



Stabilization–solidification treatment of mine tailings using Portland cement, potassium dihydrogen phosphate and ferric chloride hexahydrate

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ABSTRACT

This paper reports the investigation aimed at verifying the influence of potassium dihydrogen phosphate and ferric chloride hexahydrate on stabilization/solidification (S/S) processes applied to tailing waste from a Pb and Zn mineral processing plant. The use of cement alone (in a percentage equal to 5%) does not permit the obtaining of a final product complying with current Italian legislation. The possibility of using potassium dihydrogen phosphate, singly or combined with ferric chloride hexahydrate, has been investigated under different pH conditions, simulating the aging phase in waste–cement mixtures. The combined effect of the additives mentioned (1% KH_2PO_4 and 1% FeCl_3), together with small quantities of cement, permits production of inert material, through the physical encapsulation and formation of stable compounds.

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1. Introduction

In many countries, the gradual abandonment of mine sites and the inadequacy of systems to contain extraction waste have increased the risk of contaminant spread. This problem has global relevance: a recent study on abandoned mines in the United States (US BLM, 2012) reports nearly 31,014 sites, only for 25% of which corrective action has been planned.

Streams of water are the main vehicles of diffusion of metal contaminants. Several investigations have been carried out to analyze the contamination process of superficial and groundwater draining sites affected by mining activities. Contamination can sometimes extend for several kilometers downstream of mining sites, as demonstrated by recent studies realized in Sardinia (Italy), where in the past, mining activity was the main industrial resource (Cidu et al., 2012; Zijlstra et al., 2010; Bertocchi et al., 2006).

There are numerous remediation techniques for soils contaminated by heavy metals, including in situ or ex situ treatments (soil-washing, soil flushing, granulometric separation, phytoremediation, bioreduction, etc.), able to isolate, remove or stabilize metals in soil or wastes (Desogus et al., 2012a; Giurco and Cooper, 2012; Laguna et al., 2011; Mulligan et al., 2001). The choice of technique will hinge on a number of factors related to the future use of the areas targeted for remediation, whether for industrial activities or for public use, and on technical as well as economic and legislative considerations (Glaister and Mudd, 2010; Hilson, 2000, 2003).

The high cost of remediation based on the removal and landfilling of contaminated materials requires the development of more economical, alternative methods, such as stabilization/solidification (S/S) techniques. S/S has been identified by the U.S. EPA as the best technology available for 57 types of waste (Shi and Spence, 2004). S/S treatment combines two closely-interrelated processes which the EPA defines as follows (Cullinane and Jones, 1986):

- **Stabilization:** technique reducing the potential hazard of waste, converting contaminants into their less soluble, mobile or toxic forms. Does not lead to changes in the physical properties of the material treated.
- **Solidification:** technique encapsulating waste into a solid monolithic structure with high structural integrity. Does not necessarily involve chemical interaction between waste and solidifying agents.

The inertized material may acquire, after solidification treatment, physical properties making it suitable for reuse in various ways: for example, building material, material for the construction of pavements or road foundations or material for backfill operations (Benzaazoua et al., 2008).

This study considers the possibility of applying S/S techniques to the treatment of mine tailings, using Portland cement and chemical additives (such as potassium dihydrogen phosphate and ferric chloride hexahydrate) which, mixed with waste, minimize the mobility of contaminants and obtain a material suitable for mining backfill. This is possible only if the stability of mining waste is

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guaranteed and pollution of the soil, surface water and groundwater is prevented (Legislative Decree 117/2008 (G.U.R.I., 2008)). Considering these requirements, all concentration values of contaminants detected in leachates were compared with threshold concentrations of contamination for groundwater (Legislative Decree 152/2006 (G.U.R.I., 2006)).

The hydraulic binder determines the most significant cost, in some cases about 75% of the entire work of backfilling (Belem and Benzaazoua, 2004). Therefore, it is essential to limit the proportion of this component in mixtures, while maintaining the physical–mechanical performance and efficiency of inertization. However, low percentages of binder may not be sufficient to ensure the appropriate efficacy of waste treatment. The use of some additives, such as potassium dihydrogen phosphate and ferric chloride hexahydrate, was thus tested in order to convert the main contaminants into stable and/or slightly soluble forms.

1.1. Cement-based S/S and the use of phosphates

In S/S techniques, cement is the most widely-used type of binder, due to its availability and limited cost. Stabilization of waste in cement-based S/S treatments is the result of chemical transformations of contaminants and depends on the characteristics of the environment in which they are located. Numerous mechanisms are involved in this process: precipitation in the form of hydroxides, sulphides or substitution processes (Zhang and Reardon, 2003); adsorption of contaminants on surfaces of the monolithic structure (Batchelor, 2006); oxidation–reduction of metals and transformation into less toxic forms; degradation of some organic compounds, such as chlorinated organic compounds and pesticides, through base-catalysed hydrolyses (Schwarzenbach et al., 2003); physical encapsulation of contaminated metal enclosed within the CSH matrix (Batchelor, 2006).

The addition of water causes hydration of the clinker (tricalcium silicate, dicalcium silicate, tricalcium aluminate), with the formation of important compounds, among which calcium silicate hydrate (CSH), calcium aluminate hydrate (CAH) and Portlandite ($\text{Ca}(\text{OH})_2$). The latter gives rise to a strongly-alkaline reaction environment, with a pH generally between 12 and 13. Hydration and subsequent consolidation of the cement paste continues through several competitive exothermic reactions, forming intermediate minerals between CSH gel and the crystalline phase.

Previous studies demonstrate that the initial phase of hydration, although limited in time, constitutes the most critical moment in the entire solidification process. Indeed, the highly-alkaline environment gives rise to the release of contaminants in the waste, with higher concentrations in solution than those characterizing untreated waste. Moreover, high rates of hydraulic binder, 10–20%, are not sufficient to obtain a material with characteristics complying with the requirements imposed by regulations (Desogus et al., 2012b,c). Hence the necessity to use chemical additives producing highly-efficient stabilization, both during the transitory phase of hydration and after constitution of the monolithic form.

Pb contamination in soils has been widely studied in recent years, and several remediation techniques have been proposed. Laboratory and field experiments have shown that the use of different types of additives containing phosphorus lead to a reduction in mobility and bioavailability of Pb through the formation of pyromorphites ($\text{Pb}_5(\text{PO}_4)_3\text{X}$, X = F, Cl, Br, OH), highly stable Pb compounds with wide pH and Eh ranges (Miretzky and Fernandez-Cirelli, 2007; Ryan et al., 2001; Berti and Cunningham, 1997). The solubility of Pb compounds indicates that, under equilibrium conditions, Pb phosphates are less soluble than oxides, hydroxides, carbonates and sulfides of the same metal (Ruby et al., 1994).

Furthermore, chemical stabilization of Pb using phosphate is a widely-recognized technique for the remediation of contaminated water and soil (Ryan et al., 2001). It was found that in soils treated with phosphates, Pb absorption by plants is reduced (Hettiarachchi et al., 2000); limitation of the pollution load of acid water from mining work (Melamed et al., 2003) and minimization of the transfer of Pb from industrial wastes (Crannell et al., 2000) have also been detected.

However, it is necessary to point out that the use of phosphates may determine the mobilization of As, if present in the soil, through competitive adsorption processes between phosphates and arsenate (Miretzky and Fernandez-Cirelli, 2007; Lambkin and Alloway, 2002; Boisson et al., 1999; Peryea and Kammerek, 1997). Numerous types of natural and synthetic phosphates are used to immobilize Pb: phosphate rock, apatite and hydroxyapatite, soluble salts of phosphorus fertilizers and clays containing phosphate, and phosphoric acid. Liquid forms of phosphate are used to obtain quick reactions, while solid forms are used to decrease the release of phosphates in long-term treatment (Srinivasan et al., 2006).

Those widely used are: potassium hydrogen phosphate, potassium dihydrogen phosphate and potassium (K_2HPO_4 , KH_2PO_4); calcium mono and di-hydrogen phosphate (CaHPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$); phosphoric acid (H_3PO_4) and fertilizers with rapid phosphate release. Phosphoric acid is the most widely-used additive (U.S. EPA, 2001), both due to its availability and its ability to stabilize Pb^{2+} and transform it into pyromorphite. Furthermore, phosphoric acid is particularly effective in the treatment of calcareous soils, in which neutralization of protons favors the formation of chloropyromorphite (Miretzky and Fernandez-Cirelli, 2007). The process of nucleation of chloropyromorphite is characterized by very rapid kinetics and, with increasing reaction time, increases the stability of the precipitate, with consequent reduction in the solubility and bioavailability of Pb. The process is also influenced by the pH of the environment: the solubility of pyromorphite decreases as pH increases (Scheckel and Ryan, 2002). Berti and Cunningham (1997) utilized potassium dihydrogen phosphate (KH_2PO_4) to treat in situ a soil contaminated by Pb (1200–3500 mg/kg): adding 0.5% phosphate, Pb release was reduced below the legal limit (5 mg/l) (Miretzky and Fernandez-Cirelli, 2007; Berti and Cunningham, 1997).

2. Materials and methods

2.1. The Masua tailings

This study examines waste from the Masua mining site, located in southwestern Sardinia (Sulcis-Iglesiente), in an area of great natural value and great tourist potential. In the past, the site was one of the most important in Europe for the production of lead and zinc. Samples were collected from two ponds (2.5 mm³) containing tailing waste from the lead and zinc (carbonated and sulphides) flotation plant. The mining waste was characterized by the mineralogical, physical and chemical analysis reported in previous studies (Desogus et al., 2012b,c). The dominant mineral phases are calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and, to a lesser degree, Quartz (SiO_2). More than 55% of the material is smaller than 38 micrometers. Table 1 shows chemical analyzes using ICP-OES (PerkinElmer Optima 7000 DV). High concentrations of Zn, Cd and Pb were observed.

Leaching tests, carried out on the sample according to UNI 10802 (UNI, 2005), show concentrations of Pb equal to 0.103 mg/l, higher than the concentration (Pb = 0.010 mg/l) of contamination in groundwater (G.U.R.I., 2006).

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