Korean J. Chem. Eng., 33(3), 914-921 (2016)
DOI: 10.1007/s11814-015-0187-7

pISSN: 0256-1115
eISSN: 1975-7220

Immobilization technologies for the management of hazardous industrial waste using granite waste (case study)

Mohamed R. Lasheen, Azza M. Ashmawy, Hanan S. Ibrahim, and Shimaa M. Abdel Moniem†

National Research Centre, 33 El Bohouth St., Dokki, Giza, P. O. 12622, Egypt
(*Received 12 May 2015 • accepted 28 August 2015*)

Abstract−Full characterization of granite waste sludge (GWS) was accomplished by X-ray diffraction (XRD) and X-ray fluorescence (XRF) for identification of its phase and chemical composition. Different leaching tests were conducted to determine the efficiency of the GWS for metal stabilization in hazardous sludge. The leaching of the metals from stabilized contaminated sludge was decreased as the GWS amount increased. Only 15% of GWS was sufficient for stabilization of all metal ions under investigation. The main reason for metal immobilization was attributed to the aluminosilicates or silicates matrix within the GWS, which can transform the metals in the form of their insoluble hydroxides or absorbed in the stabilized matrix. Also, solidification/stabilization technique was used for remediation of contaminated sludge. Compressive strength test after curing for 28 days was used for measuring the effectiveness of remediation technique; it was found to be 1.88 MPa. This indicated that the remediated sludge was well solidified and safe to be used as a raw substance for roadway blocks. Therefore, this huge amount of by-product sludge derived from the granite cutting industry, which has a negative environmental impact due to its disposal, can be utilized as a binder material for solidification/stabilization of hazardous sludge.

Keywords: Compressive Strength, Leachability, Solidification, Stabilization, Granite Waste Sludge

INTRODUCTION

Sludge produced by conventional treatment of municipal and industrial wastewater is of great economic importance. It may contain xenobiotics, such as metals and persistent organic pollutants (POPs) such as phenols and polyaromatic hydrocarbons (PAHs). In Egypt, approximately 3-5% of the municipal solid waste (MSW) originates from mixing industrial activities with municipal wastewater. Therefore, it represents an immediate and long-term risk to environment and groundwater resources [1,2].

Although a number of processing strategies have the capability to recover metals from solids, metals commonly contained in sludge are still difficult to recycle. One common strategy currently adopted to dispose hazardous metal sludge is landfill. However, due to the non-degradable property of metals, leachates of landfills may contain higher levels of hazardous metals, and thus may cause potential pollution to the surrounding land and groundwater resources [3,4]. Therefore, the U.S. Environmental Protection Agency (EPA) has proposed the Land Disposal Restriction (LDR) program to set up more strict standards for land disposal of hazardous sludge. LDR regulation requires that hazardous wastes must meet protective treatment standards before disposal in landfill. It also demands these wastes be stored in secure landfills with no hydraulic contact, restricted access, and continuous monitoring [5]. Since land resources have become more limited while the quantity of wastes is continuously increasing, the cost of landfill process will inevitably be higher in the future. Therefore, strong attention has been focused on the more economical and environmentally friendly alternatives to dispose hazardous-metal bearing sludge.

Recently, increased attention has been paid to the sludge stabilization process aiming to minimize the mobility of heavy metals by using various additives, where the toxic forms present in hazardous solid sludge are physically as well as chemically fixed, to ensure the compliance with existing regulatory standards for their leachability to the environment [6]. Some promising binders are zeolite, cement, limestone, fly ash, cement clinker dust, gypsum and lime-rich industrial by-products, where physicochemical properties of the sewage sludge can be improved by their addition [7-10].

The granite cutting industry produces large amounts of solid wastes worldwide, as the cutting of cubic meter of granite gives nearly 0.75 ton sludge. In addition, it is expected to increase as the world production of granite industry has been increasing annually at a rate of 6% in the recent years. The wastes of this industrial activity can reach 20 or 25 wt% of the raw granite [11]. This large amount of granite waste is becoming a serious problem for industrial and environment, as dumping into rivers and lagoons is obviously not an environmentally safe solution. Also, transporting and dumping of waste in landfills involves substantial costs; therefore, incorporation of this waste into other industrial processes could lead to a reduction of management costs and open up new business opportunities.

Recycling of granite wastes as alternative raw materials is not a new thing and has been done successfully in many fields such as alternative ceramic raw materials in the production of ceramic bricks and tiles [12,13], incorporation in red clay roof tiles formulations [13,14], production of coloured cement-based mortars [14,15]. Furthermore, Monteiro et al. [15] studied the chemical composition

†To whom correspondence should be addressed.
E-mail: drshimaanrc@gmail.com

of granite waste sludge (GWS), and found that it contains mainly 64.14% SiO_2, 13.25% Al_2O_3, 8.18% Fe_2O_3 and 3.56% CaO, which are the major inorganic components of clay minerals that composed of SiO_2, Al_2O_3 and flux which is the mixture of Fe_2O_3, CaO, and MgO.

Furthermore, as the pozzolans are siliceous or aluminosiliceous material that, in the presence of water, chemically reacts with the calcium hydroxide to form compounds possessing cementitious properties (calcium silicate hydrate and other cementitious compounds), then the GWS can be consider as pozzolan.

Therefore, in this work, we first studied the structural characteristics of granite waste sludge. Second, for the first time, we focused on the possibility of using this waste as a binder for heavy metals in contaminated municipal and industrial hazardous sludge. Finally, we investigated the potential use of these waste matrices for producing construction materials.

MATERIALS AND METHODS

1. Materials Used and Reagents

All chemicals were supplied by Merck (Darmstadt, Germany). Synthetic stock solutions (5,000 mg/L) of cadmium, copper, nickel, lead and zinc were prepared using $CdCl_2 \cdot 5/2H_2O$, $K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$, $NiCl_2 \cdot 6H_2O$, $Pb(CH_3COO)_2 \cdot 3H_2O$ and $ZnSO_4 \cdot 7H_2O$, respectively, in deionized water. Glacial acetic acid (99.5% CH_3COOH), sulfuric acid (98% H_2SO_4) and nitric acid (65% HNO_3) were used for leachability tests.

2. Sludge Sampling

Three integrated and homogenized sludge samples were collected, one from secondary wastewater treatment plants and two from different metal-plating plants. Collection, preservation and analysis of all the sludge samples were done according to standard methods APHA [16].

3. Granite Waste Sludge (GWS)

GWS was supplied from Cairo Stone Manufacture Plant for marble and granite, it containing about 25% moisture; it was dried at room temperature than disaggregated using a hammer-mill and finally passed through different sieves for particle size analysis.

3-1. Characterization of Granite Waste Sludge

X-ray diffraction (XRD) was used for characterization of GWS and its phase identification was done using a diffractometer with CuKα1 target and second monochromator at 40 kV, 40 mA (D8 Advance, Bruker, Rheinstetten, Germany). The chemical composition of GWS was determined using X-ray fluorescence (XRF) by Axios, Sequential WD-XRF Spectrometer PANalytical 2005.

3-2. Spiking of Sludge

The spiking of sludge with heavy metals is a widely used technique for experimental purposes to distinguish between the effects of the spiked metals from that of other metals and various other contaminants present in the sludge. Therefore, one kilogram of sludge (on dry weight basis) was spiked with 100 mL of a solution containing 1,000 mg/Lof Cd, Cr, Cu, Ni, Pb and Zn in the form $CdCl_2 \cdot 5/2H_2O$, $K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$, $NiCl_2 \cdot 6H_2O$, $Pb(CH_3COO)_2 \cdot 3H_2O$ and $ZnSO_4 \cdot 7H_2O$ respectively [17,18].

4. The Immobilization Process

- For stabilization process, GWS was mixed thoroughly with the different sludge samples, using a mechanical blender, in a proportion series of 0, 2.5, 5, 15, 25 and 35% (dry weight basis) by adding approximately 5 mL of distilled water to facilitate the curing.
- The air-dried cured samples were ground to pass through a 0.2 mm sieve, and triplicate samples of the treated sludge were drawn for examining the efficiency of the immobilization technique.
- For stabilization/solidification process, the stabilized sludge with the optimum dose of GWS (20%) was mixed with fixed weight basis of 20% cement, 60% sand, and adequate mass ratio of water/cementatious material (cement and GWS) 0.55 in order to maintain the proper workability of cement mixture as recommended by American Society of Testing and Materials (ASTM) C-230-90 [19]. The mixture was poured in a mould of 5 cm×5 cm×5 cm size as recommended by ASTM designation C190-90, and allowed to cure for 28 days to simulate the worst conditions of actual field practice.

5. Analytical Methods

- **pH of Sludge Samples;** A sample corresponding to appr. 5.0 g dry sludge is diluted to a total weight of 100 g and then shaken for 15 min. The sample should be swirled before measurement. The pH reading should be done after approximately 30 to 60 s according to the European committee for standardization [23].
- Samples digestion and determination of the total heavy metals were carried out according to APHA, [16] using an atomic absorption spectrometer (SpectrAA 220, Varian, Australia) with graphite furnace accessory and equipped with deuterium arc background corrector. Quality control program for measurement of heavy metals concentration was achieved, using Blank, Quality Control Laboratory Sample and External Standards from Merck, with each series of samples analysis.

6. Evaluation of the Effectiveness of Immobilization Techniques

Several test methods were selected for evaluation of the performance of the immobilization technique;

- **The standard European leaching test** (EN 12457-2) [24]
  It is the one-stage leaching test that is used for rating the actual mobility of metals. As the European Council (European Council Decision 2003/33/EC) [21] is a criterion for classification of wastes acceptance in three main types of landfill sites, i.e., inert wastes landfill, landfill for nonhazardous wastes and hazardous wastes landfill [21]. In this test procedure, leachant (deionized water with no pH control) was added to the remediate sludge with liquid-to-solid ratio of 10 *l*/kg, rotated end-over-end for 24 hours at 30 rpm and then filtered through a 0.45 μm membrane filters. Leached metals were analyzed in the filtrate according to the "Standard Methods [16]".
- The EPA's Toxic Characteristic Leaching Procedure (TCLP) is one measure of the long-term stability of a treated waste because it simulates the leaching effect of water or acid that may come into contact with stabilized metals. In this test Leaching of the remediate sludge with an amount of extraction fluid is equal to 20 times the sludge weight (leaching fluid: 5.7 mL glacial acetic acid (99.5% CH_3COOH, BDH) diluted with deionized water to a volume of 1 liter; when correctly prepared, the pH of this fluid will be 2.88±0.05), then rotated at 30±2

rpm for 18±2 hours at ambient temperature (i.e., room temperature in which leaching takes place). pH was monitored during the experiments and additional acid was added as necessary to maintain the pH of the sludge within ±0.2 pH units of the desired value and then filtered through a 0.6 to 0.8 μm glass fiber filter [22,23]. Leached metals were analyzed in the filtrate according to the "Standard Methods [16]".

- To simulate a longer period of environmental exposure, the Multiple Extraction Procedure (MEP, USEPA [21]) test has been developed. The MEP test consists of multiple acid extractions and pH adjustments that are similar to the TCLP test. However, different leachates are used for each of ten separate extractions. A synthetic acid rain extraction fluid was prepared by adding the 60/40 weight percent sulfuric acid and nitric acid to distilled deionized water until the pH is 3.0±0.2. The sludge remaining after the TCLP was weighed and extracted immediately before drying with an amount of synthetic acid rain extraction fluid equal to 20 times the weight of the sludge sample. Then agitated the mixture for 24 hr, at temperature range between 20-40 °C. pH was recorded within 5-10 min after agitation had been started and at the end of the 24-hr extraction period; then filtration through a 0.6 to 0.8 μm glass fiber filter. Extracted metals were analyzed in the filtrate according to the "Standard Methods". Finally, steps 3, 4 and 5 were repeated eight times until the concentration of heavy metals in the extract ceased to increase.
- For UCS testing, the remediated sludge was mixed thoroughly with cement mixture prepared by fixed weight basis of cement and sand with percentages of 20 and 60 respectively, mixed with requisite amount of deionized water (water/cementations material ratio 0.55) using a Hobart-like mixer to maintain the proper workability of cement mixture as recommended by ASTM C-230-90(213). The mixture was then poured into polyethylene moulds of size 5 cm×5 cm×5 cm as recommended by ASTM designation C190-90(213). The samples were hardened for 24 hr and cured for 28 days in an air-dried.

Lo and Chen [25], calculated the percentages of metals retained in remediate sludge as the following equation.

$$\text{Retention percent of metals} = 100 - \left(\frac{V_f F}{DI}\right) \times 100$$

D: 5 g dry solids sludge

V_f: Final volume after dilution to 100 mL

F: Concentration of metal in filtrate mg L^{-1}

I: Concentration of metal in the initial dry solid sample mg kg^{-1}.

7. Statistical Analysis

Several statistical analyses were used to assess the three leaching tests: an analysis of variance (ANOVA), the post-hoc test and least significant difference (LSD). The correlation coefficient was used to make relationships between two quantities data, such as, concentrations and time.

RESULTS AND DISCUSSION

1. Component Characteristics of Granite Waste Sludge

Granite waste sludge (GWS) from Cairo Stone Manufacture for Marble and Granite provided the binder material for this study. Since every cubic meter of granite block usually weighs from 3 to 4 tons and cutting of cubic meter gives nearly 0.75 ton of sludge, the granite production of the factory per day is about 6 cubic meters, which gives about 4.5 tons wet sludge per day with 25% water content.

Table 1. Chemical composition (wt%) of selected GWS sample as determined by XRF and total content of metals in original and spiked samples of sludge

Chemical composition (%)					
SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO	MgO
68.88	14.07	ND	4.14	ND	0.21
CaO	Na_2O	K_2O	P_2O_5	SO_3	Cl
0.93	5.38	4.28	0.08	0.03	0.03
Ignition loss			pH		
0.14			8.3		

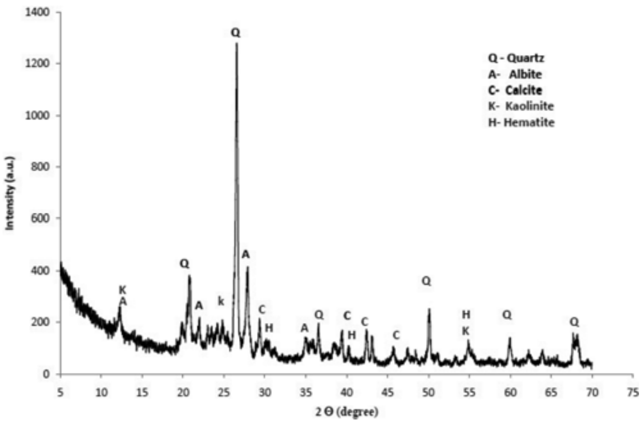

Fig. 1. XRD patterns of granite waste sludge (GWS).

Analysis of chemical composition for GWS using X-ray fluorescence (XRF) is listed in Table 1. It has chemical compositions of CaO (0.93%), SiO_2 (68.88%), Al_2O_3 (14.07%) and Fe_2O_3 (4.14%), whereas the XRD patterns confirm the presence of these minerals. The diffraction peaks of Quartz, Hexagonal (SiO_2), sodium feldspar Anorthic Albite ($NaAlSi_3O_8$), Anorthic Kaolinite ($Al_2Si_2O_5(OH)_4$), and mica are observed in Fig. 1, while calcite ($CaCO_3$) and hematite (Fe_2O_3) present as minor compounds (as shown in Fig. 1). Note that GWS is a silica-rich waste.

The particle size distributions of the GWS were analyzed, where it can be seen that 90% are of fine sand size (20-200 μm) and 10% are of corase sand size, indicating that this material can be classified as a clay-like material.

The pH of GWS was 8.3 due to presence of oxides content (particularly SiO_2, CaO, MgO and K_2O). Therefore, the GWS can act as a stabilizing agent for contaminated sludge to reduce availability of heavy metals from leaching into environment.

2. Effect of GWS Dose on Immobilization of Heavy Metals

By increasing the percentages of GWS (0, 2.5, 5, 15, 25 and 35%) added to spiked sludge for remediation of metals. Table (2) shows

Table 2. Total heavy metals concentrations and pH in sludge samples stabilized with different percentages of granite waste sludge

Parameters	0%	2.5%	5%	15%	25%	35%
pH	6.4	7.1	7.5	7.4	7.9	8.2
Cadmium	407.5±13.57	403.4±11.5	371±21.5	333±19.3	396±16.5	237±10.5
Chromium	1470±38.55	1406±13.5	1362±54.3	1202±61.1	1096±7.5	925±15.6
Copper	1942±30.36	1966±79.8	1918±58.6	1744±52.4	1551±22.3	1351±18.4
Lead	1500±9.07	1426±73.4	1405±30.4	1253±55.3	1119±22.6	903±29.1
Nickel	663±33.5	644±21.3	621±25.1	542±21.2	477±16.5	426±17.6
Zinc	3343±120.79	3274±241	2991±237	2822±122.5	2496±118	2156±99.5

that total metal concentrations in stabilized sludge were decreased by increasing different percentages of GWS, and the pH of stabilized sludge changed from 6.4 to 8.2, which would be caused by the high content of alkaline oxides in GWS such as (K_2O and Na_2O), and alkaline earth oxides (MgO and CaO) as mentioned by Monteiro et al., and Abdul Ghaffar [15,26].

To evaluate the extraction potential of metals in sludge stabilized with GWS, different standard leaching tests were applied.

Firstly, the standard European EN 12457-2 leaching test, the results are shown in Fig. 2; by increasing the percent of GWS from 0

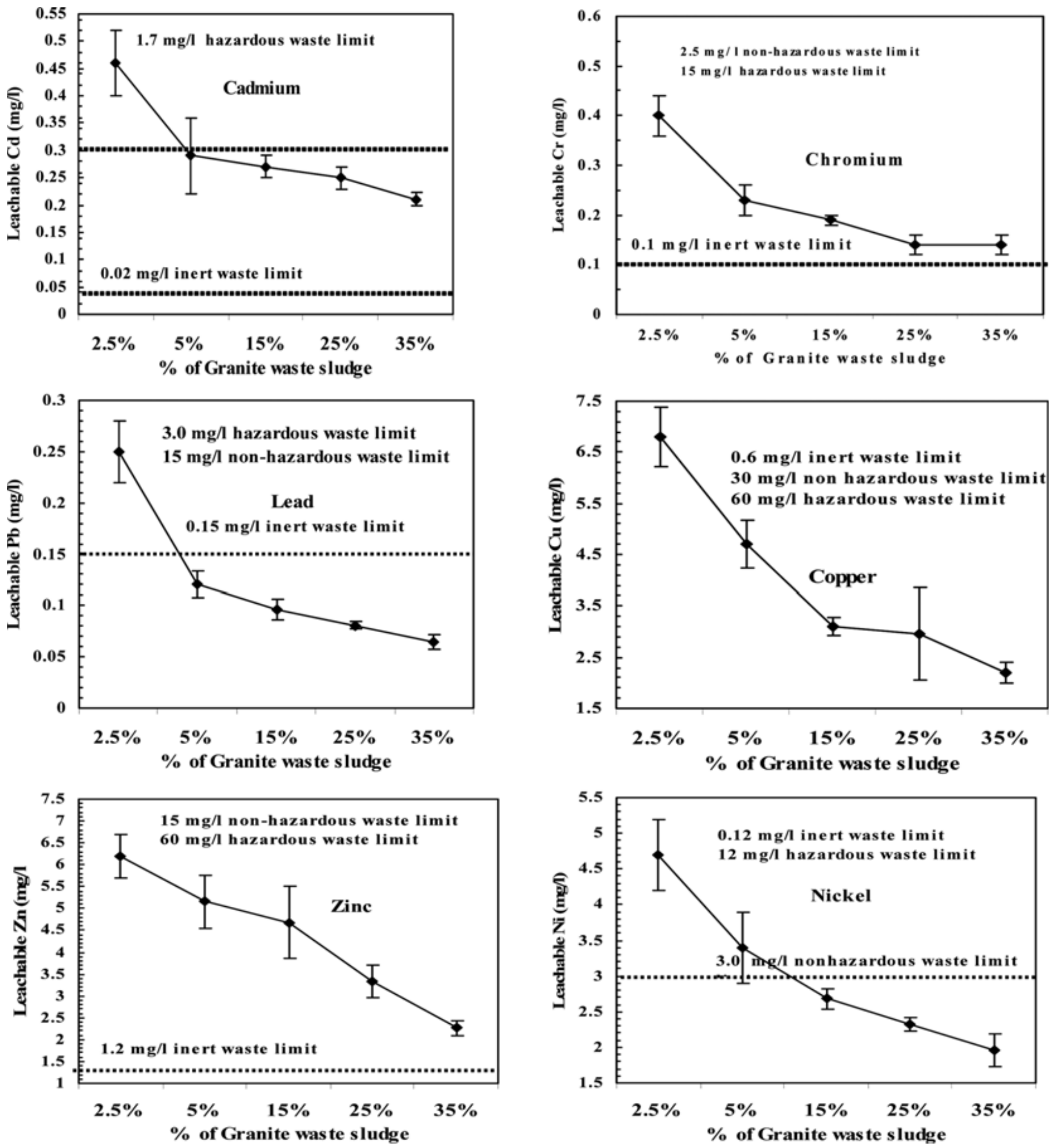

Fig. 2. Leachability of metals from stabilized sludge by granite waste sludge according to the standard EN 12457-2 test.

to 35%, the metal leaching concentrations were decreased. Where the leaching concentrations for cadmium, chromium, copper, lead, nickel and zinc decreased from 2.24, 5.2, 48.7, 5.4, 6.7 and 23.6 mg/L to 0.21, 0.14, 2.2, 0.065, 1.96 and 2.27 mg/L, respectively. Also, 15% of the GWS could reduce metal leaching concentrations that are lower than the limit values sat by the European Council decision 2003/33 for the acceptance of waste in landfills for non-hazardous waste. However, as shown in Fig. 2, availability of Pb leaching in the stabilized sludge, under the conditions of the EN 12457-2 leaching test was decreased as it can be accepted in an inert landfill. The results are in agreement with analysis of chemical composition for GWS where the high content of silica and alkaline oxides in GWS induced the immobilization of heavy metal within the solid waste: for example, silicates convert soluble metals into insoluble metal silicates, resulting in chemically stabilized solid that is easy to handle. Meanwhile the Albite and kaolinite have a high adsorption capacity for metal. Moreover, GWS contains large amount of silica, CaO, Al_2O_3 and Fe_2O_3, which is quite similar to cementitious materials. Also, these constituents are necessary for pozzolanic reactions, leading to precipitation of metals as insoluble hydroxides or to combine with products of GWS hydration to form stable complex silicate forms. Therefore, it can be used as activator for stabilization of metals in contaminated sludge [28,29].

Secondly, the TCLP test method no. 1311, Fig. 3 shows high retention percent of heavy metals with increasing the percentage of GWS, which indicates that all metals were well fixed in the applied matrix, and the retention percent of heavy metals at the optimum GWS/sludge ratio (15%) was about 79% for Ni, 88% for Cd and more than 91% for Cr, Cu, Pb and Zn.

Thirdly, the Multiple Extraction Procedure (MEP) was applied using US EPA Method, 1320. The cumulative percentages of leached heavy metals decreased with increasing leaching time and stabilized after about seven days [30].

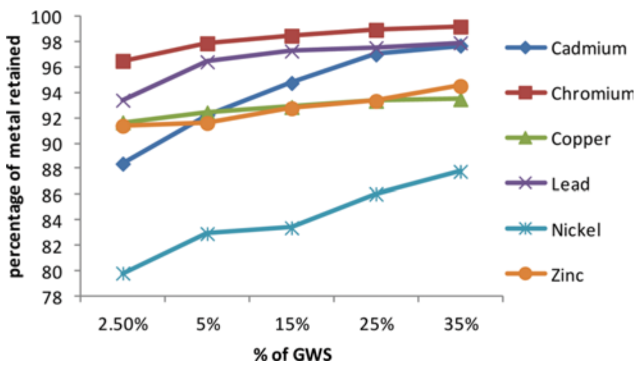

Fig. 3. Percentage of metals retained in stabilized sludge by Granite waste sludge after TCLP leaching test.

At the optimum GWS/sludge ratio (15% of GWS), the cumulative leaching percent of Cd, Cr, Cu, Pb, Ni and Zn was reduced from 0.569, 0.972, 21.63, 0.989, 1.878 and 19.88 wt% to 0.113, 0.122, 0.571, 0.178, 0.419 and 1.234 wt%, respectively. Fig. 4 reveals that the concentration of metals retained after applying US EPA Extraction Method 1320 was very high when compared to spiked sludge. This indicates that even after subjecting the stabilized sludge to rigorous leaching conditions, it exhibited good binding ability for all metals and can be considered chemically durable.

3. Statistical Analysis

To compare between the different leaching tests and heavy metals leaching concentrations in sludge stabilized with granite waste sludge, ANOVA statistical analysis was used. Based on the results from ANOVA test, there were significant variations in the concentrations of all metals where $p<0.0001$ as shown in Table 3. Regarding the applications of different leaching tests, statistical analysis revealed that there were significant variations in the metal leachate concentrations according to the applied tests. The MEP was

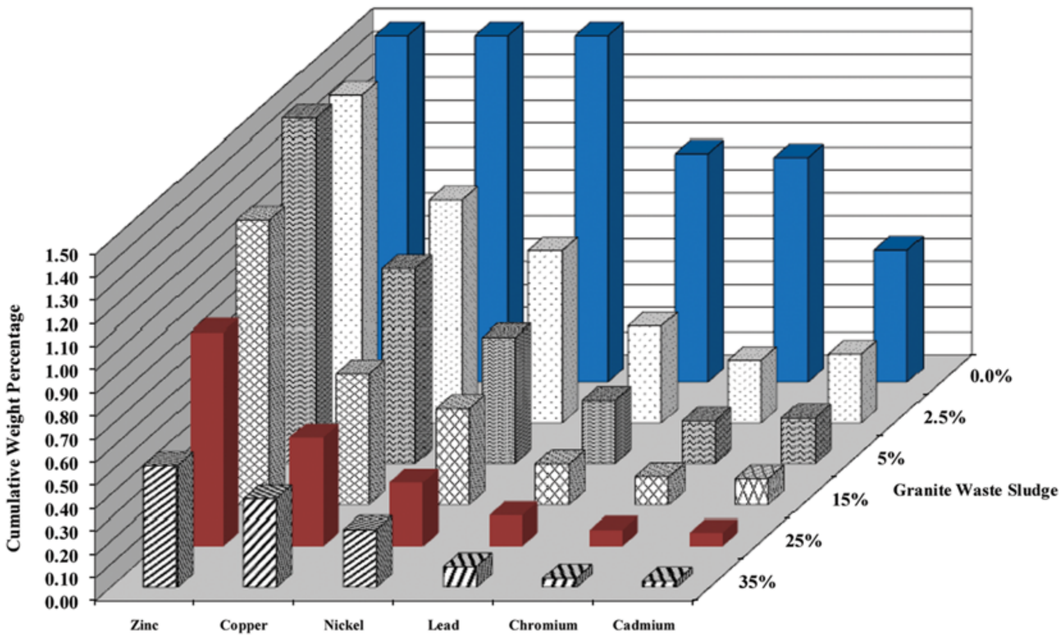

Fig. 4. The cumulative weight percentage of metals in sludge stabilized using GWS after MEP leaching test.

Table 3. Comparison between the different leaching tests and heavy metals leaching concentrations in sludge stabilized with granite waste sludge

Metal	Test	N*	Mean	SE**	F-ratio	P-value	LSD***
Cd	EN	18	0.5	0.16	266.1	P<0.0001	MEP
	TCLP	18	2.4	0.74			MEP
	MEP	180	20.7	0.91			EN, TCLP
Cr	EN	18	0.8	0.39	286.6	P<0.0001	MEP
	TCLP	18	2.3	0.63			MEP
	MEP	180	36.4	1.93			EN, TCLP
Cu	EN	18	9.0	3.62	260.3	P<0.0001	MEP
	TCLP	18	27.4	11.47			MEP
	MEP	180	793.0	46.50			EN, TCLP
Pb	EN	18	0.8	0.41	1047.0	P<0.0001	MEP
	TCLP	18	3.0	0.51			MEP
	MEP	180	43.3	1.10			EN, TCLP
Ni	EN	18	3.4	0.36	213.8	P<0.0001	MEP
	TCLP	18	7.5	1.68			MEP
	MEP	180	66.4	3.80			EN, TCLP
Zn	EN	18	6.1	1.42	315.1	P<0.0001	MEP
	TCLP	18	28.0	9.68			MEP
	MEP	180	748.6	40.05			EN, TCLP

*N: number of reading, **SE: standard error, ***LSD: least significant difference

significantly higher than both EN 12457-2 and TCLP. Whereas, there was no significant variation between the levels of the elements that leached by EN 12457-2 or by TCLP.

4. Compressive Strength

Remediation of hazardous sludge using solidified/stabilized (S/S) technique with GWS at the optimum doses was examined according to Resource Conservation & Recovery Act's (RCRA), where the minimal compressive strength necessary for disposal of solid waste at the nonhazardous waste landfill is 0.35 MPa [19,31]. The unconfined compressive strength (UCS) for S/S block was 1.88 MPa, which was greater than the recommended minimal compressive strength required for solid waste disposal at landfills by about 4 times (Fig. 5). This may be attributed to the formation of hydrated calcium silicates that is produced as a result of reaction of anhydrous silicate with water. This agent crystallizes slowly into an interlocking matrix and increases the samples strength. Longer curing period allows longer time for anhydrous silicate to react and form a strong skeleton structure throughout the material that binding the grains together, these results agree to some extent with observation, which have been achieved by several authors [27,32].

Fig. 5. A block of S/S sludge by 15% granite waste sludge in combined with cement mixture.

5. Remediation of Industrial Sludge Produced from Metal Plating Plants (Case Studies)

First, consider industrial sludge produced from Electric Water Heaters Company. Where, the inner vessel of the electric water heaters must be zinc plated to prevent corrosion. The sludge produced from the treatment of rinsing wastewater discharged from metal plating processes reached to 1.5 ton/y; it contains 43.8 g Zn/Kg at pH 7.5.

Second, industrial sludge produced from Motorcycles Industrial Co., where production of motorcycles is standardized on a metallic frame and telescopic forks which hold the front wheel. These entire components are metal zinc alloy skeletons; therefore, they must be plated with copper cyanide (first stage), nickel salts (second stage) and chromate (third stage) sequentially in separate basins to overcome of the corrosion problem, enhance appearance and durability. The metal plating sludge produced from the treatment of rinsing wastewater discharged from metal plating processes reached to 0.8 ton/y; it contained 1.8 g Cr/Kg, 2.3 g Cu/Kg, 24.8 g Ni/Kg and 4.5 g Zn/Kg at pH 9.5. The sludge produced from these two case studies represents serious ecological problems.

The sludge was collected with the purpose of field application of the optimum operating conditions of GWS/sludge for immobilization of metal in contaminated sludge and producing non-hazardous or less hazardous sludge for ensuring safe disposal.

We examined the effect of different leaching tests on stabilized sludge compared with original sludge produced from metal plating plants companies using 15% Granite waste sludge (GWS). The results revealed that by applying the standard European leaching test (EN 12457-2), the leaching concentrations of Zn, in stabilized sludge produced from Electric Water Heaters Co., decreased from 76.8 mg/L to 10.3 mg/L. However, for sludge produced from Motorcycles Industrial Co. the Cu leachate concentration decreased from 22.6 mg/L to 0.5 mg/L, Cr leachate concentration decreased from 2.86 mg/L to 0.42 mg/L, Ni leachate concentration decreased from 1.35 mg/L to 0.25 mg/L and Zn leachate concentration decreased from 33.8 mg/L to 4.2 mg/L.

The obtained results follow from the TCLP test for Electric Water Heaters stabilized sludge, where the leaching concentration of Zn decreased from 621 mg/L to 50.2 mg/L. On stabilization of contaminated sludge of Motorcycles Industrial Co. the leaching concentrations of Cu decreased from 193.7 mg/L to 7.2 mg/L. While, Cr decreased from 7.58 mg/L to 1.81 mg/L, Ni decreased from 53.8 mg/L to 3.28 mg/L and Zn decreased from 172 mg/L to 30.9 mg/L. These results agree to some extent with observation, which was achieved by Marabini et al. [33] who mention that the main reason for heavy metal immobilization was attributed to the alumino-silicates or silicates matrix within the GWS being able to transform the metals in the form of their insoluble hydroxides or may sometimes be absorbed in the stabilized matrix, which reduces their leachability, and also, due to highly alkaline and high adsorption capacity for metals. From these results we found that the metals leachate concentration did not exceed the limit specified by the US. Environmental Protection Agency.

After MEP, the results showed that the cumulative percentages of for Electric Water Heaters stabilized sludge the cumulative weight of Zn reduced from 59.3 wt% to 1.566 wt%. On stabilization of contaminated sludge of Motorcycles Industrial Co. using optimum doses of GWS showed that Cu decreased from 20.89 wt% to 0.34 wt%. While Cr decreased from 0.51 wt% to 0.14 wt%. On the other hand, Ni decreased from 3.7 wt% to 0.15 wt%, respectively. Finally, Zn decreased from 18.73 wt% to 2.62 wt%.

The unconfined compressive strength test was performed at 28 days to study the effect of the changes in the mineralogical composition of solidified/stabilized (S/S) sludge, with increasing time, and environmental exposure. The unconfined compressive strength (UCS) results were 4.63 and 2.87 MPa for Electric Water Heaters and Motorcycles Industrial Co. respectively. These UCS were greater than the recommended minimal compressive strength required for solid waste disposal at landfills.

CONCLUSIONS

The utilization of 15% of granite waste was highly efficient for immobilization of hazardous heavy metal contaminated sludge. The leachability of cadmium, chromium, copper, lead, nickel and zinc in the stabilized sludge under the conditions of the EN 12457-2 leaching test was considerably lower than the limit values set by the European Council decision for the acceptance of a waste in a landfill for non-hazardous waste. Also, the average metal concentrations in the TCLP leaching test did not exceed the limit specified by the U.S. EPA, which is the same as the limit set by the Egyptian Regulations law 4/1994 for hazardous waste management. Also, MEP confirms high retention percentages of metals in the stabilized sludge. The unconfined compressive strength, of the solidified/stabilized (S/S) sludge by using optimum ratio of GWS, was 1.88 MPa, which indicates that the remediate sludge was well solidified and safe for use in a wide variety of applications, such as a raw material used in concrete blocks.

Stabilization of the industrial sludge, produced from Electric Water Heaters Company, with the optimum doses of GWS was adequate to reduce Zn leaching concentration from 621 mg/L to 50.2 mg/L, which was lower than the limit values set by Egyptian regulations law 4/1994 for hazardous waste management. The unconfined compressive strength (UCS) for solidified/stabilized metal plating sludge of the Electric Water Heaters Industry remediate with the optimum doses of GWS was 4.63 MPa. Also, sludge produced from metal plating processes for the different parts of motorcycles industry, which was highly contaminated with 1.8 g Cr/Kg, 2.3 g Cu/Kg, 24.8 g Ni/Kg and 4.5 g Zn/Kg, could be stabilized with the optimum doses of GWS, and metals leaching concentration was lower than the limit values set by the different leaching test. Finally, the sludge produced from granite cutting industry can be used as no-cost and effective material for metal immobilization.

REFERENCES

1. Egyptian Environmental Affairs Agency (EEAA, 2010), Country report on the solid waste management. http://www.sweep-net.org/ckfinder/userfiles/files/country-profiles/rapport-Egypte-en.pdf.
2. Q. Guangren, C. Yali, C. Pengcheong and T. Joohwa, *J. Hazard. Mater.*, **129**, 274 (2006).
3. S. Alejandro and N. Jacint,*Chemosphere*, **68**, 703 (2007).
4. M. S. Bilgili, A. Demir, M. Ince and B. Ozkaya, *J. Hazard. Mater.*, **145**, 186 (2006).
5. M. A. Knecht, Overview of U.S. Federal Laws and Regulations Affecting Mixed Waste Treatment. In : *Hazardous and Radioactive Waste Treatment Technologies Handbook,* CRP Press, ISBN 978-08493-9586-4 (2001).
6. I. Buj, J. Torras, M. Rovira and J. de Pablo, *J. Hazard. Mater.*, **175**, 789 (2010).
7. A. M. Ashmawy, H. S. Ibrahim, S. M. Abdel Moniem and T. S. Saleh, *Toxicol. Environ. Chem.*, **94**(9), 1657 (2012).
8. D. Tomasevic, M. B. Dalmacija, M. D. j. Prica, B. D. Dalmacija, D. V. Kerkez, M. R. Bečelić-Tomin and S. D. Roncevic, *Chemosphere*, **92**(11), 1490 (2013).
9. M. R. Lasheen, A. M. Ashmawy, H. S. Ibrahim and S. M. Abdel Moniem, *Desalination and Water Treatment*, **51**, 2644 (2013).
10. F. Garrido, V. Illera, M. T. Garcı and a-Gonza lez, *Appl. Geochemistry,* **20**(2), 397 (2005).
11. P. Torres, H. R. Fernandes, S. Agathopoulos, D. U. Tulyaganov and J. M. F. Ferreira, *J. Eur. Ceram. Soc.*, **24**, 3177 (2004).
12. R. R. Menezes, H. S. Ferreira, G. A. Neves, H. de L. Lira and H. C.

Ferreira, *J. Eur. Ceram. Soc.*, **25**(7), 1149 (2005).
13. P. Torres, H. R. Fernandes, S. Olhero and J. M. F. Ferreira, *J. Eur. Ceram. Soc.*, **29**(1), 23 (2009).
14. I. Mármol, P. Ballester, S. Cerro, G. Monrós, J. Morales and L. Sánchez, *Cem. Concr. Compos.*, **32**(8), 617 (2010).
15. S. N. Monteiro, L. A. Peçanha and C. M. F. Vieira, *J. Eur. Ceram. Soc.*, **24**, 2349 (2004).
16. American Public Health Association, *Standard Methods for the Examination of Water and Wastewater*, 22nd Ed. Washington D.C. (2012).
17. R. G. McLaren and L. M. Clucas, *J. Environ. Qual.*, **30**, 1968 (2001).
18. G. Kandpal, B. Ram, P. C. Srivastava and S. K. Singh, *J. Hazard. Mater.*, **106B**, 133 (2004).
19. American Society of Testing and Materials (ASTM, 1991). Annual Book of ASTM Standards, Part II, Philadelphia: ASTM.
20. European Committee for Standardization, (ENV 12176, 2000). Characterization of sludge - Determination of pH-value. Brussels, Belgium. http://www.ecn.nl/docs/society/horizontal/hor15_ph.pdf.
21. European Council Decision 2003/33/EC. Establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. Journal of the European Communities.
22. U.S. EPA, Toxicity characteristic leaching procedure (TCLP), Federal Register, 40 CFR 50, No. 286, 406 (1986).
23. U.S. EPA, Training module on Hazardous Waste Identification (40 CFR Parts 261), Solid Waste and Emergency Response (5305W), EPA 530-K-05-012 (2005).
24. U.S. EPA, Multiple Extraction Procedure (MEP) Method 1320, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846), 4 (1986).
25. K. S. L. Lo and Y. H. Chen, *Sci. Total Environ.*, **90**, 99 (1990).
26. Abdul Ghaffar, *Removal and stabilization of chromium metal ions from industrial effluents*, Electronic Journal of Environmental, Agricultural and Food Chemistry, (EJEAFCHE), **5**(2), 1286 (2006).
27. R. A. Shawabkeh, *J. Hazard. Mater.*, **B125**, 237 (2005).
28. C. Pérez-Sirvent, M. L. García-Lorenzo, M. J. Martínez-Sánchez, M. C. Navarro, J. Marimón and J. Bech, *Environment International*, **33**, 502 (2007).
29. G. Xu, M. Liu and G. Li, *J. Hazard. Mater.*, **260**(15), 74 (2013).
30. H. Zhang, Y. Zhao and J. Qi, *J. Hazard. Mater.*, **141**(1), 106 (2007).
31. U.S. EPA, Stabilization/Solidification of CERCLA and RCRA Wastes: Physical Tests, Chemical Testing Procedures, Technology Screening, and Field Activities. EPA/625/6-89/022, U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, Ohio (1989).
32. J. Naji, *Journal of Science and Technology-Yemen*, **7**(2), 2002 (2002).
33. A. M. Marabini, P. Plescia, D. Maccari, F. Burragato and M. Pelino, *Int. J. Miner. Process.*, **53**(1-2), 121 (1998).