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Small hazardous waste generators in developing countries: use of stabilization/solidification process as an economic tool for metal wastewater treatment and appropriate sludge disposal

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Abstract

The aim of this study was to propose a profitable destination for an industrial sludge that can cover the wastewater treatment costs of small waste generators. Optimized stabilization/solidification technology was used to treat hazardous waste from an electroplating industry that is currently released untreated to the environment. The stabilized/solidified (S/S) waste product was used as a raw material to build concrete blocks, to be sold as pavement blocks or used in roadbeds and/or parking lots. The quality of the blocks containing a mixture of cement, lime, clay and waste was evaluated by means of leaching and solubility tests according to the current Brazilian waste regulations. Results showed very low metal leachability and solubility of the block constituents, indicating a low environmental impact. Concerning economic benefits from the S/S process and reuse of the resultant product, the cost of untreated heavy metal-containing sludge disposal to landfill is usually on the order of US$ 150–200 per tonne of waste, while 1 tonne of concrete roadbed blocks (with 25% of S/S waste constitution) has a value of around US$ 100. The results of this work showed that the cement, clay and lime-based process of stabilization/solidification of hazardous waste sludge is sufficiently effective and economically viable to stimulate the treatment of wastewater from small industrial waste generators.

Keywords: Stabilization/solidification; Industrial hazardous waste; Heavy metal encapsulation; Small waste generators

1. Introduction

Environmental management in developing countries is a complex issue because environmental problems are linked with social and economic aspects, which must be considered in the development of any environmental program or regulation. Concerning waste management, recognition that not all generators produce the same quantities of hazardous waste is an essential step. In this sense, in terms of hazardous waste, large quantity generators (LQGs) are subject to more stringent regulations, while small quantity generators (SQGs) generally do not fulfill environmental regulations. Nowadays, there are many SQGs that release wastewater directly into receiving waters without treatment due to high costs of treatment and proper disposal of the generated sludge, which is generally disposed of in industrial landfills, sometimes not designed to handle hazardous waste [1].

Heavy metals are present in many industrial sludges and they are considered as hazardous waste. Conventionally, chemical precipitation has been the method most often used to remove heavy metals from wastewater [2]. Of the few precipitation methods, hydroxide and sulfide are the two main methods currently used, and hydroxide precipitation is by far the most widely used method to precipitate heavy metal contaminants in wastewater, which employs alkaline materials such as caustic soda, soda ash, lime, magnesium hydroxide or a combination thereof. This technique has the disadvantage of producing large quantities of sludge. The metals generally present in the electroplating industry sludges are cadmium, chromium, cobalt, copper, iron, lead, nickel, and zinc.

To avoid environmental metal release, a successful management technique for small generators of hazardous wastes must link sludge destination with economic benefits of this practice.

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This could stimulate wastewater treatment and sludge collection, since sludge reuse could yield economic benefits, allowing, in this manner, prevention of pollution at its source. Based on this idea, stabilization/solidification (S/S) of sludge originating from wastewater treatment is a potential tool to stimulate correct industrial sludge disposal, i.e., in a safe and profitable manner. In this regard, we propose incorporation of this contaminated sludge into non-structural concrete blocks used in paving. According to USEPA [3], stabilization refers to techniques that chemically reduce the hazard potential of a waste by converting the contaminants into less soluble, mobile, or toxic forms, while solidification refers to techniques that encapsulate the waste, forming a solid material, and does not necessarily involve a chemical interaction between the contaminants and the solidifying additives. The product of solidification, often called the waste form, may be a monolithic block, a clay-like material, granular particulates, or some other physical form commonly considered "solid."

Technology involving the S/S processes is currently being used to treat a wide variety of wastes containing contaminants such as metals, organics, soluble salts, and others [4,5]. This technology is cheap and easy to apply, but its application should be analyzed case-by-case. Briefly, the process involves mixing hazardous wastes, either in the form of sludge, liquid or solid, into a cementitious binder system. It is most suitable for treating wastes that are predominantly inorganic, as these are considered to be more compatible with the types of cementitious materials normally used. After water, concrete is one of the most used resources in the world and can be employed for various purposes, including environmental application as inert roadbed gravel, concrete ducts for sewage and wastewaters, and runoff and erosion barriers.

The aim of this study was to propose a profitable destination for an industrial sludge as a concrete constituent, where the concrete application benefits can cover the wastewater treatment costs of small quantity generators. To achieve this objective, the effectiveness of a pre-stabilization/solidification with clay-lime and subsequent use of this material in a cement-based system for the stabilization and solidification of heavy metals from an electroplating industry sludge was evaluated by means of economic, physical and leachability/solubility aspects.

2. Materials and methods

2.1. Sludge source and analysis

The industrial sludge used in this study came from a small electroplating industry that works as a general electroplating unit providing a protective and decorative coating for metals. Metal analysis was carried out according to standard methods [6].

2.2. Stabilization/solidification treatment

2.2.1. Step 1

The industrial sludge (3 kg dry weight) was placed in a 20 L mixer. Clay (1 kg) and lime (2 kg) were added and the mixture stirred for 2 h. The lime was added 30 min after the clay. After homogenization, the mixture was allowed to stabilize/solidify for 7 days (exothermic phase). Initially, a clod mixture was formed, but after 7 days (end of exothermic phase) a fine powder was obtained.

2.2.2. Step 2

The stabilized solid waste product obtained in Step 1 was resolidified by mixing with Portland cement (6 kg), sand (2 kg), and water (6 L). After homogenization, the concrete hexagonal block manufactured was allowed to stabilize/solidify for 28 days (curing time) at 25 ± 2 °C and a relative humidity of 83 ± 3%.

2.3. Leachability and solubility tests

One concrete hexagonal block was fragmented (sieved at 0.1 mm), homogenized and used to carry out leachability and solubility tests. The leachability and solubility tests were carried out according to the Brazilian standard methods [7,8]. In the leachability test, a solid sample size of 20 g was placed in a 500 mL bottle, 320 mL of distilled water was added along with a sufficient quantity of acetic acid (80 mL, 0.5N) to adjust the pH to 5.0. The initial pH was 11.2, which was adjusted under stirring to 5.0, and the final pH was 5.1. The suspension was stirred for 24 h. After filtration with a GF membrane (20 μm) the leached contaminants were analyzed. In the solubility test, a solid sample size of 25 g was placed in a 500 mL bottle with addition of 100 mL of distilled water. After 1 h of homogenization, the suspension was allowed to stand for 7 days. After filtration, soluble contaminant concentrations were determined according to the standard methods [6].

3. Results and discussion

To treat electroplating wastewaters and reduce sludge generation, current technologies are based on ultrafiltration, crystallization, electrolysis, evaporation, ion exchange and adsorption. However, in developing countries, the cost of these technologies is generally prohibitive for wide application in small factories. If the treated waste had some value to partially, or completely, offset treatment costs, this would certainly stimulate waste treatment/disposal by the SQGs, given the general awareness of the environmental impact of chemical pollutants. One way to achieve economic benefits from sludge is to reuse this waste as a raw material for making concrete. In this regard, many stabilization/solidification methods have recently been proposed for the treatment of hazardous and other wastes from industrial and governmental sources [4,5]. For more detailed discussions on this technology, critical reviews of S/S have been published [9–11,13]. Unfortunately, in most countries, there is no mechanism for reclassifying a treated, previously hazardous, waste as non-hazardous, and at present, the regulations regarding this question are not based on risk analysis. In Brazil, federal guidelines classify industrial waste products based on the waste constitution and on leaching and solubility tests [12]. Thus, in this study, the effectiveness of the S/S process in fixing heavy metals was evaluated according to current Brazilian legislation, which classifies electroplating sludge as a hazardous waste

Table 1
Chemical composition of the constituents before application of the stabilization/solidification process

Parameters	Detection limit	Solid Industrial sludge	Clay (CEC = 245 meq kg^{-1})	Sand	Portland cement	Lime
Aluminum		10,742	21,248	3,182	19,072	956
Arsenic	0.5	ND	5.8	5.0	7.5	5.0
Barium	0.01	33,395	147	38.9	182	37.5
Cadmium	0.005	3.495	ND	ND	ND	ND
Calcium	–	23,568	189	978	33,3501	402,452
Lead	3.0	300.1	6.7	ND	5,9	ND
Cobalt	2.5	ND	10.6	7.6	8.7	ND
Copper	0.5	8,897	8.3	ND	7.7	ND
Chromium	1.0	5,082	60.4	9.3	25.3	1.0
Iron		1,163	25,412	5,606	17,766	579
Fluorides	2.5	6.0	ND	ND	25.1	29.1
Manganese		148.0	153	348	201	74.4
Nickel	1.0	8,283	13.3	4.3	20.2	5.1
Potassium		188.2	147	470	4,674	577
Silicon		71,956	204,929	369,661	86,366	6,743
Sodium		875	101	307	791	453
Vanadium	5.0	ND	33.1	10	50.7	13.3
Zinc	0.1	1,380	17.1	16.6	24.9	ND

Data are in mg kg^{-1}. ND: not detected.

(Class I) [12]. Before the application of the S/S technology, an initial analysis of all constituents of this process was carried out (Table 1).

Table 1 gives a chemical overview of all constituents used in the S/S process. The treatment reagents also contain the heavy metals of concern. After initial characterization, the S/S process was carried out. In the first step the clay acts as a metal adsorbent, which is immobilized by lime addition [13–16]. In the second step, solidification occurs following the addition of cement [10,14]. This two-step S/S process: (i) reduces the potential environmental impact due to the very low metal leachability (Table 2); and (ii) ensures a commercial product at the end of process since the solidified waste can be used to manufacture concrete blocks (e.g., roadbed blocks).

Table 2 shows the results of the chemical analysis of the leachable and soluble components of solid industrial sludge, as well as the composition of solid sludge after the first step of immobilization and its leachable and soluble components. In

Table 2
Chemical analysis of galvanic industrial sludge and stabilized/solidified sludge, as well as theirs leachate and soluble contaminants

Parameter	Industrial sludge[a]		First step stabilized/solidified mixture		
	Leaching test (legal limit value[b])	Solubility test (legal limit value[b])	S/S solid mixture[c] (mg kg^{-1})	Leaching test (legal limit value[b])	Solubility test (legal limit value[b])
Aluminum	–	0.17 (0.20)	21,892	–	0.14 (0.20)
Arsenic	ND (5.0)	ND	6.1	ND (5.0)	ND
Barium	0.1 (100.0)	ND (1.0)	7,498	10.8 (100.0)	4.4 (1.0)
Cadmium	1.0 (0.5)	ND (0.005)	ND	ND (0.5)	ND (0.005)
Calcium	–	–	111,686	–	–
Cobalt	–	–	9.51	–	–
Copper	15.2	0.21 (1.0)	1,017	ND	0.15 (1.0)
Iron	–	ND (0.3)	–	–	ND (0.3)
Lead	0.1 (5.0)	ND (0.05)	32.1	ND (5.0)	ND (0.05)
Chromium	9.1 (5.0)	1.7 (0.05)	528.0	0.1 (5.0)	0.20 (0.05)
Manganese	–	0.14 (0.1)	369.0	–	ND (0.1)
Mercury	ND (0.1)	ND (0.001)	ND	ND (0.1)	ND (0.001)
Molybdenum	–	–	ND	–	–
Nickel	23.2	ND	832.0	ND	ND
Selenium	ND (1.0)	ND (0.01)	ND	ND (1.0)	ND (0.01)
Silver	ND (5.0)	ND (0.05)	ND	ND (5.0)	ND (0.05)
Vanadium	–	–	12.8	–	–
Zinc	8.0	3.80 (5.0)	186.0	1.4	0.02 (5.0)
Hardness	–	1,355 (500.0)	–	–	2,135 (500.0)

ND: not detected.
[a] Solid industrial sludge composition is given in Table 1.
[b] According to ABNT/NBR 10004/2004 (in mg L^{-1}).
[c] Mixture of industrial sludge, clay, sand, Portland cement and lime.

Table 3
Results of chemical analysis for both the normal concrete block (control) and the waste incorporated concrete block, as well as their leachable and soluble contaminants

Parameter	Concrete block with waste (mg kg^{-1})	Leaching test (legal limit value[a])	Solubility test (legal limit value[a])	Normal concrete block (control) (mg kg^{-1})	Leaching test (legal limit value[a])	Solubility test (legal limit value[a])
Aluminum	9,288	–	0.41 (0.20)	8,271	–	0.22 (0.20)
Arsenic	ND	ND (5.0)	ND	ND	ND (5.0)	ND
Barium	586.0	0.89 (100.0)	5.92 (1.0)	103.0	0.40 (100.0)	1.2 (1.0)
Cadmium	ND	ND (0.5)	ND (0.005)	ND	ND (0.5)	ND (0.005)
Calcium	54,389	–	–	72,556	–	–
Cobalt	9.6	–	–	7.3	–	–
Copper	65.2	–	ND (1.0)	5.0	–	ND (1.0)
Iron	14,779	–	ND (0.3)	12,203	–	ND (0.3)
Lead	ND	ND (5.0)	ND (0.05)	ND	ND (5.0)	ND (0.05)
Chromium	43.4	ND (5.0)	ND (0.05)	31.7	0.0 (5.0)	ND (0.05)
Manganese	555.0	–	ND (0.1)	481.0	–	ND (0.1)
Mercury	ND	ND (0.1)	ND (0.001)	ND	ND (0.1)	ND (0.001)
Molybdenum	24.1	–	–	26.5	–	–
Nickel	58.6	–		37.7	–	–
Selenium	ND	ND (1.0)	ND (0.01)	ND	ND (1.0)	ND (0.01)
Silver	ND	ND (5.0)	ND (0.05)	ND	ND (5.0)	ND (0.05)
Vanadium	21.1	–	–	19.4	–	–
Zinc	32.4	–	0.02 (5.0)	27.2	–	ND (5.0)
Hardness	–	–	1,531 (500.0)	–	–	1,464 (500.0)
Strenght resistance (MPa)[b]	37.4 (7.9)	–	–	37.7 (5.9)	–	–

ND: not detected.

[a] According to ABNT/NBR 10004/2004 (in mg L^{-1}).

[b] Mean and coefficient of variation (in parenthesis) ($n = 6$).

this table, comparison of leachable or soluble metals (or semimetals) in industrial sludge with the amounts in solid industrial sludge (Table 1) show mobilization of dangerous contaminants (e.g., chromium).

The values in this table allow us to evaluate the efficiency of the first stabilization/solidification step. A comparison between leachate compositions shows that chromium mobility is very reduced after the first step of the S/S process. A comparison of solubility test results shows that after the first step of the S/S process Al, Cu, Cr, Mn and Zn values were lower than values from industrial sludge solubility test. On the other hand, Ba and hardness values increase after the first step of the S/S process. Thus, the use of clay and lime in the first step of the S/S process was effective in the immobilization of waste contaminants. Barium, chromium and hardness values in the solubility test were higher than the legal limits but, despite this fact, the waste classification improved from Class I (dangerous waste) to Class II A (non-dangerous and non-inert waste).

In Table 3 the chemical analysis results for the concrete block and leachable and soluble components are shown for both the normal concrete block (control) and the waste incorporated concrete block. The results for the unconfined compressive strength test is also shown in Table 3.

The quantities of leached or solubilized contaminants determined for the concrete blocks with and without waste incorporation were the same. Thus, using the proposed methodology there will be no additional environmental pollution compared to the concrete block without waste incorporation. According to Brazilian regulations [17], these concrete blocks must be assayed using an unconfined compressive strength test before use in paving, where the mean value must be 35 MPa. This is the same value as that used in the Australian compressive strength standard. Table 3 shows that both the normal and the waste-incorporated concrete blocks for paving achieve this standard value with similar coefficients of variation.

Comparison of Tables 1–3 allows us to conclude that the stabilization/solidification process was effective in changing, according to Brazilian regulations, the initial waste classification from hazardous (Class I) to non-hazardous (Class II). It was considered Class II A (non-inert) due to the presence of aluminum, barium and hardness values above legal limits in the soluble fraction. The origin of these soluble quantities could be attributed to any concrete constituent, not necessarily to the industrial waste.

With respect to concrete-waste reuse, the increase in the final waste volume is a disadvantage when this waste is disposed of to landfills (3 kg of dry waste yields 14 kg of commercial concrete blocks), but when it is incorporated into the concrete blocks, this becomes an advantage. Furthermore, if we consider the potential environmental impact caused by the use of the blocks in road construction, these blocks are less ecotoxic and less costly than the other paving option of asphalt. Regarding the ecotoxicity potential of the concrete blocks (with and without waste incorporation), the final S/S product showed relative hardness of the leachate (Table 3), which is caused by a variety of dissolved polyvalent metallic ions, predominantly calcium and magnesium cations, although other cations, e.g., barium, iron, manganese, strontium and zinc, also contribute. These ions are natural constituents of the clay, lime, and cement. There does not appear to be any convincing evidence that water hardness causes adverse environmental impact. Furthermore, it must be remembered that soil roadbeds are very compacted and metal percolation may not occur due to the relatively high adsorption capability of the clays present in the soils under paving [16].

Concerning economic benefits of the S/S process and reuse of the resultant product, the cost of untreated heavy metal-containing sludge disposal to landfill is usually in the order of US$ 150–200 per tonne of waste. A profitable application for the waste concrete is in the manufacturing of hexagonal blocks used as roadbeds. With population growth, urbanization and consequent road/street construction are inevitable and asphalt paving is costly. In relation to the production of concrete roadbed blocks, the final economic balance is positive. For example, costs of heavy metal-contaminated sludge landfilling (including transport) are usually in the order of US$ 150–200 per tonne of waste, while 1 tonne of concrete roadbed blocks (with 25% of waste constitution) yields about US$ 100. We have not detailed the costs for concrete block manufacture since there are not an international standardization of raw material prices, but the economic balance is simple: normal (without waste addition) concrete block manufacture is already profitable and, thus, a 25% saving on constituent costs will increase the profit, which will cover the wastewater metal-precipitation treatment cost.

Furthermore, cement material suppliers and the equipment used for mixing concrete constituents to built roadbeds are generally locally available, and the latter is also simple, which contributes to the lower cost for the application of this methodology. Small quantity generators of waste where this methodology could be optimized include: metal finishing sludges, metal refining sludges and emission control dusts, inorganic chemical industry sludges and dusts, and metal contaminated soils. This methodology could be applied to other SQGs, where costs inhibit the proper management of wastes, by establishing collection/reuse programs to improve environmental performance.

4. Conclusions

Environmental management of small quantity generators of waste in developing countries is a difficult task due to the economic aspects of waste treatment/disposal. Thus, the search for innovative solutions for the treatment/disposal of industrial wastes is necessary to achieve technical goals in public/private environmental programs. Incorporation of industrial solid waste in commercial products can provide the funds to improve industrial wastewater treatment, and in this regard, the clay-lime stabilization/solidification followed by Portland cement stabilization/solidification was efficient in immobilizing the hazardous heavy metal constituents of electroplating industry sludge. This treated waste is safe enough to be used in environmental applications, like roadbeds. Thus, due to the relatively low cost of this sequential treatment together with the possibility for the beneficial use of the immobilized material, this type of industrial sludge treatment appears to offer a promising way to improve environmental quality in developing countries. It should be noted that more research is necessary to gain a better understanding of the effects of waste incorporation into a cement product.

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