



Nickel speciation in cement-stabilized/solidified metal treatment filtercakes



Amitava Roy^a, Julia A. Stegemann^{b,*}

^a J. Bennett Johnston, Sr., Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, LA 70806, USA, USA

^b Centre for Resource Efficiency & the Environment, Department of Civil, Environmental & Geomatic Engineering, University College London, Chadwick Building, Gower Street, London WC1E 6BT, UK, UK

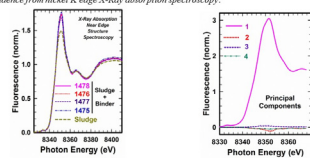
HIGHLIGHTS

- XAS shows the same Ni speciation in untreated and stabilized/solidified filtercake.
- Ni solubility is the same for untreated and stabilized/solidified filtercake.
- Leaching is controlled by pH and physical encapsulation for all binders.

GRAPHICAL ABSTRACT

Solidification/ Stabilization Waste + binder
Physical encapsulation? Or chemical reaction?

Evidence from nickel K edge X-Ray absorption spectroscopy:



- Same nickel species in waste and binders
- No change in speciation from waste to binders
- Only one nickel species

Physical encapsulation!

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ABSTRACT

Cement-based stabilization/solidification (S/S) is used to decrease environmental leaching of contaminants from industrial wastes. In this study, two industrial metal treatment filtercakes were characterized by X-ray diffractometry (XRD), thermogravimetric and differential thermogravimetric analysis (TG/DTG) and Fourier transform infrared (FTIR); speciation of nickel was examined by X-ray absorption (XAS) spectroscopy. Although the degree of carbonation and crystallinity of the two untreated filtercakes differed, α -nickel hydroxide was identified as the primary nickel-containing phase by XRD and nickel K edge XAS. XAS showed that the speciation of nickel in the filtercake was unaltered by treatment with any of five different S/S binder systems. Nickel leaching from the untreated filtercakes and all their stabilized/solidified products, as a function of pH in the acid neutralization capacity test, was essentially complete below pH \sim 5, but was 3–4 orders of magnitude lower at pH 8–12. S/S does not respeciate nickel from metal treatment filtercakes and any reduction of nickel leaching by S/S is attributable to pH control and physical mechanisms only. pH-dependent leaching of Cr, Cu and Ni is similar for the wastes and s/s products, except that availability of Cr, Cu and Zn at decreased pH is reduced in matrices containing ground granulated blast furnace slag.

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1. Introduction

Treatment by stabilization/solidification with cement-based binders (S/S) is an option for wastes that cannot be prevented or

reduced, such as metal-bearing industrial wastes and wastewaters. S/S aims to provide a chemical environment where contaminants have lower solubility, and a physical matrix of low hydraulic conductivity, to minimize leaching when the resulting cement-based product is utilized or land-disposed.

Metal-bearing wastewaters are usually acidic, and are typically treated by neutralization with excess calcium hydroxide to produce a hydroxide sludge that is dewatered by filter pressing. The filtercake tends to undergo carbonation from the atmosphere, before

* Corresponding author.

E-mail addresses: reroy@lsu.edu (A. Roy), j.stegemann@ucl.ac.uk (J.A. Stegemann).

possible further treatment by S/S. The mineralogical composition of such metal treatment filtercakes, and the speciation of contaminants in them, is controlled by both kinetic and thermodynamic factors and has not been well-characterized. In fact, the initial precipitate is often colloidal and the solid phases are unstable or metastable and therefore different from predictions based on thermodynamic equilibrium.

Characterization of waste mineralogy and speciation of contaminants in wastes and their stabilized/solidified (s/s) products is critical for understanding contaminant leachability in laboratory tests and the environment, as well as development of effective treatments. The effect of S/S on metal contaminant speciation and leachability is of particular interest, as respeciation of contaminants is arguably a primary goal of the treatment. In theory, S/S results in precipitation or co-precipitation of metal ions, e.g., as hydroxides, or up-take by cement hydration products, e.g., in calcium silicate hydrate, or ettringite and/or monosulphate-type phases, possibly including a change in oxidation state [1]. Papers about S/S commonly speculate about contaminant speciation without evidence, e.g., reporting leaching results for regulatory tests such as the USEPA Toxicity Characteristic Leaching Procedure (e.g. [2,3]), and/or as “% immobilization” (the difference between the total concentration and the leached amount as a percentage of the total concentration (e.g., [3–5])). Such results are arbitrary in relation to potential environmental leaching, since they can be manipulated by changing the leaching conditions (pH, liquid-to-solid ratio, contact method), and are unhelpful in elucidating the contaminant immobilization mechanism. Questionable evidence of respeciation is often based on application of a sequential extraction procedure (e.g. [6]), such as that originally proposed by Tessier et al. [7], though this has been shown to be highly inaccurate for s/s products [8].

A variety of instrumental techniques are available to examine mineralogy and contaminant speciation of wastes and cement-based materials. X-ray diffractometry (XRD) is widely used for mineralogical characterization of crystalline samples, but is of limited help for non-crystalline materials. Fourier transform infrared (FTIR) microscopy and thermal analysis are also routinely used to investigate cementitious materials. None of these techniques is element specific and they are not useful for study of elements at low concentrations. In contrast, X-ray absorption spectroscopy (XAS) can track a particular element at relatively low concentrations in a complex host matrix and probe its local structure and speciation, without a requirement for crystallinity.

The application of XAS to complex matrices in relation to environmental fate and behavior of contaminants is still relatively rare, but it has been employed in a limited number of studies of the speciation of metals in cement pastes, including chromium [9], cobalt [10], copper [11], lead [12], neodymium [13], selenium [14], tin [15], uranium [16], and zinc [17], as well as nickel [18–20]. Apart from Rinehart et al. [9], who examined the oxidation state of chromium in a s/s contaminated soil and showed that this was not affected by S/S, and Hsaio et al. [11], who indicated that S/S respeciated CuCl_2 and reduced forms of copper in municipal waste incinerator air pollution control residues to $\text{Cu}(\text{OH})_2$, other studies have all prepared hydrated cement pastes by mixing pure solutions of soluble metal salts with cement powder. This contact mechanism is unrealistic, as contaminants in wastes are rarely fully dissolved, and the speciation observed in this way may not apply in cement-based systems containing real wastes. Previous scanning electron microscopy work has shown encapsulation of sludge particles, tens of μm in size, in the cement matrix [21]. Microscopy, however, cannot infer whether respeciation occurred.

This study therefore used multiple techniques, including XAS, to investigate the mineralogy and speciation of nickel in two real metal treatment filtercakes, as well as in five different s/s products prepared from one of the filtercakes using different S/S

formulations. pH-dependent leaching of Ni, Cr, Cu and Zn in both filtercakes and their s/s products were also examined.

Nickel was studied as an element of environmental concern that is more common in metal treatment filtercakes than other industrial wastes usually treated by S/S. Previous work with these materials found the trivalent oxidation state of chromium to be unaltered by S/S, but indicated that hydroxo complexes with similar coordination but slightly different bond distances were formed in s/s products [22]. Speciation of copper and zinc, also present in these wastes, has not yet been investigated. This work was conducted in the context of a larger project led by University College London (UCL) to increase transparency of S/S technology by developing process envelopes for generic S/S of the most common/problematic residual waste types, i.e., to investigate relationships between engineering and leaching properties and s/s product composition [23,24].

2. Experimental materials and methods

2.1. Filtercakes

Two metal treatment filtercakes were obtained by UCL from anonymous industrial sources, designated “ST” and “TX” in the following text. The filtercakes were produced by filterpressing sludges from neutralization of plating wastes with calcium hydroxide, in a process that is open to the atmosphere. The residual moisture contents of ST and TX were 57% and 78% wet mass, respectively. To obtain representative results in the S/S trials, the filtercakes were dried to constant mass at 60 °C, crushed to a particle size of <1 mm, homogenized and reconstituted to a moisture content of 50% wet mass before being treated by S/S. The chemical compositions of the dried filtercakes were determined by inductively coupled plasma optical emission or mass spectroscopy (ICP-OES/MS) following aqua regia digestion, with measurement of anions by ion chromatography of the extract from a 10:1 water extraction. Loss-on-ignition (LOI) of the filtercakes was determined at 550 °C, and total organic carbon (TOC) content was measured in a LECO furnace. The typical composition ranges of the filtercakes for several samples taken over more than a year are shown in Table 1, including the specific samples used in this work (i.e., totals shown in Fig. 5 and used in Table 3). The variations in element concentrations observed are typical of industrial wastes, whereby concentrations of the soluble ions potassium, sodium and nitrate were particularly variable, but quite low. The TOC content of both sludges was low (<3.3%), so the much higher LOI values (<61%) suggest the presence of inorganic compounds that decompose at a relatively low temperature (see also 3.1.3). Nickel was present at % levels in both sludges, with a four-fold concentration variation in sludge ST and a two-fold variation in sludge TX.

2.2. Preparation of stabilized/solidified products

The binders used in S/S were Portland cement on its own, or Portland cement or hydrated lime ($\text{Ca}(\text{OH})_2$) blended with power plant fly ash (from combustion of pulverized bituminous coal, i.e., “Class F” or “pfa”) or ground granulated blast furnace slag. The five formulations studied in this work are summarized in Table 2. The overall concentrations of selected elements in each formulation (Table 3) were calculated based on the elemental compositions and proportions of filtercake and binder, and the moisture contents of the s/s products determined by drying at 60 °C after 28-day curing. The dried s/s products were also ground and used for the following XAS, mineralogical characterization, and leaching studies.

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