Journal of Hazardous Materials 141 (2007) 591–606

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Release of Zn, Ni, Cu, SO_4^{2-} and CrO_4^{2-} as a function of pH from cement-based stabilized/solidified refinery oily sludge and ash from incineration of oily sludge

Athanasios K. Karamalidis [1], Evangelos A. Voudrias *

Department of Environmental Engineering, Democritus University of Thrace, GR 671 00 Xanthi, Greece

Received 14 February 2006; received in revised form 30 June 2006; accepted 11 July 2006

Abstract

A framework for the evaluation of leaching behavior of inorganic constituents from stabilized/solidified refinery oily sludge and ash produced from incineration of oily sludge with cement was employed. Metal and anion release as a function of pH was investigated. The leaching test consisted of multiple parallel extractions at pH range from 2 to 12. Remarkably good immobilization >98% was observed for metals of solidified ash at pH > 6 and >93% of solidified oily sludge at pH > 7. Sulfate leaching was high at pH range 2–12. The leaching behavior of metals and anions was simulated by VMINTEQ. The calculations showed that leaching behavior of Zn, Ni and Cu was controlled by chemical equilibrium and surface complexation onto ferrihydrite, at the pH range 2–12. The dominant solid phases that controlled metal leachability were metal hydroxides. The dominant mechanism that described sulfate leaching was found to be chemical equilibrium. Sulfate and also chromate leachability was controlled by Ettringite and Cr(VI)Ettringite as the major minerals affecting their release.

Keywords: Refinery oily sludge; Incinerated oily sludge; Cement; Leaching; Metal; Anion; Stabilization/solidification; Sorption; Surface complexation

1. Introduction

Many leaching tests have been developed, evaluated and applied to a variety of materials and waste for regulatory purposes, waste management, environmental impact assessment and for scientific purposes [1,2]. Toxicity Characteristic Leaching Procedure (TCLP) is a leaching test that has been used for most of these purposes. Although TCLP is one of the most widely used leaching tests, it has come to unfavorable criticism. There are limitations of using the TCLP for simulating the leaching of contaminants in landfills. These limitations have resulted in legal challenges concerning the failure of the US EPA to provide adequate justification for specifying the TCLP for the classification of several industrial wastes [3]. Recent studies have shown that the TCLP may not accurately measure the ability for arsenic to migrate from a landfill [4]. Poon and Lio [5] has reported TCLP limitations and the EPA Science Advisory Board criticized the protocol on the basis of several technical considerations, such as leaching kinetics, liquid to solid ratio, pH, potential of colloid formation, particle size reduction, aging, volatile losses, and codisposal with other waste [6]. In the present study, an alternative to TCLP framework was used for the evaluation of leaching of inorganic constituents from stabilized/solidified oily sludge and ash. This alternative was a leaching test for alkalinity, solubility and release of metals and anions as a function of pH [6].

A metal ion may be immobilized into the cement matrix. It may either be bound in the alkaline cement matrix as an oxide or mixed oxide, be sorbed to surfaces, or be incorporated into cement minerals [7]. Recently, incorporation of Zn to the interlayer or sorption to internal surface of Calcium Silicate Hydrate (CSH; $CaOSiO_2 \cdot xH_2O$) which is a mineral formed during cement hydration, have been proved [8–10]. Surface complexation modeling, with a modified triple layer model, was used to describe Zn sorption onto ferrihydrite ($Fe(OH)_{3(s)}$) [11]. Zhu has estimated surface precipitation constants for sorption of divalent metals M^{2+} (e.g. Ni^{2+}, Cu^{2+}, Zn^{2+}) onto ferrihydrite, and concluded that surface complexation dominates sorption at

---

* Corresponding author. Tel.: +30 25410 79377; fax: +30 25410 79376.
E-mail addresses: akaramal@env.duth.gr (A.K. Karamalidis), voudrias@env.duth.gr (E.A. Voudrias).

[1] Tel.: +30 25410 79395; fax: +30 25410 79376.

0304-3894/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2006.07.034

low dissolved metal concentrations [12]. Ni uptake by blended cement has been attributed to the formation of a 4:1 Ca:Ni phase, which was thought to replace $Ni(OH)_2$ as the solubility-limiting phase in cement systems. However, X-ray diffraction of Ni-doped cement pastes showed only the presence of a poorly crystallized $Ni(OH)_2$ gel [13]. Under highly alkaline conditions, Ni–Al–oxyhydroxides were potential host phases for Ni in cement, but, nevertheless, $Ni(OH)_2$ was present to some extent [13]. The pH-dependent adsorption and coprecipitation of Cu with the hydrous oxides of Fe and Al were previously reported by Karthikeyan et al. [14]. They also applied a generalized two-layer model on Cu adsorption onto ferrihydrite over a range of pH and surface loading conditions, and found that it was satisfactory for low sorbate/sorbent ratios where metal oxide interaction is adequately described as Cu^{2+} coordination to surface functional groups [15].

Another mineral affecting metal immobilization in the cement matrix is Ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3\cdot 26H_2O$), because of its abundance and appropriate structure [7,16]. Several publications [17–19] showed that Ettringite is one of those minerals that can contain in its structure anions and oxyanions as well as cations. Anion substitution in Ettringite can take place either by reacting with surface sites (ligand exchange) or by substituting inside the channels for sulfate (isomorphic substitution) [14,18]. Anionic substituted Ettringites have been reported and synthesized for $AsO_4{}^{3-}$, $B(OH)_4{}^{-}$, $CO_3{}^{2-}$, $CrO_4{}^{2-}$, $NO_3{}^{-}$, OH^{-}, $SeO_4{}^{2-}$, $SO_3{}^{2-}$, and $VO_4{}^{3-}$. In cementitious material, $B(OH)_4{}^{-}$, $CrO_4{}^{2-}$, $MoO_4{}^{2-}$, $SeO_4{}^{2-}$, and $SO_3{}^{2-}$ also have been shown to serve as interlayer anions [17]. In such cement-matrices, because of their high alkaline environment, it is common that chromium speciation is dominated by $CrO_4{}^{2-}$ above pH 8 [20]. Ettringite can also be found in cement-related materials, such as in cement-solidified waste. Contrary to substitution, at extremely low concentrations, below the threshold for precipitation, contaminant availability tends to be controlled by sorption mechanisms [21].

In this study, the leaching behavior of metals and anions released from solidified/stabilized refinery oily sludge and ash produced by incineration of refinery oily sludge, was examined by means of the alkalinity, solubility and release as a function of pH test. Refinery oily sludge and ash are classified as hazardous wastes. Metals and anions, contained in such waste are potential contaminants to groundwater and soil. Cement-based stabilization/solidification is a low cost treatment process, which has been widely applied to waste containing radioactive contaminants, heavy metals, and other hazardous substances. In some cases treatment technologies, such as incineration, are not a feasible option, either because of unavailable infrastructure or of high cost. Thus, alternative treatment technologies must be applied. Stabilization/solidification aiming to landfill disposal is certainly one of them. Data about metal and anion leaching from real refinery oily sludge and incinerated refinery sludge, stabilized/solidified with II-45 ordinary Portland cement (OPC) as a function of pH, are scarce or do not exist. Much work has been done about leachability of metals using the TCLP protocol, but because of its recent criticism, in this work a new leaching framework [6] was applied. The work focuses on the immobilization mechanisms, which control the leaching behavior of metals and anions. For this purpose, in addition to leaching experiments, the computer program Visual MINTEQ was employed. Metals were assumed to be mainly in the form of hydroxides and simulated by chemical equilibrium and surface complexation using diffuse layer model (DLM). Sulfate leaching was simulated by chemical equilibrium and chromate by chemical equilibrium and surface complexation. Cr(VI)Ettringite, Ettringite, $ZnSO_{4(s)}$, and $Fe_2(SO_4)_{3(s)}$ were considered for sulfate leaching and $CaCrO_{4(s)}$ for chromate leaching.

2. Materials and methods

2.1. Oily sludge and incinerated oily sludge

Sludge samples were obtained from a Greek refinery (R). The R samples originated from a centrifuge unit, which contained a mixture of different kinds of oily sludge, such as API type gravity separator sludge and dissolved air flotation (DAF) sludge. The purpose of the centrifuge unit was to recover and reuse the hydrocarbon fraction contained in the sludge. The incinerated oily sludge (IR) (ash) was produced by incineration of the R samples in a laboratory kiln.

2.2. Binding materials

The ordinary Portland cement (OPC), II-45, was obtained from TITAN Cement Company SA. The II-45 OPC contains pozzolanic material (natural pozzolan 7%, w/w). The chemical composition of the cement and its pozzolanic component was determined by XRF analysis (Table 1). For the stabilization/solidification (S/S) process, ultra-pure water was used in order to minimize contamination of the solidified specimens by constituents contained in the water. Ultra-pure water (ASTM Type I, ISO 3696) was prepared using the system USF-ELGA, UHQ II.

2.3. Incineration procedure

Measured amounts of R oily sludge samples were placed into a stainless steel container, capable of resisting temperature above 1200 °C, without being disintegrated. The temperature of

Table 1
Chemical composition of II-45 OPC and natural pozzolan contained in II-45 OPC, determined by XRF analysis

Component	II-45 OPC (wt.%)	Natural pozzolan of II-45 OPC (wt.%)
SiO_2	28.3	64
Al_2O_3	8.7	14
Fe_2O_3	3.6	5
CaO	50.8	7
MgO	2.2	1.5
K_2O	2.0	2.5
SO_3	3.2	–
Lost on ignition		5
Total	98.8	99