a review of the problem of contaminated sediments, available stabilization techniques, assessments of contaminant leaching, and risk to groundwater regulatory framework. Objectives and hypotheses are stated and methodology described. Results of sediments characterization, XAS speciation study of Zn which was abundant in the sediments studied, sequential extraction, and leaching assessments, are presented and discussed. Finally, conclusions are drawn and future research described.

CHAPTER 2

LITERATURE REVIEW

Sustainable management of dredged sediments through treatment and reuse requires an understanding of the amended structure. This chapter addresses the problem of contaminated sediments and reviews available treatment methods. Phosphate addition and thermal treatment is reviewed as a potential sediment stabilization technique for reuse in construction. Procedures for assessment of metal speciation to elucidate stabilization mechanisms are examined. Finally, leaching assessments for management of wastes and other materials and applicable regulations are reviewed.

2.1 The Problem of Contaminated Sediments

Sediments are continuously deposited in rivers, lakes, and shorelines through the natural processes of erosion, transportation, and deposition. Because of their capacity to adsorb contaminants, sediments act as an important sink (Thibodeaux, 1996; Vdović et al., 2006); their contamination can adversely affect the health of aquatic organisms impacting the food chain (Lyman et al., 1987; Peplow and Edmonds, 2005). The U.S. EPA (2004) reported that some of the most severely contaminated sediments in the U.S. were found in harbors and waterways. Harbors are an important focus for industrial and urban activities which, however, release pollutants through oil spills, leaks of industrial products, corrosion of vessels, and emissions of wastewater. Because harbors are designed to minimize hydrodynamic energy, the pollutants usually accumulate in sediments (Guevara-Riba et al., 2004). Harbors and waterways are dredged regularly to maintain and sometimes extend water depths. The amount of material excavated is enormous; for example, 3 to 5 million m^3 annually in maintenance and improvement (Douglas et al., 2003) and 55.5 million m^3 in a deepening project (Yozzo et al., 2004) at the New York/New Jersey (NY/NJ) Harbor, which raises the question of disposal. Historically, dredged materials have been relocated to open waters, rivers, and estuaries or placed in wetlands (Lager et al., 2005; Yozzo et al., 2004). However, enactment of stringent ocean disposal criteria under the Marine and Protection, Research and Sanctuaries Act (MPRSA, 2000) reduced the volume of materials acceptable for open sea disposal (Jones et al., 2001). Consequently, contaminated sediments are managed through placement in confined disposal facilities which is expensive. Consideration is increasingly being given to reuse applications such as remediation and redevelopment of brownfields and reclamation of abandoned mines (Douglas et al., 2003; Gardner et al., 2007). Furthermore, beneficial reuse in road-base construction has been considered (e.g., Siham et al., 2008). Before reuse, sediments are screened with site specific criteria and in some cases stabilized with lime and cement (Douglas et al., 2003). However, these reuse applications may be inappropriate as continued volatilization of polychlorinated biphenyls (PCBs) was observed in cement-stabilized sediments used as fill (e.g., Miskewitz et al., 2008). Furthermore, Gardner et al. (2007) found organic matter in sediments enhanced release of heavy metals, Cd, Cu, Ni, Pb, and Zn, through complexation. Therefore, a sustainable sediment treatment which addresses organics as well as heavy metals is needed.

Existing treatment technologies include physical separation, washing, stabilization/solidification, thermal processes, and biological decontamination (Mulligan et al., 2001). These technologies have been for the most part adopted from those applied on contaminated soil and in the mining industry; however, comparatively, sediment treatment is more expensive because of the high water content (over 50%) and the large quantities involved (Burt and Fletcher, 1998; Mulligan et al., 2001). Many treatment technologies for reuse in construction involve thermal application to produce cement, lightweight aggregates, bricks, and ceramic and glass tiles (Hamer and Karius, 2002; Jones et al., 2001; Mulligan et al., 2001; Dalton et al., 2004). The appeal of high temperature processes stems from their capacity to mineralize organics and immobilize metals by incorporating them in glassy-like matrix (Jones et al., 2001; Karius et al., 2001). However, because of the high costs involved, few of these technologies are commercially used (Mulligan et al., 2001); as such, there is need for further development.

2.2 Phosphate Addition and Thermal Treatment

Beneficial reuse of dredged sediments requires that contaminants are removed or immobilized so that they do not pose danger to the environment. The potential for phosphate addition followed by calcination at 700 to 900 °C to stabilize heavy metals into sediments was demonstrated by Kribi et al. (2004). Addition of phosphoric acid at 3 to 10% of sediment by dry weight followed by drying and aging, and calcination at 700 °C (Figure 2.1) reduced metal leachability to within the U.S. Resource Conservation and Recovery Act (RCRA) limits for hazardous material (40CFR, Part 261.24). All organics were mineralized and/or volatilized below 700 °C with off-gas treated by carbon adsorption; further heating sintered minerals resulting in increased density and reduced surface area.

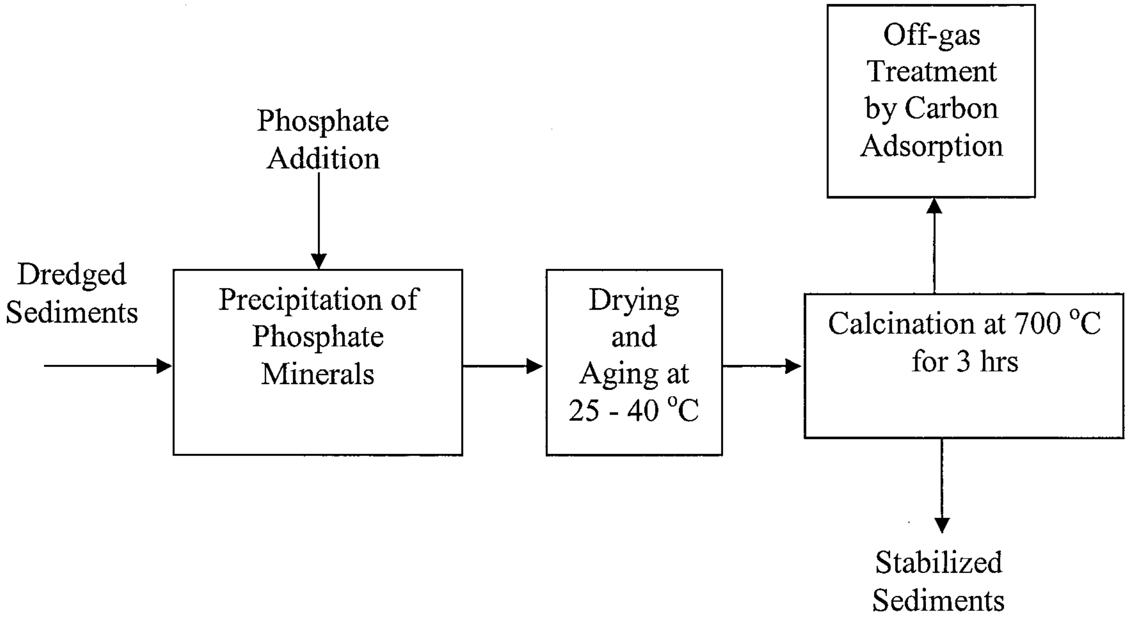

Figure 2.1 Flow diagram of phosphate and thermal treatment of dredged sediments, with the off-gas treated by carbon adsorption.

Phosphate minerals are used widely to stabilize heavy metals in wastes, contaminated soils, and sediments, because of the low solubility of many phosphate minerals (Ma et al., 1995; Chen et al., 1997; Traina and Laperche, 1999; Crannel et al., 2000; Seaman et al., 2001; Kribi et al., 2004). Crannell et al. (2000) along with Chen et al. (1997) found stabilization is predominantly through dissolution of the phosphate form followed by precipitation, and, to a lesser extent, ion exchange, adsorption, and complexation; these studies demonstrated the potential for immobilizing Pb as phosphate minerals, reducing the potential impact to surface and ground waters. Although phosphate stabilization of metals in sediments has been observed (Kribi et al. 2004), the resulting speciation, and the most appropriate source of phosphate have not been identified. Phosphate sources investigated in the past include apatite, natural (rock phosphate and bonemeal) and synthetic ($Ca_5(PO_4)_3(OH, F, Cl)$, phosphoric acid (H_3PO_4), and the phosphates of Ca, Na, and Mg (Ma et al., 1995; Hodson et al., 2000; Wang et al. 2001; Yang and Mosby, 2006). Precipitation of metal phosphates is dependant on an initial availability of phosphate ions in solution and therefore, solubility of the phosphate source. For example, Sugiyama et al. (2002) found β-$Ca_3(HPO_4)_2$, $(CaHPO_4)\cdot 2H_2O$, and $Ca(H_2PO_4)_2\cdot H_2O$ immobilized Pb to a greater degree than did apatite because of greater solubility. Typically, pH conditions of 4 to 7, are necessary for precipitation of metal phosphates, including pyromorphite ($Pb_5(PO_4)_3OH$) and hopeite ($Zn_3(PO_4)_2\cdot 4H_2O$); alkaline conditions precipitated lead oxide fluoride (Pb_2OF_2), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), zincite (ZnO), and hydrozincite ($Zn_5(OH)_6(CO_3)_2$ at the expense of phosphate minerals (Arnich et al., 2003; Chen et al., 1997; Lee et al., 2005). However, more acidic conditions, for example, pH values of 3 to 4 from H_3PO_4 addition, reduced precipitation resulting in increased mobility (Zhang et al., 1998; Arnich et al., 2003; Bournonville et al., 2004). Purity of phosphate forms is important if they are not to result in significant sources for contamination, specifically, groundwater. Consequently, Ma et al. (1993) measured Pb in natural apatite while Zupanic et al. (2004) measured Zn, Cr, Cu, and Co in $Ca(H_2PO_4)_2$ and ($Ca_5(PO_4)_3(OH, F, Cl)$).

The thermal treatment of contaminated sediments is not well understood. Heavy metals in sediments are often observed sorbed to hydrous iron oxide (HFO), hydrous manganese oxides (HMO), and clays; complexed with organics; precipitated as carbonates; or, under reducing conditions, present as metal sulfides (Carroll et al., 2002; Brydie and Polya, 2003; Ibhadon et al., 2004; Boughriet et al., 2007). Chang et al. (2004) observed amorphous HMO crystallized into trivalent manganese oxide (Mn_2O_3) when heated at 500 °C and into hausmannite (Mn_3O_4) at 700 °C. Sørensen et al. (2000) observed crystallization of HFO as hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) when HFO was heated from 600 to 900 °C; interestingly, with crystallization oxide capacity for metal ions decreased. Heavy metals expulsion from inorganic sorbents by calcination coupled with mineralization of organics could initiate their precipitation as minerals; therefore, their mobility in treated sediments would be governed by dissolution.

Combined phosphate addition and thermal treatment was first applied to fly ash (Iretskaya et al., 1999; Nzihou and Sharrock, 2002) where the thermal step was used to agglomerate hydroxylapatite particles by sintering. However, on the basis of reduced leachability of Cu after calcination only, Nzihou and Sharrock (2002) hypothesized that Cu was incorporated into the glassy phase. Similar observations were made for Cu in doped-kaolin heated at 900 °C (Wei et al., 2002) and for Cd and Zn sorbed to HFO after calcination at 900 °C compared to 600 °C (Sørensen et al., 2000). Jones et al. (2001) along with Hamer and Karius (2002) attributed thermal stabilization of metals in soils and sediments to their incorporation in glassy matrix. For nickel-laden sludge sintered with kaolinite, Shih et al. (2006) identified the spinel, nickel aluminate ($NiAl_2O_4$), as the stabilized phase.

2.3 Metal Speciation in Elucidation of Stabilization Mechanisms

Metal speciation in sediments dictates mobility and hence bioavailability, the potential for impact to the surrounding environment. Therefore, understanding speciation helps elucidate precipitation/sorption mechanisms in metal stabilization. Metal forms in sediments have in the past been investigated using sequential extraction (Tessier et al., 1979; Mulligan et al., 2000; Scheinost et al., 2002). Several studies have used microscopic observations such as X-ray diffraction (XRD) and scanning electron microscopy (SEM) to assist in determining metal forms and morphology, respectively, in sediments (Carroll et al., 2002; Isaure et al., 2002; Brydie and Polya, 2003). However, although the microscopic techniques are capable of identifying crystalline compounds of sufficient concentration, they are less effective for measuring the amorphous, poorly crystalline, or low-concentration crystalline phases observed in sediments (Roberts et al, 2002; Wei et al., 2002; Lee et al., 2005; Struis et al., 2004). On the other hand, X-ray absorption spectroscopy (XAS) has proven to be a useful tool for direct assessment of metal speciation in soils and sediments (Isaure et al., 2002; Struis et al., 2004; Kirpichtchikova et al., 2006). Sequential extraction and XAS assessments of metal speciation in sediments are reviewed below.

2.3.1 X-ray Absorption Spectroscopy (XAS)

XAS provides information at the molecular level which allows the molecular structure of a metal to be determined, whether precipitated in a pure mineral, adsorbed, precipitated on another surface, or coprecipitated (Manceau, 1996; Isaure et al., 2002). The XAS measures energy absorption when electrons are excited from a targeted central atom. Above the absorbance edge, scattering of electron waves by neighboring atoms modulates the absorption coefficient. Therefore, the above edge spectra are sensitive to the local structure and can be analyzed to provide molecular details, near neighbor atoms, coordination number, bond lengths, and the mean variation in distances (Bunker, 2003). However, because of heterogeneity in sediments, the bulk XAS spectra are a weighted sum for all species present and, therefore, require deciphering. Multi-shell fitting using crystallographic data (ab initio technique) can determine the most predominant species, but those with weak second shell backscattering can be easily overlooked (Manceau et al., 2000). Linear combination fitting (LCF) of reference mineral spectra can identify and quantify up to three main species; however, it is uncertain whether a complete set of species is obtained and whether the set is unique (Wasserman et al., 1999; Scheinost et al., 2002). An alternative technique, principal component analysis (PCA) addresses the number of species present by deconvolution of spectra into constituent components (Malinowski, 1991). These species are then identified by target transformation (TT) of reference spectra with the principal components, and quantified with LCF.

2.3.2 Sequential Extraction

Extraction is performed by subjecting a waste sample to a sequence of leachants of differing types or strengths where the metals extracted in each step are assumed to be associated with a mineral phase within the matrix (Tessier et al., 1979; Quevauviller, 1998; Filgueiras et al., 2002). Numerous techniques and reagents have been developed and applied to soils, sediments, and sludges; however, none is completely specific (Mulligan et al., 2001; Brydie and Polya, 2003; Ibhadon et al., 2004; Boughriet et al., 2007). Furthermore, the results can vary even with the same reagents, pH, temperature, extractant strength, and liquid to solid ratio (Mulligan et al., 2001). In review of these procedures, Kirpichtchikova et al. (2006) attributed the poor reproducibility to dissolution of non-target metal phases, incomplete dissolution, readsorption and reprecipitation, and modification of the original metal oxidation states. One of the commonly used procedures

(Tessier et al., 1979), groups associated mineral phases into five fractions of increasing stability, namely: ion exchangeable, carbonates, adsorbed to iron and manganese oxides, bound to organic matter, and residuals, with estimated uncertainties of up to 10%. Another procedure is the BCR which was developed by the Standards, Measurements, and Testing (SM&T) programme in an attempt to harmonize the different extraction schemes for comparability of data (Filgueiras et al., 2002). The procedure employs three metal fractions, acid extractable (exchangeable and bound to carbonates), reducible (bound to iron and manganese oxides), and oxidizable (bound to sulfides and organics) (Rauret et al., 1999; Kartal et al., 2006). Sutherland and Tack (2002) found uncertainty in an optimized BCR procedure is typically 15%.

Despite numerous limitations, sequential extraction has been routinely applied on a comparative basis to indicate shifts in metal associations following treatment. Wong and Selvam (2006) investigated transformations of various forms of Cu, Mn, Ni, Pb, and Zn in treatment of sewage sludge. Liu and Zhao (2007) used sequential extraction to show the effectiveness of Pb treatment in soils using stabilized iron phosphate nanoparticles, where a 33 to 93% decrease of exchangeable Pb^{2+} and carbonate-bound fractions and an increase in residual fractions were observed.

2.4 Leaching Tests for Management of Wastes and other Materials

Leaching experiments are widely employed to assess the mobility of toxic substances in wastes and other materials (Van der Slot, 1996; Wang et al., 2001; Halim et al., 2003; Kribi et al., 2004); theoretically, these studies simulate release in the field when the material is exposed to ambient conditions associated with its utilization or ultimate disposal. The results of leaching studies can also be interpreted to qualitatively predict retention mechanism(s) for toxic species and, therefore, the efficacy of applied treatment (Cohen and Petrie, 2005). For regulatory purposes, tests need to be easy to conduct and provide reproducible results; consequently, regulatory tests usually involve batch systems (Scott et al., 2005). However, it is apparent that the simpler the tests the greater the digression from actual environmental conditions, which raises questions of their suitability (Hooper et al., 1998; Halim et al., 2003). The alternative dynamic tests, column and field, potentially simulate field conditions such as kinetics and mass transfer more accurately; however, they require more time (up to three months) and are more costly and sensitive to channeling and achievement of local equilibrium (Park and Batchelor, 2002).

The Washington State Department of Ecology (WSDE, 2003) along with Scott et al. (2005) reviewed available leaching procedures including the U.S. EPA toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP), the State of California waste extraction test (WET), American Nuclear Society (ANS) semi-dynamic test, and the German Nederlands Normalisatie-instituut (NEN) column test DNN. Internationally, TCLP is the most commonly used extraction test for regulatory purposes and it is the only method currently recognized by RCRA for assessing hazardous wastes (Scott et al., 2005; 40CFR, Part 261.24). The WET test (CCR, 1991) is used to supplement the TCLP procedure in accordance with the California Code of Regulations (CCR). In the U.S., the SPLP is employed by several states including New Jersey, Florida, and Wisconsin for assessment of soil remediation and acceptability of waste materials in beneficial reuse (FDEP, 2005; NJDEP, 2008;

W.A.C., 2008). The U.S. EPA TCLP and SPLP, the California WET procedures and other batch tests are reviewed in the following sub-sections.

2.4.1 Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP (U.S. EPA, 1992) is a regulatory test designed to assess whether industrial wastes are non-hazardous for co-disposal with municipal waste in landfills, a potentially worst-case disposal scenario. Sample particle size is reduced to less than 9.5 mm prior to extraction to account for breakage during compression and in freezing and thawing cycles (Scott et al., 2005). Extractions are carried out with an acetate buffer to simulate landfill leachates (Scott et al., 2005). The initial pH of the extraction fluid is 4.93 ± 0.05 for sample pH less than 5 and 2.88 ± 0.05 for sample pH greater than 5, while the liquid to solid ratio (L/S) is 20:1 (U.S. EPA, 1992). Extraction of contaminants is impacted by the low extraction pH, buffer intensity, and complexation with the acetate ligand. Additionally, samples are subjected to 18 hours of end-over-end tumbling at 30 rpm designed to attain equilibrium. Questions exist as to how well acetic acid approximates municipal landfill leachate; for example, Hopper et al. (1998) found that the TCLP underestimated leaching of oxyanion forming elements, As, Cr, Mo, Sb, Se, and V. Furthermore, the 18 hours extraction period was set arbitrarily (Scott et al., 2002); therefore, leaching as a function of time is necessary to assess whether equilibrium or pseudo-equilibrium is achieved. However, among the various leaching parameters that control the leachability of metals, pH, extraction fluid, leaching duration, particle size, and L/S, Halim et al. (2003) found the final leachate pH was the most important factor, potentially because of its influence on solubility and partitioning.

The TCLP extract is subjected to analysis of 39 contaminants including eight metals (Table 2.1) that are regulated by RCRA (40CFR, Part 261.24). Concentration limits were derived from the National Interim Primary Drinking Water Standards, which were the available health-based criteria (U.S. EPA, 1995). To cater for the expected natural dilution and attenuation of contaminants in moving from landfill to drinking-water sources, a groundwater model-based dilution-attenuation factor (DAF) of 100 was applied to the drinking water standards, specifically, chronic toxicity reference levels (55 Federal Register 11804, 1990; U.S. EPA, 1995). U.S. EPA (1996b) found that for waste piles, the applied DAF of 100 was conservative for all metals except Ba, where a DAF of 54 was deemed acceptable.

2.4.2 California Waste Extraction Test (WET)

The WET test (CCR, 1991) is used to supplement the TCLP procedure in accordance with the California Code of Regulations (CCR). The test was developed in 1984, before TCLP, as a more appropriate leaching procedure than the then EPA regulatory method, extraction procedure (EP) (WSDE, 2003). Extraction is conducted with a 0.2 M sodium citrate solution at pH 5.0 ± 0.1, L/S ratio 10:1, and a 48 hour extraction period. The sodium citrate solution was considered to describe mobility of toxicants under a wide variety of conditions more adequately than did the acetic acid solution used in EP (WSDE, 2003). However, more recent studies found that the WET test overestimated leaching of cationic metals by more than an order of magnitude, which was attributed to the greater chelation of the citrate buffer (Hooper et al., 1998; WSDE, 2003; Townsend et

Table 2.1 Maximum Allowable Contaminant Concentrations in the TCLP Leachate for the Toxicity Characteristic (U.S. 40 CFR, Part 261.24)

EPA Hazardous Waste (HW) No.	Contaminant	Chemical Abstract Service No.	RegulatoryLevel (mg /L)
D004	Arsenic	7440-38-2	5.0
D005	Barium	7440-39-3	100.0
D018	Benzene	71-43-2	0.5
D006	Cadmium	7440-43-9	1.0
D019	Carbon tetrachloride	56-23-5	0.5
D020	Chlordane	57-74-9	0.03
D021	Chlorobenzene	108-90-7	100.0
D022	Chloroform	67-66-3	6.0
D007	Chromium	7440-47-3	5.0
D023	-	95-48-7	200.0
D024	m-Cresol	108-39-4	200.0
D025	p-Cresol	106-44-5	200.0
D026	Creso	----------	200.0
D016	2,4-D	94-75-7	10.0
D027	1,4-Dichlorobenzene	106-46-7	7.5
D028	1,2-Dichloroethane	107-06-2	0.5
D029	1,1-Dichloroethylene	75-35-4	0.7
D030	2,4-Dinitrotoluene	121-14-2	0.13
D012	Endrin	72-20-8	0.02
D031	Heptachlor (and its epoxide)	76-44-8	0.008
D032	Hexachlorobenzene	118-74-1	0.13
D033	Hexachlorobutadiene	87-68-3	0.5
D034	Hexachloroethane	67-72-1	3.0
D008	Lead	7439-92-1	5.0
D013	Lindane	58-89-9	0.4
D009	Mercury	7439-97-6	0.2
D014	Methoxychlor	72-43-5	10.0
D035	Methyl ethyl ketone	78-93-3	200.0
D036	Nitrobenzene	98-95-3	2.0
D037	Pentrachlorophenol	87-86-5	100.0
D038	Pyridine	110-86-1	5.0
D010	Selenium	7782-49-2	1.0
D011	Silver	7440-22-4	5.0
D039	Tetrachloroethylene	127-18-4	0.7
D015	Toxaphene	8001-35-2	0.5
D040	Trichloroethylene	79-01-6	0.5
D041	2,4,5-Trichlorophenol	95-95-4	400.0
D042	2,4,6-Trichlorophenol	88-06-2	2.0
D017	2,4,5-TP (Silvex)	93-72-1	1.0
D043	Vinyl chloride	75-01-4	0.2

al., 2004; U.S. EPA, 1996b). For regulatory purposes, CCR applies soluble threshold limit concentrations (STLC) (Table 2.2) which are equivalent to RCRA limits (40 CFR, Part 261.24) and regulates additional 12 metals including, Zn, Ni, Cu, and Co. Furthermore, CCR (1991) sets total threshold limit concentrations (TTLC) for total metal concentrations. By regulating more contaminants than the federal government and capping their total concentration, the California provides greater safeguards for human and environmental health. In any event, for amended waste materials including dredged sediments to be applicable in California, these additional metals and the TTLC need to be addressed.

2.4.3 Synthetic Precipitation Leaching Procedure (SPLP)

Whereas TCLP addresses disposal of waste materials in landfills, questions on environmental acceptability of non-hazardous materials for beneficial reuse persist (Townsend et al., 2006). For assessing the potential impact to a drinking water source, groundwater, a leaching procedure to gauge release of contaminants by conditions affecting the environment, for example, weathering from rainfall and snow, is necessary. A survey by the Association of State and Territorial, Solid Waste Management Officials (ASTSWMO) found at least 10 states in the U.S. specified the SPLP (U.S. EPA, 1994) for determining leaching characteristics for (beneficial) reuse of waste materials (ASTSWMO, 2000). The SPLP is similar to TCLP except the extraction fluid is a simulation of acid rain with a 60/40 by weight concentrated nitric and sulfuric acid solution. The initial extraction fluid pH is 4.20 ± 0.05 for sites east of Mississippi River,

Table 2.2 California Code of Regulations: Soluble Threshold Limit Concentration (STLC) and Total Threshold Limit Concentration (TTLC) for Inorganic Toxic Substances (CCR, 1991) and the RCRA Regulatory Levels (U.S. 40 CFR, Part 261.24)

Element	STLC (WET Test extract) (mg/L)	TTLC (Total Concentration) (mg/kg)	RCRA Regulatory Level (mg/kg)
Antimony	15	500	N/R [a]
Arsenic	5	500	5.0
Asbestos (as percent)	N/A	1	N/R
Barium	100	10,000	100.0
Beryllium	0.75	75	N/R
Cadmium	1	100	1.0
Chromium (VI)	5	500	
Chromium (III)	5	2,500	5.0
Cobalt	80	8,000	N/R
Copper	25	2,500	N/R
Fluoride	180	18,000	N/R
Lead	5	1,000	5.0
Mercury	0.2	20	0.2
Molybdenum	350	3,500	N/R
Nickel	20	2,000	N/R
Selenium	1	100	1.0
Silver	5	500	5.0
Thallium	7	700	N/R
Vanadium	24	2,400	N/R
Zinc	250	5,000	N/R

[a] N/R refers to not regulated

which have high organic matter, and 5.00 ± 0.05 for sites west of Mississippi River (U.S. EPA, 1994; Townsend et al., 2006). Townsend et al. (2003) found the SPLP tests resulted in less leaching of most metals as compared to the TCLP because of a lack of buffer and complexation capacity.

Assessment of the risk to groundwater quality with SPLP is necessary before treated sediments can be applied as construction material in states where SPLP is mandated for beneficial reuse. Although the phosphate and thermal treatment of sediments was developed for beneficial reuse (Kribi et al., 2004), the treated sediments have not been assessed with SPLP.

2.4.4 Other Batch Tests

Although the regulatory tests, TCLP, WET, and SPLP target the material of interest, they have numerous limitations among them:

(i) Failure to consider the high alkalinity of some wastes which would reduce leaching by retention of sparingly soluble metal hydroxides (van der Sloot, 1996).

(ii) Failure to consider the low liquid to solid ratio of some of the materials (USEPA, 1995).

(iii) Not applicable to waste destined for monofills that are neutral or alkaline in nature, and where there is no possibility of contact with acetic acid (USEPA, 1995).

(iv) Where there is no possibility of particle size reduction, overestimate the leachate by drastically increasing surface area and potentially contaminating samples through grinding.

(v) Focuses only on one or two stages of extraction, without providing a analysis of partitioning processes or speciation of contaminants within the test materials (Li et al., 2001).

(vi) Does not provide mechanistic behaviour or kinetics of metal release under field conditions (Tack, 1999).

In additional to the issues raised above, the large number of factors involved in leaching limit the information that can be obtained from these batch tests. For example, Gardner et al. (2007) found metal leaching exceeded the U.S. EPA maximum contaminant levels (MCL) for drinking water at pH less than 5 and greater than 9 for NY/NJ Harbor sediments. Townsend et al. (2006) observed a fivefold increase in Cr leaching for L/S reduction from 20 to 2, while Norrström (2005) observed Cd and Zn leaching increased by up to two orders of magnitude through complexation with Cl. Consequently, a comprehensive approach incorporating a better understanding of contaminant speciation and behavior may include assessing speciation and comparing experimental behavior to that predicted, when evaluating leaching as a function of pH, L/S, redox potential, and complexing ligands (van der Sloot, 1996; Kosson et al., 2002; Townsend et al., 2006). Speciation may be evaluated, for example, with sequential extraction and X-ray absorption spectroscopy (XAS) and modeled with thermodynamic analysis to aid in interpretation of the leaching results.

2.5 Risks to Groundwater in Beneficial Reuse of Wastes

Land application of waste materials treated for beneficial reuse must address potential risk associated with their use including that to groundwater used as a drinking water source. This type of risk has been evaluated with models based on the total contaminant concentration and the distribution coefficient (K_d) or through leaching studies (van der Sloot, 1996; NJDEP, 2008). Use of K_d implies that distribution can be described with simply adsorption; furthermore, because K_d does not account for variation in pH, ionic strength, temperature, and presence of complexing ligands, appropriate coefficients may not be available. Townsend et al. (2006) found that modeling the leaching of granular wastes with K_d underestimated the pore water concentrations of Sb, Mo, B, As, Cr, and Al, by as much as 80%.

Several states including New Jersey, Florida, and Wisconsin require an assessment of the risk to groundwater for reuse of granular wastes through application of the U.S. EPA SPLP (U.S. EPA, 1994; FDEP, 2005; NJDEP, 2008; W.A.C., 2008). Criteria for assessing risk to groundwater in reusing granular wastes is derived from state based groundwater quality limits (GQL) which are, in some cases, MCL for drinking water, multiplied with dilution attenuation factors (DAF) that account for dilution in an aquifer. However, in defining the criteria, states differ in their interpretation as to what the SPLP leachate represents. Florida and Wisconsin consider SPLP leachate to have an inherent 20:1 dilution and compare it directly to GQL (DAF 1) (Table 2.3) (FDEP, 2005; W.A.C., 2008). Other states assume the leachate represents pore-water and specify DAF values which, however, are often site specific. For example, the New Jersey Department of Environmental Protection (NJDEP) develops remediation standards on a site-by-site

Table 2.3 Groundwater Quality Levels and SPLP Leachate Criteria for the States of New Jersey (NJDEP, 2008), Florida (FDEP, 2005), and Wisconsin (W.A.C., 2008)

	New Jersey		**Florida**	**Wisconsin**
Contaminant	**Health Based Groundwater Quality Criteria (μg/L)**	**Impact to Groundwater Leachate Criteria [a] (μg/L)**	**Groundwater [b] Cleanup Target Levels (μg/L)**	**Groundwater [b] Enforcement Standards (μg/L)**
Aluminum	200	43 [c]	200	NA
Antimony	6	78	6	6
Arsenic	0.02	3 [d]	10	10
Barium	6,000	78,000	2,000	2,000
Beryllium	1	13	4	4
Boron	NA	NA	1,400	96
Cadmium	4	52	5	5
Cobalt	NA	NA	140	40
Copper	1,300	16,900	1,000	1,300
Chromium	NA	NA	NA	100
Lead	5	65	15	15
Manganese	50	650	50	NA
Mercury	2	26	3	2
Nickel	100	1,300	100	100
Selenium	40	520	50	50
Silver	40	520	100	50
Thallium	0.5	6	2	2
Vanadium	NA	NA	49	30
Zinc	2,000	26,000	5000	NA

[a] Computed by applying DAF 13 on the health based groundwater quality criteria (second column).
[b] Typically primary and secondary drinking water standards.
[c] Adjusted so as not to exceed water solubility.
[d] Based on aqueous practical quantitation limit.

basis; without such, a default DAF of 13 is applied based on their hydrogeological studies (Table 2.3) (NJDEP, 2008). The U.S. EPA specifies two default DAF values of 1 (for no dilution) and 20 (U.S EPA, 2002; NJDEP, 2008). Because of the different criteria for reuse of granular waste among states, there is a need for further understanding of the risk involved.

CHAPTER 3

OBJECTIVES AND HYPOTHESES

Regular dredging of sediments in harbors and waterways is necessary for maintenance of navigable systems. Contaminants in the dredged sediments can impact the ecosystem adversely and, therefore, disposal of the sediments poses a major challenge for harbor dredging projects. Development of effective methods for stabilization and beneficial reuse of the dredged sediments as opposed to disposal would provide a sustainable solution for their management. In this study, treatment of dredged sediments by phosphate addition and calcination at 700 °C for beneficial reuse is investigated. Objectives of the study are:

1. Investigate metal speciation in dredged and treated sediments using a suite of analytical procedures including, X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), and sequential extraction to elucidate stabilization mechanisms.
2. Conduct TCLP to assess immobilization of metal contaminants and compare results and spectroscopic analyses to thermodynamic analysis.
3. Assess risks to groundwater quality in beneficial reuse of sediments, with the U.S. EPA SPLP and other batch tests as a function of pH, L/S, and alternative phosphate forms.
4. Determine compliance of the phosphate addition and thermal treated sediments with regulatory standards for hazardous materials and for beneficial reuse of waste materials in construction.

The following hypotheses are tested:

1. Phosphate addition and thermal treatment shifts metal speciation in sediments from labile phases, ion exchangeable and carbonates, to immobilized residual forms as determined by XAS and sequential extraction.
2. Mineralization of organics and crystallization of amorphous iron and manganese oxides by heat treatment implies precipitation rather than adsorption is the dominant mechanism for metal sequestration. Therefore, thermodynamic analysis of the metal species observed with XRD and XAS in treated sediments can predict leaching.
3. The effectiveness of phosphate sources in immobilizing heavy metals is dependant on their solubility, capacity to buffer the system, and purity to avoid introducing contaminants into the sediments. For example, $Ca(H_2PO_4)_2 \cdot 2H_2O$, NaH_2PO_4, and H_3PO_4 are relatively soluble while $CaHPO_4$ is not. $Ca(H_2PO_4)_2 \cdot 2H_2O$, NaH_2PO_4, and $CaHPO_4$ may result in a solution pH within the 4-7 range, while with 5% by dry weight H_3PO_4 addition, the pH may drop to 3.0. Also, commercially, a higher purity (by weight) is available for $CaHPO_4$ (>99.9997%), NaH_2PO_4 (>99.999%), and H_3PO_4 (>99.999%) than for $Ca(H_2PO_4)_2 \cdot 2H_2O$ (>99.995%).

CHAPTER 4

METHODS AND ANALYSES

To test the research hypotheses, a suite of analytical methods were applied on untreated and phosphate addition and thermal treated sediments. Metal speciation was assessed with XAS for Zn specifically because it was the most abundant heavy metal in sediment samples from both the U.S. and Europe. The forms of other metal contaminants were examined with sequential extraction. Leaching studies were applied to evaluate the efficacy of the sediment treatment and assess compliance with criteria for beneficial reuse.

4.1 Materials

Laboratory quality assurance and quality control procedures were based on Standard Methods for the Examination of Water and Wastewater (Greenberg et al., 2005). Milli-Q Type I de-ionized water was employed in all experiments. All reagents were of certified analytical grade or trace metal quality; phosphate forms were trace metal grade (H_3PO_4) and analytical grade ($CaHPO_4$ (Fisher Scientific®), $Ca(H_2PO_4)_2 \cdot 2H_2O$, and $NaH_2PO_4 \cdot H_2O$ (Sigma-Aldrich®)). All glassware, plastic-ware, and associated materials were washed with a detergent and then soaked in 10% HNO_3 acid bath for a period of two days for glassware and one day for high density polyethylene (HDPE). Subsequently, all materials were rinsed in de-ionized water and stored in a particle free environment.

Dredged sediments were obtained from Dampremy, Belgium and Passaic River Estuary courtesy of Solvay Company and the New Jersey Office of Maritime Resources, respectively. Moisture content was determined by drying sediments to constant weight at 105 °C, while organic matter was estimated by loss on ignition at 445 ± 10 °C for six hours (AASHTO, 1986). Total metal concentrations were obtained by HNO_3 and HCl (aqua regia) digestion (U.S. EPA, 1996a). Sediment mineralogy was characterized by X-ray diffraction (XRD) with a Philip's X'Pert X-ray diffractometer.

4.2 Sediment Treatment

Sediment treatment was carried out by phosphate addition and calcination at 700 °C. Phosphate was applied to stabilize metal contaminants in sparingly soluble phosphate precipitates (e.g., Chen et al., 1997; Traina and Laperche, 1999; Crannell et al., 2000; Wang et al. 2001; Yang and Mosby, 2006). Additionally, phosphate binding of metals may prevent excessive evaporation during calcination. In fly ash, Jakob et al. (1995) observed 3, 9, 23, and 85% evaporation of Zn, Cu, Cd, and Pb, respectively, at 670 °C over 3 hours which increased to 38, 82, 97, and 95% respectively at 1030 °C and then decreased drastically between 1100 and 1300 °C due to formation of vitrification products. For dredged sediments, Rio et al. (2007) found phosphate addition limited evaporation of Pb to about 20%. A lower temperature of 700 °C would limit evaporation of metals and reduce the cost of the product yet mineralize (or volatilize) organics and improve mechanical properties through sintering (Kribi et al., 2004).

Dredged sediments were treated with addition of 14.7 M H_3PO_4 at 3 and 5% by dry weight phosphate under completely mixed conditions. The mixtures were left to dry and cure for 14 days (Wang et al., 2001) at 40 °C. The aged sediments were ground and treated by calcination at 700 °C in a Thermolyne® tube furnace for 3 hours based on

Kribi et al. (2004). Both dredged and treated sediments were investigated for Zn speciation with XAS, metal forms with sequential extraction, and leaching characteristics with TCLP, SPLP, and other batch tests as a function of time, alternative phosphate forms, pH, and L/S.

4.3 XAS Data Collection and Analyses

X-ray absorption spectroscopy was conducted at beamline X11A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, where the average electron beam energy was 2.8 GeV with a current of 260-280 mA. All spectra were collected at the Zn *K*-edge (9,659 eV) using a double Si (111) crystal monochromator over the energy range 9,630-10,410 eV. Ground sediments and adsorbed reference phases were measured in fluorescence mode using a Lytle detector (Stern and Heald, 1979) with soller slits, a z-1 filter, and filled with Ar. Reference minerals were measured in transmission mode with nitrogen gas in the ion chamber before the sample (I_0). Harmonic rejection was achieved by detuning to 70% of I_0.

XAS spectra were analyzed using WinXAS (version 3.1) (Ressler, 1998) following standard procedures (Bunker, 2003). The background X-ray absorbance was subtracted by fitting a linear polynomial through pre-edge region and the edge jump normalized with a zero order polynomial over 9.759-9.859 keV. The threshold energy (E_o) was determined from the first inflection point in the edge region and was used to convert the spectra from energy to *k*-space. A spline function was employed to enhance the isolated atomic absorption over the range 2.6-13.9 Å^{-1} and to convert the data to $\chi(k)$ that was then weighted by k^3 to enhance the higher k-space data. A Bessel window function was used in Fourier transforms to produce the radial structure functions (RSF) which were then fit with theoretical models generated using FEFF7 (Zabinsky et al., 1995). The amplitude reduction factor (S_0^2) for spectra collected in fluorescence was obtained by fixing the first shell coordination numbers (CN) at crystallographic values and floating all the other parameters. Errors in first and second shells were estimated as ± 0.02 and ± 0.05 Å for distances (R), respectively, and ± 20 and ± 40% for CN respectively.

4.3.1 Selection of Reference Spectra

The success of PCA, TT, and LCF analyses depends on the availability of an exhaustive set of reference spectra. Because samples in this study were sediments, dredged and treated by phosphate addition and calcination, potential Zn phases in these environments were considered (Table 4.1). Compounds used in previous studies were also considered (Table 4.2). The selected reference minerals included, sphalerite (ZnS), zincite (ZnO), smithsonite ($ZnCO_3$), hydrozincite ($Zn_5(OH)_6(CO_3)_2$), willemite (Zn_2SiO_4), hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}2H_2O$), gahnite ($ZnAl_2O_4$), franklinite ($ZnFe_2O_4$), hopeite ($Zn_3(PO_4)_2{\cdot}4H_2O$), and scholzite ($CaZn_2(PO_4)_2{\cdot}2H_2O$). Others selected were ones addressing sorption to ubiquitous heavy metal scavengers in the environment: hydrous iron oxides (HFO), hydrous manganese oxide (HMO), and montmorillonite, important sorbents for Zn (Gadde and Laitinen, 1974; Trivedi and Axe, 2000; Lee et al., 2004). Reference Zn minerals, gahnite, scholzite, willemite, and hemimorphite, were obtained from mineral vendors; to confirm their mineralogy, crystallographic structures were measured with XRD (Appendix A).

Table 4.1 Selection of Reference Minerals

Mineral	Justification	References
Sphalerite (ZnS)	Stable Zn phase in reducing environments	Carroll et al. (2002)
Hydrous manganese oxides (HMO)	Ubiquitous in sediments and important Zn sorbent	Gadde et al. (1974)
Hydrous iron oxides (HFO)	Ubiquitous in sediments and important Zn sorbent	Trivedi and Axe (2000)
Montmorillonite ($(Na,Ca)(Al,Mg)_6 (Si_4O_{10})_3(OH)_6 \cdot nH_2O$)	Important Zn sorbent in sediments	Lee et al. (2004)
Hemimorphite ($Zn_4Si_2O_7(OH)_2.2H_2O$)	Observation of silica (as quartz) with XRD	This study
Willemite (Zn_2SiO_4)	Observation of silica (as quartz) with XRD	This study
Smithsonite ($ZnCO_3$)	On of main Zn species in estuarine waters	Brydie and Polya (2003)
Hydrozincite ($Zn_5(OH)_6(CO_3)_2$)	Presence of carbonates in sediments	
Zincite (ZnO)	Formed from $ZnCO_3$ above 295 °C	Bailar et al. (1973)
Hopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$)	Product of Zn reaction with phosphate	Crannel et al. (2000)
Scholzite ($CaZn_2(PO_4)_2 \cdot 2H_2O$)	Product of Zn reaction with phosphate	Crannel et al. (2000)
Franklinite ($ZnFe_2O_4$)	Formation at high temperatures and observation of iron oxides with XRD	Guaita et al. (1999)
Gahnite ($ZnAl_2O_4$)	Formation at temperatures above 600 °C and observation of aluminosilicates with XRD	Mousa et al. (1990)

Table 4.2 Reference Zn Minerals used in Previous PCA-TT-LCF Analyses

Sample	Reference Spectra	References
Zn smelter contaminated soil	ZnS (sphalerite) Zn_2SiO_4 (willemite) ZnHFO (Zn sorption to hydrous iron oxide) ZnO (Zincite)	Isaure et al. (2002)
Incineration fly ash after heat treatment	ZnO (zincite) Γ-$Zn(OH)_2$ (γ-zinc hydroxide) $Ca(Zn_2(OH)_6)\cdot 2H_2O$ (calcium zincate) $Zn_5(OH)_6(CO_3)_2$ (hydrozincite) Zn_2SiO_4 (willemite) $Zn_4Si_2O_7(OH)_2\cdot 2H_2O$ (hemimorphite) (gahnite) $ZnFe_2O_4$ (franklinite) $ZnCO_3$ (smithsonite) $ZnSO_4\cdot 7H_2O$ (goslarite) ZnS (wurtzite) ZnS (sphalerite) ZnO (Zinicite) $ZnCl_2$ Zn^0 (metal foil)	Struis et al. (2004)
Soil contaminated with ZnO containing filter dust from a brass foundry	Zinc carbonate Gahnite Sphalerite Willemite Zincite Zincochromite ($ZnCr_2O_4$) Hydroxyapatite ($Ca_5(PO_4)_3(OH)$) Hopeite ($Zn_3(PO_4)_2.4H_2O$) Phosphate dehydrate ($CaHPO_4\cdot 2H_2O$) Goethite (α-FeOOH) Ferrihydrite ($Fe_5HO_8\cdot 4H_2O$) Hematite (α-Fe_2O_3) Zn Kerolite ($Si_4(Mg_{1.65}Zn_{1.35})_3O_{10}(OH)_2\cdot nH_2O$) Montmorillonite ($(Na,Ca)(Al,Mg)_6(Si_4O_{10})_3(OH)_6\cdot nH_2O$) Birnessite ($Na_4Mn_{14}O_{27}\cdot 9H_2O$) Humic and fulvic acids Bacterial exopolymers Fungi cell walls	Kirpichtchikova et al. (2006)

4.3.2 PCA-TT-LCF Analysis

Determination of the number of species with PCA requires the number of spectra to exceed that of the sample species and a varying species composition (Scheinost et al., 2002). In this study, bulk spectra were collected for samples of fixed composition and, therefore, PCA was used primarily to facilitate TT identification of the likely end-members of the sample spectra. Sample $\chi(k)\cdot k^3$ spectra in the range 3.0-10.0 Å^{-1} for dredged sediments and 2.7-10.5 Å^{-1} for treated sediments were loaded into SixPACK PCA program (Webb, 2006) and decomposed mathematically into the minimum number of orthogonal components necessary to describe variance in the data (Malinowski, 1991). The likelihood of reference spectra to be end-members of the sample spectra was determined by target transformation of the reference spectra using the decomposed components, and assessed by a fitting factor $R = \sum(\chi_{exp} - \chi_{model})^2/(\chi_{exp})^2$ (Isaure et al., 2002). Proportions of the identified member compounds were quantified by LCF. Reference spectra with the lowest R were combined first and other spectra added until the contribution of the last member was less than 10% the approximate method precision (Isaure et al., 2002).

4.4 Sequential Extraction.

Metal distribution among acid extractible (exchangeable and carbonates), reducible (adsorbed to iron and manganese oxides), and oxidizable (bound to sulfides and organics) phases was evaluated with the modified three step BCR sequential extraction procedure of the Standards, Measurements and Testing (SM&T) Programme (Rauret et al. 1999). An aqua regia digestion of residuals, which comprise sparingly soluble minerals and refractory organic material (Tessier et al., 1979), was incorporated to assess recovery (e.g., Rauret et al. 1999). Extractions were performed in 40 ml Sorvall® polypropylene centrifuge tubes on an end-over-end shaker rotated at 30 rpm. Between successive extractions, separation of extract from residue was carried out by centrifugation at 3,000 g for 20 min. The supernatant was decanted into HDPE Naglene® bottles, acidified to pH less than 2, and refrigerated until analysis with flame atomic absorption spectrometry (U.S. EPA, 1998a). The residues were washed with 20 mL of deionized water, centrifuged for 20 min, and the supernatant discarded.

To allow direct comparison of concentration measurements for dredged and treated sediments, samples with the equivalent 1.00 g dry weight were used for both cases; for dredged sediments, moisture content was applied to the 1.00 g dry weight to obtain an equivalent wet weight of 2.30 g. In Step 1, extraction for exchangeables and carbonates involved 0.11 M acetic acid solution (CH_3COOH), while in Step 2 0.5 M hydroxylammonium chloride ($NH_2OH{\cdot}HCl$) and 0.05 M HNO_3 solution were used to extract adsorbed to iron and manganese phases from remaining residue. In Step 3, residue from Step 2 was treated at 85 ± 2 ^{o}C with two sequential 10 ml portions of 30% H_2O_2 adjusted to pH 2 with HNO_3, and then extracted with 1.0 M ammonium acetate (CH_3COONH_4) solution at pH 2.0 ± 0.1 for the organics and sulfides fraction. Step 4 employed HCl and HNO_3 (aqua regia) digestion (U.S. EPA, 1996) to measure total metals in residue from Step 3; this residual represents metals in sparingly soluble minerals and refractory organic material that are not available to plants and other environmental media.

4.5 Leaching Tests

This section describes leaching tests conducted to evaluate the efficacy of the phosphate addition and thermal treatment, assess whether equilibrium or pseudo-equilibrium was achieved, and determine compliance with regulatory criteria. The tests included the U.S. EPA (1992) TCLP and leaching as a function of time. Impacts to groundwater quality in beneficial reuse of treated sediments for construction were investigated with the U.S. EPA (1992) SPLP and other batch tests as a function of phosphate forms, pH and L/S ratio.

4.5.1 Leaching with the U.S. EPA TCLP

The TCLP (U.S. EPA 1994) was conducted to determine the efficacy of treatment (e.g., Wei et al., 2001) and evaluate whether the sediments would be classified as hazardous materials (40 CFR, Part 261.24; CCR, 1991). Extraction was carried out on sediments, dredged, 3% phosphate addition only, 700 °C calcinations only, and phosphate addition followed by calcination. Acetic acid buffer solution at pH 2.88 ± 0.05 was used as extraction fluid based on the pH of the sediments (U.S. EPA, 1992). Extractions were carried out at 20:1 liquid to solid ratio in 2 L HDPE bottles tumbled at 30 rpm for 18 hours. The pH was measured and the extract filtered through acid washed 0.7 μm borosilicate filters, acidified, and stored in closed Nalgene® bottles under refrigeration at 4 °C until analyzed (U.S. EPA, 1992; Geenberg et al., 2005). Analysis for metals was carried out by flame atomic absorption (FAA) spectrometry using AAnaylst 400 spectrometer (U.S. EPA, 1998a).

4.5.2 TCLP Leaching as a Function of Time

The TCLP (U.S. EPA, 1994) was extended to 28 days to investigate whether equilibrium or pseudo-equilibrium was achieved. Extractions were carried out with 20:1 liquid to solid ratio in an acetate solution at an initial pH 2.88 ± 0.05, based on the sediment pH, in 2 L HDPE bottles tumbled at 30 rpm. After the standard 18 hr TCLP leaching period, the pH was measured and 10 mL sample withdrawn with syringes, filtered through 0.22 μL Millex-GV® filters (Shih et al., 2006), acidified, and refrigerated at 4 °C until analysis. Extraction was continued with pH maintained at 5.0 ± 0.1 by HNO_3 and NaOH addition as necessary over sampling intervals not exceeding 4 days for up to 28 days. The selected extraction pH was envisioned from continuous exposure to landfill leacheate of pH 5 to 8 (Van der Sloot, 1996; Halim et al., 2003). Analysis of the extract was carried out with flame atomic absorption spectrometry (FAA) (U.S.EPA, 1998a).

4.5.3 SPLP Leaching Tests

SPLP was conducted on dredged and treated sediments following U.S. EPA method 1312 (U.S. EPA, 1994). The tests were performed in triplicate with blanks used to isolate contaminants in the reagents and procedures. The extraction fluid was prepared by mixing H_2SO_4 and HNO_3 at 60/40 by weight ratio to achieve a pH of 4.20 ± 0.05. Similar to other studies, the pH fluctuated widely because of absorption of CO_2 and a lack of buffering capacity (Townsend et al., 2003); however, the pH stabilized after 15 minutes under completely mixed conditions. To ensure uniformity of the extraction fluid for the samples, 1500 mL stock solutions were prepared and split equally to among the extraction reactors. Extractions were carried out in 2 L HDPE bottles tumbled head-over-head at 30 rpm for 18 hours. Subsequently, the pH was measured and the extract filtered through 0.7 μM borosilicate filter, acidified to less than pH 2, and stored for analysis in closed Nalgene® bottles under refrigeration at 4 °C. Metal analysis was accomplished with flame atomic absorption (FAA) spectrometry (U.S. EPA, 1998a) and graphite furnace atomic absorption (GFAA) spectrometry (U.S. EPA, 1998b). The extract metal concentrations were compared to risk to groundwater criteria (Table 2.3) (FDEP, 2005; NJDEP, 2008; W.A.C., 2008).

4.5.4 SPLP Study of Alternative Phosphate Forms

The sediments were treated by addition of 3 and 5% by dry weight phosphates, $NaH_2PO_4{\cdot}H_2O$, $Ca(H_2PO_4)_2{\cdot}2H_2O$, and $CaHPO_4$; transferred with 50 ml DI water. After mixing, the pH was measured, the sediments dried, and aged for 14 days at 40 °C followed by calcination at 700 °C for 3 hours (Kribi et al., 2004, Wang et al., 2004). The pH of the treated sediments was measured upon addition of 96.5 mL de-ionized water to 5 g of sample followed by complete mixing for 5 minutes (U.S. EPA, 1992). Leaching was conducted following the U.S. EPA SPLP, initial extraction fluid pH 4.20 ± 0.05, L/S 20:1, and 18 hours equilibration.

4.5.5 Leaching as function of pH and L/S

Metal leaching was investigated over a pH range of 4 to 9, potentially including the lower to more alkaline pH conditions observed, for example, under lime and partly cement application (van der Sloot, 1996, 2003). The extraction fluid was prepared as described for the SPLP (U.S. EPA, 1994) with an initial pH 4.20 ± 0.05 and adjusted to experimental pH with HNO_3 and NaOH. During extraction, the pH was monitored and readjusted as necessary.

Leaching as a function of L/S was conducted with a modified SPLP procedure over L/S 5, 8, 10, 20, 50, and 100 to investigate the effect of pore water L/S on transient leaching. The lowest L/S selected was based on the need to separate sufficient extract samples, 100 mL, from the solids for subsequent acid digestion. Other L/S investigated included the U.S. EPA SPLP L/S 20, and an order of magnitude larger L/S 100. Following the U.S. EPA SPLP (1994) and similar to other studies (e.g., Townsend et al., 2006; Gardner et al., 2007), extractions were conducted with buffering from the sediment system after an initial pH of 4.20.

CHAPTER 5

XAS SPECIATION STUDY

This chapter first presents results of sediment characterization. XAS data which comprised spectra for dredged and treated sediments and 13 reference Zn minerals are then treated to isolate the extended absorption fine structure, and fitted with crystallographic models. Subsequently, the spectra are analyzed with PCA, TT and LCF to identify and quantify the potential Zn species in the sediments, and the results interpreted to elucidate stabilization mechanisms. The chapter concludes with thermodynamic analysis to determine the stability of the species identified in the treated sediments.

5.1 Sediment Characterization

Sediments from both the U.S. (Passaic River Estuary) and Belgium exhibited similar characteristics (Table 5.1) with heavy metal concentrations falling within the same order of magnitude. This result implies that treatment methods developed for one region would potentially be applicable to the other. Zn was the most abundant heavy metal with 1,067 and 3,400 mg kg^{-1} dry sediments for Passaic River Estuary and Dampremy, Belgium, respectively. Consequently, Zn in the Belgium sample was selected for study of speciation with XAS. Mineralogy assessment with XRD (Figure 5.1) revealed that in dredged sediments quartz (α-SiO_2) was the predominant mineral followed by calcite ($CaCO_3$), hematite (α-Fe_2O_3), and aluminosilicates ($(Na,Ca)Al_xSi_yO_z$) (Appendix A). After phosphate addition and calcination, quartz (α-SiO_2) and hematite (α-Fe_2O_3) were

TABLE 5.1 Dredged Sediments Characteristics: Moisture Content, Organics and Total Metal Concentrations determined with HCl and HNO_3 (Aqua Regia) Digestion EPA Method 3050B (U.S. EPA, 1996a)

	Sediments	
	Passaic River Estuary, U.S.	**Dampremy, Belgium**
Moisture content (%)	56.5	N/A [a]
Organics (mg/kg dry weight)	132	161
Metals (mg/kg)		
Zn	1067 ± 12	3400 ± 130
Co	33 ± 0.1	30 ± 0.1
Ni	971 ± 3.5	105 ± 1.3
Mn	519 ± 4.1	1467 ± 47
Cu	520 ± 0.1	120 ± 4.5
Pb	662 ± 7.2	878 ± 9.8
Cd	18 ± 0.01	11 ± 2.3

[a] The sediments were supplied as a dry sample

predominant while calcium oxide (CaO), hydroxylapatite ($Ca_5(PO_4)_3(OH)$) and calcium phosphate ($Ca_3(PO_4)_2$) were present in smaller amounts. Similar to other studies (Roberts et al., 2002; Struis et al., 2004), Zn minerals and those of other heavy metals were not detected by XRD, probably due to their low concentration (< 0.5% by weight) and/or presence of amorphous phases. Therefore, evaluation of speciation requires the use of other techniques such as spectroscopy and chemical extraction.

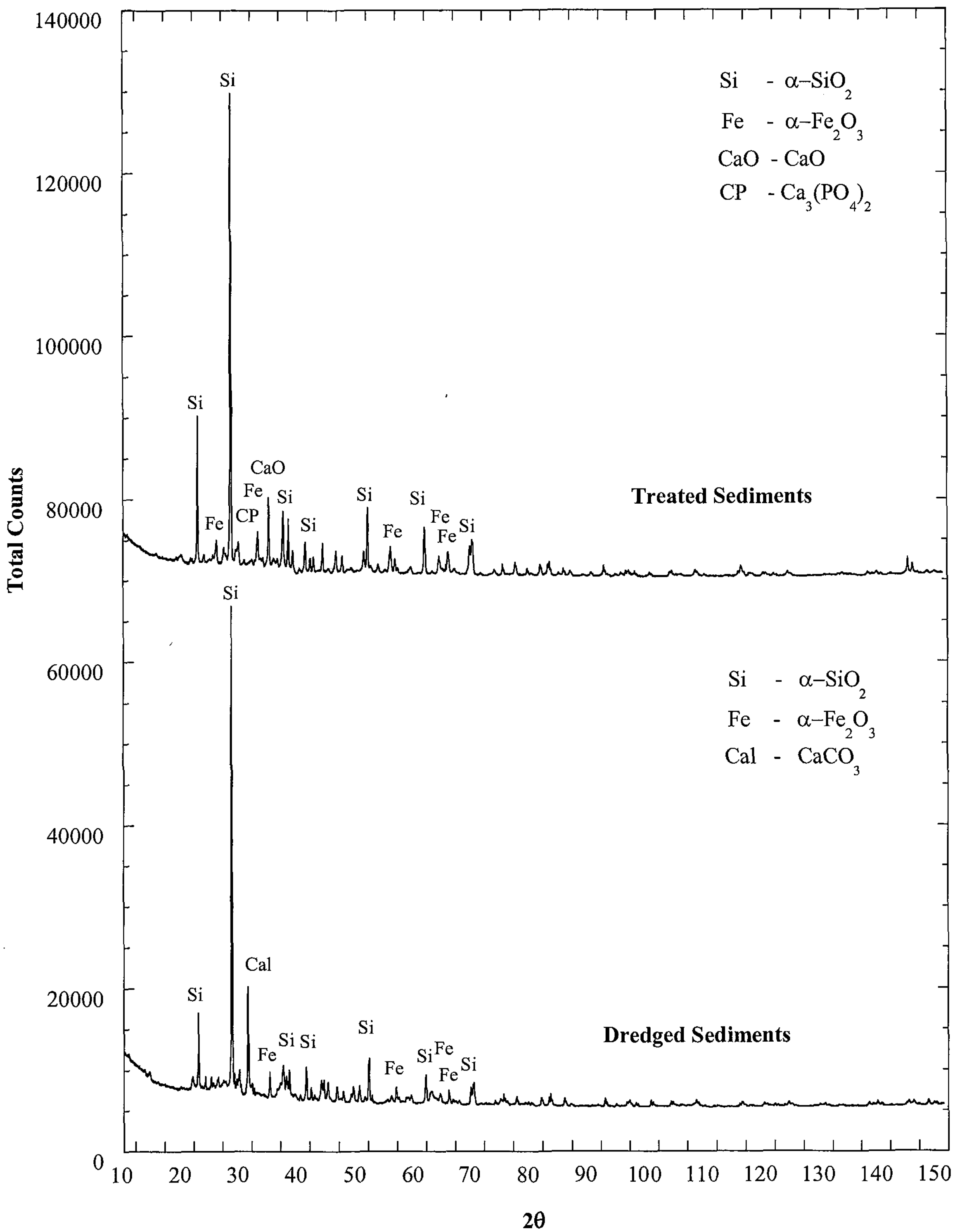

Figure 5.1 XRD patterns for dredged and treated sediments.

5.2 Analysis of reference spectra

Reference spectra (Figures 5.1) show characteristic structural details; crystalline Zn minerals $\chi(k)\cdot k^3$ show more structure compared to adsorption systems because of stronger backscattering from higher shells and less degree of disorder. Results of fitting the RSF with theoretical models (Table 5.2) were consistent with XRD crystallographic data, (Appendix B). Gahnite, franklinite, hopeite, hemimorphite, willemite, scholzite, and zincite exhibited first shell average distances of 1.95 ± 0.02 Å indicating tetrahedral structure with oxygen. Hopeite consists of tetrahedral and octahedral sheets in a 2:1 ratio (Hill and Jones, 1976), and while in this study tetrahedral dominates the signal, there is a 20% error in the coordination number (CN). For smithsonite and hydrozincite, contributions from the weaker backscattering carbon atoms were negligible because of greater contributions from stronger backscatters, Zn and O (Manceau et al., 2000).

Waychunas et al. (2002) found aqueous Zn^{2+} sorbed on ferrihydrite as a tetrahedral complex with Zn-Fe coordination depending on sorption density and observed a minimum second shell CN of 0.8 ± 0.2 Fe atoms. Although in this study tetrahedral structure was observed for the 10^{-2} mole Zn g^{-1} HFO, the second shell could not be isolated most likely due to a high degree of disorder. Results from fitting Zn adsorption to montmorillonite compare well with those found by Lee et al. (2004), 6 O atoms at 2.02-2.07 Å for 10^{-3} mole Zn g^{-1} of montmorillonite; however, unlike in their study, second shell contributions could not be isolated.

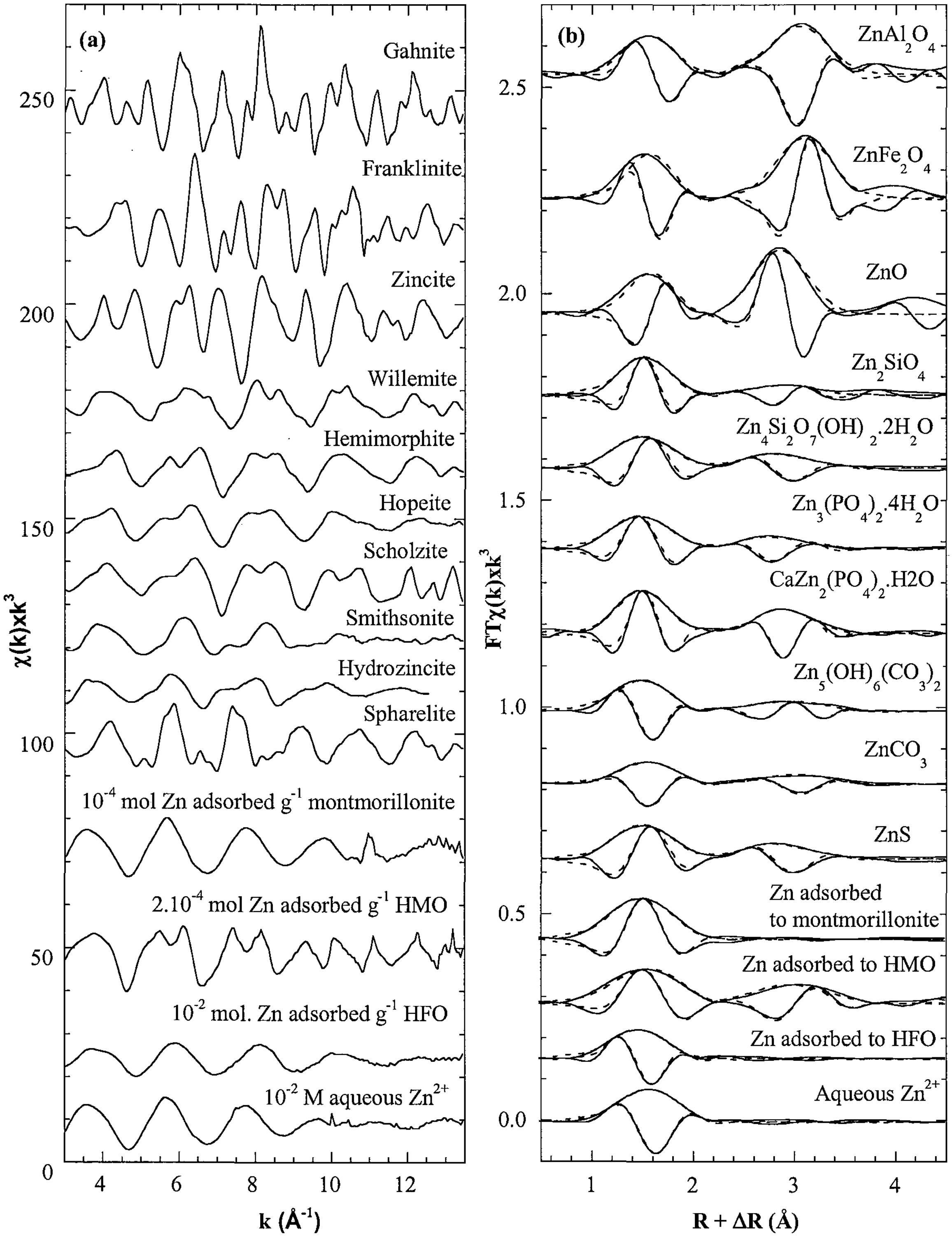

Figure 5.2 Zn K-edge for crystalline minerals and Zn sorption species (a) Background subtracted, normalized, and averaged $\chi(k)\cdot k^3$ spectra and (b) Fourier transformation of $\chi(k)\cdot k^3$ spectra (solid lines) over 3.0-10 $Å^{-1}$ for dredged sediments and 2.7-12.5 $Å^{-1}$ for treated sediments and fitted (dashed lines) with models.

Table 5.2 Fitting Results for the First and Second Shells Zn *K*-edge $\chi(k)\cdot k^3$ Spectra Fourier Transforms for Zn Minerals. Coordination Numbers (CN), Interatomic Distances (R, Å), Debye-Waller Factors (σ^2, Å^2), Shift in E_0 (eV)

Compound	Atoms	CN	R (Å)	σ^2 (Å)^2	Atoms	CN	R (Å)	σ^2 (Å)^2	ΔE_o (eV)
Gahnite ($ZnAl_2O_4$)	O	4.42	1.97	0.0043	Al	7.88	3.34	0.0034	2.21
					Zn	4[a]	3.58	0.0040	
Franklinite ($ZnFe_2O_4$)	O	3.73	1.98	0.0033	Fe	17.28	3.52	0.0102	-1.71
					Zn	5.85	3.67	0.0121	
Zincite ZnO	O	4.03	1.95	0.0037	Zn	12.37	3.21	0.0097	-1.48
Willemite (Zn_2SiO_4)	O	4	1.93	0.0040	Si	2.13	3.23	0.0013	-3.90
					Zn	4.37	3.20	0.0079	
Hemimorphite ($Zn_4Si_2O_7(OH)_2.2H_2O$)	O	4	1.95	0.0045	Si	3	3.01	0.0157	-2.20
					Zn	4	3.28	0.0118	
Hopeite ($Zn_3(PO_4)_2$)	O	4	1.95	0.0049	P	4	3.03	0.0293	-4.60
					Zn	3	3.28	0.0108	
Scholzite ($CaZn_2(PO_4)_2.H_2O$)	O	4.24	1.93	0.0033	P	3.24	3.42	0.0020	-4.78
					Zn	1.57	3.23	0.0101	
Smithsonite ($ZnCO_3$)	O	5.61	2.12	0.0075	O	3.57	3.04	0.0071	-4.80
					Zn	9.45	3.65	0.0193	
Hydrozincite ($Zn_5(OH)_6(CO_3)_2$)	O	4.23	2.00	0.0055	Zn	7.72	3.46	0.0161	1.08
Sphalerite (ZnS)	S	4.32	2.33	0.0071	Zn	5.44	3.80	0.0105	2.24
					S	7.91	4.46	0.0095	
Zn adsorbed to montmorillonite[b]	O	6.67	2.05	0.0029					-4.72
Zn adsorbed to HMO	O	5.2	2.08	0.006	Mn	1.3	3.33	0.005	-1.15
					Mn	5.5	3.51	0.009	
Zn adsorbed to HFO[b]	O	3.55	1.98	0.0017					-4.25
Aqueous Zn (Zn^{2+})	O	5.70	2.07	0.0142					-1.82

[a] Integer values indicate parameter fixed at crystallographic value.

[b] No backscattering contribution from the second shell. Highlighted cells refer to second shell backscatters identified by LCF for sediments.

Errors in first and second shells were estimated as ± 0.02 and ± 0.05 Å respectively for distances (R), and ± 20 and ± 40% respectively for CN.

5.3 Analysis of Sediment Spectra

The $\chi(k)\cdot k^3$ spectra for dredged and treated sediments (Figure 5.3) are significantly different indicating substantial change in structure. Dredged sediments show backscattering from potentially lighter elements and/or more disorder with much less structure than the treated system spectra. The structure is more closely associated with Zn sorption phases, for example, sorption to HFO, HMO, and montmorillonite, than to crystalline minerals (Figure 5.2). On the other hand, the treated sediments reveal significant structure with a much greater signal than the dredged sediment. The treated ones closely resemble gahnite and franklinite: pronounced peaks at 4.0, 6.1, 8.1, and 10.3 $Å^{-1}$, but without the peak splitting exhibited by franklinite at 4.0 and 8.1 $Å^{-1}$.

5.3.1 Dredged Sediments

Spectra in the k range 3.0-10 $Å^{-1}$ were decomposed into components using SixPACK PCA program (Webb, 2006). Analysis of the eigen values (Appendix C) revealed one principal component contributing 51% of the variance with each of the remaining components contributing less than 4% and therefore mainly experimental noise (Malinowski, 1991). The result is consistent with collection of bulk XAS spectra with no chemical variation (Malinowski, 1991; Roberts et al., 2002). Target transformation with smithsonite yielded the best spectra reconstruction ($R = 0.061$) (Table 5.3) followed by Zn sorption to montmorillonite (0.090), hydrozincite (0.116), and Zn sorption to HFO (0.169) and HMO (0.264). Other minerals including gahnite and franklinite resulted in poorer fits with an R 0.604 and 0.643, respectively. Because the statistic R does not consider interaction of a spectrum with other member spectra, the ranking does not

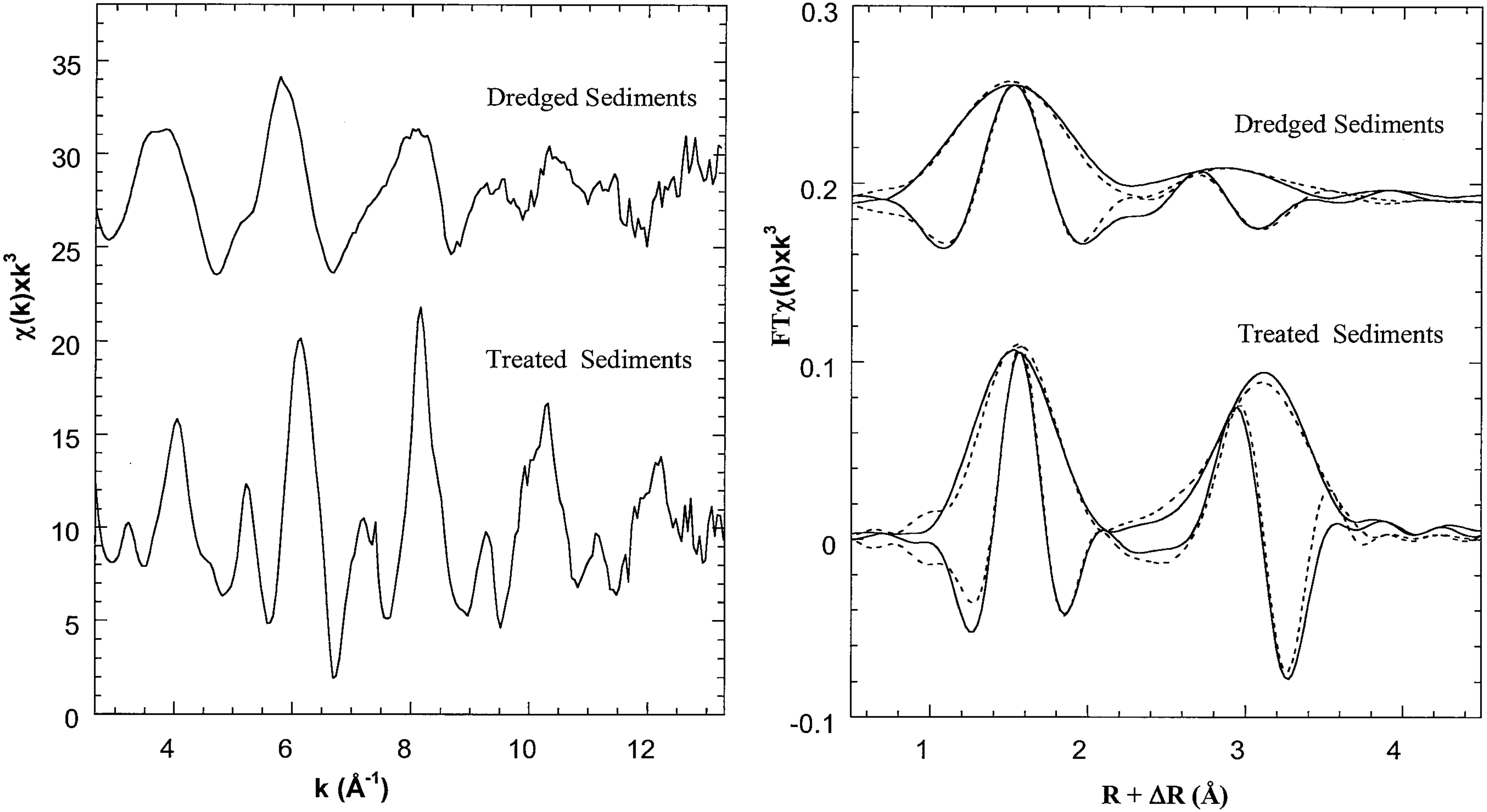

Figure 5.3 Zn K-edge spectra for Zn sorption species (a) Background subtracted, normalized, and averaged $\chi(k)\cdot k^3$ spectra and (b) Fourier transformation of $\chi(k)\cdot k^3$ (solid lines) over 3.0-10 Å^{-1} for dredged sediments and 2.7-12.5 Å^{-1} for treated sediments and fitted (dashed lines) with models. Radial distances are not corrected for phase shift and therefore do not reflect actual bond lengths.

Table 5.3 Fitting Factor R Values for Zn Reference Minerals Target Transformation with the Principal Components Decomposed from the Dredged and Treated Sediments Spectra

Dredged Sediments		**Treated Sediments**	
Reference Models	**Fitting Factor R**	**Reference Models**	**Fitting Factor R**
Smithsonite	0.061	Gahnite	0.223
Zn-Montmorillonite	0.090	Franklinite	0.243
Hydrozincite	0.116	Willemite	0.494
HFO	0.169	HFO	0.509
HMO	0.264	Hopeite	0.516
Sphalerite	0.449	Smithsonite	0.599
Willemite	0.484	Hemimorphite	0.601
Hopeite	0.538	HMO	0.604
ZnO hydrate	0.575	Scholzite	0.610
Gahnite	0.604	ZnO hydrate	0.640
Scholzite	0.617	Zincite	0.648
Zincite	0.622	Hydrozincite	0.662
Hemimorphite	0.630	Zn-Montmorillonite	0.736
Franklinite	0.643	Spharelite	0.843

determine the spectrums contribution to the sample spectrum or even guarantee its presence. Nevertheless, by prioritizing spectra, this ranking can greatly reduce the number of spectra to be processed in subsequent least squares fitting.

Linear combination fitting (Figure 5.4) showed that Zn in the dredged sediments were best represented by smithsonite (67%) and Zn sorption to HMO (18%) and HFO (15%) with an improved R 0.038. Contributions from Zn sorption to montmorillonite and precipitation as hydrozincite were insignificant. The first shell was fit with 5.26-6.21

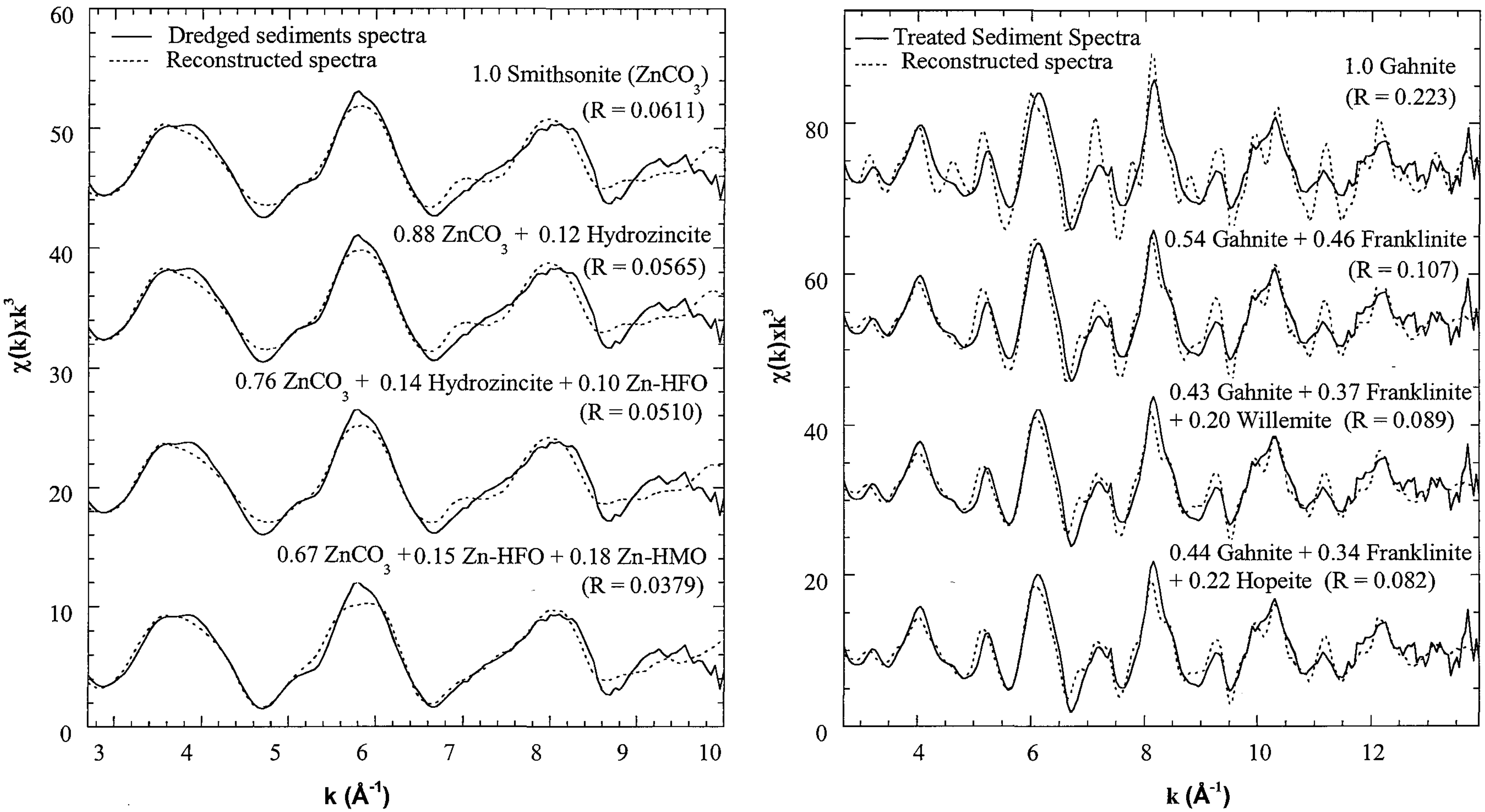

Figure 5.4 Experimental and LCF reconstructed $\chi(k)\cdot k^3$ spectra for dredged and treated sediments. Only spectra with more than 10% contributions are included. Fitting factor $R = \sum[(\chi_{exp} - \chi_{model})/\chi_{exp}]^2$ where χ_{model} refers to spectra reconstruction with PCA decomposed components.

± 1.24 O atoms at 2.03 ± 0.02 Å (Table 5.4) indicating octahedral coordination around the Zn atoms. The second shell was fit with 5.26 ± 1.05 Fe, 4.0 ± 1.6 Zn, and 3.54 ± 1.41 Mn atoms. The fitting suggests Zn is present in a number of configurations: precipitated as smithsonite and adsorbed to HFO and HMO, consistent with the LCF findings. In other studies on estuarine sediments using sequential extraction (Brydie and Polya, 2003; Hé et al., 2006), Zn was found to be primarily associated with the carbonate-bound fraction. On the other hand, Carroll et al. (2002) observed Zn formed sulfides under reducing conditions. When dredged, the sulfides were highly reactive with seawater; however, release of Zn was limited by sorption and co-precipitation with hydrous iron oxide. In this work, no attempt was made to preserve redox conditions that may exist before dredging, which may explain why sphalerite was not significant while sorption to HFO and HMO was.

5.3.2 Treated Sediments Spectra

In the analysis of the treated sediments spectra, the best reconstruction was obtained for gahnite (R = 0.223) followed by franklinite (0.243), willemite (0.494), HFO (0.509), and hopeite (0.516). LCF spectra reconstruction with gahnite, franklinite, and willemite improved the fitting factor R to 0.089 (Figure 5.4). When hopeite was included the contribution of willemite became insignificant, implying it was fully described by hopeite, while R improved to 0.082. Attempts to improve the fit further by including HFO were not successful. Therefore, Zn in treated sediments was best represented by gahnite (44%), franklinite (34%), and hopeite (22%). Gahnite and franklinite are spinels with Zn in tetrahedral coordination with oxygen while hopeite is orthorhombic with a 2:1 tetrahedral

Table 5.4 First and Second Shells Fitting Results using Models for Dredged and Treated Sediments, Zn *K*-Edge $\chi(K)\cdot K^3$ Spectra Fourier Transform, Coordination Numbers (CN), Interatomic Distances (R, Å), Debye-Waller Factors (Σ^2, Å^2), Shift in E_0 (Ev)

		First Shell				Second Shell			
Sample (model)	**Element**	**CN**	**R (Å)**	**σ^2 (Å)^2**	**Element**	**CN**	**R (Å)**	**σ^2 (Å)^2**	**ΔE_0 (eV)**
Dredged Sediments									
(Smithsonite)	O	6.21	2.03	0.0091	O	4[a]	3.40	0.0006	-2.79
					Zn	4[a]	3.61	0.0095	
(Chacolphanite)	O	5.26	2.02	0.0049	Fe	4.63	3.55	0.0150	-4.71
(Chacolphanite)	O	5.78	2.03	0.0055	Mn	3.73	3.54	0.0112	-5.07
Treated Sediments									
(Gahnite)	O	4.60	1.95	0.0032	Al	4.20	3.26	0.0018	-2.78
					Zn	3.78[a]	3.50	0.0025	
(Franklinite)	O	3.55	1.95	0.0005	Fe	8.79	3.43	0.0073	-4.82
					Zn	3.78[a]	3.54	0.0040	
(Hopeite)	O	4.81	1.96	0.0035	P	3.16	3.21	0.0025	0.21
					Zn	3.78[a]	3.49	0.0026	

[a] CN fixed at weighted average based on contributions obtained from LCF.

Errors in first and second shells were estimated as ± 0.02 and ± 0.05 Å respectively for distances (R), and ± 20 and ± 40% respectively for CN.

to octahedral coordination (Hill and Jones, 1976). Therefore, the treated sediments would be expected to exhibit a predominantly tetrahedral Zn coordination with oxygen.

Fitting the RSF first shell (Figure 5.3) revealed Zn-O distances 1.95 ± 0.02 Å and CN 3.55-4.81 ± 0.96 O atoms (Table 5.4) suggesting tetrahedral coordination. The second shell was fit with 4.20 ± 1.68 Al, 8.79 ± 3.52 Fe, or 3.16 ± 1.26 P atoms, and 3.78 ± 1.51 Zn atoms. The RSFs were therefore consistent with the presence of gahnite, franklinite, and hopeite in the treated sediments as determined by LCF. Other XAS studies using PCA, TT, and LCF have observed and quantified gahnite in incineration fly ash (Isaure et al., 2002) and franklinite in smelter waste in contaminated soil (Scheinost et al., 2002; Roberts et al., 2002), materials that are produced at elevated temperatures. Crannell et al. (2000) observed formation of several zinc phosphate phases including tertiary zinc phosphate ($Zn_3(PO_4)_2$), after treating incineration bottom ash with phosphate.

5.3.3 Dissecting Changes in Zn Speciation

The XAS analyses of the sediment spectra have shown phosphate addition and 700 °C thermal treatment changed Zn speciation from mainly carbonate and adsorbed phases to the crystalline minerals, hopeite, franklinite, and gahnite. While hopeite was identified in the treated sediments, it was not significant in untreated ones indicating it was formed primarily from phosphate addition. When heated, hopeite was observed to lose its waters of hydration in three steps at approximately 116, 158, and 296 °C (Hill and Jones, 1976; Pawlig and Trettin, 1999), yet remain stable up to 1000 °C (Hill and Jones, 1976). Observation of hopeite in the treated sediments is therefore consistent with its stability at elevated temperatures and suggests a role in Zn sequestration.

Sørensen et al. (2000) investigated the effect of heat on HFO and observed formation of crystalline iron oxides, hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) between 600 and 900 °C; sorbed metals including Zn were either incorporated into the crystal structure or expelled. Chang et al. (2004) observed thermal treatment transformed amorphous HMO into the crystalline trivalent manganese oxide (Mn_2O_3) at 500 °C and hausmannite (Mn_3O_4) at 700 °C. Although the fate of sorbed metals was not investigated, it is likely similar to that for HFO. $ZnCO_3$ has been reported to loose CO_2 between 150 and 295 °C to form ZnO (Bailar et al., 1973) which potentially reacts with aluminum and iron oxides on further heating to precipitate gahnite and franklinite. Perales-Perez and Umetsu (2002) observed franklinite precipitation from aqueous Fe^{3+} and Zn^{2+} at ambient temperatures under mildly oxidizing conditions and adequate Fe^{2+}/Zn^{2+} mole ratio. Typically, however, formation takes place at elevated temperatures and was observed to nucleate at 500-800 °C depending on precursors (Guaita et al., 1999). Mousa (1990) found gahnite precipitated from a ZnO-Al_2O_3 system at 600 °C; at 700 °C, its formation would be thermodynamically favored in a mixture of ZnO and Al_2O_3 ($\Delta G^o = -38.409$ KJ · mol^{-1} at 700 °C) (Jacob, 1976; Essene et al., 1987).

5.4 Thermodynamic Analysis of Zn Species in Treated Sediments

The Zn phases observed with XAS in treated sediments gahnite, franklinite, and hopeite are crystalline minerals; therefore, leaching of Zn would be controlled by dissolution. Consequently, thermodynamic analysis (Appendix D) was carried out to determine the expected concentration of Zn in solution in contact with the treated sediments. Concentrations of Zn species (Figures 5.5 and 5.6) were computed with MINEQL+

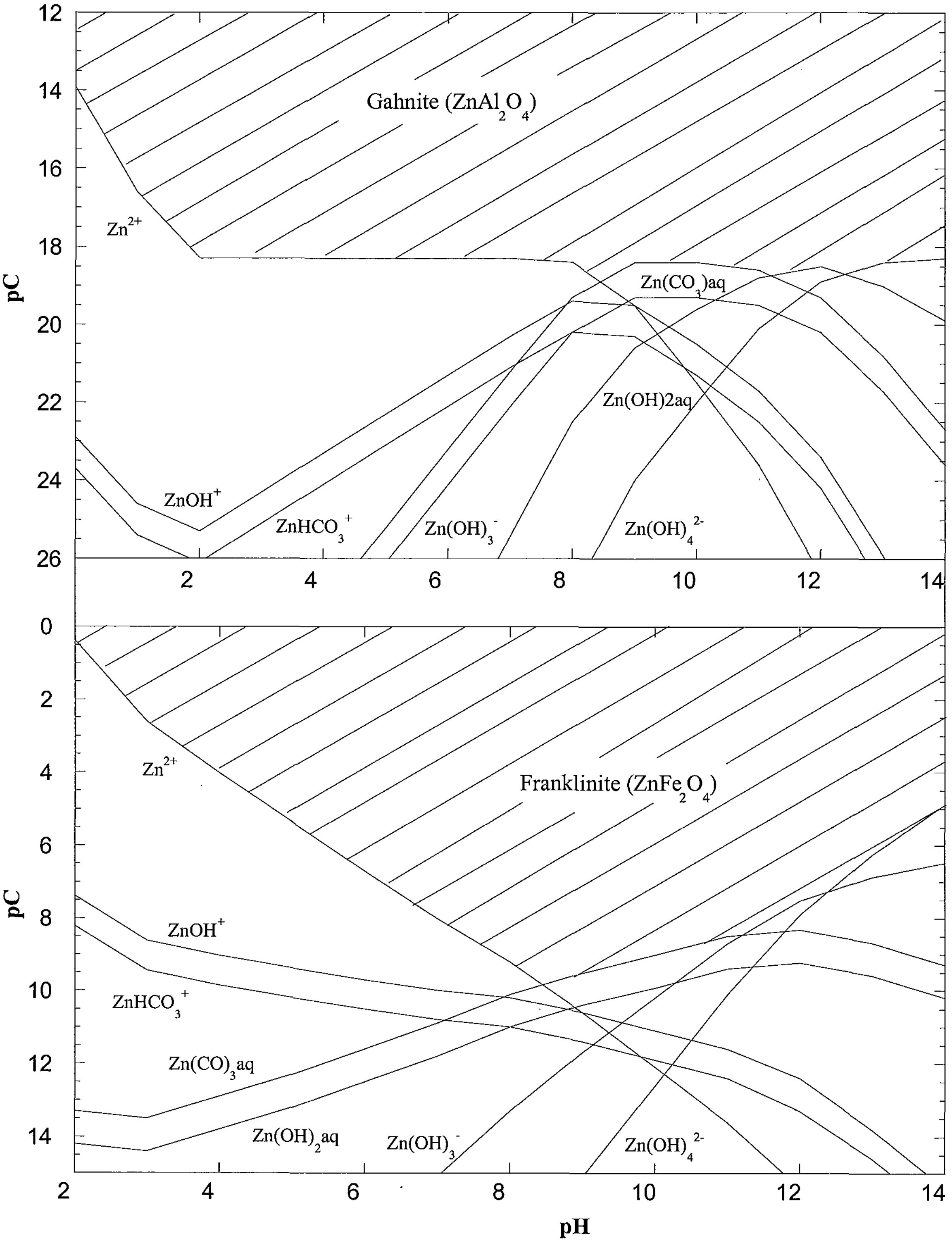

Figure 5.5 Solubility diagram of Zn species in equilibrium with gahnite ($ZnAl_2O_4$) and franklinite ($ZnFe_2O_4$) in an open system, computed using MINEQL+ (Schecher and McAvoy, 1998).

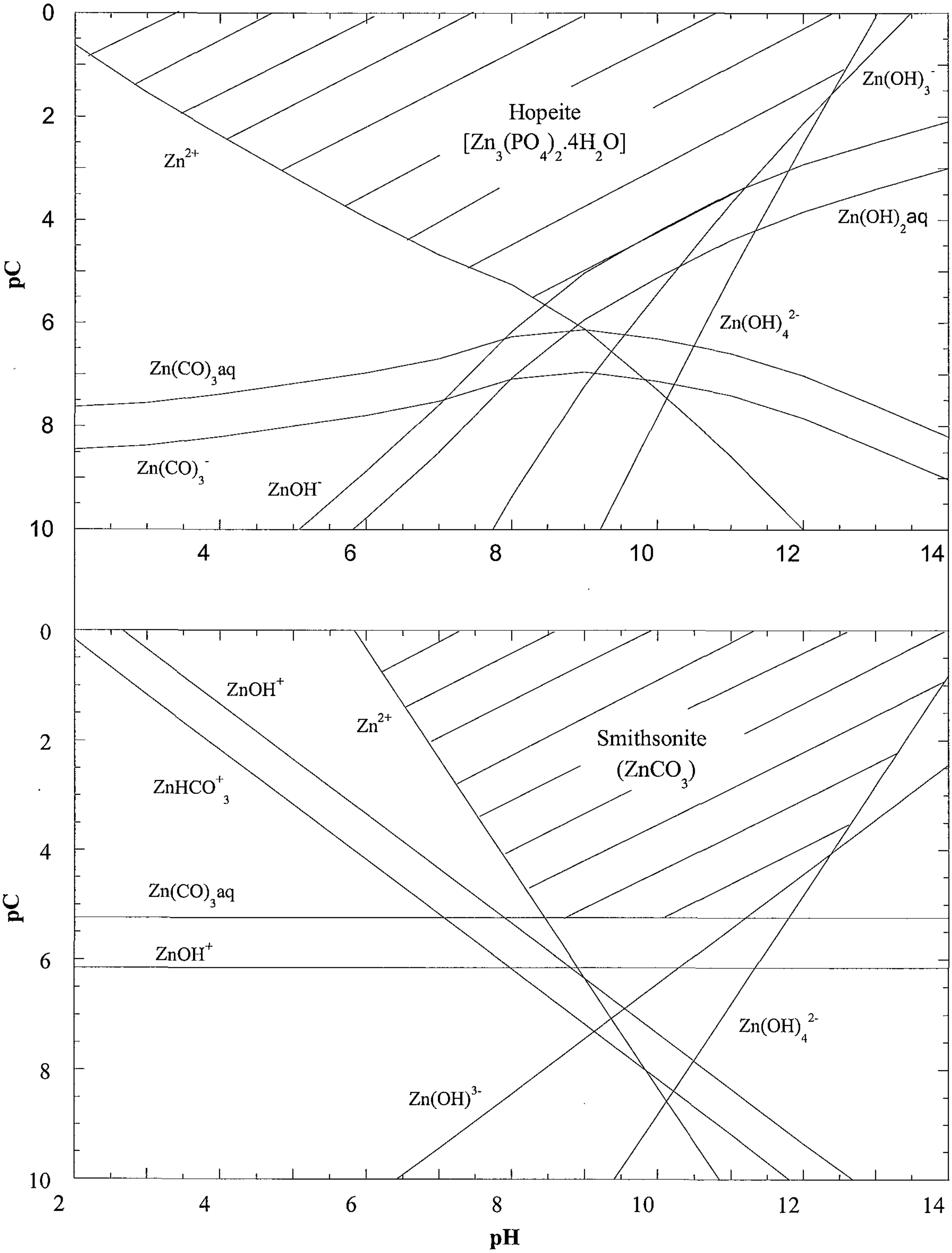

Figure 5.6 Solubility diagram of Zn species in equilibrium with smithsonite ($ZnCO_3$) and hopeite ($Zn_3(PO4)_2 \cdot 4H_2O$) in an open system, computed using MINEQL+ (Schecher and McAvoy, 1998).

(Schecher and McAvoy, 1998) for open to atmosphere conditions, ionic strength 1.0 × 10^{-4}, pH 0-14, and Zn in equilibrium with the solid phase under analysis only: gahnite, franklinite, and hopeite for treated sediments, and smithsonite for dredged sediments. The analyses showed gahnite is sparingly soluble for the entire pH range studied, while franklinite and hopeite are sparingly soluble under mildly acidic to neutral conditions with franklinite less soluble than hopeite. These results indicate that in treated sediments Zn is sequestered in sparingly soluble forms suggesting a reduction in leachability. In contrast, smithsonite in the dredged sediments would be relatively soluble in acidic and neutral conditions.

5.5 Implications of Results to Sediment Treatment

The aim of phosphate addition followed by calcination treatment is to stabilize dredged sediments for beneficial reuse as construction materials. This speciation study showed structural changes in mineralogy of Zn phases to more thermodynamically stable phases. The changes in speciation for other metals need to be investigated as well. Because of the need of a large library of reference spectra for each metal, sequential extraction was applied for the other metals in this study. Additionally, for reuse of the treated product, it is necessary to demonstrate, the ability to predict leaching based on speciation, reduction in leachability, and compliance with regulatory leaching criteria, by conducting leaching tests.

CHAPTER 6

SEQUENTIAL EXTRACTION

This chapter presents the determination of metal forms with sequential extraction. The total metal concentration in dredged sediments are restated from Table 5.1 and compared with those from other estuaries. Recovery of metals from sequential extraction as a proportion of the total metals is discussed and the total metals in dredged and treated sediments compared. Subsequently, the changes in metal forms following treatment are discussed and stabilization mechanisms elucidated. Finally, the implications of the sediment treatment are enumerated.

6.1 Total Metals in Sediments

Comparison of total metal concentrations in the NY/NJ Harbor's Passaic River Estuary sediments with those from other estuaries and bays (Table 6.1) reveal they are in the same range as those observed in Belgium sediments and the maximum concentrations overall for the NY/NJ Harbor Newark Bay. The concentrations of metals in these locations are up to four orders of magnitude greater than those of pristine estuaries such as the Florida Bay. In harbors, contamination results from harbor, industrial, and urban activities such as oil spills, releases of industrial products, wastewater emissions, and corrosion of ships (e.g., Guevara-Riba et al., 2003). These results indicate that the heavy metals are not native to the harbor sediments. Consequently, it can be hypothesized that most of the metals would be in the exchangeable, carbonates, adsorbed to metal oxides, and organic phases with limited incorporation into the crystal structure of the residuals.

Table 6.1 Total Metal Concentrations in Sediments from Passaic River Estuary at the NY/NJ Harbor and other Pristine and Polluted Estuaries and Bays

	Total Metal Concentrations (mg/kg)							
Site	**Zn**	**Ni**	**Mn**	**Pb**	**Cd**	**Cu**	**Co**	**Reference**
Passaic River Estuary at NY/NJ Harbor	1067 ± 12	971 ± 3.5	519 ± 4.1	662 ± 7.2	18 ± 0.0	520 ± 0.1	33 ± 0.1	This study
Newark Bay (NY/NJ Harbor)	21-1900	7.1-369	NR [a]	5.6-2500	0.13-29	0.44-2470	NR	Jones et al. (2001)
Dampremy, Belgium	3400 ± 130	105 ± 1.3	NR	878 ± 9.8	11 ± 2.3	120 ± 4.5	30 ± 0.1	This study
Florida Bay	0.5-3.14	0.30-0.89	11.6-62.7	0.62-3.25	NR	0.44-2.03	0.04-0.57	Caccia et al. (2003)
Large Marda, Texas	4.11-69.8	4.16-24.5	9.74-150	11.5-69.8	1.2-2.7	1.61-18.5	2.01-35.4	Sharma et al. (1999)

[a] NR refers to not reported

6.2 Sequential Extraction Recoveries

Recoveries of sequential extraction fractions were computed based on the total metal concentrations determined by aqua regia digestion (Table 6.2). The recoveries were within the 15% method error (Sutherland and Tack, 2002), with the exception of Zn in treated sediments (126%). Kartal et al. (2006) reported recoveries of between 87.5 and 178% from a number of studies using the standard reference material SRM 2711, a soil sample. In a study of concentration in topsoil samples from refuse dump sites, Umoren et al. (2007) found recoveries in the range 68 to 93% for Ni and Zn, respectively. These errors are attributed to dissolution of non-target metal phases, incomplete dissolution, readsorption and reprecipitation, and modification of the original metal oxidation states (Kirpichtchikova et al., 2006). Therefore, it is concluded that the results obtained are within the method variability.

6.3 Comparison of Total Metals in Dredged and Treated Sediments

Total metals measured in treated as a percentage of those in dredged were Cd (105), Mn (104), Ni (83), Cu (80), Pb (65), Co (105), and Zn (58) (Table 6.2, Figure 6.1). The relatively small concentration of Pb measured in the treated sediments is most likely due to evaporation during calcination. Rio et al. (2007) observed up to 20% evaporation of Pb from phosphate treated dreged sediments. For Zn, the reduced concentration in the treated sediments possibly resulted from inability of the aqua regia digestion to dissolve some of the resulting phases in the treated sediment. XAS showed 34% of Zn was in form of the spinel, gahnite, which has an extremely small solubility (Figure 5.5). This spinel was most likely not dissolved by aqua regia digestion and may have been part

Table 6.2 Sequential Extractions Metal Concentrations, Percentages, and Recoveries

	Concentrations (Percentage of Sum of Fractions)							Total Metals in Treated/ Untreated Sediments
	Exchangeable/ Carbornates mg/kg (%)	**Sorption to Fe/Mn Oxides mg/kg (%)**	**Organics/ Sulfides Mg/kg (%)**	**Residuals mg/kg (%)**	**Sum of Fractions mg/kg**	**Total Digestions mg/kg**	**Recovery [a] %**	**%**
Untreated Sediment								
Zn	757.7 (59)	207.0 (18)	168.9 (14)	100.4 (9)	1234.0	1066.5	115.7	N/A [b]
Ni	34.5 (33)	6.8 (6)	27.0 (25)	38.0 (36)	106.2	111.97	94.9	N/A
Mn	366.2 (68)	24.9 (2)	28.2 (8)	85.1 (21)	504.4	519.5	97.0	N/A
Pb	320.0 (43)	320.0 (43)	65.8 (9)	45.5 (6)	751.6	859.0	87.5	N/A
Cd	8.3 (43)	5.7 (29)	4.0 (20)	1.5 (8)	18.2	17.3	112.8	N/A
Cu	3.8 (1)	189.0 (36)	303.1 (58)	30.4 (6)	526.3	570.1	92.3	N/A
Co	6.2 (19)	1.0 (3)	6.4 (19)	19.4 (59)	32.9	32.5	101.5	N/A
Treated Sediments								
Zn	110.6 (14)	139.3 (18)	23.4 (3)	507.8 (66)	781.1	620.77	125.8	58
Ni	5.6 (7)	4.9 (6)	1.0 (1)	70.3 (86)	81.7	93.31	87.5	83
Mn	154.4 (29)	81.6 (15)	10.4 (2)	271.7 (54)	518.1	539.3	96.1	104
Pb	9.1 (2)	200.0 (33)	75.5 (12)	321.9 (53)	606.4	560.0	108.3	65
Cd	1.2 (7)	1.7 (9)	0.4 (2)	15.2 (82)	18.5	18.2	101.6	105
Cu	37.6 (8)	66.9 (14)	60.3 (13)	302.9 (65)	467.7	456.1	102.6	80
Co	3.3 (9)	2.8 (8)	1.1 (3)	27.9 (80)	35.1	34.0	103.3	105

[a] Recoveries are computed by expressing the sum of fractions as a percent of the total digestions.

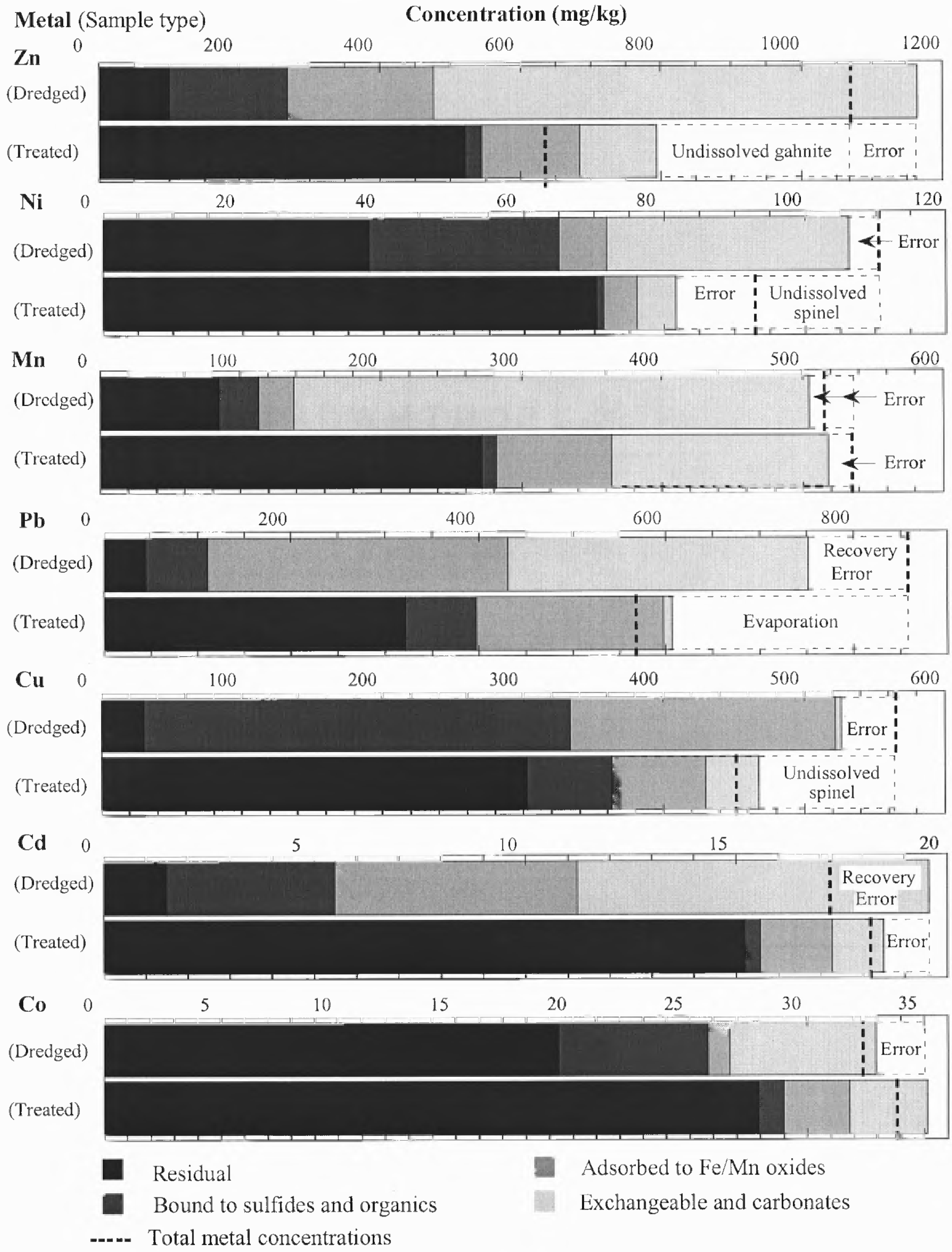

Figure 6.1 Mass balances of sequential extraction fractions and the total metal concentrations evaluated with aqua reqia (HCl/HNO_3) digestion for dredged and treated sediments and the likely causes of discrepancies. Estimated error in the extractions is ± 15% (Sutherland and Tack, 2002).

of the residual observed after filtration. Similar to Zn, the smaller concentrations of Ni and Cu in treated sediments as compared to the dredged most likely resulted from heat induced precipitation of sparingly soluble spinels (Shih et al., 2006; Lu et al., 2008).

6.4 Observed Metal Phases and Implications of Treatment

In untreated sediments (Figure 6.1, Table 6.2), Zn was distributed with exchangeable and carbonate phases, 59%, iron and manganese oxide minerals, 18%, sulfide and organic phases, 14%, and residual, 9%. These results compare well with the XAS observation of 67% Zn in the carbonate, smithsonite ($ZnCO_3$), and 33% adsorbed to iron and manganese oxides phases. In the XAS study, phases with less than 10% contributions, for example, organics and residuals are not measurable. Furthermore, small backscatters such as carbon atoms in the organics are insignificant as compared to heavier backscatters in the spectra such as Zn, Mn, and Fe (e.g., Manceau, 2000). Phosphate addition and calcination resulted in the dissolution of the carbonate to ZnO and CO_2 decreasing the exchangeable and carbonate phase to 13.9%. Similarly, calcination resulted in destruction of the organic matter reflected by a decline of Zn concentration in the oxidizable phase from 169 to 23 mg/kg. Adsorption to iron and manganese oxides phases also decreased from 207 to 139 mg/kg, which is attributed to transformation of the amorphous oxides to crystalline minerals induced by calcination (e.g., Sørensen, 2000). The decrease in the acid extractable, reducible, and oxidizable phases was accompanied by an increase of the residual phases from 100 to 521 mg/kg and which, based on the XAS measurements, comprised $Zn_3(PO_4)_2.4H_2O$, $ZnAl_2O_4$, and $ZnFe_2O_4$. As discussed earlier, the Zn concentration in residual phase of the treated sediment may have been greater than that observed because some of the minerals, for example, gahnite may not have been measured by aqua regia digestion.

The transformation of Ni through treatment was similar to that of Zn, although typical recoveries of total metals in the treated sediments were observed in the case of Ni. In the dredged sediments, a relatively greater portion of Ni was in the residual and organic and sulfide phases and a smaller in the exchangeable and carbonates phase as compared with Zn. Following treatment, the proportion of residual forms increased from 36 to 86% reflecting significant immobilization. Thermodynamic analysis (Appendix D) reveals that $Ni_3(PO_4)_2$ is acid extractible with a minimum Ni^{2+} equilibrium concentration of $10^{-3.5}$ M (pH 6.4) and, therefore, not likely to be part of the residuals. Similar to observations of spinels in Zn immobilization, Shih et al. (2006) found the spinel, nickel aluminate ($NiAl_2O_4$), was the stabilized phase in Ni-laden sludge sintered with Al rich ceramic precursors such as kaolinite. Precipitation of $NiAl_2O_4$ may have been partly responsible for the drastic increase in residual forms. Thermodynamic analysis of the spinels, $NiAl_2O_4$ and $NiFe_2O_4$ (Figure 6.2), reveal they are sparingly soluble with solubility similar to that of gahnite for pH greater than 3. Interestingly, the Ni spinels are more soluble than gahnite around the pH of 0 which may explain the greater aqua regia recovery of total metal in treated sediments obtained for Ni as compared to Zn.

Manganese was mainly associated with exchangeable and carbonate phases, 68%. Interestingly, Mn adsorption to iron and its own oxides was limited (2%) with the remaining 21% Mn bound in the crystal structure of sparingly soluble minerals. In the treated sediments, however, these phases increased to about 15 and 54% for the adsorbed and residual phases respectively implying a change of structure, for example, from

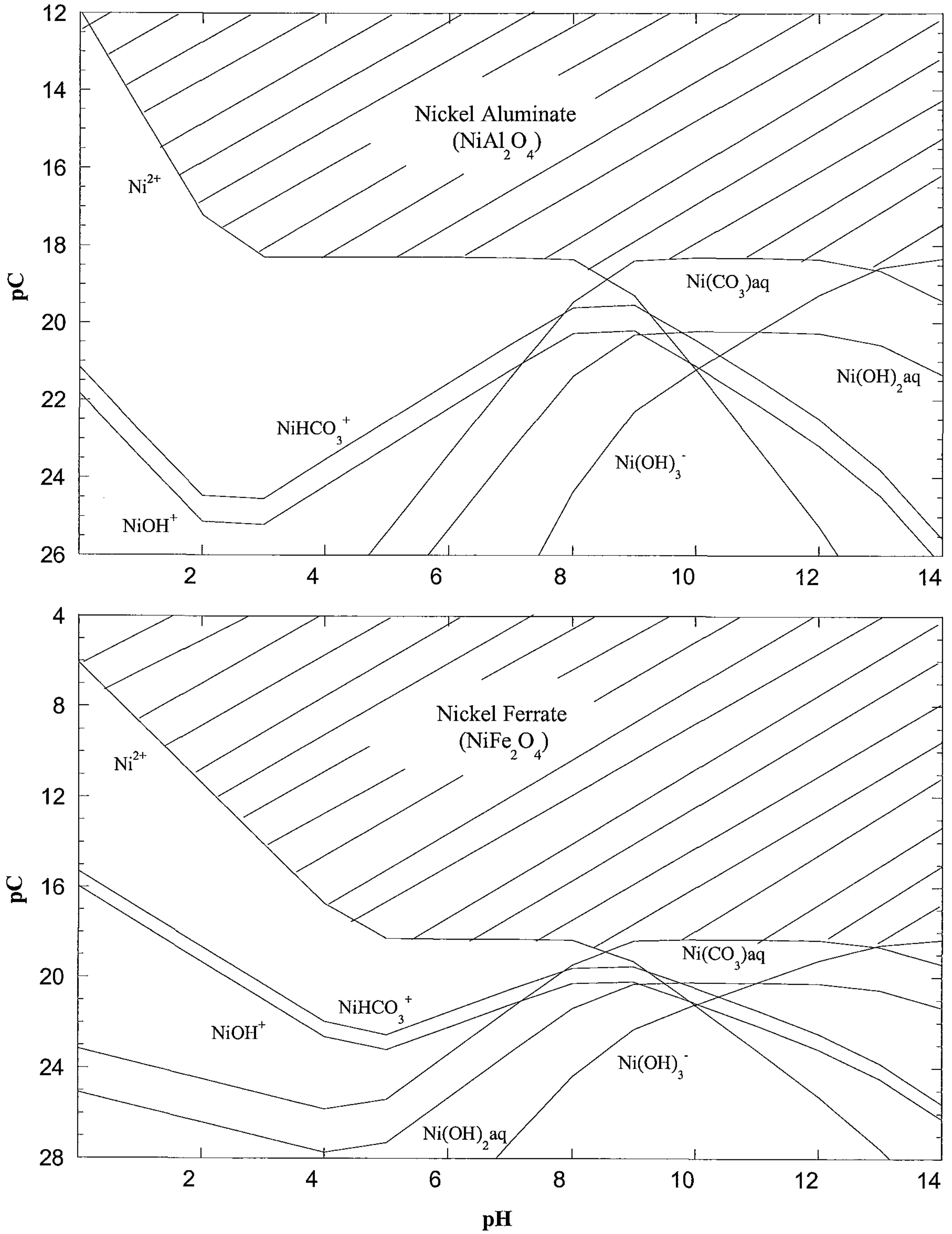

Figure 6.2 Solubility diagrams for Ni^{2+} in equilibrium with $NiAl_2O_4$ and $NiFe_2O_4$in an open system, computed using MINEQL+ (Schecher and McAvoy, 1998).

amorphous oxides to the crystalline trivalent manganese oxide (Mn_2O_3) and hausmannite (Mn_3O_4) (e.g., Chang et al., 2004), which has been observed to complex with Mn. The treatment was accompanied by a substantial reduction of exchangeable and carbonates forms, from 68 to 29%, most likely due dissolution of carbonates to oxides and CO_2 through addition of phosphoric acid and subsequent calcination. Incorporation of resulting manganese oxides into spinels such as manganese ferrate (III) and crystallization of amorphous oxide may have been responsible for the increase in residual forms from 21 to 54%. As a result of calcination, Mn binding to organics and sulfides diminished from 8 to less than 2%.

Cadmium in the dredged sediments was mainly in exchangeable and carbonates phase (43%), adsorbed to iron and manganese oxides (29%), with a smaller portion in the organic and sulfide phases (20%) (Table 6.2). Following treatment, the residual phases increased drastically from 8 to 82%, while the other phases declined. The minerals comprising Cd in the residual formed are not known. Although sorption and coprecipitation of Cd with apatite ($Ca_5(PO_4)_3(OH, F, Cl)$) was observed (Ma et al. 1994; Xu and Swartz, 1994), cadmium phosphate minerals were not observed with XRD while otavite ($CdCO_3$) and cadmium hydroxide were (Chen et al., 1997). However, in calcination, Uberol and Shadman (1991) observed formation of a cadmium aluminate silicate compound ($CdO{\cdot}Al_2O_3{\cdot}2SiO_2$) when metakaolinite ($Al_2O_3{\cdot}2SiO_2$) was exposed to $CdCl_2$ at 800 °C.

In the untreated sediments, Pb was distributed almost evenly between exchangeable and carbonate phases and adsorbed to iron and manganese oxides (Figure 6.1), representing 85% of the total. After treatment, the exchangeable and carbonate phases diminished to less than 2% while adsorbed phases dropped to 12%. This change in form is attributed to reaction with phosphate precipitating sparingly soluble forms such as pyromorphite ($Pb_5(PO_4)_3OH$) (Ma et al., 1995; Chen et al., 1997; Traina and Laperche, 1999; Crannell et al., 2000) with a corresponding increase in residuals from 6 to 53%. The increase in Pb associated with organics and sulfides from 66 to 76 mg/kg was unexpected given destruction of organics; it may imply association of Pb with sulfides yet, given the 15% error for the BCR method, the distribution is not significant different (Sutherland and Tack, 2002).

A relatively large proportion of Cu in the untreated sediments (58%) was in the oxidizable (organics and sulfides) phase consistent with affinity of copper for organics; for example, Caccia et al. (2003) found a correlation between metals and the percent of organic carbon (OC) in the order V > Cu > Ni > Cr > Co > Zn > Pb > Mg. This same trend was observed in our study for the metals analyzed. Burton et al. (2005) found Cu partitioning to organic phases was two times that to amorphous oxide minerals compared to 50 and 75% less for Pb and Zn, respectively. The high affinity of copper for organic matter is attributed to multidentate complexation with such groups as carboxylic and phenolic. Kinniburgh et al. (1999) observed a greater molar H^+/Cu^{2+} exchange ratio in Cu binding to humic acid, 1.3 to 1.8, compared to 0.3 to 0.5 for Ca and 0.4 to 0.8 for Cd. Interestingly, this affinity for organics and manganese and iron oxide phases resulted in scavenging of Cu leaving only 2% in the labile exchangeable and carbonate phases. Following treatment, metal forms in the organic and sulfide phases declined from 58 to 13%, which is assumed to be due to destruction or volatilization of organics by calcination. On the other hand, the concentration of the residual increased from 6 to 65%, consistent with formation of low solubility phase such as spinels. Nzihou and Sharrock (2002) hypothesized that Cu was incorporated into the glassy phase from observations of reduced Cu leachability after calcination only. Similarly, Wei et al. (2001) observed that heating in the temperature range of 105-900 °C reduced leaching more markedly for Cu-doped kaolin than for Cu-doped SiO_2 suggesting formation of a stabilizing phase with the aluminum rich kaolin. Lu et al. (2008) likewise found stabilization of copper by incorporation into $CuFe_2O_4$ structures when sludge from the surface finishing industry was heated above 800 °C.

Co in untreated sediments had the largest portion in the residual at 59%, while 38% was equally distributed between the exchangeable and carbonates and organics and sulfides phases with the remaining 3% adsorbed to iron and manganese oxides. Although the nature of the residuals is not known, Backes et al. (1995) suggest that these phases may comprise ones where Co is strongly adsorbed to crystalline manganese minerals, for example, cryptomelane ($K_2Mn_8O_{16}$) which has a point of zero charge below a pH of 3 and a high surface area. Co adsorption to such a phase could explain the very small portion sorbed to amorphous iron and manganese oxides, 2%. Upon treatment, the exchangeable and carbonates and organics and sulfides phases decreased, while adsorption to iron and manganese oxides and residual phases increased.

In summary, sequential extraction revealed that metals in dredged sediments are associated mainly with exchangeable, carbonates, metal oxides, and organic/sulfide phases with only small proportions in residual as hypothesized earlier. Following treatment, the residual phases increased significantly indicating metals are incorporated into crystalline structure of sparingly soluble minerals. The potential minerals in the

Table 6.3 Potential Sparingly Soluble Minerals in Treated Sediments

	Potential Minerals	Observed Materials and Temperature (Detection Method)	Reference
Zn	$ZnAl_2O_4$ $ZnFe_2O_4$ $Zn_3(PO4)_2\cdot 4H_2O$	Treated dredged Sediments, 700 °C (XAS)	This Study
Ni	$NiAl_2O_4$	Nickel-laden sludge sintered with kaolinite, 800 -1480 °C (XRD)	Shih et al. (2006)
Mn	Mn_2O_3 Mn_3O_4	Synthesized Hydrous Manganese oxide, 500-700 °C. (XRD, SEM)	Chang et al. (2004)
Cu	Cu-Kaolin phase	Soil analogue minerals, quartz and kaolin (XAS)	Wei et al. (2001)
	$CuFe_2O_4$	Surface finishing industry Sludge, 800 °C (XRD)	Lu et al. (2008)
Pb	$Pb_5(PO_4)_3OH$	Bottom Ash from Municipal solid waste treated with soluble phosphate (XRPD)	Crannell et al. (2000)
Cd	$CdO\cdot Al_2O_3\cdot 2SiO_2$	metakaolinite ($Al_2O_3\cdot 2SiO_2$) was exposed to $CdCl_2$’ 800 °C. (XRD)	Uberol and Shadman (1991)
Co	Adsorption to $K_2Mn_8O_{16}$	Oxides of Fe and Mn in soil	Backes et al. (1995)

SEM - Scanning Electron Microscope
XRPD - X-ray powder diffraction

residuals (Table 6.3) were deduced above from the XAS speciation study for Zn and inferred from sequential extraction results and literature. Knowledge of these phases is useful in geochemical modeling of contaminant leaching behavior.

6.5 Implications to Sediment Treatment

Sequential extraction revealed that phosphate addition and thermal treatment at 700 °C transferred metal contaminants from the chemically labile forms, such as exchangeable and carbonates to recalcitrant residual forms. These findings corroborate XAS observations of Zn immobilization in sparingly soluble minerals. Metal concentrations in the oxidizable phase (organics and sulfides) decreased substantially to less than 5% for all metals, except for Pb and Cu at 12.5 and 12.9%, respectively, demonstrating the mineralization/volatilization of organics in sediments through calcination. Although with sequential extraction, metal speciation was not determined explicitly, as with the XAS, results obtained indicate that the metals studied were stabilized (Table 6.2, 6.3). Consequently, reduced leachability of these metals is expected.

CHAPTER 7

LEACHING STUDIES

This chapter describes the leaching of sediments with TCLP (U.S. EPA 1994) for the standard 18 hr period to assess the efficacy of treatment and evaluate whether the sediments would be classified as hazardous materials. Extended TCLP to investigate whether equilibrium or pseudo equilibrium was achieved is also presented. The chapter concludes with SPLP assessment of risk to groundwater quality in beneficial reuse of treated sediments as construction material and compares this standard test to a more comprehensive analysis of the affect of pH and L/S ratio under transient conditions.

7.1 TCLP Assessment of Phosphate Addition and Calcination Treatments

Leaching of metals from dredged sediments as a percentage of the total metal concentration (Table 7.1) varied widely from 0.8% for Pb to 32% for Cd. Nevertheless, phosphate addition and calcination resulted in substantial reduction in leaching of up to 89%, when adjusted for loss of 16.1 % by dry weight organic matter. Approximately 22% of the total Zn or 740 mg kg^{-1} dry sediments (and 5.6×10^{-4} M Zn^{2+}) leached from dredged sediments at pH 5.56, where, based on XAS and speciation studies, over 50% of the Zn was in exchangeable and carbonate phases. After phosphate addition and calcination, leaching reduced to 3% of the total Zn or 102 mg kg^{-1} dry sediments (and 7.8×10^{-5} M Zn^{2+}) despite the more acidic pH of 5.37. Based on speciation, the observed reduction in the leachability of Zn can be attributed to immobilization

Table 7.1 Sediments Total Metal Concentrations, Hazardous Materials Regulatory Limits, and TCLP Results for Dredged and Treated Sediments for Dampremy, Belgium Samples

	Total Metal [a, b] in Dredged Sediments [b] (mg/kg)	Amount Leached from Dredged Sediments [b, c] (mg/kg)	Hazardous Materials Regulatory Limit [d] (mg/l)	TCLP Extract pH and Metal Concentration (mg/L)				
				Dredged	3% H_3PO_4 Addition	Calcined	3% H_3PO_4 & Calcined	Reduction in Leaching [e] (%)
pH				5.56 ± 0.03 [f]	5.02 ± 0.06	6.04 ± 0.17	5.37 ± 0.15	
Zn	3400 ± 130	740 ± 36	250	37 ± 1.8	19.8 ± 0.36	3.7 ± 0.87	5.1 ± 0.49	89 ± 1.3
Co	30 ± 0.1	3.1 ± 0.02	80	0.16 ± 0.003	0.15 ± 0.003	0.16 ± 0.003	0.14 ± 0.008	28 ± 3.5
Ni	105 ± 1.3	9.9 ± 0.24	25	0.50 ± 0.012	0.55 ± 0.004	0.24 ± 0.006	0.23 ± 0.009	62 ± 1.5
Cu	120 ± 4.5	1.8 ± 0.08	20	0.09 ± 0.004	0.07 ± 0.008	0.07 ± 0.005	0.08 ± 0.011	29 ± 0.2
Pb	878 ± 9.8	7.0 ± 0.30	5.0	0.35 ± 0.015	0.15 ± 0.019	0.25 ± 0.004	0.22 ± 0.035	48 ± 5.5
Cd	11 ± 2.3	3.5 ± 0.08	1.0	0.18 ± 0.004	0.10 ± 0.001	0.04 ± 0.001	0.04 ± 0.009	82 ± 2.3

[a] EPA Method 3050B (US EPA, 1996).
[b] Based on dry weight.
[c] Values were computed by multiplying leachate concentrations in Column 5 with the TCLP L/S ratio of 20.
[d] RCRA limits for Pb, Cd and California Code of Regulations limits for Zn, Ni, Co and Cu.
[e] Adjusted to account for loss of 16.1% by weight organic matter content during calcination.
[f] Error refers to 2 × standard error.

in sparingly soluble spinels such a $ZnAl_2O_4$, $ZnFe_2O_4$, and the phosphate mineral $Zn_3(PO_4)_2{\cdot}4H_2O$. Thermodynamic analyses (Figures 5.5 and 5.6) showed that at the extract pH, 5.37, equilibrium concentrations for Zn^{2+} are 3.47×10^{-4} M with hopeite, 1.37×10^{-6} M with franklinite, and 5.01×10^{-19} M with gahnite. Complexation of Zn with the acetate in the extraction fluid is negligible at 2.16×10^{-7} M or less than 0.3 % of Zn^{2+} (Schecher and McAvoy, 1998). Because the leachate was undersaturated with respect to hopeite, dissolution may be limited by reaction kinetics.

Phosphate addition was most effective with Pb (Figure 7.1) which is attributed to precipitation of sparingly soluble minerals such as pyromorphite ($Pb_5(PO_4)_3OH$) (Chen et al., 1997; Traina and Laperche, 1999; Crannell et al., 2000). In contrast, the leachability of Ni increased with phosphate addition; Seaman et al. (2001) along with Zupančič et al. (2004) attributed similar observations to Ca^{2+} competition for ion exchange sites, complexation with dissolved organic matter, and reduced pH. Calcination was most effective with Zn, Cd, and Ni with an over 50% reduction in leaching. The combined phosphate addition and calcination treatment reduced the leaching of Cd, Ni, and Co further. Based on results for Zn, formation of spinels such as $CdFe_2O_4$ and $NiAl_2O_4$ could be responsible for the reduced leaching observed for the calcined sediments compared to untreated and phosphate treated ones.

The leached metal concentrations (Table 7.1) were below RCRA (40 CFR, 2003) and California (CCR, 1991) criteria for the toxicity characteristic including total threshold limit concentrations (Table 2.2); therefore, the sediments would not be classified as hazardous materials for the metals studied. The leaching results obtained here were for the 18 hr U.S. EPA (1992) leaching period, which appears to have been

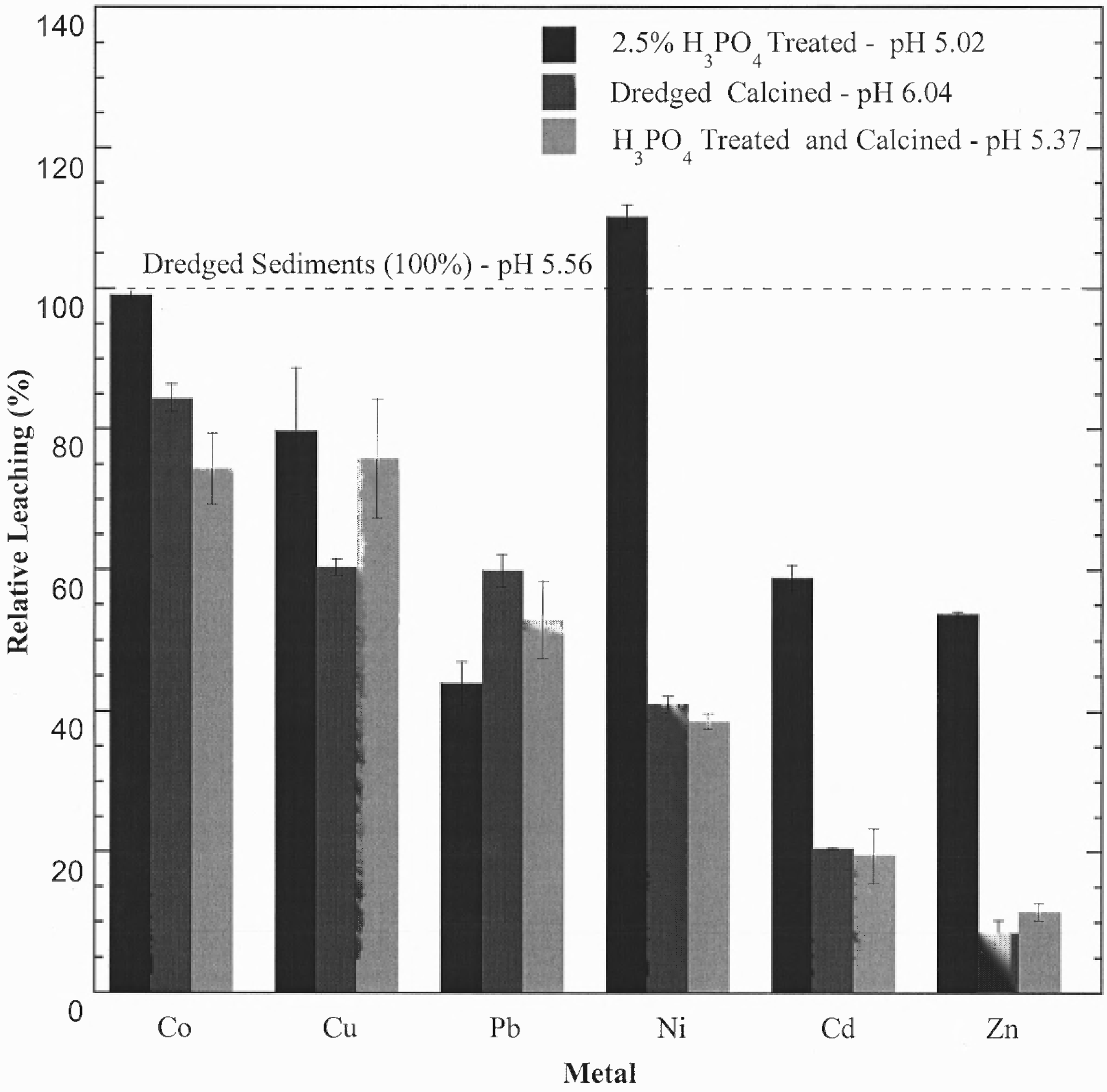

Figure 7.1 TCLP metal leaching for sediment treatments relative to amount leached from dredged sediments. Percentage leaching from calcined sediments are adjusted for loss of organic matter. Error bars indicate 2 x standard error.

selected arbitrarily period, which appears to have been selected arbitrarily (Scott et al., 2005) and, therefore, may not be indicative of equilibrium or leaching from long-term weathering. Consequently, leaching with TCLP was conducted for an extended period of 28 days.

7.2 Extended TCLP Leaching Tests

Extended TCLP showed similar trends as a function of time for Zn, Ni, and Co in dredged and treated sediments. Leached metal concentrations increased rapidly for the first day and then gradually approached equilibrium after 28 days (Figure 7.2). Reductions in metal leachability for the treated sediments of up to 80% were observed. The U.S. EPA TCLP 18 hr leaching represented between 51 and 83% of the total leached over 28 days for Zn in treated and untreated sediments, respectively. These results indicate that TCLP can underestimate the equilibrium concentration, or leachable concentration by as much as 50%; however, Scott et al. (2005) reported that this loss of accuracy needs to be weighed against the benefit of obtaining results within a reasonable period arguably essential for a regulatory test (e.g., Scott et al., 2005). Nevertheless, for more concentrated wastes, potential risk may be overlooked with the TCLP.

For Pb, initially a significant reduction in the leachable concentration is observed for the treated systems. However, after about 10 days, Pb concentrations in the aqueous phase for the untreated sediments began to decrease. Halim et al. (2005) observed a similar behavior with Pb and attributed it to initial complexation with dissolved organic matter followed by kinetically slower hydroxide precipitation. Interestingly, a similar phenomenon was observed for Cd in untreated sediments, where after 18 h the treated sediments leached about 25% of that from untreated sediments. Yet, after the first day, Cd underwent redistribution, either precipitating or adsorbing to other phases. Similar to Pb, results for Cu in treated sediments suggest an initial complexation with dissolved organic matter followed by a gradual precipitation from solution. Interestingly, an artifact of this study was a white precipitate which was identified with XRD as dichlorodimethyl

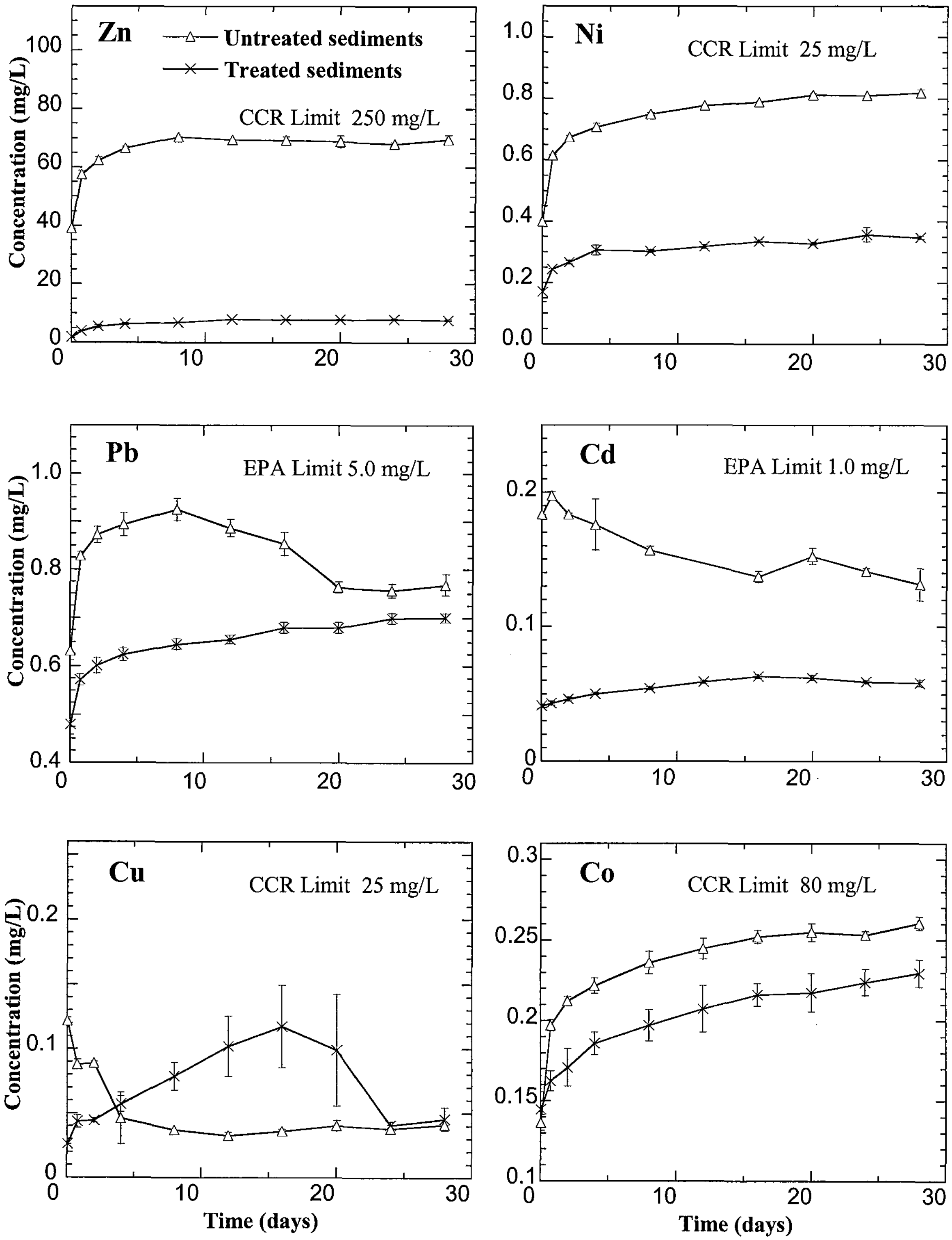

Figure 7.2 TCLP leaching of dredged and treated sediments as a function of time at pH of 5.0 ± 0.1. CCR refers to California Code of Regulations (CCR, 1991).

glyoxime (or gloxime) copper (II) ($C_4H_8Cl_2CuN_2O_2$) (Appendix A). This compound is prepared by reaction of anyhydrous copper (II) chloride with dimethyl glyoxime ($C_4H_8N_2O_2$), which is synthesized by catalytic reaction of alcohol (C_2H_5OH) and nitrous acid (HNO_2) (Semon and Damerell, 1943; Svedung, 1969). In this study, the synthesis precursors may have formed through potentially microbial transformation of the acetic acid/acetate used in the extraction fluid to an alcohol (Chen and Rosazza, 1994) coupled with the HNO_3 used for pH adjustment and combined with copper chloride from the sediments.

Metal leaching was below RCRA (40 CFR, 2003) and California (CCR, 1991) limits for hazardous materials even over the extended period (Figure 7.2); therefore, the sediments would not be classified as hazardous material based on the metals studied. Nevertheless, discrepancies between the standard TCLP leachate concentrations and the equilibrium concentrations demonstrate the need for improved understanding of speciation and mechanistic models prior to characterizing a waste as "non-hazardous" or in beneficial reuse of waste material. SPLP is required by several states including New Jersey, Florida, and Wisconsin (FDEP, 2005; W.A.C., 2008; NJDEP, 2008) in considering waste or treated waste for beneficial reuse.

7.3 SPLP Assessment of Risk to Groundwater

7.3.1 Results of Leaching with SPLP

Passaic River Estuary sediments treated with H_3PO_4 at 5% by dry weight phosphate addition and calcinations at 700 °C were extracted with the U.S. EPA SPLP (1994). Only a small fraction of the total metals was mobilized, less than 0.6% for Zn, Ni, Cu, Pb, and

Cd, 1.27% for Co, and 6.32% for Mn (Table 7.2). This observation is similar to the results from roadside soils extracted with NaCl and de-ionized water, where only 0.15% of total Pb was mobilized (Norrström, 2005). While these results would appear to suggest sequestration of metals in recalcitrant phases, sequential extraction (Figure 6.1) showed the percent of metals in the residual phases reflecting stable forms was relatively small, less than 10%, with the exception of Mn (21%), Ni (36%), and Co (59%). Therefore, results reflect the limited capacity of SPLP extraction fluid in mobilizing metals from these matrices, resulting from a lack of buffering at a lower pH and complexation (e.g., Townsend et al., 2003). The treated sediments showed a 93% reduction in Zn concentration compared to the dredged sediment (Table 7.2). The reduction in leaching is similar to the 89% reduction observed with the TCLP study even though the latter concentrations were greater by more than two orders of magnitude. The greater leaching with TCLP was due to the lower pH (5.37) of the acetate buffered extraction fluid as compared to the SPLP (6.70). Significant reductions in leaching were also observed for Cu, Ni, and Mn, 52-82%, and smaller reductions for Pb, Cd, and Co, 13 to 27%. These findings were also corroborated by sequential extraction where a large increase in metal concentration in the residual phases was observed upon treatment, from 36 to 86% for Ni and from 6 to 65% for Cu (Table 6.2, Figure 6.1).

The results for treated sediments were based on 5% by dry weight phosphate addition with 14.7 M H_3PO_4. However, while H_3PO_4 potentially increases dissolution of labile metal phases, given its acidity it could inhibit subsequent precipitation of phosphate phases. Therefore, other forms of phosphates were examined to optimize reduction in metal leachability.

Table 7.2 Passaic River Estuary Dredged Sediments Characteristics: Moisture Content, Organics and Total Metal Concentrations (U.S. EPA, 1996), and SPLP Extract Metal Concentrations

	Dredged Sediments			Treated Sediments [a]	
	Moisture, Organics and Total Metal Concentrations (mg/kg) [b]	**SPLP Extract Metal Concentration (mg/kg) [c]**	**Percent Metals Leached (%)**	**SPLP Extract Metal Concentration (mg/kg) [c]**	**Percent Reduction in Leaching (%)**
Moisture	56.5%				
Organics	131				
Zn	1067 ± 12	5.46 ± 0.66	0.51	0.380 ± 0.106	93.0
Ni	971 ± 3.5	1.36 ± 0.12	0.14	0.480 ± 0.150	64.7
Mn	519 ± 4.1	32.80 ± 5.32	6.32	6.000 ± 2.660	81.7
Cu	520 ± 0.1	0.14 ± 0.03	0.03	0.067 ± 0.005	52.1
Pb	662 ± 7.2	0.68 ± 0.03	0.10	0.548 ± 0.006	19.4
Cd	18 ± 0.0	0.10 ± 0.01	0.56	0.088 ± 0.001	13.2
Co	33 ± 0.1	0.42 ± 0.03	1.27	0.308 ± 0.018	26.7

[a] Sediments treated by 5% H_3PO_4 addition and 700 °C calcination.
[b] Except for moisture which is expressed in percent.
[c] Obtained by applying the SPLP L/S of 20 to the SPLP extract concentration measured in mg/L.

7.3.2 Evaluation of Alternative Phosphate Forms

The initial pH (6.96) of dredged sediments was reduced by addition of 3 and 5% by dry weight phosphate to respectively 6.47 and 6.56 for $CaHPO_4$, 5.25 and 5.30 for $NaH_2PO_4{\cdot}H_2O$, 4.54 and 4.23 for $Ca(H_2PO_4)_2{\cdot}2H_2O$, and 3.55 and 3.07 for H_3PO_4. After calcination, however, the sediment pH rose to the 6.2-7.0 range for all the phosphates most likely due to dissolution of carbonates to oxides and carbon dioxide. In achieving this final pH range, the phosphate addition and thermal treatment has an advantage over stabilization with cement where resulting alkaline conditions, pH values of 11 to 12, increased leachability of amphoteric metals such as Ni, Cd, Cu, and Pb (e.g., Gardner et al., 2007).

Reduction of metal leachability by alternative phosphate forms was statistically similar for Zn and Ni (Figure 7.3). Based on XAS, 78% of Zn was precipitated in sparingly soluble heat induced spinels, gahnite and franklinite, while Ni potentially formed the spinel, nickel aluminate (Shih et al., 2006). This transformation by calcination combined with the narrow range of final extract pH, 6.70 - 7.2 (Figure 7.3) may have eclipsed differences in the phosphate forms applied. For Mn, the calcium phosphates were more effective in reducing leachability possibly due to ion exchange with the less soluble calcium phosphates (e.g., Chen et al., 1997). The greater reduction in leachability by 5% phosphate addition as compared to 3% suggests less competition for phosphate. Treatment with H_3PO_4 was more effective than with $NaH_2PO_4{\cdot}H_2O$ in reducing the leachability of Mn and Cu, indicating that an initial dissolution of the metals by the more acidic conditions through H_3PO_4 addition may be important in their stabilization.

Sediment treatment with calcium phosphates, sodium phosphate, and H_3PO_4 at 3% by dry weight phosphate increased leachability of Pb and Cd as compared to dredged sediments (Figure 7.3). This increment is partly due to loss of 13.1% of dry weight organic matter in calcination subsequent to phosphate addition, where metals were concentrated in the remaining sediments. The smaller solubilities 0.032 $g{\cdot}(100\ g\ H_2O)^{-1}$ and 1.8 $g{\cdot}(100\ g\ H_2O)^{-1}$ for $CaHPO_4$ and $Ca(H_2PO_4){\cdot}2H_2O$, respectively, compared to 59.9 $g{\cdot}(100\ g\ H_2O)^{-1}$) for $NaH_2PO_4{\cdot}H_2O$ (Weast and Astle, 1983) may have limited availability of phosphate for reaction with Pb and Cd following dissolution of their

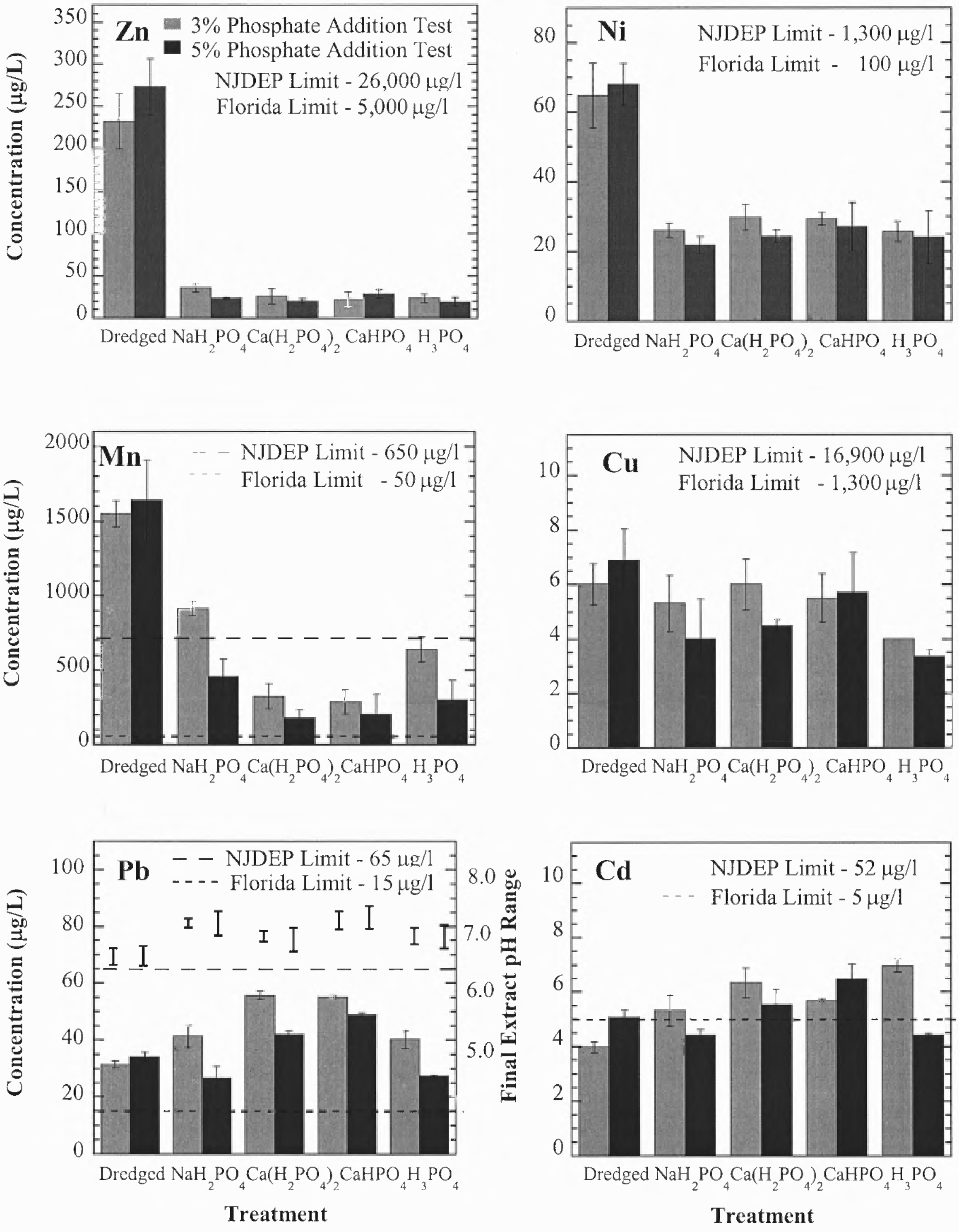

Figure 7.3 SPLP leaching of metals from dredged sediments and sediments treated with alternative phosphate forms and calcination, and states risks to groundwater criteria. The final extract pH shown for Pb applies to the other metals as well. Waters of hydration are omitted in labeling phosphate forms for clarity.

carbonates to oxides by calcination (and with no notable formation of sparingly soluble spinels). Based on reagent blanks, the purity of $Ca(H_2PO_4)·2H_2O$ was marginally less than that of $CaHPO_4$, potentially contributing, for example, 5 μg/l of the 25 μg/l Zn in the $Ca(H_2PO_4)·2H_2O$ addition leachate. However, the lesser purity did not affect the treatment significantly most likely due to the greater solubility of $Ca(H_2PO_4)·2H_2O$ compared to CaH_2PO_4. Overall, H_3PO_4 applied at 5% was most consistent in reducing metal leachability suggesting solubility, stoichiometry, and initial dissolution of metals from their native phases are important factors in the treatment.

7.3.3 Risks to Groundwater in Beneficial Reuse of Sediments

Several states in the U.S. require applying the SPLP for assessing risk to groundwater before reuse of waste materials. In determining this risk, regulators apply a dilution attenuation factor to the groundwater quality levels (GQL) to generate the impact to groundwater criteria for leachate as discussed earlier. The DAF accounts for dilution of pore water once it enters the groundwater. The NJDEP (2008) employs a DAF of 13, while Florida and Wisconsin assume an implicit dilution from the SPLP given the L/S ratio of 20:1 and apply a DAF of 1. The NJDEP criteria were exceeded only for Mn (Table 7.2, Figure 7.3) in dredged sediments and achieved in treated sediments with the exception of treatment with $NaH_2PO_4·H_2O$ and H_3PO_4 applied at 3% phosphate by dry weight. On the other hand, applying Florida and Wisconsin criteria based on a DAF of 1 (Table 2.3) resulted in exceedances for both dredged and treated sediments of Mn, Pb, and most treatments for Cd. Sequential extraction applied on treated sediments suggests that Pb is adsorbed to iron and manganese oxides (33%) and present in residual forms

(53%). Considering the more stable residual forms, thermodynamic analysis based on pyromophite ($Pb_5(PO_4)_3OH$) (Figure 7.4) reveals that Pb aqueous concentrations were undersaturated, suggesting dissolution is likely controlled by reaction kinetics. At the DAF of 13 applied by NJDEP, the 65 μg/L groundwater quality criterion for Pb is greater than the Pb concentration in equilibrium with pyromorphite over the pH range of 7 to 8.2. On the other hand, the 15 μg/L criterion applied in Florida and Wisconsin (FDEP, 2005; W.A.C., 2008) is less than pyromorphite solubility. Therefore, thermodynamically, the criterion is not achievable; however, it may be attained through slow dissolution kinetics.

While SPLP is an approach used to evaluate leaching from acid rain for regulatory purposes, it does not provide a mechanistic basis and therefore a magnitude of leaching as a function of environmental conditions especially pH. Consequently, leaching was evaluated over the possible range of pH in the environment.

7.3.4 Leaching as a Function of pH

Variation of pH over the range 4 to 9 resulted in large changes in leachate metal concentrations ranging over two to four orders of magnitude for both treated and dredged sediments (Figure 7.5). Leaching decreased as pH increased consistent with cation adsorption (e.g., Phillips and Sheehan, 2005), where as the pH increases, the surface charge becomes more negative increasing the affinity of cations for the surface. Acidic pH values revealed elevated metal concentrations, which approached or surpassed the NJDEP impact to groundwater criteria (NJDEP, 2008). However, for Pb, leaching showed less of an effect of pH, which can be attributed to the forms of Pb present,

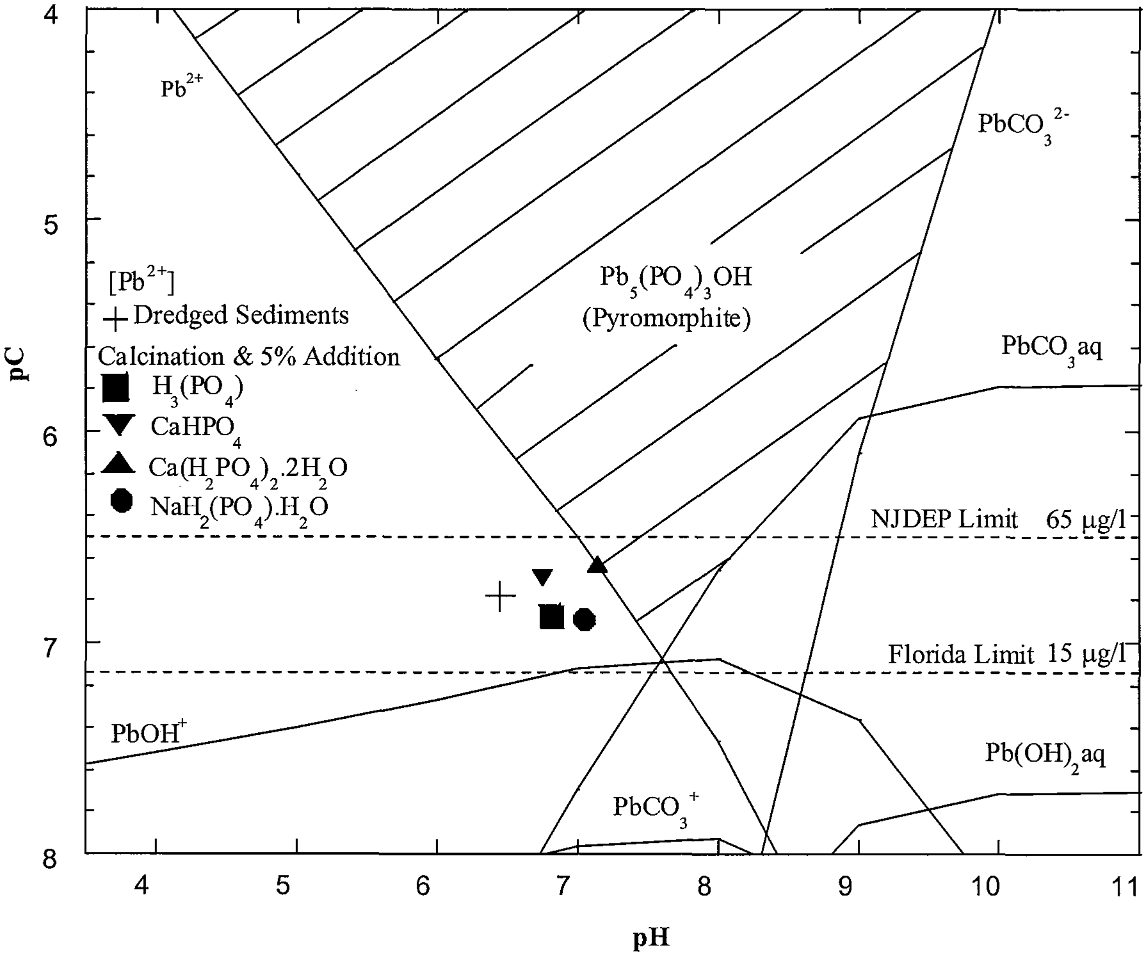

Figure 7.4 Solubility diagram of Pb species in equilibrium with pyromophite in an open system, computed using MINEQL+ (Schecher and McAvoy, 1998), and the impact to groundwater limits for New Jersey (NJDEP Limit) and Florida.

potentially pyromorphite and sorption to iron and manganese oxides. Leaching of untreated dredged sediments exceeded that for treated sediments for Cu under acidic pH conditions and Pb under alkaline conditions. However, leached concentrations were below the New Jersey, Florida, and Wisconsin criteria for Cu, but as discussed earlier exceeded Florida and Wisconsin criteria for Pb. For all other metals, treated sediments leached less than the untreated dredged sediments over the entire pH range 4 to 9. This observation is consistent with the sequential extraction results where residual forms

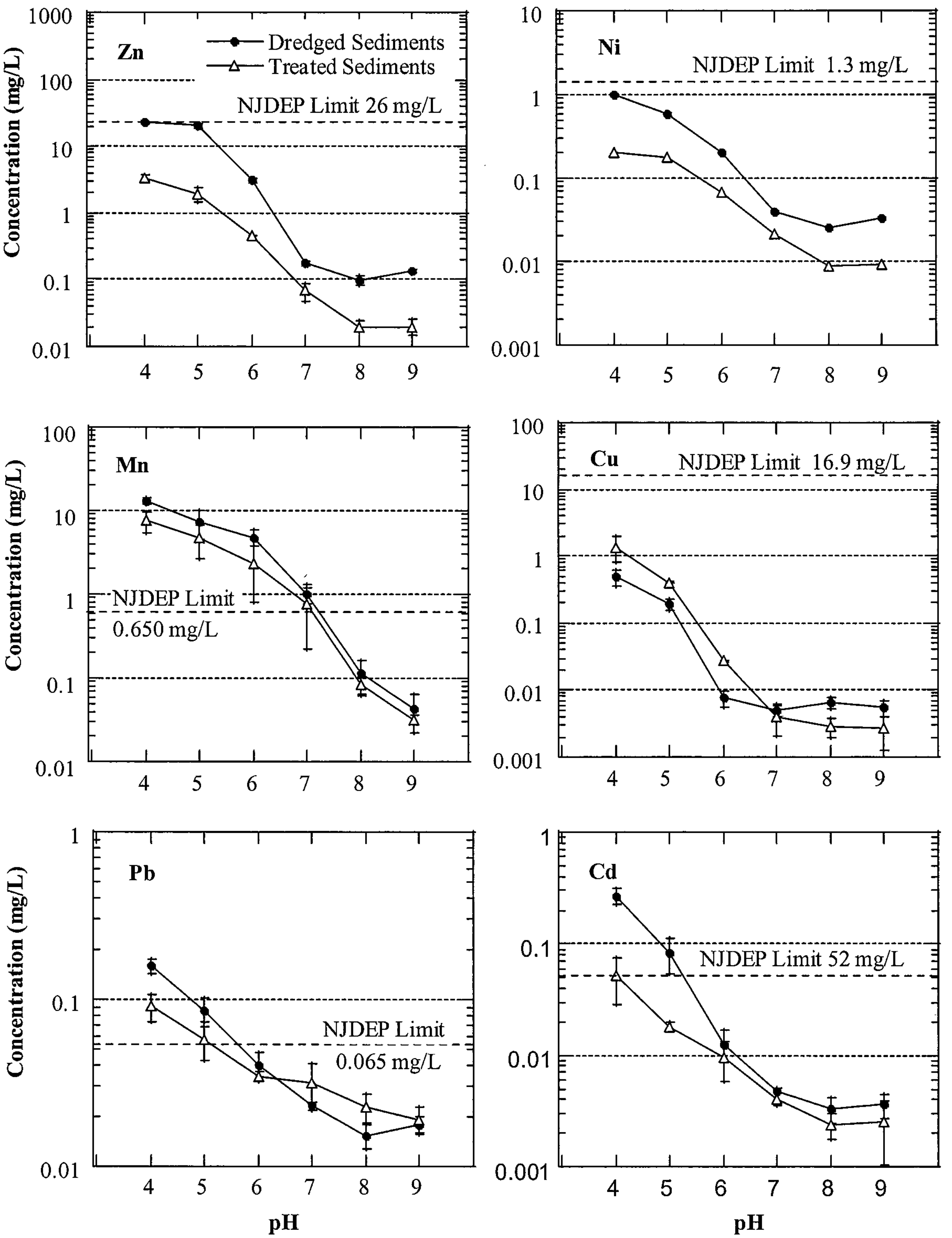

Figure 7.5 SPLP leaching of metals as a function of pH for dredged and treated sediments at L/S 20 showing two to four order of magnitude change in leaching over pH values of 4-9. NJDEP refers to New Jersey Department of Environmental Protection.

increased at the expense of exchangeable and carbonates phases. The above results show the criteria for an impact to groundwater requirement would be met under alkaline conditions and exceeded under acidic conditions; however, for the sediments, and particularly the treated ones, buffering capacity may control solution pH around neutral.

7.3.5 Leaching at various L/S

The difference in risk to groundwater criteria between the State of New Jersey on one hand and Florida and Wisconsin States on the other is based on interpretation of the U.S. EPA SPLP L/S of 20. The implications of L/S to the risk to groundwater were therefore investigated. Varying L/S between 5 and 100 (Figure 7.6) showed a much smaller change in metal leaching compared to the effect of pH, an increase of 4 to 10 times as L/S was reduced from 100 to 5. Townsend et al. (2006) similarly observed a two to fivefold increase in leaching of Ba, Mo, Sr, Cr, As, and Pb for L/S reduction from 20 to 2 where the extraction pH was allowed to vary. The increase in metal leaching with decreased L/S is partly explained by a drop in pH from 7.00 for L/S 100 to 6.55 and 6.74 for L/S 5 in dredged and treated sediments, respectively. While the effect of L/S was not isolated from that of pH, it is evident that it was comparatively small. The increase in leaching with decreased L/S is consistent with kinetically limited processes associated with adsorption/desorption influencing leaching; these phases were observed with sequential extraction in both dredged and treated sediments. As a result, the contaminant behavior may not be described with the distribution coefficient as its use assumes equilibrium partitioning only; other kinetic based models are needed.

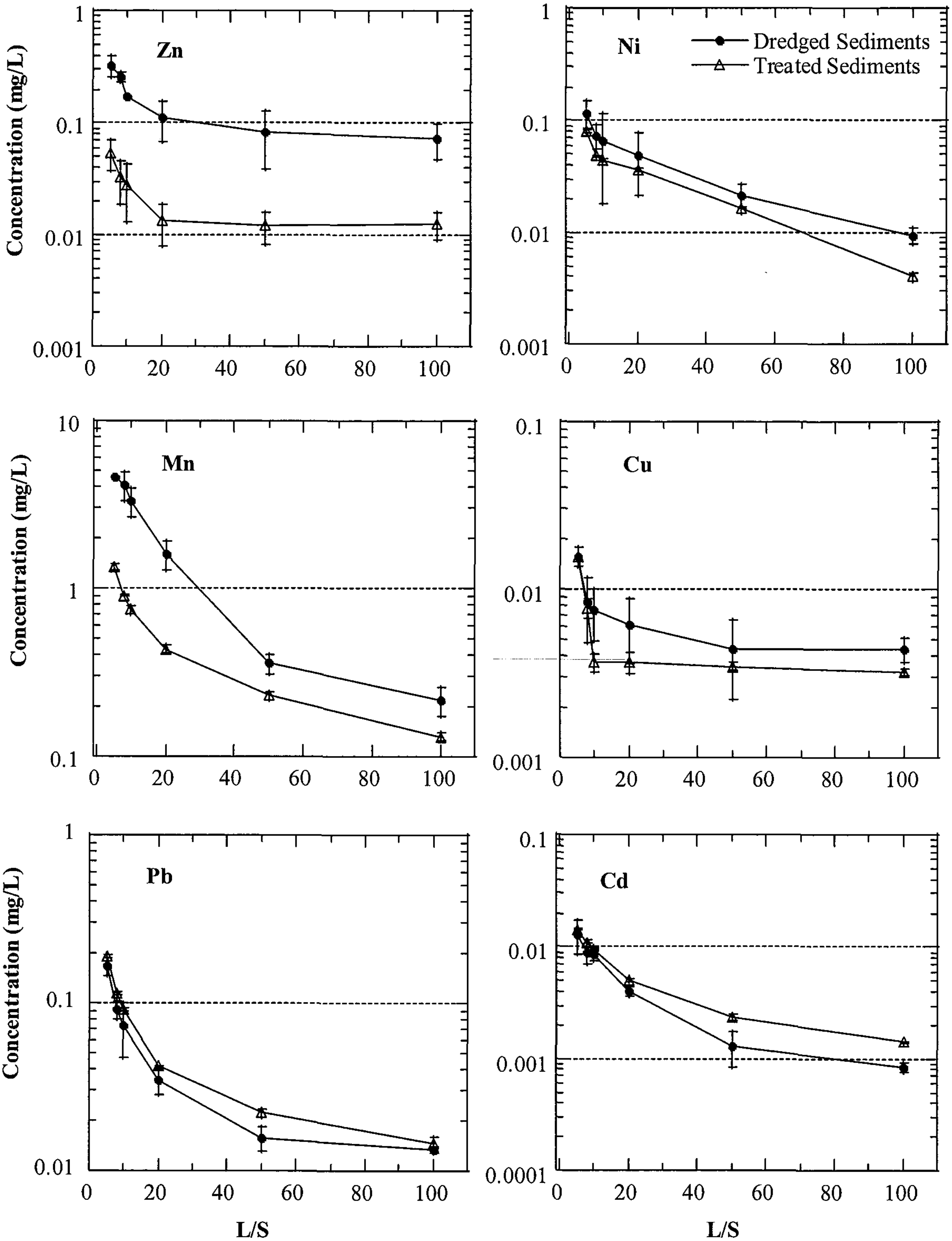

Figure 7.6. SPLP leaching of metals at various L/S values for dredged and treated sediments showing comparatively less effect of L/S than of pH.

7.4 Implications to Sediment Treatment

Treatment of dredged sediments with phosphate addition and 700 °C calcination resulted in substantial reduction in leaching of metals by TCLP of up to 89% when adjusted for loss of organic matter. Based on the metals studied, leaching with TCLP revealed that both the treated and untreated sediments would not be categorized as RCRA and California (CCR, 1991) hazardous materials. In beneficial reuse of the treated sediments as construction material, SPLP showed that the treated system buffered the pH in the range 6.7 to 7.2, which resulted in minimal leaching of metals. Furthermore, the treated sediments met the NJDEP impact to groundwater criteria for Zn, Ni, Mn, Cu, Pb, and Cd. Florida and Wisconsin criteria for Mn, Pb, and Cd were not met. These results show that phosphate and thermal treated sediments do have potential for reuse in construction, based on metals studied.

CHAPTER 8

CONCLUSIONS

The aim of phosphate addition followed by calcination treatment is to stabilize dredged sediments for beneficial reuse in construction. Analysis of the New York/New Jersey Harbor Passaic River Estuary and Dampremy, Belgium sediments revealed elevated heavy metal concentrations compared to pristine estuaries such as the Florida Bay. Zinc was the most abundant heavy metal with 1,067 and 3,400 mg/kg for Passaic River Estuary and Dampremy, respectively. Examination of Zn speciation with XAS, PCA, TT, and LCF showed that in untreated sediments Zn was precipitated as smithsonite ($ZnCO_3$) (67%) and adsorbed to hydrous iron oxide (15%) and hydrous manganese oxide (18%). In the treated sediments, Zn was precipitated in heat induced spinels, gahnite (44%) and franklinite (34%), and the phosphate mineral, hopeite (22%). Thermodynamic analysis showed that the treated sediment phases were dominated by sparingly soluble precipitates compared to the untreated sediments. Therefore, the treatment results in structural changes to more thermodynamically stable Zn crystalline phases.

Sequential extraction corroborated the results of XAS where Zn in exchangeable and carbonate phases and that adsorbed to iron and manganese oxides declined from 758 and 207 to 111 and 139 mg/kg, respectively, while that in residuals increased from 100 to 508 mg/kg. Other metals analyzed, Ni, Mn, Pb, Cu, Cd, and Co showed similar trends, an increase in the sparingly soluble residual phases at the expense of such phases as exchangeable and carbonates where the metals are labile. Destruction of organic materials was demonstrated by large declines in the percentage of metals bound to the organics and sulfide phase, for example, from 58 to 13% for Cu and from 25 to 1% for Ni. Again, these findings demonstrate a shift in metal speciation by phosphate addition and thermal treatment from phases where the metals are labile to sparingly soluble phases implying reduction in leachability of metals.

TCLP studies showed that both phosphate addition and calcination treatment resulted in a substantial reduction in the leaching of metals when adjusted for loss of 16.1% by dry weight organic matter. The combined treatment achieved up to an 89% reduction in leaching. Extended TCLP experiments illustrated that the standard 18 hr procedure underestimated the equilibrium leachate concentrations, which were presumably achieved after 28 days, by up to 50%. Leaching from both the dredged and the treated sediments was below the RCRA (40 CFR, 2003) and California (CCR, 1991) limits for the toxicity characteristic even for the extended leaching periods; therefore, these sediments would not be classified as RCRA or CCR hazardous materials.

Environmental acceptability of dredged sediments in beneficial reuse as construction material was assessed with the SPLP based on states where regulations require an assessment of the risk to groundwater used as a drinking water source. Leaching based on the SPLP showed H_3PO_4 applied at 5% by dry weight phosphate was the most effective phosphate form in reducing metal leachability. Over the pH range of 4 to 9, metal leachability varied by two to four orders of magnitude while varying L/S over 5 to 100 revealed little difference. The New Jersey State impact to groundwater criteria which apply a dilution attenuation factor (DAF) of 13 on groundwater quality levels (GQL) was achieved. On the other hand, Florida and Wisconsin criteria which apply a DAF of 1 based on the assumption that the SPLP leachate has an inherent dilution of 20 (with an L/S of 20), were exceeded for Pb, Cd, and Mn. A thermodynamic analysis of pyromorphite ($Pb_5(PO_4)_3OH$) demonstrates that the criteria cannot be satisfied should dissolution control pore water concentrations.

Based on the metals studied here, phosphate addition and thermal treated sediments have potential for reuse as construction materials. However, further work is needed to fully characterize the sediments and validate the treatment. Recommendations for future work are enumerated in the following chapter.

CHAPTER 9

FUTURE RESEARCH

Phosphate addition and thermal treatment of dredged sediment was found to result in a reusable construction material based on the metals studied. This research demonstrated that the U.S. EPA leaching procedures TCLP and SPLP are not adequate when evaluating the risk posed to the environment. Specifically, a more rigorous analysis is needed for speciation and leaching behavior with respect to kinetics and equilibrium conditions. Therefore, there is need to incorporate an assessment of speciation and leaching as a function of time, pH, and other factors such as ionic strength and complexation with ligands in evaluation of risk.

In this research, only seven metals, Zn, Ni, Mn, Cu, Pb, Cd, and Co were in investigated. To fully characterize the sediments and validate the treatment, the remaining regulated metals; namely, Ag, Al, As, Ba, Be, Bo, Cr, Hg, Sb, Se, Ti, and V (40 CFR, 261.4; CCR, 1991; FDEP, 2005; NJDEP, 2008; W.A.C., 2008) need to be assessed for both toxicity characteristic and/or impact to groundwater quality. While Zn speciation was investigated with XAS, the mineral forms of other metals were evaluated with sequential extraction. Based on sequential extraction along with leaching tests, thermodynamic analysis, and literature, likely minerals precipitated in the treatment include for example, spinel, nickel aluminate, copper ferrate, and the Pb phosphate, pyromorphite. These minerals need be confirmed, for example, with direct molecular probes such as XAS.

Both TCLP and SPLP showed that only a small portion of the total metal in the dredged sediments is leached. At the same time, XAS and sequential extraction showed that only a small fraction of the metals are associated with residuals; the larger proportion of the metals being associated with forms where the metals are more labile such as exchangeable and carbonates. Understanding the relationships between the sediment matrix, metal forms, and dissolution is important in predicting leaching. Furthermore, in beneficial reuse of waste materials, the difference in interpretation between states as to what the SPLP leachate represents needs to be resolved.

This research elucidated the stabilization mechanisms for seven heavy metals and characterized their leaching behavior. Along with extending the study to other metals, as discussed earlier, the feasibility of setting up a pilot treatment plant should be investigated. The required technology already exists in the chemical industry for phosphoric acid addition, cement manufacturing for calcination, and carbon adsorption for off-gas treatment. Assuming such a plant is feasible, treated sediments can be produced for field studies to evaluate leaching under actual environmental conditions, and for evaluation of mechanical properties.

APPENDIX A

XRD PATTERNS

This appendix presents XRD patterns for crystalline minerals observed in dredged and treated sediments, Zn reference minerals used in XAS speciation study, and the white substance that precipitated in the TCLP leaching as a function of time study.

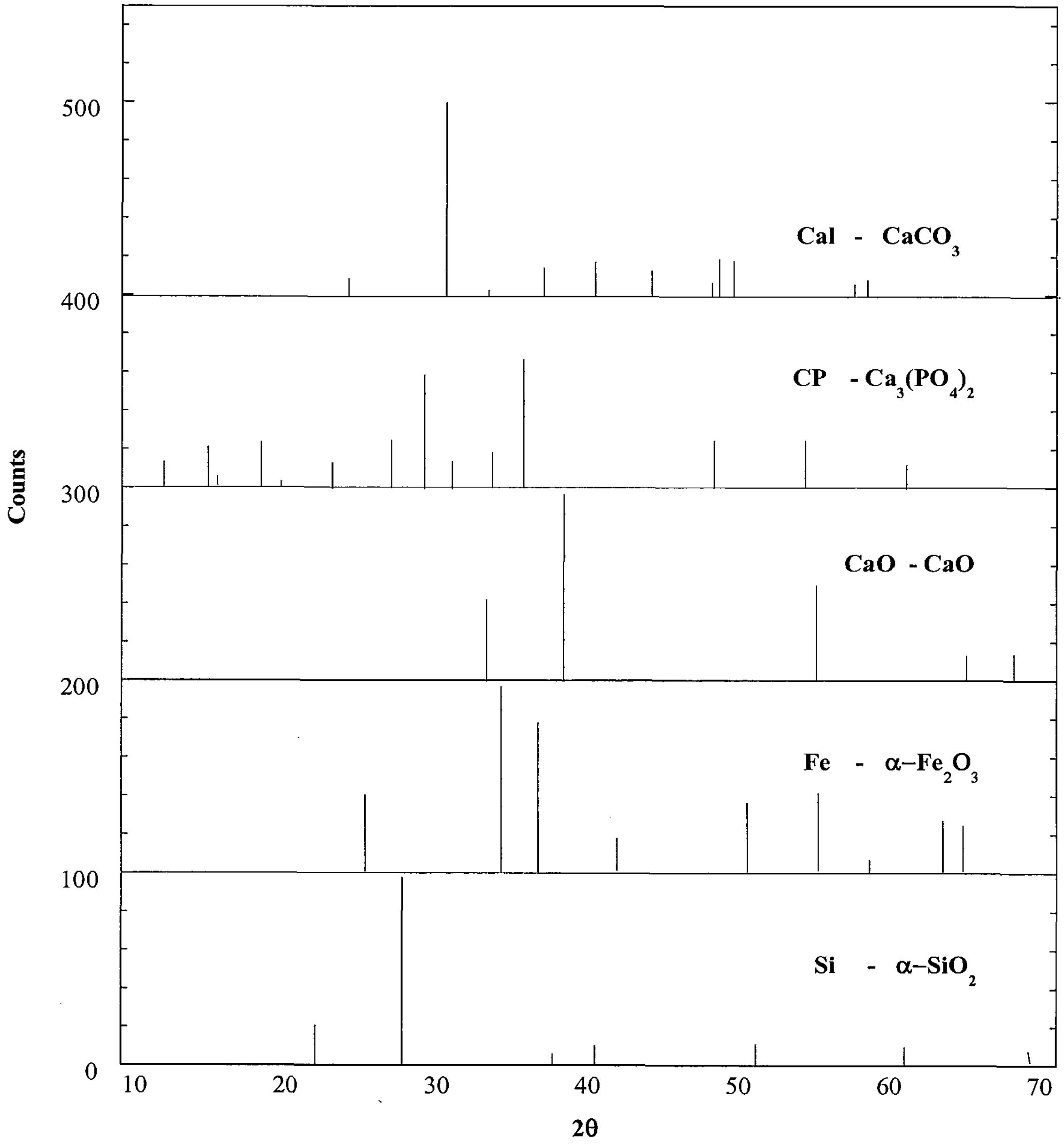

Figure A.1 XRD peaks for minerals in dredged and treated sediments.

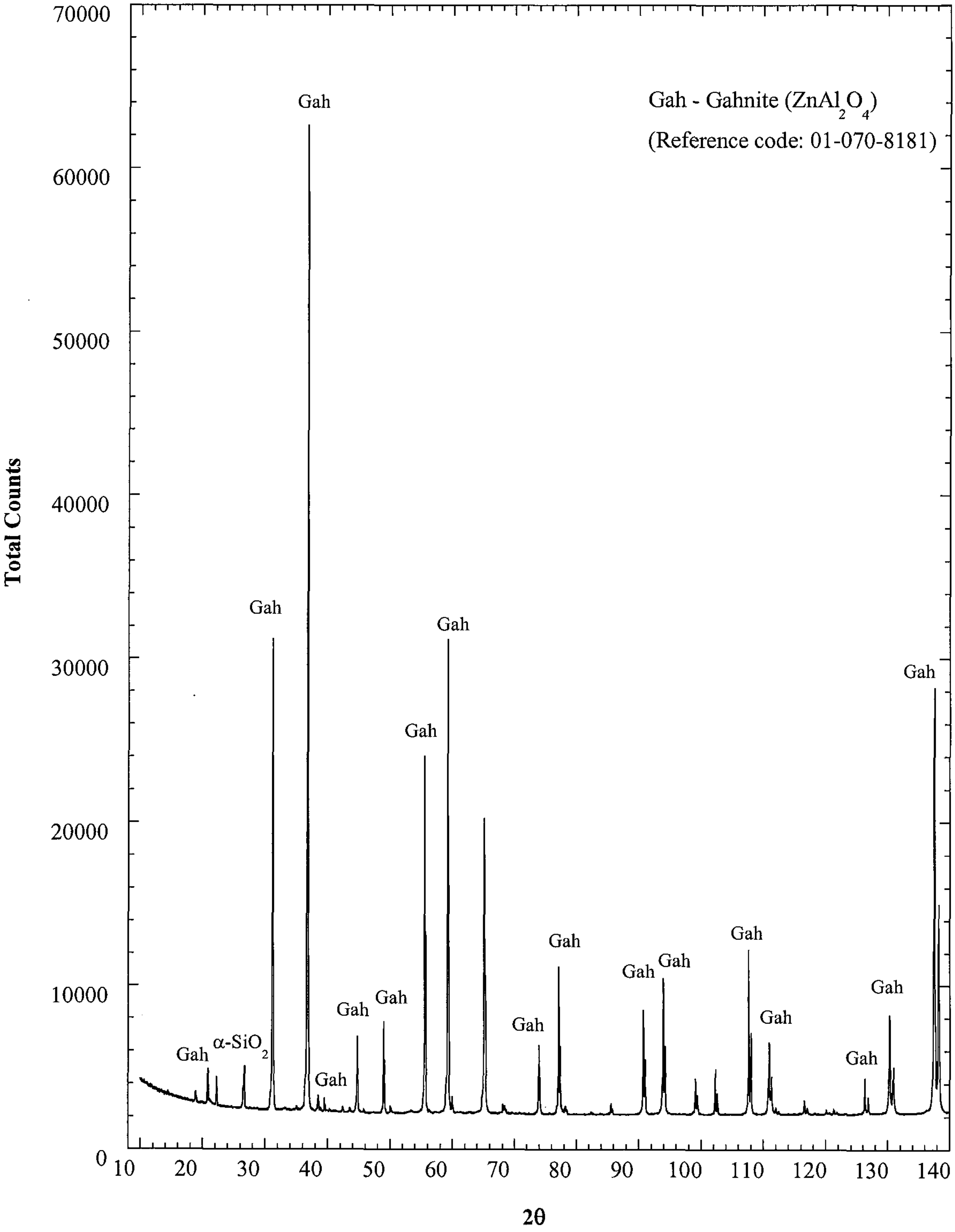

Figure A.2 XRD patterns for Zn mineral, gahnite, used in collection of XAS reference spectra

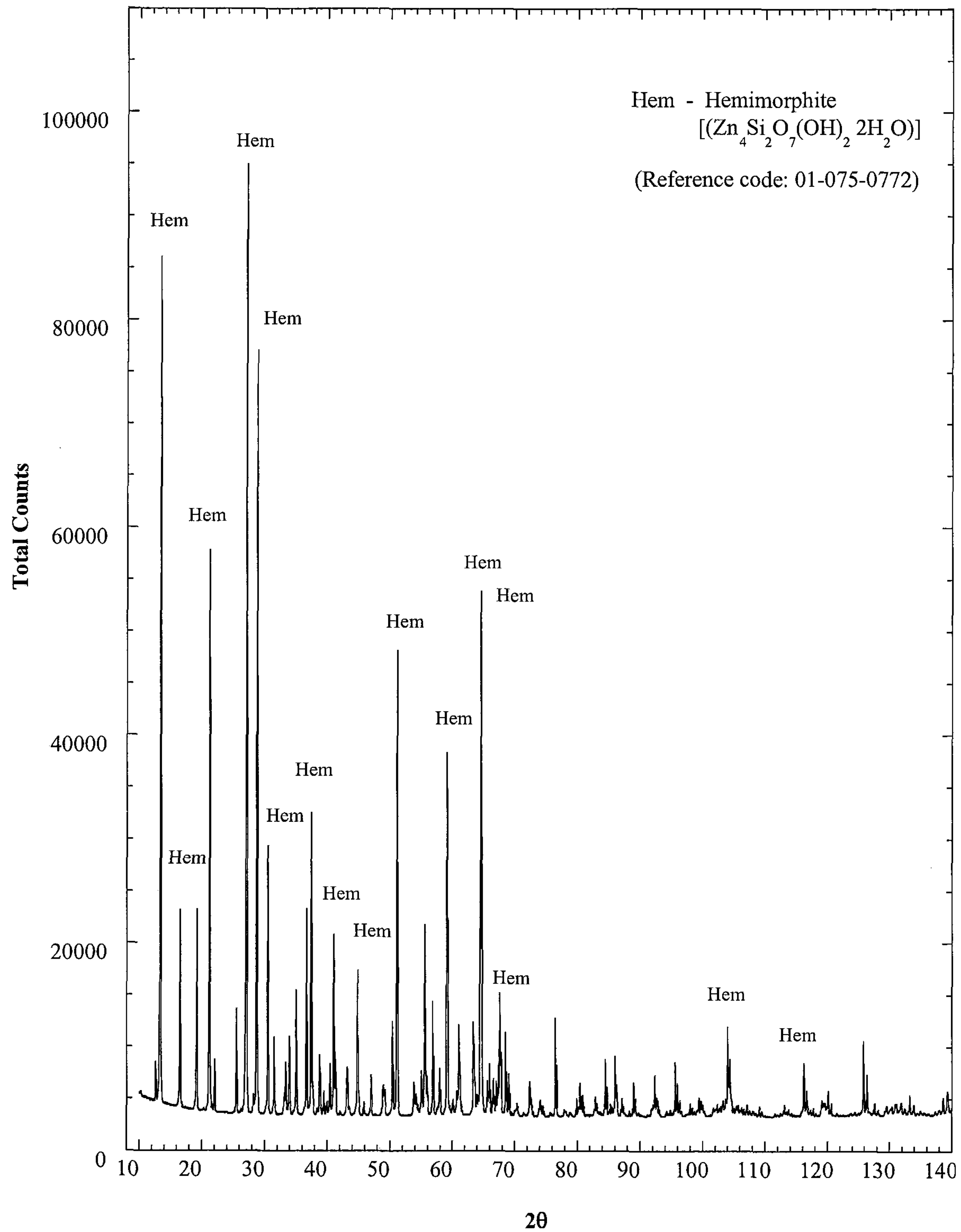

Figure A.3 XRD patterns for Zn mineral, hemimorphite, used in collection of XAS reference spectra

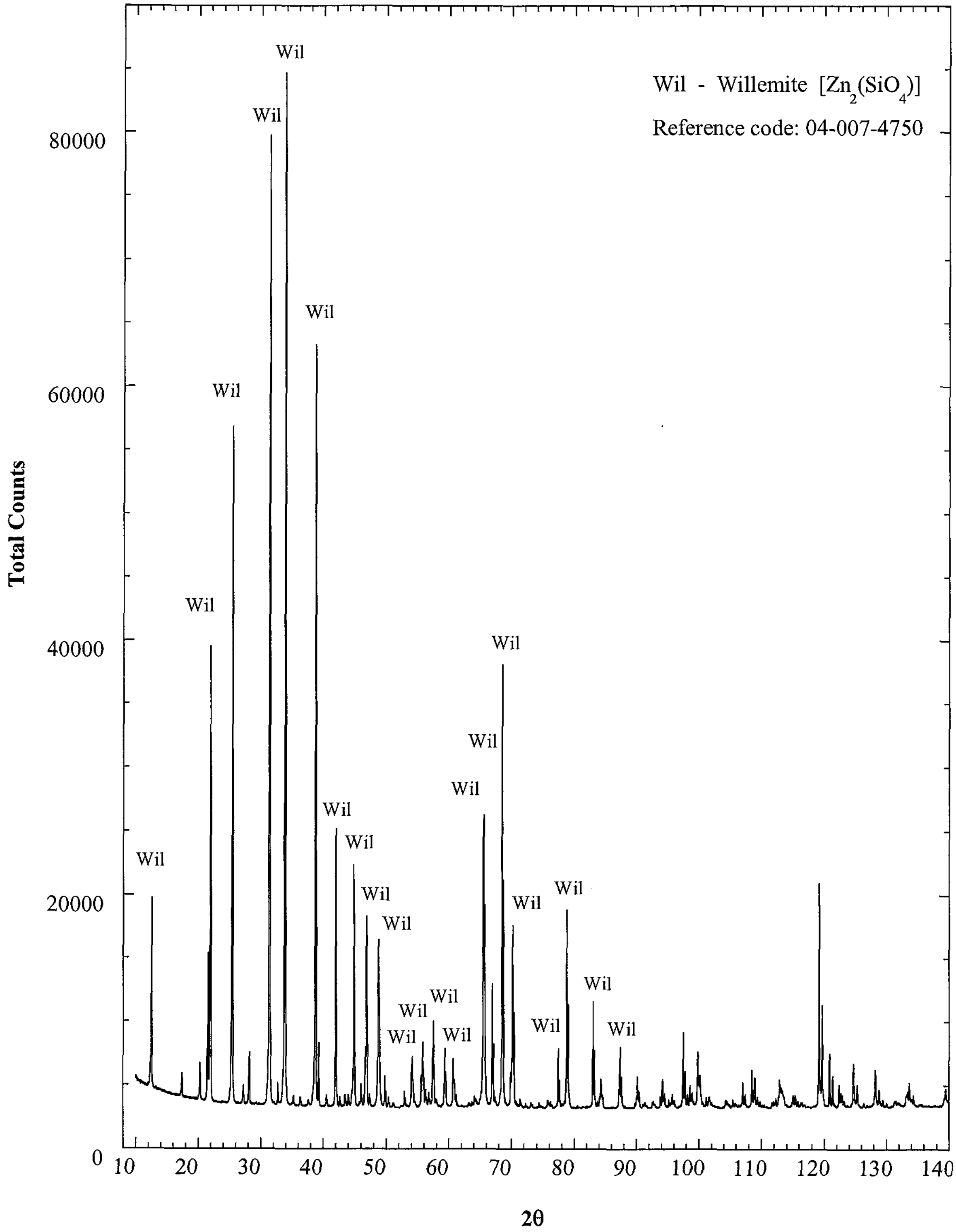

Figure A.4 XRD patterns for Zn mineral, willemite, used in collection of XAS reference spectra

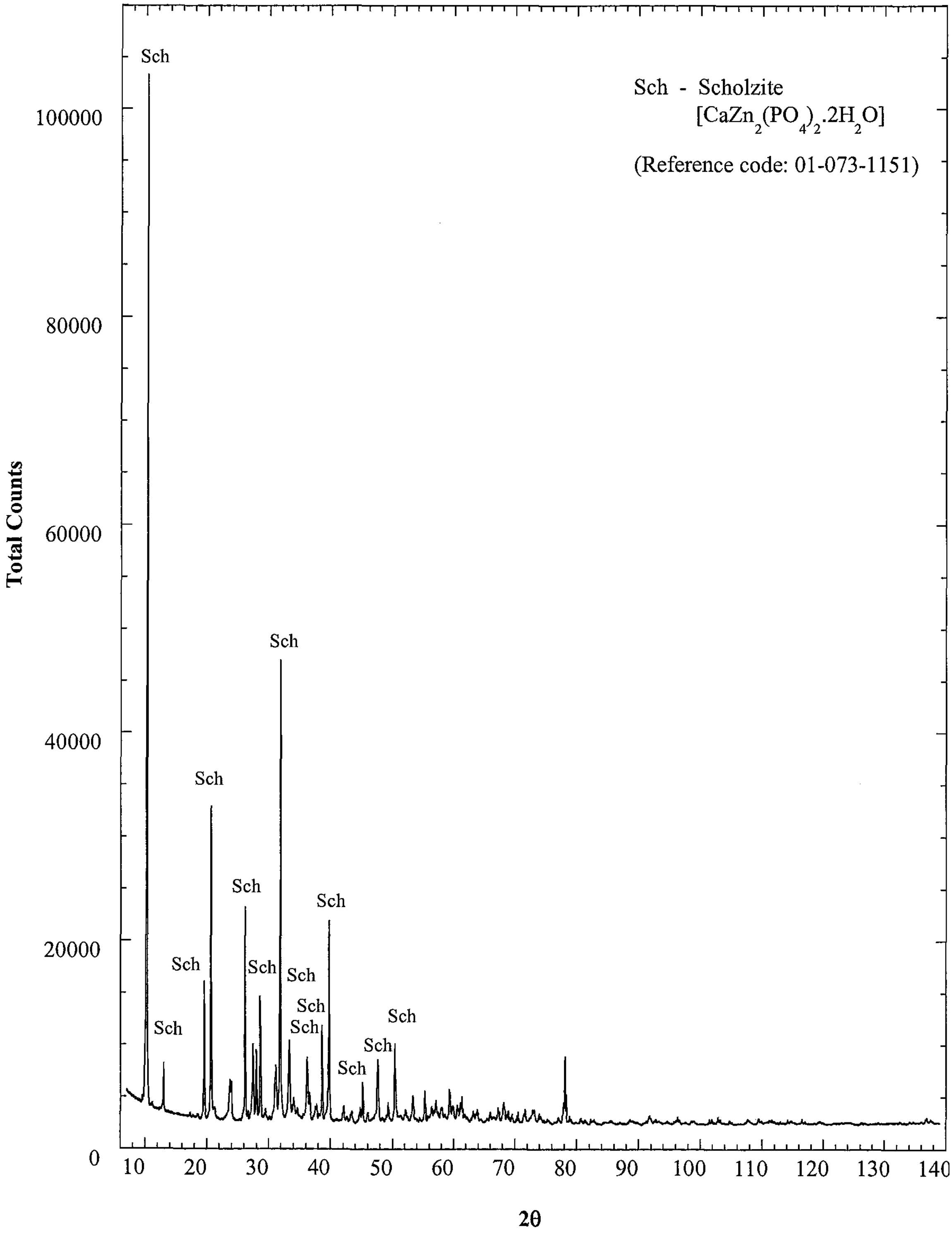

Figure A.5 XRD patterns for Zn mineral, scholzite, used in collection of XAS reference spectra

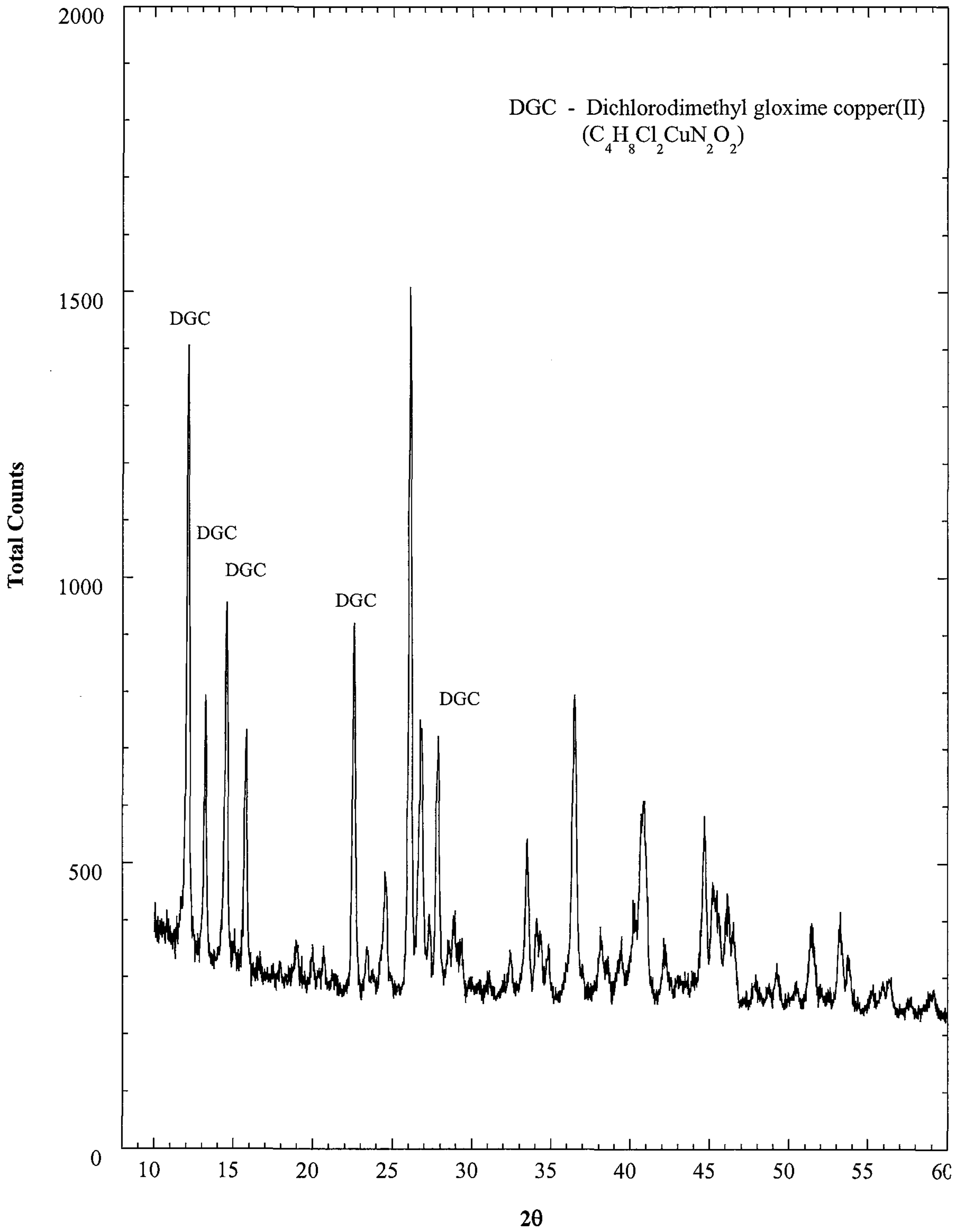

Figure A.6 XRD patterns for the white substance that precipitated the TCLP leaching as a function of time study, with peaks matching those of dichlorodimethyl gloxime copper (II) ($C_4H_8Cl_2CuN_2O_2$)

APPENDIX B

CRYSTALLOGRAPHIC DATA FOR ZN REFERENCE MINERALS BASED ON XRD

This appendix presents crystallographic data for the reference minerals used in XAS speciation study.

Table B.1 Elements, Number of Atoms and radial Distances for Zn Reference Minerals

Mineral/ Adsorbed Phase	Element	N (atoms)	R (Å)
Gahnite	O	4	1.95
	Al	12	3.36
	Zn	4	3.51
Franklinite	O	4	2.00
	Fe	12	3.51
	Zn	4	3.65
ZnO	O	3	1.97
	O	1	1.99
	Zn	6	3.21
	Zn	6	3.25
Willemite	O	4	1.94 - 1.98
	Si	4	3.09 - 3.32
	Zn	4	3.11 - 3.24
Hemimorphite	O	4	1.94 - 1.97
	Si	3	3.05 - 3.22
	Zn	2	3.28
	Zn	2	3.42 - 3.46
Hopeite	O	1	1.90 - 2.00
	P	4	3.02 - 3.19
	Zn	2	3.39
	Zn	1	3.67
Scholzite	O	4	1.91 - 1.99
	P	4	3.06 - 3.15
	Zn	2	3.34
	Zn	2	3.83

Table B.1 Continued

Mineral/ Adsorbed Phase	Element	N (atoms)	R (Å)
ZnCO3 (Smithsonite)	O	6	2.11
	O	6	3.23
	Zn	6	3.67
Sphalerite	S	4	2.33
	Zn	12	3.83
	S	12	4.49
HMO	O	3	2.07
	O	3	2.14
	Mn	3	3.49
	Mn	3	3.50
HFO	O	3	1.97
	O	1	1.99

APPENDIX C
XAS PRINCIPAL COMPONENTS ANALYSIS

In this appendix, the scree of eigen values and cumulative variance for the dredged and treated sediments spectra are presented.

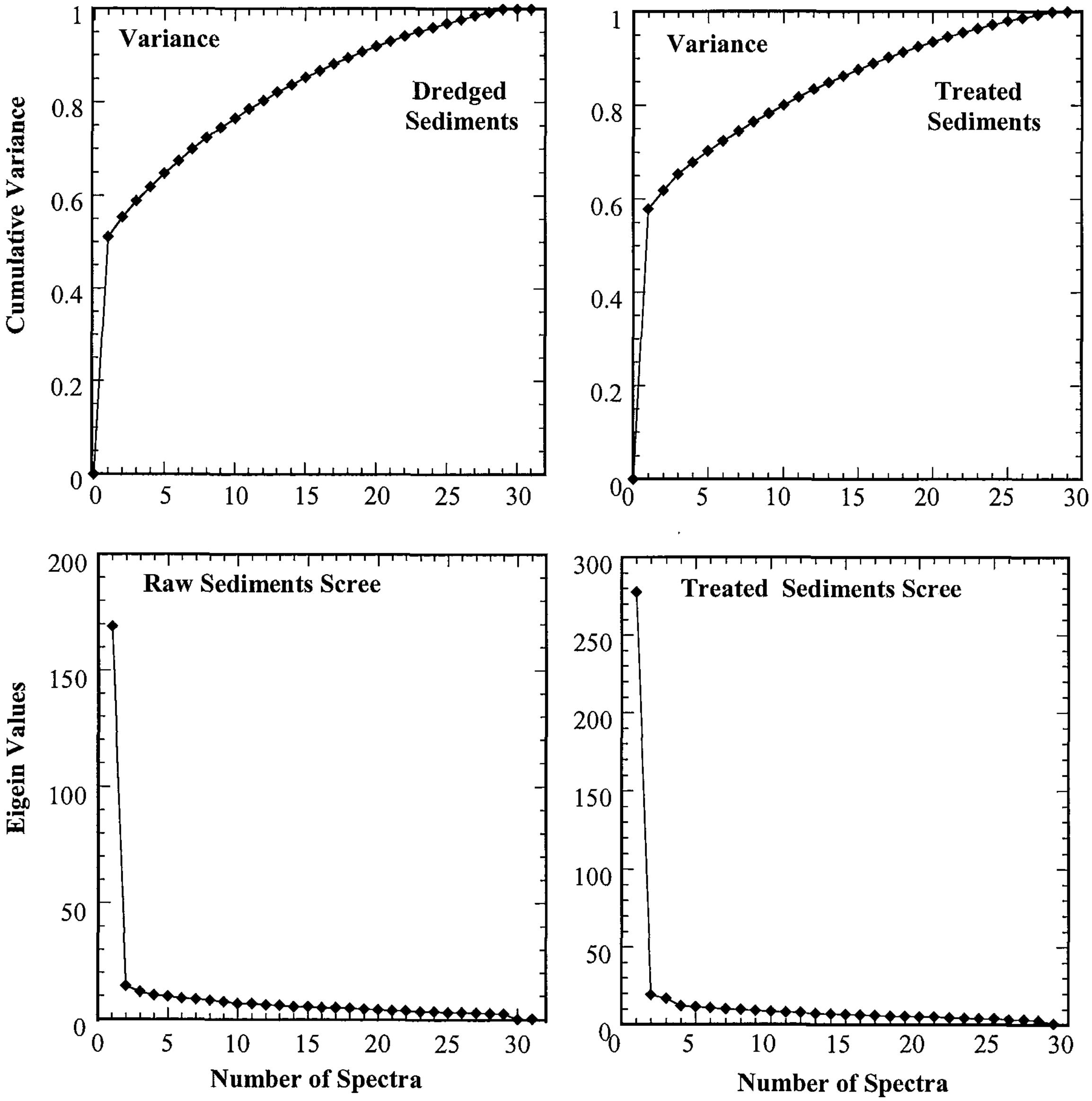

Figure C.1 Principal components analysis (PCA) eigen values and variance showing one principal component, with the remaining components as mainly noise.

APPENDIX D

THERMODYNAMIC ANALYSIS

The formation constants k used in thermodynamic analysis of gahnite, franklinite, nickel aluminate, and nickel ferrate are computed in this appendix. The appendix also includes solubility diagrams for $Ni_3(PO_4)_2$ and $Cd_3(PO_4)_2$.

Computation of formation constant for Gahnite $ZnAl_2O_4$

Heat of formation at 298 °Cin KJ mol^{-1}K^{-1}: $ZnAl_2O_4$ (-2071.3), ZnO (-350.5), Al_2O_3 (-1662.3) (Binnewics and Mike, 1999)

$$\Delta G^o_{298}{}^oC = H_f\,(ZnAl_2O_4) - H_f\,(ZnO) - H_f\,(Al_2O_3) = -58.5\ KJmol^{-1}K^{-1}$$

$$\Delta G^o_{298}{}^oC = -RTInK_{298}{}^oC$$

$$-58.5\ KJ/mol = -8.314 \times 10^{-3}\ KJ/mol\cdot K \times 298K \times InK_{298}{}^oC$$

$$K_{298}{}^oC = 1.80 \times 10^{10}, \quad pK = 10.254$$

$$\begin{array}{llllllll}
H_2O & + & Zn^{2+} & = & 2H^+ & + & ZnO & pK = 11.334\ * \\
3H_2O & + & 2Al^{2+} & = & 6H^+ & + & Al_2O_3 & pK = 19.652\ * \\
ZnO & + & Al_2O_3 & = & ZnAl_2O_4 & & & pK = 10.254 \\
\hline
4H_2O & + & Zn^{2+} + 2Al^{3+} & = & 8H^+ & + & ZnAl_2O_4 & pK = 41.240
\end{array}$$

* From MINEQL+ Database (Schecher and McAvoy, 1998)

Computation of formation constant for Franklinite $ZnFe_2O_4$

Heat of formation at 298 °C (KJ mol^{-1}K^{-1}): $ZnFe_2O_4$ (-1179.1), ZnO (-350.5), Fe_2O_3 (-823.4) (Binnewics and Mike, 1999)

$\Delta G^{o}{}_{298}{}^{o}{}_{C} = H_f\,(ZnAl_2O_4) - H_f\,(ZnO) - H_f\,(Al_2O_3) \;=\; -5.2\ KJmol^{-1}K^{-1}$

$\Delta G^{o}{}_{298}{}^{o}{}_{C} \;=\; -RTInK_{298}{}^{o}{}_{C}$

99

$-5.2\ KJ/mol \;=\; -8.314 \times 10^{-3}\ KJ/mol{\cdot}K$ ‹× $InK_{298}{}^{o}C$

$K_{298}{}^{o}{}_{C} \;=\; 8.15, \quad pK = 10.254$

$$\begin{array}{llcllll}
H_20 & + \; Zn^{2+} & = & 2H^{+} & + & ZnO & pK = 11.334\ * \\
3H_2O & + \; 2Fe^{2+} & = & 6H^{+} & + & Fe_2O_3 & pK = \;\; 1.418\ * \\
 & & & 99 & & & \\
ZnO & + \; Fe_2O_3 & = & Zn & & & pK = \;\; 0.908\ * \\
\hline
4H_2O & + \; Zn^{2+} + 2Fe^{3+} & = & 8H^{+} & + & ZnFe_2O_4 & pK = 13.660
\end{array}$$

* From MINEQL+ Database (Schecher and McAvoy, 1998)

Computation of formation constant for Nickel Aluminate $NiAl_2O_4$

Heat of formation at 298 °Cin KJ $mol^{-1}K^{-1}$: $ZnAl_2O_4$ (-1921.5), ZnO (-350.5), Al_2O_3 (-1662.3) (Binnewics and Mike, 1999)

$\Delta G^{o}{}_{298}{}^{o}{}_{C} = H_f\,(ZnAl_2O_4) - H_f\,(ZnO) - H_f\,(Al_2O_3) \;=\; -19.5\ KJmol^{-1}K^{-1}$

$\Delta G^{o}{}_{298}{}^{o}{}_{C} \;=\; -RTInK_{298}{}^{o}{}_{C}$

$-58.5\ KJ/mol \;=\; -8.314 \times 10^{-3}\ KJ/mol{\cdot}K \times 298K \times InK_{298}{}^{o}C$

$K_{298}{}^{o}{}_{C} \;=\; 2.620 \times 10^{3}, \quad pK = 3.148$

$$\begin{array}{llcllll}
H_2O & + \; Ni^{2+} & = & 2H^{+} & + & NiO & pK = 12.446\ * \\
3H_2O & + \; 2Al^{2+} & = & 6H^{+} & + & Al_2O_3 & pK = 19.652\ * \\
NiO & + \; Al_2O_3 & = & NiAl_2O_4 & & & pK = \;\; 3.148 \\
\hline
4H_2O & + \; Zn^{2+} + 2Al^{3+} & = & 8H^{+} & + & NiAl_2O_4 & pK = 35.246
\end{array}$$

* From MINEQL+ Database (Schecher and McAvoy, 1998)

Computation of formation constant for Nickel Ferrate $NiFe_2O_4$

Heat of formation at 298 °C (KJ $mol^{-1}K^{-1}$): $NiFe_2O_4$ (-1084.5), NiO (-350.5), Fe_2O_3 (-823.4) (Binnewics and Mike, 1999)

$\Delta G^o{}_{298^oC} = H_f\,(NiAl_2O_4) - H_f\,(NiO) - H_f\,(Al_2O_3) = -21.4\ KJmol^{-1}K^{-1}$

$\Delta G^o{}_{298^oC} = -RTInK_{298^oC}$

$-21.4\ KJ/mol = -8.314 \times 10^{-3}\ KJ/mol\cdot K \times 298K \times InK_{298}{}^oC$

$K_{298^oC} = 5641.3$, $pK = 3.751$

H_20	+	Ni^{2+}		=	$2H^+$	+	NiO	pK = 12.446 *
$3H_2O$	+	$2Fe^{2+}$		=	$6H^+$	+	Fe_2O_3	pK = 1.418 *
NiO	+	Fe_2O_3		=	$NiFe_2O_4$			pK = 3.751
$4H_2O$	+	Ni^{2+}	+ $2Fe^{3+}$	=	$8H^+$	+	$NiFe_2O_4$	pK = 17.615

* From MINEQL+ Database (Schecher and McAvoy, 1998)

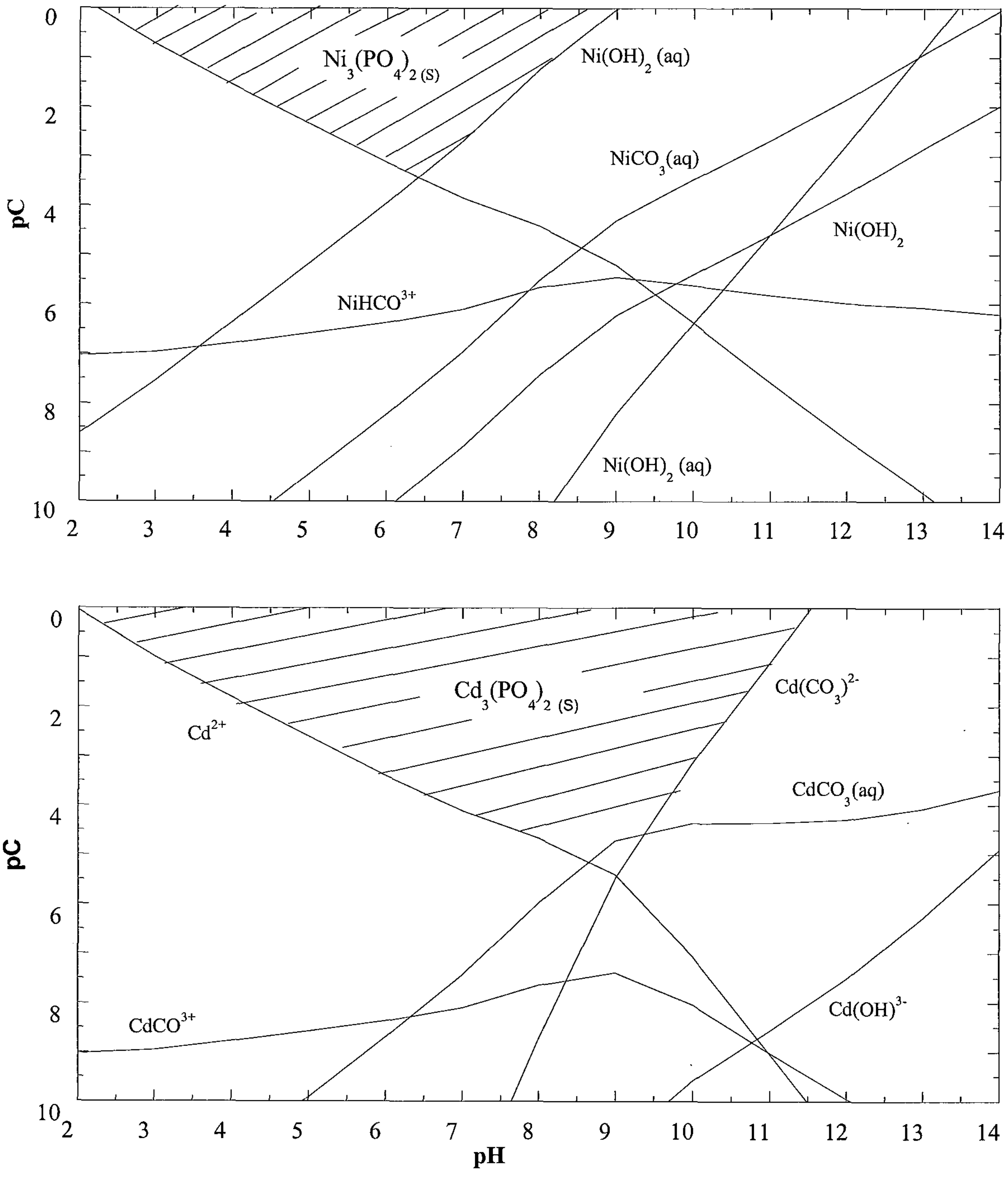

Figure D.1 Solubility diagrams for Ni^{2+} in equilibrium with $Ni_3(PO_4)_2$ and Cd^{2+} in equilibrium with $Cd_3(PO_4)_2$ in an open system, computed using MINEQL+ (Schecher and McAvoy, 1998).

APPENDIX E

SEQUENTIAL EXTRACTION DATA

Sequential extraction measurements of metal concentration for the Passaic River Estuary Sediments are presented. Extractions are for 1.0 g by dry weight samples in 40 ml de-ionized water measured with flame atomic absorption spectroscopy (FAA) for dredged sediments (D) and Treated (T) Sediments with extraction fractions, exchangeable/ carbonates (1), reducible (bound to iron and manganese oxides) (2), oxidizable (bound to sulfides and organics) (3), and residual (4). The number after the dash is the replicate samples number.

Table E.1 Metal concentrations for on 1.0 g sediment samples in 40 ml extraction fluid

	Concentration in mg/L						
Sample	**Zn**	**Ni**	**Mn**	**Pb**	**Cu**	**Cd**	**Co**
D1-1	16.790	0.7775	8.5150	7.1824	0.0294	0.1860	0.1229
D1-2	18.060	0.8598	9.4230	7.0024	0.0289	0.1870	0.1352
D1-3	18.510	0.9004	9.3950	9.1534	0.1333	0.2546	0.1470
D1-4	18.370	0.9154	10.0510	5.1164	0.0255	0.1052	0.1604
D1-5	12.690	0.7833	7.9270	8.3874	0.1133	0.2151	0.1366
D1-6	15.870	0.8842	9.3560	9.0634	0.0736	0.2423	0.1562
D1-7	18.090	0.8638	9.2900	8.4164	0.0476	0.2213	0.1671
D1-8	18.290	0.9104	9.4020	10.1374	0.4186	0.2608	0.1852
D1-9	17.920	0.8629	9.5860	7.2524	0.0309	0.1833	0.1723
D1-10	17.740	0.8717	9.3680	8.2994	0.0516	0.2289	0.1729
T1-6	2.739	0.1579	3.8520	0.2235	0.9518	0.0307	0.0760
T1-7	2.687	0.1302	3.9150	0.2714	0.9021	0.0307	0.0792

Table E.1 Continued

	Concentration in mg/L						
Sample	**Zn**	**Ni**	**Mn**	**Pb**	**Cu**	**Cd**	**Co**
T1-8	2.789	0.1343	3.9070	0.2174	0.9417	0.0300	0.0830
T1-9	2.908	0.1423	3.9240	0.2088	0.9765	0.0310	0.0887
T1-10	2.698	0.1336	3.8110	0.2174	0.9324	0.0308	0.0869
D2-1	4.699	0.1311	0.2640	7.3981	4.2856	0.1337	0.0132
D2-2	5.309	0.1757	0.3980	8.7381	4.8136	0.1635	0.0188
D2-3	5.073	0.1506	0.3100	7.0081	4.8596	0.1110	0.0150
D2-4	6.552	0.2398	0.3390	12.2881	4.9506	0.2757	0.0294
D2-5	4.509	0.1468	0.2880	6.3141	4.4486	0.0997	0.0226
D2-6	5.175	0.1709	0.3100	7.4631	4.8686	0.1212	0.0218
D2-7	4.993	0.1656	0.3160	7.6221	4.7016	0.1266	0.0255
D2-8	4.836	0.1557	0.3280	6.3441	4.6826	0.0971	0.0287
D2-9	5.577	0.1808	0.3410	9.1821	4.9286	0.1760	0.0321
D2-10	5.025	0.1771	0.3260	7.6991	4.7106	0.1280	0.0302
T2-6	2.676	0.1220	1.8500	4.9831	1.6896	0.0433	0.0688
T2-7	2.425	0.1130	1.8940	4.7091	1.5596	0.0405	0.0664
T2-8	2.692	0.1174	2.0290	5.0071	1.6926	0.0419	0.0670
T2-9	3.032	0.1219	2.0770	5.2831	1.7486	0.0444	0.0751
T2-10	6.589	0.1227	2.6170	5.0111	-	0.0416	0.0743
D3-1	3.946	0.6306	1.1032	1.4717	7.1015	0.0967	0.1418
D3-2	4.234	0.7017	1.1632	1.7147	7.6245	0.0987	0.1635
D3-4	4.942	0.7457	1.2202	2.0187	8.5885	0.1152	0.1706
D3-5	3.655	0.5942	1.0552	1.3547	6.7295	0.0879	0.1477
D3-9	4.335	0.6805	1.1592	1.7317	7.8385	0.1029	0.1661
D3-10	-	0.6898	-	1.5797	-	0.0990	0.1664
T3-6	0.691	0.0410	0.3459	2.5097	1.7795	0.0132	0.0264
T3-7	0.451	0.0146	0.2486	1.9517	1.4235	0.0096	0.0234
T3-8	0.598	0.0316	0.2689	1.7267	1.5635	0.0071	0.0216

Table E.1 Continued

	Concentration in mg/L						
Sample	**Zn**	**Ni**	**Mn**	**Pb**	**Cu**	**Cd**	**Co**
T3-9	0.525	0.0279	0.1908	1.4847	1.3065	0.0066	0.0310
T3-10	0.663	0.0293	0.2581	1.7677	1.4655	0.0085	0.0314
D4-1 x 1	0.872	0.3760	1.0970	0.4105	0.3119	0.0148	0.1901
D4-2 x 1	1.383	0.3794	1.1590	0.4679	0.2904	0.0172	0.1945
D4-4 x 1	1.107	0.4040	1.1780	0.5327	0.3418	0.0126	0.2035
D4-5 x 1	0.655	0.3595	1.0540	0.4086	0.2720	0.0152	0.1880
T4-1 x 1	5.017	0.8274	2.9560	3.3060	3.0600	0.1591	0.2839
T4-2 x 1	5.057	0.8059	2.9240	3.1040	3.0170	0.1512	0.2762
T4-10 x 1	5.160	0.8187	2.8970	3.2460	3.0090	0.1461	0.2779

Table E.2 Total Metal Determination with Aqua Regia Digestion EPA Method 3050B (U.S. EPA, 1996) with Flame Atomic Absorption Spectroscopy (FAA) for Passaic River Estuary Dredged Sediments (TD) and Treated Sediments (TT)

	Concentration in mg/L						
Sample	**Zn**	**Ni**	**Mn**	**Pb**	**Cu**	**Cd**	**Co**
TD-2 x 1	9.910	0.9922	7.9300	6.6600	5.2000	0.1840	0.3243
TD-3 x 1	10.140	0.9498	8.2600	6.5720	5.2010	0.1839	0.3248
TT-1 x 1	5.350	0.9293	8.4200	5.5970	4.3250	0.1894	0.3415
TT-2 x 1	5.350	0.9243	8.2800	5.5900	4.3870	0.2016	0.3402
TT-3 x 1	5.280	0.9291	8.4300	5.6120	4.3290	0.1866	0.3384

APPENDIX F

LEACHING STUDIES DATA

In this appendix metal concentrations in for TCLP, extended TCLP, SPLP, Alternative phosphate forms, leaching as a function of pH, and leaching at various L/S, evaluated with FAA and GFAA is presented.

Table F.1 TCLP Leachate Concentrations for Dampremy, Belgium Dredged Sediments and Treated with Phosphate addition, Calcination, and Combined Phosphate addition and Calcination

		pH/Concentration (mg/L)			
pH/ Metal	**Replicate Sample No.**	**Dredged Sediments**	**2.5% Phosphate Addition**	**Dredged Sediments Calcination Only**	**2.5% Phosphate addition and Calcination**
pH		5.560	5.020	6.040	5.370
Pb	1	0.342	0.137	0.255	0.190
	2	0.376	0.176	0.256	0.250
	3	0.358	0.158	0.250	0.229
	4	0.357	0.146	-	0.250
Zn	1	38.400	20.200	3.090	5.120
	2	37.600	19.500	2.960	5.470
	3	39.200	-	4.820	4.620
	4	37.600	19.700	4.000	-
Cd	1	0.174	0.104	0.043	0.034
	2	0.177	0.104	0.044	0.042
	3	0.177	-	0.042	0.035
	4	0.180	0.102	0.044	0.053
Ni	1	0.496	0.542	0.242	0.217
	2	0.504	0.551	0.237	0.233

Table F.1 Continued

pH/ Metal	Replicate Sample No.	Dredged Sediments	2.5% Phosphate Addition	Dredged Sediments Calcination Only	2.5% Phosphate addition and Calcination
		pH/Concentration (mg/L)			
	3	0.509	0.542	0.248	0.237
	4	0.495	0.546	0.249	0.229
Cu	1	0.086	0.064	0.061	0.087
	2	0.086	0.070	0.063	0.074
	3	0.086	0.080	0.064	-
	4	0.098	0.072	0.072	0.084
Co	1	0.156	0.152	0.158	0.127
	2	0.158	0.155	0.154	0.136
	3	0.155	0.153	0.160	0.142
	4	0.155	0.153	0.156	0.148
Mn	1	8.500	8.900	0.880	2.820
	2	7.700	8.400	0.770	2.670
	3	8.000	9.800	0.940	3.550
	4	7.700	7.900	1.000	1.930

Table F.2 Total metal determination with aqua regia digestion EPA Method 3050B (U.S. EPA, 1996) with flame atomic absorption spectroscopy (FAA) for dredged sediments (TD) and treated sediments (TT)

Metal	Replicate Sample No	Concentration (Based on 1 g dry sample in 100 mL) (mg/L)
Pb	1	8.847
	2	8.682
	3	8.798
Zn	1	35.500
	2	33.400
	3	33.700
Cd	1	0.126
	2	0.125
	3	0.091
Ni	1	1.060
	2	1.041
	3	1.060
Cu	1	1.205
	2	1.159
	3	1.236
Co	1	0.303
	2	0.302
	3	0.302
Mn	1	15.100
	2	14.300
	3	14.600

Table F.3 Leaching as a Function of Time extended TCLP Leachate Concentrations for Dampremy, Belgium Dredged Sediments (D) and Treated (T) with H_3PO_4 at 3% Phosphate addition and 700 °C Calcination at pH 5 ± 0.1

	Concentration (mg/L)									
Time (Days)	**0.04**	**0.75**	**2**	**4**	**8**	**12**	**16**	**20**	**24**	**28**
Metal (Sample Type)										
Zn										
(D)	38.8	55.9	-	66.9	70.3	69.4	70.3	-	67.3	71.8
	38.6	59.0	63.7	65.5	-	69.0	70.3	70.8	69.2	66.6
	39.6	-	60.8	67.1	-	69.8	67.3	66.7	67.4	70.2
(T)	1.6	-	4.80	5.90	6.70	-	-	7.60	8.20	7.10
	1.57	3.90	6.10	6.20	6.90	7.90	7.90	8.10	8.00	8.00
	2.44	-	-	6.70	-	-	7.70	7.60	7.60	7.80
Cd										
(D)	-	0.196	0.184	0.126	0.158	0.120	0.139	0.149	0.142	0.137
	0.183	0.200	0.184	0.210	0.261	0.248	0.225	0.208	0.189	0.168
	-	0.196	0.182	0.191	0.155	0.127	0.135	0.155	0.140	0.125
(T)	0.042	0.044	0.047	0.051	0.055	0.060	0.064	0.059	0.059	0.059
	0.042	0.045	0.048	0.051	0.056	0.061	0.064	0.066	0.061	0.054
	0.038	0.040	0.043	0.048	0.052	0.057	0.060	0.062	0.057	0.062
Pb										
(D)	0.662	0.816	0.887	0.888	0.922	0.904	0.892	0.783	0.729	0.790
	0.630	0.844	0.891	0.937	0.966	0.903	0.859	0.760	0.778	0.724
	0.600	0.824	0.837	0.854	0.887	0.850	0.809	0.745	0.762	0.791
(T)	0.444	0.580	0.625	0.623	0.667	0.666	0.694	0.684	0.702	0.691
	0.516	0.587	0.607	0.648	0.642	0.662	0.686	0.687	0.716	0.691
	0.477	0.549	0.572	0.600	0.627	0.638	0.657	0.665	0.679	0.719

Table F.3 Continued

Ni											
	(D)	0.404	0.610	0.673	0.698	0.756	0.779	0.799	0.832	0.810	0.831
		0.395	0.618	0.683	0.730	0.748	0.775	0.786	0.789	0.808	0.795
		0.394	0.617	0.665	0.693	0.742	0.773	0.780	0.810	0.808	0.826
	(T)	0.106	-	0.277	0.293	0.309	0.322	0.335	0.334	0.400	0.353
		0.201	0.244	0.267	0.287	0.304	0.324	0.328	0.336	0.343	0.350
		0.197	-	0.255	0.337	0.294	0.304	0.319	0.323	0.325	0.335
Cu											
	(D)	0.120	0.085	0.088	0.036	0.142	0.034	0.037	0.040	0.037	0.041
		0.124	0.088	0.090	0.111	0.037	0.077	0.060	0.044	0.041	-
		0.121	0.091	0.088	0.056	0.037	0.031	0.035	0.037	0.036	-
	(T)	-	-	0.043	0.054	0.068	0.080	0.087	0.038	0.043	0.041
		0.026	0.041	0.044	0.054	0.085	0.120	0.119	0.091	0.041	0.050
		0.026	0.046	0.046	0.063	0.083	0.106	0.146	0.168	0.038	-0.83
Co											
	(D)	0.141	0.200	0.213	0.225	0.229	0.250	0.254	0.260	0.255	0.264
		0.135	0.197	0.214	0.223	0.240	0.239	0.248	0.251	0.251	0.257
		0.133	0.194	0.209	0.217	0.239	0.245	0.254	0.253	0.253	0.26
	(T)	-	0.165	0.176	0.187	0.198	0.212	0.219	0.220	0.225	0.233
		0.150	0.166	0.177	0.191	0.205	0.217	0.220	0.226	0.230	0.221
		0.139	0.156	0.159	0.179	0.188	0.193	0.209	0.206	0.216	0.234
Cu											
	(D)	-	0.077	0.080	0.026	0.031	0.026	0.023	0.024	0.018	0.018
		0.118	0.082	0.082	0.101 -		0.066	0.045	0.027	0.020	0.015
		-	0.082	0.079	0.050	0.026	0.022	0.019	0.018	0.016	0.02
	(T)	-	0.048	0.020	0.030	0.044	0.058	0.061	0.015	0.016	0.012
		0.080	0.018	0.023	0.032	0.062	0.091	0.095	0.064	0.017	0.025
		0.070	0.023	0.026	0.041	0.063	0.081	0.116	0.142	0.015	0.013

Table F.4 Alternative phosphate forms treated and dredged sediments leachate metal concentrations flame atomic absorption spectroscopy (FAA)

	Concentration in mg/L						
Sample	**Zn**	**Ni**	**Mn**	**Pb**	**Cu**	**Cd**	**Co**
3% Phosphate Addition							
31 NaH_2PO_4	49.0	27.0	956.7	40.0	5.0	5.1	14.7
32 NaH_2PO_4	48.0	27.0	870.0	41.8	4.6	5.4	15.7
33 NaH_2PO_4	43.0	24.0	916.7	41.8	6.3	5.4	15.9
34 $Ca(H_2PO_4)_2$	44.0	32.0	406.7	57.7	6.1	6.9	18.3
35 $Ca(H_2PO_4)_2$	36.0	26.0	276.7	51.7	5.2	6.1	16.9
36 $Ca(H_2PO_4)_2$	29.0	31.0	286.7	57.4	6.8	6.0	17.8
37 $CaHPO_4$	36.0	29.0	366.7	54.8	5.1	6.2	17.5
38 $CaHPO_4$	37.0	31.0	236.7	54.0	5.0	5.3	16.3
39 $CaHPO_4$	24.0	28.0	590.0	56.4	6.4	5.5	17.4
40 H_3PO_4	37.0	23.0	703.3	39.6	4.0	7.0	14.9
41 H_3PO_4	33.0	28.0	610.0	40.5	4.0	7.0	15.9
42 H_3PO_4	36.0	26.0	610.0	40.2	4.0	6.9	15.8
43 Dredged	205.0	56.0	1543.3	28.6	5.4	3.8	15.6
44 Dredged	235.0	72.0	1623.3	31.5	6.7	3.9	16.7
45 Dredged	279.0	66.0	1476.7	33.9	6.0	4.2	18.8
46 Reagent Blank	12.0	0.0	246.7	8.2	0.0	0.0	0.0
47 Purity $Ca(H_2PO_4)_2$	16.0	24.0	66.7	37.8	8.4	3.7	14.7
48 Purity $CaHPO_4$	11.0	0.0	80.0	6.9	1.9	-0.1	1.5
5% Phosphate Addition							
51 NaH_2PO_4	37.0	24.0	400.0	25.2	2.6	3.9	14.3
52 NaH_2PO_4	40.0	20.0	766.7	27.1	4.3	4.6	15.8
53 NaH_2PO_4	39.0	21.0	516.7	27.8	5.1	4.7	16.7
54 $Ca(H_2PO_4)_2$	52.0	24.0	136.7	40.7	4.4	5.3	15.9
55 $Ca(H_2PO_4)_2$	34.0	23.0	180.0	39.4	4.6	5.5	17.5
56 $Ca(H_2PO_4)_2$	35.0	26.0	223.3	45.8		5.8	18.2
57 $CaHPO_4$	39.0	30.0	96.7	48.7	4.5	6.6	19.7
58 $CaHPO_4$	45.0	20.0	326.7	47.6	5.5	6.5	19.6
59 $CaHPO_4$	35.0	31.0	183.3	49.8	7.0	6.3	21.0
60 H_3PO_4	35.0	18.0	340.0	27.6	3.2	4.5	15.5
61 H_3PO_4	47.0	23.0	390.0	27.9	3.5	4.5	16.2
62 H_3PO_4	30.0	31.0	170.0	26.7	6.6	4.2	14.6
64 Dredged	255.0	71.0	1873.3	33.9	6.2	4.5	19.7
65 Dredged	338.0	65.0	1413.3	34.2		6.0	21.4
66 Dredged	298.0	0.0	1633.3	0.0	7.6	4.7	21.7
67 Purity $CaHPO_4$	20.0	0.0	0.040	0.0	0.0	0.0	0.0
68 Purity $Ca(H_2PO_4)_2$	14.0	67.0	0.663	74.2	6.0	5.9	23.5

Table F.5 SPLP leaching of Dredged (D) and Treated (T) Sediments as a Function of pH Leachate concentrations

	Concentration (mg/L)						
Sample	**Zn**	**Ni**	**Mn**	**Pb**	**Cu**	**Cd**	**Co**
1D pH4	23.732	1.0666	13.2181	0.1676	0.4206	0.3092	0.1839
2D pH4	21.793	0.9711	12.0161	0.1412	0.5406	0.2676	0.1683
3D pH4	22.672	1.0356	14.0565	0.1649		0.2311	0.1835
1D pH5	22.217	0.6403	9.0565	0.0687	0.1723	0.0801	0.1172
2D pH5	18.985	0.5171	5.6424	0.0964	0.2062	0.0593	0.0937
3D pH5				0.0907		0.1100	0.1162
1D pH6	2.833	0.2152	4.1676	0.0411	0.0086	0.0131	0.0544
2D pH6		0.1781	5.4504	0.0329	0.0066	0.0089	0.0446
3D pH6	3.418	0.2283		0.0461		0.0158	0.0530
1D pH7	0.198	0.0419	1.1683	0.0239	0.0056	0.0046	0.0187
2D pH7	0.153	0.0412	0.8064	0.0221	0.0046	0.0049	0.0181
3D pH7	0.175	0.0365	0.9978	0.0455			0.0161
1D pH8	0.127	0.0222	0.1420	0.0131	0.0054	0.0041	0.0139
2D pH8	0.091	0.0255	0.1298	0.0156	0.0070	0.0025	0.0140
3D pH8	0.074	0.0274	0.0655	0.0173	0.0070	0.0032	0.0137
1D pH9	0.144	0.0290	0.0327	0.0176	0.0047	0.0043	0.0143
2D pH9	0.130	0.0367	0.0655	0.0200	0.0062	0.0038	0.0141
3D pH9	0.128	0.0344	0.0339	0.0164		0.0028	0.0167
4T pH4	3.864	0.2783	9.7495	0.0936	1.9140	0.0762	0.1837
5T pH4	2.789	0.1691	6.1896	0.0935	1.0350	0.0385	0.1181
6T pH4	3.477	0.1766	6.7154	0.0848	1.1250	0.0424	0.1249
4T pH5	2.789	0.2119	6.6813	0.0673	0.4020	0.0324	0.1212
5T pH5	1.530	0.1165	3.7253	0.0546	0.4000	0.0122	0.0820
6T pH5	1.428	0.1170	3.6032	0.0516	0.4070	0.0103	0.0778
4T pH6	0.460	0.0794	3.6846	0.0272		0.0070	0.0387
5T pH6	0.464	0.0822	2.2523	0.0423	0.0266	0.0132	0.0438
6T pH6		0.0822	1.0334	0.0345	0.0278	0.0085	0.0476
4T pH7	0.088		1.1104	0.0455	0.0059	0.0047	0.0302
5T pH7	0.048	0.0345	0.4129	0.0220	0.0029	0.0040	0.0181
6T pH7		0.0337		0.0269	0.0032	0.0037	0.0173
4T pH8	0.025	0.0261	0.0645	0.0254	0.0036	0.0030	0.0136
5T pH8	0.022	0.0134	0.0824		0.0029	0.0024	0.0133
6T pH8	0.012	0.0251	0.1011	0.0200	0.0020	0.0019	0.0126
4T pH9	0.029	0.0261	0.0335	0.0214	0.0033	0.0033	0.0137
5T pH9	0.010	0.0226	0.0274	0.0170	0.0020	0.0018	0.0111
6T pH9	0.019	0.0173	0.0342				

Table F.6 SPLP leaching of Dredged (D) and Treated (T) Sediments as a Function of L/S Leachate concentrations

	Concentration (mg/L)						
Sample	**Zn**	**Ni**	**Mn**	**Pb**	**Cu**	**Cd**	**Co**
1D L/S 005	0.1811	0.1011	2.6414	0.1505	-	0.0087	0.0469
2D L/S 005	0.1019	0.1331	3.5589	0.1641	0.0147	0.0138	0.0651
3D L/S 005	0.6908	0.0000	7.5450	0.1850	0.0167	0.0160	0.0930
4T L/S 005	0.0439	0.0782	1.2332	0.1843	0.0140	0.0144	0.0605
5T L/S 005	0.0707	0.0824	1.3465	0.1932	0.0154	0.0139	0.0605
6T L/S 005	0.0471	0.0825	1.2794	0.1905	0.0175	0.0145	0.0611
1D L/S 008	0.1556	0.0827	-	0.0871	0.0079	0.0091	0.0414
2D L/S 008	0.1285	0.0649	-	0.0843	0.0055	0.0072	0.0360
3D L/S 008	0.4868	0.0000	4.1276	0.1015	0.0115	0.0104	0.0578
4T L/S 008	0.0240	0.0475	0.8966	0.1139	0.0072	0.0114	0.0428
5T L/S 008	0.0406	0.0495	0.9032	0.1112	0.0072	0.0099	0.0441
6T L/S 008	-	0.0478	-	0.1170	0.0087	0.0109	0.0349
1D L/S 010	0.0514	0.0424	-	0.0469	-	-	0.0194
2D L/S 010	0.0482	0.0905	-	0.0883	0.0087	0.0079	0.0377
3D L/S 010	0.4146	0.0000	3.2233	0.0865	0.0062	0.0091	0.0480
4T L/S 010	0.0165	0.0429	0.7074	0.0895	-	0.0093	0.0371
5T L/S 010	0.0253	0.0434	0.7723	0.0915	0.0039	0.0097	0.0373
6T L/S 010	0.0424	0.0455	0.7558	0.0936	0.0035	0.0094	0.0194
1D L/S 020	0.0295	0.0531	0.3036	0.0308	0.0072	0.0038	0.0195
2D L/S 020	0.0717	0.0233	0.8724		0.0016		0.0090
3D L/S 020	0.2373	0.0711	1.5842	0.0382	0.0097	0.0042	0.0248
4T L/S 020	0.0090	0.0357	0.4202	0.0419	0.0032	0.0049	0.0207
5T L/S 020	0.0185	0.0372	0.4587	0.0415	0.0037	0.0052	0.0220
6T L/S 020	0.0127	0.0362	0.4268	0.0421	0.0042	0.0051	0.0213
1D L/S 050	0.0372	0.0169	0.3330	0.0131	0.0044	0.0009	0.0063
2D L/S 050	0.0752	0.0241	0.3823	0.0172	-	0.0017	0.0093
3D L/S 050	0.1387	0.0273		0.0168	-	0.0014	0.0100
4T L/S 050	0.0081	0.0179	0.2208	0.0220	-	0.0023	0.0105
5T L/S 050	0.0140	0.0182	0.2309	0.0209	0.0007	0.0023	0.0103
6T L/S 050	0.0137	0.0183	0.2419	0.0232	0.0005	0.0025	0.0110
1D L/S 100	0.0504	0.0087	0.0649	0.0138	0.0016	0.0009	0.0052
2D L/S 100	0.0949	0.0087	0.1960	0.0130	0.0063	0.0008	0.0048
3D L/S 100	0.0712	0.0109	0.2396	0.0134	0.0054	0.0008	0.0057
4T L/S 100	-	0.0037	0.1344	0.0135	0.0014	0.0014	0.0059
5T L/S 100	-	0.0040	0.1241	0.0141	0.0011	0.0014	0.0057
6T L/S 100	0.0124	0.0042	0.1358	0.0160	0.0073	0.0014	0.0055

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