



Field methods for rapidly characterizing paint waste during bridge rehabilitation



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HIGHLIGHTS

- Metal leaching mechanisms from paint waste generated during bridge rehabilitation were investigated.
- The diffuse layer model demonstrated the importance of complexation with the iron oxide surface.
- Statistically-based models developed in this research predicted metal leaching from paint waste.
- The study may assist DOT agencies with applying a predictive tool for waste classification.

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ABSTRACT

For Department of Transportation (DOT) agencies, bridge rehabilitation involving paint removal results in waste that is often managed as hazardous. Hence, an approach that provides field characterization of the waste classification would be beneficial. In this study, an analysis of variables critical to the leaching process was conducted to develop a predictive tool for waste classification. This approach first involved identifying mechanistic processes that control leaching. Because steel grit is used to remove paint, elevated iron concentrations remain in the paint waste. As such, iron oxide coatings provide an important surface for metal adsorption. The diffuse layer model was invoked ($\log K_{Me} = 4.65$ for Pb and $\log K_{Me} = 2.11$ for Cr), where 90% of the data were captured within the 95% confidence level. Based on an understanding of mechanistic processes along with principal component analysis (PCA) of data obtained from field-portable X-ray fluorescence (FP-XRF), statistically-based models for leaching from paint waste were developed. Modeling resulted in 96% of the data falling within the 95% confidence level for Pb (R^2 0.6–0.9, $p \leq 0.04$), Ba (R^2 0.5–0.7, $p \leq 0.1$), and Zn (R^2 0.6–0.7, $p \leq 0.08$). However, the regression model obtained for Cr leaching was not significant (R^2 0.3–0.5, $p \leq 0.75$). The results of this work may assist DOT agencies with applying a predictive tool in the field that addresses the mobility of trace metals as well as disposal and management of paint waste during bridge rehabilitation.

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1. Introduction

The majority of the steel bridges in the interstate system were constructed between 1950 and 1980 (Appleman, 1997), all were protected from corrosion with paint coatings containing lead and chromate (Strivens and Lambourne, 1999). Currently, a number of transportation agencies (i.e., New York State Department of Transportation (NYSDOT, 2008); Minnesota Department of Transportation (MnDOT, 2004); and Missouri Department of Natural Resources, 2006) apply a conservative approach by assuming all

waste generated from bridges rehabilitated before 1988 or with lead concentrations greater than 5000 ppm as hazardous. This practice stems from the fact that there is no approved reliable, fast, and efficient method for classifying paint waste in-situ as non-hazardous.

In earlier work (Shu, 2014), elevated iron was observed (as great as 80 wt.%) in the paint waste due to the use of steel grit as blasting abrasive during bridge rehabilitation. Although magnetic separation is applied to remove the steel grit, a fraction remains in the paint waste. Iron oxide formed on the steel grit surface plays an important role in the system (Shu et al., 2015). In our companion paper (Shu et al., 2015) despite the elevated concentrations of trace metals, leached concentrations evaluated using the U.S. Environmental

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Protection Agency (U.S. EPA) toxicity characteristic leaching procedure (TCLP) (U.S. EPA, 1992) were less than the toxicity characteristic (TC) levels. Furthermore, the multiple extraction procedure (MEP) (U.S. EPA, 1986, 2004) studies simulating long-term leaching behavior in a landfill environment demonstrated that 19 out of 24 samples resulted in concentrations less than the TC level. To better understand the phases metals and metalloids were associated with, sequential extraction (Tessier et al., 1979) revealed the importance of the iron oxide surfaces in the leaching process (Shu et al., 2015).

The objective of this study was to develop a model that can predict the leachability of metals in paint waste and to apply this model in the field on waste generated during bridge rehabilitation. This research builds on previous work (Shu, 2014; Shu et al., 2015). Through mechanistic modeling, the iron oxide coating formed on the steel grit surface was assessed for its role in metal mobility. Subsequently, statistically-based models that address leaching from paint waste were developed for field application. Results of this work assist in applying a predictive tool in the field that addresses the mobility of trace metals as well as disposal and management of paint waste during bridge rehabilitation.

2. Materials and methods

2.1. Data collected

A total of 117 paint waste samples were obtained from 24 bridges under rehabilitation in seven regions (Regions 1, 2, 3, 5, 7, 10, and 11) in NYS between October 2010 and November 2011 (Shu, 2014). To investigate metal distribution in the paint waste, eight Resource Conservation and Recovery Act (RCRA) metals (i.e., As, Ba, Cr, Cd, Pb, Hg, Se, and Ag) along with Fe, Ca, Ti, and Zn were analyzed with the NITON XL3t-600 series FP-XRF following Method 6200 (U.S. EPA, 1998) using either Soil Mode (metal concentrations < 2 wt.%) or Mining Mode (metal concentrations \geq 2 wt.%) (Shu, 2014). Additional details including detection limits for the FP-XRF in these two modes are provided in Supporting Information (Tables S1 and S2). Results from using FP-XRF on eight paint samples with Pb concentrations ranging from 210 to 168,093 mg/kg were compared to applying digestion with hydrogen fluoride (HF) (Method 3052) (U.S. EPA, 2004) followed by inductively coupled plasma mass spectroscopy (ICP-MS) (Method 6020A) (U.S. EPA, 2007). FP-XRF correlated ($R = 0.85\text{--}0.98$) (Details are provided in Supporting Information) with the ICP-MS analysis (Figs. S1 and S2 in Supporting Information). This work demonstrates the effectiveness of using FP-XRF as a field method to analyze the RCRA metals as well as iron and zinc concentrations in bridge paint waste.

In managing paint waste disposal from bridge structures, state DOT agencies are required to investigate waste leaching behavior and determine waste classification. In this study, trace metal concentrations in the leachate solution were detected using ICP-MS (Method 6020A; U.S. EPA, 2007). This instrument was calibrated using National Institute of Standards and Technology (NIST)

Standard Reference Material (SRM). The calibration curve was developed with ten standards covering the range of 2–1700 $\mu\text{g L}^{-1}$ using Multi-Element Solution 2A (Spex Certiprep). Detection limits included As = 0.7 $\mu\text{g L}^{-1}$, Ba = 0.4 $\mu\text{g L}^{-1}$, Cd = 0.5 $\mu\text{g L}^{-1}$, Cr = 0.7 $\mu\text{g L}^{-1}$, Pb = 0.5 $\mu\text{g L}^{-1}$, Se = 0.2 $\mu\text{g L}^{-1}$, Ag = 0.3 $\mu\text{g L}^{-1}$, Fe = 2.5 $\mu\text{g L}^{-1}$, Zn = 1.0 $\mu\text{g L}^{-1}$, and Hg = 2.0×10^{-3} $\mu\text{g L}^{-1}$. Data collected (Shu, 2014; Shu et al., 2015) from studying the leaching behavior were applied in mechanistic modeling, in the analysis of key variables, and then in the resulting statistically based-model.

2.2. Mechanistic processes

Based on the results from sequential extraction along with leaching studies (Shu et al., 2015), adsorption/desorption and dissolution/precipitation are considered plausible processes. Because ferrihydrite is a dominant surface (Shu et al., 2015) and because of its significant adsorbent characteristics including a large surface area and high affinity for metal ions, this oxide surface was used in modeling sorption (Kendall, 2003; Apul et al., 2005). The hydrous ferric oxide (HFO) surface has low-affinity and high-affinity sites (Dzombak and Morel, 1990), represented as Fe^{WOH} and Fe^{OH} , respectively. The weak-affinity site density of 0.2 mol/mol Fe and the high-affinity site density of 0.005 mol/mol Fe were used in this study (Dzombak and Morel, 1990; Meima and Comans, 1998; Apul et al., 2005). Dominant surface complexes with ferrihydrite have been shown to include FeOPb^+ and FeOCrOH^+ (Supporting Information, Tables S3 and S4) (Dzombak and Morel, 1990; Kendall, 2003; Jing et al., 2006).

In this study, two models were trialed for Pb and Cr leaching over the pH of 4.5–7. Sorption onto the ferrihydrite surface was considered using the surface complexation diffuse layer model (DLM) coupled with 2-pK formalism. Surface acid–base reactions and equilibrium constants used in the DLM are from the compilation of studies reviewed in Dzombak and Morel (1990). Inputs such as background electrolyte, adsorbate, and sorbent concentrations were based on the TCLP leaching experiments, XRF analyses, and sequential extraction results (Table 1) (Shu et al., 2015). An ionic strength of 0.1 was applied in the calculations to simulate the leaching conditions considered. The second modeling approach involved precipitation/dissolution. Barnes and Davis (1996) demonstrated $\text{PbCO}_{3(s)}$ (cerussite) (pH < 8) and $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2(s)$ (hydrocerussite) (pH \geq 8) as the dominant Pb minerals in lead-based paint. In fact, the primary lead compound used in paints was white lead ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2(s)$) with concentrations as great as 40 wt.% of dry paint (Gooch, 1993). Lead chromate (chrome yellow $\text{PbCrO}_{4(s)}$) was used in (colored) paint at 5–7% (Clark, 1976), while lead tetraoxide (red lead Pb_3O_4 , Pb_2O_4 , $\text{PbO}_2 \cdot 2\text{PbO}$) was also a component of paints (Clark, 1976; Gooch, 1993). Boy et al. (1995) found $\text{Cr}(\text{OH})_3(s)$ (chrome oxide green) as the dominant phase when they investigated chromium stabilization in paint waste with Portland cement and blast furnace slag. Jing et al. (2006) further demonstrated that $\text{Cr}(\text{OH})_3(s)$ and $\text{Ca}_2\text{Cr}_2\text{O}_5(s)$ were the dominant phases when they evaluated Cr leaching behavior in

Table 1
Total and leached concentrations^a used in surface complexation modeling.

	Pb			Cr		
	Mean	Min	Max	Mean	Min	Max
Total Concentrations in the paint (mg kg^{-1}) ^b	4.6×10^4	5	1.7×10^5	3018	21	1×10^4
Leached concentrations over TCLP procedure (M or mol/L)	1.4×10^{-6}	BDL ^c	1.0×10^{-5}	1.5×10^{-5}	BDL	1.8×10^{-4}
Desorbed metal concentrations over TCLP procedure (% of total metal)	0.011	BDL	0.048	0.62	BDL	3.7

^a Shu et al. (2014, 2015).

^b The values are based on results from FP-XRF.

^c BDL refers to below detection limit.

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