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Pozzolanic-based materials for stabilization/solidification of contaminated sludge with hazardous heavy metal: case study

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ABSTRACT

In this study, the efficiency of metals immobilization in sludge using pozzolanic materials fly ash and cement clinker dust (CCD) was investigated. Also, estimation of the optimum binder to waste ratio was determined. Different leaching tests such as the standard European (EN) 12457-2 leaching tests; the toxicity characteristic leaching procedure; and the multiple extraction procedure test were used to evaluate the efficiency of metals stabilization in sludge matrix, and they showed that the availability of metals leaching (Cd, Cu, Cr, Pb, Ni, Zn) from the stabilized sludge were lower than the permissible limit set by National and International regulations for hazardous waste management. Examination of the solidified sample for its compressive strength after curing for 28 days yielded a value of 1.55 and 4.57 MPa for fly ash, and CCD which indicates that the treated sludge was well solidified and safe to be used in a wide variety of applications, for instance as a raw material for pavement blocks.

Keywords: Heavy metals; Immobilization; Pozzolanic-based materials; Fly ash; Cement clinker dust; Leachability; Compressive strength

1. Introduction

The management of solid wastes has been seriously recognized and tackled worldwide. In developing countries the problem is still hindered by social and economic predicaments and priorities. In Egypt, the generation of solid wastes has become an increasingly important environmental issue over the last decade, due to the escalating growth in populations and the changing life style, leading to new trends of unsustainable consumption patterns.

Also, in Egypt, approximately 3–5% of the municipal solid waste (MSW) collected from urban centers originated from industrial activities and considered to be hazardous. This waste presented an immediate and/or long-term threat to the nation's surface, soil, and groundwater resources [1,2].

Heavy metal pollution of sludge is a very serious problem all over the world. Heavy metals, unlike organic contaminants, are generally immutable, not degradable, and persistent in soil and sewage sludge [3]. Although sludge have a natural capacity to attenuate the bioavailability and the movement of metals through them by means of different mechanisms (precipitation, adsorption process, and redox reactions), when the concentrations of heavy metals become too high to allow the sludge to be used as a soil fertilizer and it is considered as hazardous waste, it is neces-

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sary to take action to remediate contaminated sludge [4,5].

The management of sludge produced from wastewater and concentrated contaminants which present in this sludge is still one of the most difficult and expensive problems in the field of wastewater engineering [6]. Nevertheless, if the beneficial use of sludge in agriculture is not possible or feasible, other technical solutions for final sludge disposal, such as use for landscaping, recultivation, and landfill, will be implemented [7–11].

Currently, solidification and stabilization (S/S) techniques are recognized by the Environment Protection Agency (EPA) as the best demonstrated available technology for land disposal of most toxic elements [12,13]. S/S of heavy metal in contaminated sludge utilizing pozzolanic materials has shown to be a cost effective technique [14]. Moreover, immobilization of heavy metals contaminated sludge using waste materials also has added advantage of reusing waste materials which otherwise would also be disposed of at landfills. The most commonly used pozzolan today is Portland cement, cement dust, and fly ash. Cement dust considered the most large by-product material generated from Ordinary Portland Cement (OPC) manufacture [15]. In Egypt, more than three million tons per year of cement dust are generated [16]. Therefore, these industrial by-product materials should be managed to insure a clean and safe environment, the cost associated with cement dust disposal is high. Also, coal fly ash, which is the residues produced during the burning of coal, can be used as a stabilizing binder for sewage sludge [17].

By applying immobilization techniques, hazardous contaminants in sludge can be converted to much less mobile, less soluble, and toxic forms. Also, the contaminants can be incorporated into a monolithic solid with reduced surface area that physically encapsulates the contaminants yielding lower leachability results [18,19].

The mechanism of stabilization process is based on hydraulic reactions or pozzolanic reactions between lime and pozzolanic materials such as cement clinker dust (CCD) and fly ash [20–25]. The development of hydration products of calcium silicate hydrate ($CaO·SiO_2·nH_2O$), ettringite hydrate ($3CaO·Al_2O_3·3CaSO_4·32H_2O$), and monosulfate ($3CaO·Al_2O_3·CaSO_4·12H_2O$) in the matrix where the heavy metals can be chemically fixed in the lattice of hydration production combined with physically encapsulated in the matrix that provided an interlocking framework to physically encapsulate waste particles and was responsible for the strength development of the monolithic solid [26]. The possible immobilization mechanisms of heavy metals could be (1) sorption, (2) chemical incorporation (surface complexation, precipitation, or co-precipitation), and (3) micro- or macro-encapsulation [27,28].

Katsioti et al. [29] have studied the effect of bentonite/cement mortar for the stabilization/solidification of sewage sludge containing heavy metals, and they found that the S/S products had been proven throughout the study as a viable solution for stabilizing heavy metals. They can be used in many applications such as in landfill liners, slurry walls, and building blocks. Also Malliou et al. [30] have investigate the utilization of several mixtures of sludge–cement–calcium chloride and calcium hydroxide (CH) for S/S of sewage sludge containing heavy metals and found that sewage sludge from wastewater treatment plants (WWTPs) can be solidified and stabilized in a matrix of Portland cement.

Several tests were used to evaluate the efficiency of the stabilization and solidification of heavy metal in sludge. The EN 12457-2 leaching test allows comparison of experimental results with the corresponding limit guideline values set out by the European Council Decision 2003/33/EC for the acceptance of waste for each landfill class (*landfills for inert waste, landfills for non-hazardous waste, and landfills for hazardous waste*) [31]. The waste may be accepted at a landfill only if it fulfills the acceptance criteria of the relevant landfill class. The toxicity characteristic leaching procedure (TCLP, USEPA method 1311) and the multiple extraction procedure (MEP) are typically compliance tests. The TCLP is designed to determine the mobility of both organic and inorganic analytes that present in liquid and solid wastes. This test is simulation for leaching that takes place in a sanitary landfill as shown in Table 1 (some selected constituents are listed) [32,33].

Earlier studies were conducted for the immobilization of heavy metals by OPC. For the generation of one ton of Portland cement, about one ton of

Table 1
USEPA regulation for metals using TCLP leaching test (some selected constituents are listed)

Metals	Maximum concentration (mg/L)	Metal	Maximum concentration (mg/L)
Cadmium (Cd)	1.0	Lead (Pb)	5.0
Chromium (Cr)	5.0	Nickel (Ni)	5.0
Copper (Cu)	100	Zinc (Zn)	100

green house gas CO_2 is released to the atmosphere as a result of de-carbonation of lime in the kiln during manufacturing of cement and causes major problem of global warming [34,35]. To reduce this CO_2 emission, Portland cement is replaced by fly ash and CCD. These materials are stabilizing agents for metals, which are used for their physical and chemical actions. They are cheap and available material that encourages their use. Furthermore, CCD is generated from the second grinding process of the cement clinker. It produced in large quantities and its known hazards to human beings and environment. This hazard is assessed and updated in the health effects sections, HSE, of an earlier report of Portland Cement Association [36,37]. In addition, this type of waste has not been widely applied in stabilization of heavy metals in contaminated sludge. Therefore, our study aimed to assess the simplest and cost effective immobilization technique for hazardous sludge contaminated with heavy metals using these waste materials or industrial by-products whose themselves have negative impact on the environment such as CCD and fly ash, and to evaluate the efficiency of the proposed immobilization techniques according to the international and national regulations. Examining the remediate sludge to be considered for use in a wide variety of applications such as a raw material used in concrete blocks or to be sold as pavement blocks or used in roadbeds and/or parking lots.

2. Materials and methods

2.1. Reagent

Inorganic chemicals were supplied by Merck as analytical-grade reagents and deionized water was used. Synthetic stock solutions of cadmium, copper, nickel, lead, and zinc were prepared using $CdCl_2 \cdot 5/2H_2O$, $CuSO_4 \cdot 5H_2O$, $NiCl_2 \cdot 6H_2O$, $Pb(CH_3COO)_2 \cdot 3H_2O$, 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.

2.2. Sludge sampling

Integrated sludge samples were collected from secondary WWTP, its capacity is approximately 1,700,000 m^3/day which serves municipal and industrial areas at the east of Cairo. Collection and preservation of all the sludge samples was done according to Standard Methods (section 1060 B, C) [38].

2.2.1. Case study

Integrated sludge samples were collected from Balaqus WWTP. It designed to operate as a biological treatment process with activated sludge. It currently provides both primary and secondary treatment of approximately 600,000 m^3/day which serves municipal industrialized north of Cairo.

Collection and preservation of all the sludge samples was done according to Standard Methods (section 1060 B, C) [38]. In addition, to avoid excessive chemical transformations within the sludge samples, which might be produced from prolonged storage, the experiments were initiated within the shortest possible time after obtaining the samples from the different WWTPs.

2.3. Pozzolanic-based materials (binding material)

Fly ash, it is the residues produced during the burning of coal from the Egyptian National Railways. Also, CCD is generated from the second grinding process of the cement clinker (National Cement Company). Characterization of the different binding materials conducted by using X-ray fluorescence (XRF) and their chemical compositions are

Table 2
The pH, heavy metals, and elementary chemical analysis expressed in weight percent of oxides for the different binders used for immobilization technique

Chemical composition	Fly ash	CCD
pH	11.9	12.9
SiO_2	40.08	19.58
TiO_2	0.78	0.36
Al_2O_3	5.83	4.7
MgO	4.21	1.5
$Fe_2O_3^{tot.}$	5.53	4.67
CaO	14.10	66.49
Na_2O	2.79	0.55
K_2O	10.82	ND
P_2O_5	2.73	0.14
SO_3	1.57	0.47
Cl	1.01	0.01
Loss on ignition (L.O.I)	10.10	1.10
Heavy metals (mg/kg)		
Cd	2.5	2.5
Cr	15.0	20.0
Cu	15.0	18.0
Pb	16.0	17.5
Ni	20.0	23.5
Zn	4.0	57.5

listed in Table 2. The XRF analyses were performed on AXIOS Sequential WD-XRF spectrometer PANalytical 2005.

2.4. The immobilization process

The spiking of sludge with heavy metals is a widely used technique for experimental purposes in order to distinguish between the effects of the spiked metals from that of other metals and various other contaminants present in the sludge [39]. Therefore, spiked sewage sludge samples were used for application of the immobilization techniques by applying the following steps:

- The sludge samples were processed to remove the non-recyclable materials and passed through a 2 mm sieve.
- One kilogram of sludge (on dry weight basis) was spiked with 100 mL of a solution containing 1,000 mg/L of Cd, Cu, Ni, Pb, and Zn in the form $CdCl_2{\cdot}5/2H_2O$, $CuSO_4{\cdot}5H_2O$, $NiCl_2{\cdot}6H_2O$, $Pb(CH_3COO)_2{\cdot}3H_2O$, and $ZnSO_4{\cdot}7H_2O$, respectively.
- Spiked sludge was thoroughly stirred and incubated at room temperature for one month. After incubation, the treated sludge was again thoroughly stirred. The heavy metals content in the spiked sludge compared to the original sludge are shown in Table 3.
- Pozzolanic materials were mixed thoroughly using a mechanical blender with the samples in a proportion series of 0, 2.5, 5, 15, 25, and 35% (dry weight basis) by adding of approximately 5 mL of distilled water to facilitate curing.
- The air-dried cured samples were grounded to pass through a 0.2 mm sieve and triplicate samples of metal spiked, sludge, and pozzolanic materials were drawn for chemical analysis.

2.5. Analytical methods

- **pH measurements**: a sample corresponding to approximately 5.0 g dry matter was diluted to a total weight of 100 g and then shaken for 15 min. The sample swirled before measurement. Reading done after approximately 30 to 60 s according to the European committee for standardization [40].
- The digestion of samples and determination of total contents of heavy metals were carried out according to Standard Methods (section 1060 B, C and 3030 D) [38] using Atomic Absorption Spectrometer Varian SpectrAA (220) with graphite furnace accessory and equipped with deuterium arc background corrector.

2.6. Quality control

(i) Blank was run with each set of analysis. (ii) Quantifications of metal were carried out using external standards with coefficient of calibration curves higher than 0.995. (iii) The calibration program was verified on each working day by measuring one or more standard. (iv) A random sample was run in triplicate. (v) Laboratory control sample was analyzed with each series of samples.

2.7. Evaluation of the performance of the immobilization techniques

In order to evaluation of the performance of the immobilization schemes different methods were selected:

(1) The standard European leaching test (EN 12457-2) according to **European Council Decision 2003/33/EC** [35]. Triplicate samples of one gram remediate sludge transferred to a shaking bottle. Add 10 ml of leachant (deionized water), the bottles were then sealed with Parafilm, lids and secured, rotated end-over-end for 24 h at 30 rpm, and then filtered through a 0.45 m membrane filters. Leached metals were analyzed in the filtrate.

(2) TCLP according to **USEPA** [36,37], which the Egyptian regulation follows (law 4/1994). Triplicate samples of five grams sludge were transferred to a shaking bottle. Leaching with an

Table 3
Total content of heavy metals in original and spiked samples of sludge

Metal (mg/kg)	Cd	Cu	Pb	Ni	Zn
Original	4.0 ± 0.05	538.0 ± 9.5	750.0 ± 4.9	81.0 ± 1.6	1204.0 ± 7.6
Spiked sludge	407.5 ± 2.5	1942.0 ± 88.4	1500.0 ± 11.7	663.0 ± 5.99	3343.0 ± 22.4

amount of extraction fluid 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 L, when correctly prepared, the pH of this fluid will be 2.88 ± 0.05). Slowly add the amount of appropriate leaching fluid to the extractor vessel. Close the extractor bottle tightly (teflon tape was used to ensure a tight seal), secure in shaking device, mechanical reciprocating shaker "Julapo-SW-20C", and rotate at 30 ± 2 rpm for 18 ± 2 h at ambient temperature (i.e. room temperature in which leaching takes place). The 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 0.6–0.8 μm glass fiber filter. Leached metals were analyzed in the filtrate.

(3) MEP according to **USEPA** [41]. Triplicate samples of five grams sludge were transfer to a shaking bottle, to which the TCLP mentioned above was done. A synthetic acid rain extraction fluid was prepared by adding the 60/40 weight percent sulfuric acid (98% H_2SO_4, BDH) and nitric acid (65% HNO_3, Merck) 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. Agitate the mixture for 24 h, at temperature range between 20 and 40 ℃, pH was recorded within 5–10 min after agitation has been started and at the end of the 24-h extraction period, then filtration through a 0.6 to 0.8 μm glass fiber filter. Extracted metals were analyzed in the filtrate. Repeat steps 3, 4, and 5 eight times until the concentration of heavy metals in the extract ceases to increase.

(4) Unconfined Compressive Strength test (UCS) after 28 days according to **ASTM** [42]. The compressive strength was selected as the benchmark parameter. For UCS testing, cubes of 5 × 5 × 5 cm were prepared using different waste binder ratios. They were 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. The mixture was then poured into polyethylene molds of size 5 cm × 5 cm × 5 cm as recommended by ASTM designation C190-90. The samples were hardened for 24 h and cured for 28 days in an air-dried. Five different sludge binder ratios were made. The compressive strength test was performed after 28 days.

The UCS test was performed on a Universal Testing Machine (Model—Instron 5500 R), this type of instron has a self-calibration, zero adjusting, and automatic balance which are done daily before testing or during testing.

The retention percentage of metals for stabilized samples was calculated as mentioned by Lo and Chen, [43].

Retention percentage of metals = 100 − (V_f F/D I)* 100

D: 5 g dry solids sludge

V_f: Final volume after dilution to 100 mL

F: Concentration of metal in filtrate mg/L

I: Concentration of metal in initial dry solid sample mg/kg.

To compare between the different leaching tests and heavy metals leaching concentrations in sludge stabilized with different pozzolanic materials, statistical analysis was done.

2.8. Statistical analysis

Statistical analysis was done through SPSS statistical program version 14.0. For each element, an analysis of variance (ANOVA) and the post hoc test least significant difference (LSD) were performed to compare between the three leaching test. Correlation coefficient was used to test the relationships between two quantities data (time and concentrations).

3. Results and discussion

3.1. Chemical and physical characteristics of binding materials

Table 2 shows the elementary chemical analysis of binder materials using XRF expressed in weight percent of oxides. Their main chemical compositions are CaO, SiO_2, Al_2O_3, and Fe_2O_3, which is quite similar to those of complementary cementitious materials, that indicating their cementitious properties in addition to pozzolanic properties due to presence of reactive silica and free lime which are necessary for pozzolanic reactions. They satisfy the requirements of cementitious stabilizers that having a hydration modulus [$CaO/(Al_2O_3 + SiO_2 + Fe_2O_3)$] so they behave as stabilizers in a manner similar to that of Portland Cement as proposed by several authors [44,45]. The pH of fly ash and CCD were 11.9 and 12.9, respectively. The high pH of fly ash and CCD are due to the large amounts of CaO. As the presence of CaO in high concentration can stabilize heavy metals effectively then other compositions as they raise the pH of the stabilized sludge causing metal precipitation within the sludge matrix. So, they can be used as a stabilizing agent for sewage sludge to reduce heavy metal availability [46–49]. The use of fly ash and CCD as stabilized materials for hazardous waste considered an advantage for reusing these substances, which otherwise would also be disposed of at hazardous landfills [20,49].

3.2. *Evaluation of the performance of the stabilization and solidification techniques of heavy metals in sludge using pozzolanic-based materials*

Tables 4 and 5 showed the pH and the total heavy metals concentration of stabilized spiked sludge with different percentages of fly ash and CCD (0, 2.5, 5, 15, 25, and 35%). The results revealed that the total metal concentrations in stabilized samples were decreased with increasing the percentages of fly ash and CCD. These were expected as a result of the dilution effect and it were also in agreement with the observations of several authors who mentioned that increasing amendment rates of stabilized materials significantly reduced the total metal contents in the sludge [50–52]. In addition as the percent of fly ash and CCD increases, the stabilized sludge pH increases from 6.4 to 9.2 and 12.34, respectively, due to high content of CaO in stabilized materials. Raising the pH levels of stabilized sludge by using the pozzolanic hydration reactivity coincide with pH level that stabilized leachable metals. Also, these findings are emphasized by several authors [53–55].

The results of metal leaching concentrations after application of EN (12457-2) are graphically represented in Figs. 1 and 2. The obtained results revealed that the low leaching of all metal concentration from stabilized sludge was achieved by gradual increasing the percentages of pozzolanic materials from 0 to 35%. And it was found that CCD was more efficient than fly ash as it could reduce metal leaching concentrations from 2.24, 5.2, 48.7, 5.4, 6.7, and 23.6 mg L^{-1} to 0.024, 0.028, 0.13, 0.041, 0.63, and 0.1 mg L^{-1}, for cadmium, chromium, copper, lead, nickel, and zinc, respectively. While fly ash reduce metal leaching concentrations to 0.2, 0.073, 0.22, 0.05, 0.93, and 0.16 mg L^{-1} for cadmium, chromium, copper, lead, nickel, and zinc, respectively. This was due to that these pozzolanic-based materials can substantially reduce heavy metal solubility as a result of precipitation, adsorption

Table 4
Total heavy metals concentrations and pH in sludge samples stabilized with different percentage of fly ash

Parameters	Unit	0%	2.5%	5%	15%	25%	35%
pH	–	6.4	8.6	8.8	8.9	8.9	9.2
Cadmium	mg/kg	407.5 ± 13.57	377 ± 13.5	335 ± 30.5	300 ± 11.93	255 ± 6.55	200 ± 5.5
Chromium	mg/kg	1,470 ± 38.55	1,400 ± 13.05	1,230 ± 69.3	1,100 ± 3.51	945 ± 8.62	730 ± 5.6
Copper	mg/kg	1942 ± 30.36	1,840 ± 26.45	1,650 ± 24.66	1,446 ± 39.23	1,260 ± 10.36	966 ± 9.3
Lead	mg/kg	1,500 ± 9.07	1,400 ± 41.78	1,266 ± 10.41	1,110 ± 70.53	966 ± 6.55	780 ± 19.13
Nickel	mg/kg	663 ± 33.5	625 ± 10.59	565 ± 12.89	489 ± 15.04	430 ± 5.5	328 ± 9.8
Zinc	mg/kg	3,343 ± 120.79	3,100 ± 225	2,800 ± 74.3	2,497 ± 35.1	2,150 ± 39.07	1,650 ± 11.4

Table 5
Total heavy metals concentrations and pH in sludge samples stabilized with different percentages of CCD

Parameters	Unit	0%	2.5%	5%	15%	25%	35%
pH	–	6.4	9.7	10.65	11.48	11.98	12.38
Cadmium	mg/kg	407.5 ± 13.57	385 ± 11.5	368 ± 22.5	335 ± 9.65	297 ± 10.21	210.7 ± 9.5
Chromium	mg/kg	1,470 ± 38.55	1,399 ± 19.98	1,280 ± 39.4	1,133 ± 26.1	1,006 ± 11.3	765 ± 6.6
Copper	mg/kg	1,942 ± 30.36	1,855 ± 86.8	1,646 ± 38.76	1,465 ± 36.4	1,256 ± 15.66	963 ± 18.9
Lead	mg/kg	1,500 ± 9.07	1,422 ± 113.8	1,257 ± 65.5	1,119 ± 90.53	932 ± 65.5	719 ± 39.7
Nickel	mg/kg	663 ± 33.5	661 ± 24.4	595 ± 29.7	527 ± 19.7	455 ± 9.6	365 ± 8.6
Zinc	mg/kg	3,343 ± 120.79	3,305 ± 368	3,004 ± 257	2,641 ± 204	2,311 ± 183	1,810 ± 99.3

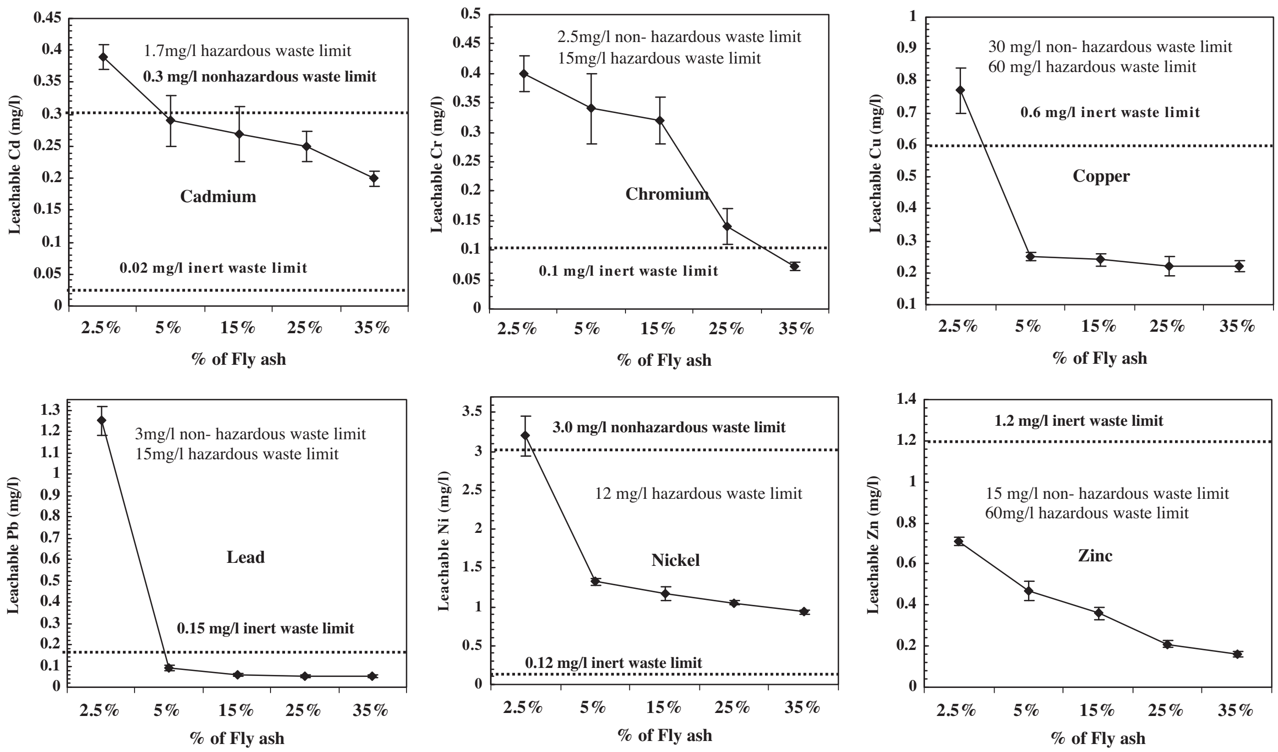

Fig. 1. Leachability of metals from stabilized sludge by fly ash according to the standard EN 12457-2 test.

to the surfaces, and incorporation. As heavy metal cations may sorb quite strongly to calcium silicate hydrate (C–S–H). The cations diffuse into the C–S–H particles where they are probably sorbed to the silicate chains [56].

Also, Figs. 1 and 2 showed that only 5% of pozzolanic materials to waste is the optimum percent that required to produce a waste form with high physical stability, where the availability of investigated metals in the stabilized sludge under the conditions of the EN 12457-2 leaching test were considerably lower than the permissible limits set by the European Council Decision 2003/33 for the acceptance of waste in landfills for non-hazardous waste. Moreover, the leaching level of Cu, Pb, and Zn in the stabilized sludge with fly or Cr, Cu, Pb, and Zn in sludge stabilized with CCD met also the limit values for inert waste [35].

The TCLP test method No. 1311 is designed to simulate leaching that takes place in a sanitary landfill. The results of TCLP leaching test indicate a high retention percent of heavy metals in the pozzolanic materials/sludge matrix. The leaching concentrations of Cd, Cr, Cu, Pb, Ni, and Zn were decreased from 9.0, 133, 6.8, 22.5, and 117 $mg\,L^{-1}$ to 0.36, 0.42, 0.77, 0.05, 1.42, and 0.4 $mg\,L^{-1}$ for fly ash and decreased to 0.12, 0.04, 0.83, 0.08, 0.81, and 0.19 $mg\,L^{-1}$ for CCD. The retention percent of heavy metals was more than about 79% for Cd, Pb, and Ni and more than 93% for Cr, Cu, and Zn after TCLP. The order of metal retained in pozzolanic materials/sludge matrix was found to be as following.

Zinc $\geq$ Lead > Chromium > Copper > Cadmium > Nickel (For fly ash)

Zinc > Chromium > Lead > Copper > Cadmium > Nickel. (For CCD)

Heavy metals stabilization with CCD cement S/S process relies on the formation of calcium silicate hydrate in the matrix, on the extensive ion substitution and adsorption. Due to the hydration reaction of cement matrixes, the heavy metals can be chemically fixed in the lattice of hydration production combined with physically encapsulated in the matrix [32,57].

In order to assess the long-term stability of heavy metal-contaminated sludge stabilized with pozzolanic materials and to simulate a longer period of environmental exposure, the MEP was conducting on the stabilized sludge using US EPA Method, 1320. The results showed that, the cumulative percentages of heavy metals leached decrease with leaching time and stabilize after about 7 days. Similar results were also reported by Giergiczny and Król [58] who mentioned that, the increase of the so-called immobilization

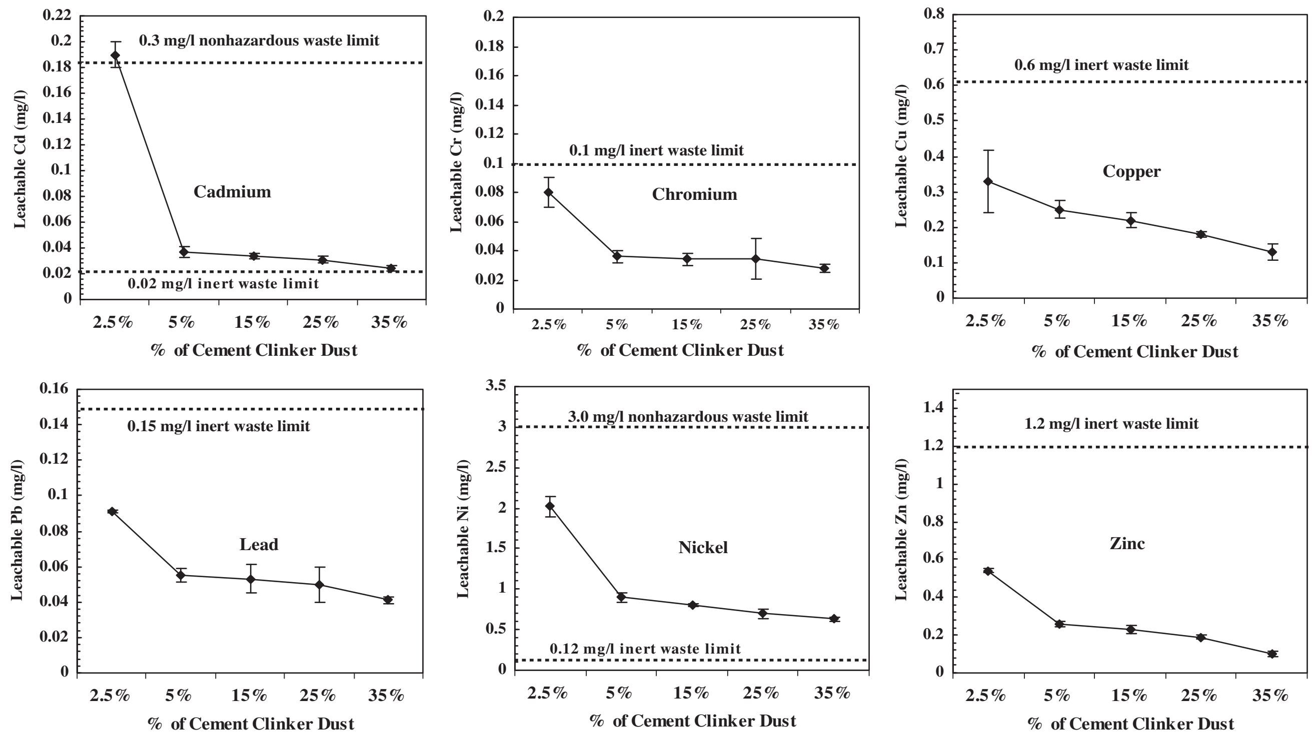

Fig. 2. Leachability of metals from stabilized sludge by CCD according to the standard EN 12457-2 test.

degree with time of hardened material maturing was found. This should be attributed to the pozzolanic or pozzolanic/hydraulic properties of the binding materials used. The cumulative leaching of heavy metal from stabilized sludge with fly ash and CCD is graphically represented in Figs. 3 and 4, respectively. Where the Cd, Cr, Cu, Pb, Ni, and Zn cumulative leaching percentages of stabilized sludge with 5% of fly ash (the optimum binder/sludge percent) were reduced from 0.569, 0.972, 21.63, 0.989, 1.878, and 19.88 wt.% to 0.071, 0.125, 0.273, 0.014, 0.26, and 0.061 wt.%, respectively. Moreover, the corresponding values of sludge stabilized by 5% of CCD were reduced to 0.036, 0.075, 0.155, 0.017, 0.208, and 0.045 wt.%, respectively. The obtained results revealed that, the cumulative metal leaching percent were very low comparable to original sludge, which indicated that the heavy metals present in the stabilized sludge are highly stable and have low ability to be dissolved even through repetitive leaching under acid rain in a natural environment [59]. Also, the highest concentration of the metals extracted by the MEP was below the prescribed limits in USEPA 40 CFR Part 261 [60] for the metals covered under this standard.

Finally, the results in present sludge agree with previous authors, which reported that the addition of pozzolanic materials can facilitate the binding of

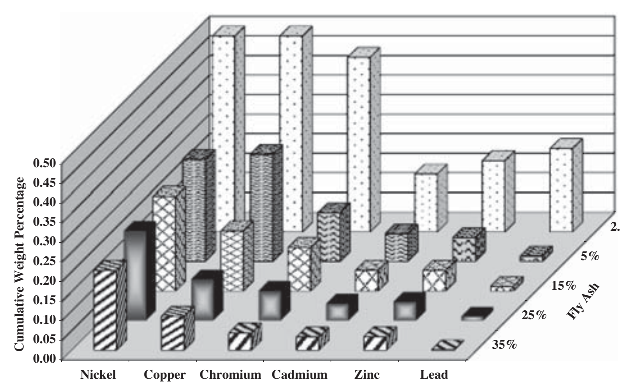

Fig. 3. The cumulative weight percentage of metals in sludge stabilized using fly ash after MEP leaching test, the cumulative weight percentages at 0% fly ash was 1.878% for Ni, 21.63% for Cu, 0.9725% for Cr, 0.569% for Cd, 19.88 for Zn, and 0.989 for Pb.

heavy metal in contaminated sludge. The main reason of heavy metal immobilization in stabilized sludge is due to the highly alkaline nature and buffering capacity of these materials that would cause the metals to precipitate as insoluble hydroxides or by combination with them components to form complex silicate forms [61,62]. These phenomena can be interpreted on the basis of more than one predominant mechanism of

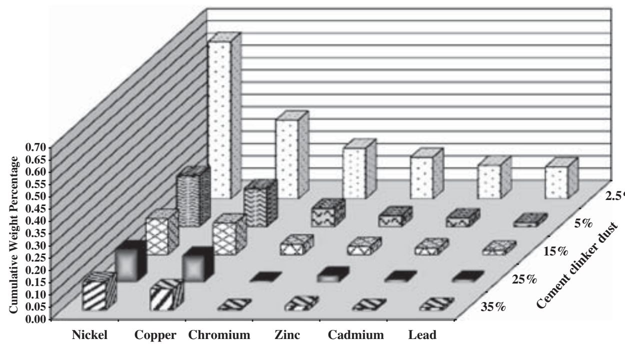

Fig. 4. The cumulative weight percentage of metals in stabilized sludge using CCD after MEP leaching test. The cumulative weight percentages at 0% CCD was 1.878% for Ni, 21.63% for Cu, 0.9725% for Cr, 0.569% for Cd, 19.88 for Zn, and 0.989 for Pb.

metal binding to the binder matrix similar to cement products some of those suggestions are ionic adsorption to the calcium silicate hydrated C–S–H in the hydrated cement paste, ionic incorporation into the crystalline network of some compounds of the hydrated cement such as sulfates in the ettringite hydrate and, finally, physical retention in the porous structure [63,64].

3.3. Statistical analysis

Statistical analysis was done using ANOVA to compare between the different leaching tests and heavy metals leaching concentrations in sludge stabilized with different pozzolanic materials. The obtained result showed that there were significant variations in concentration of all metals where $p \leq 0.05$ for sludge stabilized with fly ash and $p < 0.0001$ for sludge stabilized with CCD. Statistical results revealed that there was no significant correlation between the two EN 12457-2 and TCLP leaching standard methods to estimate the mobility of heavy metals under their specific condition, while the MEP was significantly higher than both EN 12457-2 and TCLP.

Furthermore, statistical results showed that the metal leachate concentrations were significantly affected by the two factors, the percent of binding materials used and the time of the test. Where, the leaching metal concentrations were inversely correlated with both percent of binding materials and time of MEP test.

3.4. The compressive strength of solidified/stabilized sludge with pozzolanic materials matrix

As the recommended minimal compressive strength required for solid waste disposal at landfills in Resource Conservation & Recovery Act's (RCRA) is 0.35 MPa [41,65]. For applying the compressive strength test on the stabilized/solidified (S/S) sludge at the optimum percent of pozzolanic materials to waste. Experimental study was conducted using 20% solidified sludge by 5% pozzolanic materials in combined with cement mixture that prepared by fixed weight basis of cement and sand with percentages of 20 and 60, respectively, and adequate mass ratio of water/cementatious material (cement and pozzolanic materials) 0.55 was used to maintain the proper workability of cement mixture as recommended by American Society of Testing and Materials (ASTM) C-230-90 [41].

The mixture were placed in the mold of $5 \times 5 \times 5$ cm size as recommended by ASTM designation C190-90 [41], as shown in Fig. 5, and allowed to

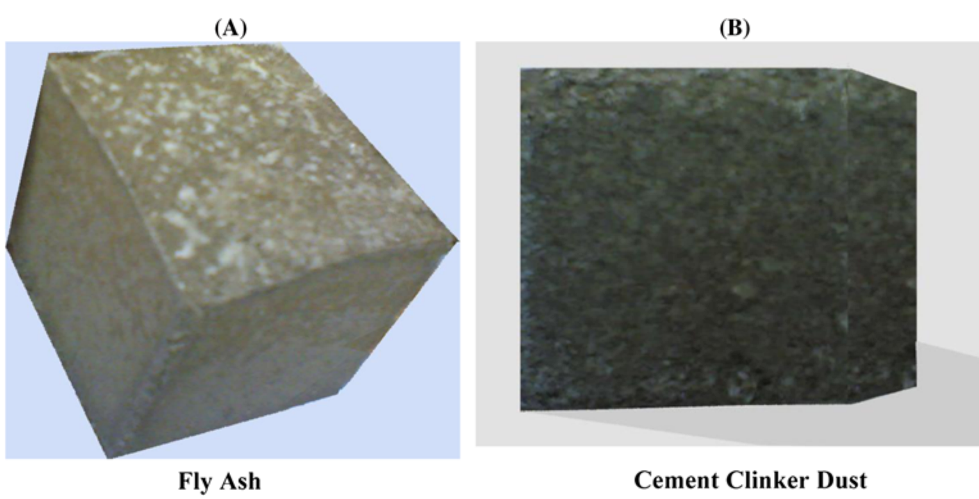

Fig. 5. Block A and B of S/S sludge by 5% of pozzolanic-based materials in combined with cement mixture.

Table 6
The UCS results of sludge solidified with the optimum doses of the different binders after (28 days)

Matrices	UCS (MPa)
Fly ash/sludge	1.55
CCD/sludge	4.57
Minimal compressive strength required for solid waste disposal	0.35

cure for 28 days to simulate the worst conditions of actual field practice for disposal of solidified sludge. Our results are represented in Table 6. The results showed that, the compressive strength was greater than the recommended minimal compressive strength required for solid waste disposal at landfills by about 3- and 12-fold for fly ash and CCD, respectively.

Our results are substantiated by several authors [66,67] who mentioned that, shortly after water addition almost all of the CaO (free lime), originally present in the pozzolanic binders (fly ash and CCD), was converted to CH, which became a major component. Also, due to long-term pozzolanic reactions and lime reactivity which depends on the proportion of reactive silica, they are considered as highly self-cementing material (binder).

3.5. Case study: hazardous sludge produced from Balaqus WWTP

Sludge produced from Balaqus WWTP found to be highly contaminated with lead (Pb); it reached to 13,500 mg/kg which is about 44 times that of the limit of Pb (300 mg/kg) adopted by Egyptian regulations in Decree 214/1997 for sludge permitted to be reused in agriculture [68]. Therefore, applying the optimum percents of different binders for immobilization of Pb in hazardous contaminated sludge was very important.

The environmental availability of heavy metals from the stabilized sludge can be studied through applying the different leaching tests. The standard European leaching test (EN 12457-2) for Pb-contaminated sludge produced from Balaqus WWTP which stabilized with the optimum percent (5%) of the pozzolanic-based materials as binders. The results revealed that, low solubilization of Pb concentration was achieved for the stabilized sludge with optimum percent. Where, the leaching concentrations of Pb were decreased from 5.9 to 0.66 and 0.37 mg/L for fly ash-stabilized sludge and CCD-stabilized sludge, respectively. Furthermore the leachability of Pb in the stabilized materials under the conditions of the EN 12457-2 leaching test were considerably lower than (3 mg/L) which is the limit values set by the European Council Decision 2003/33 for the acceptance of waste in landfills for non-hazardous waste. Various studies have evaluated the interactions of Pb with the pozzolanic matrix, Pb ions could homogeneously dispersed in the calcium silicate hydrated matrix by adsorption or precipitation with calcium or silicate compounds present in the cement [69]. Other study suggests that Pb generally replace calcium in the cement hydrates phases [70].

The TCLP test was carried out to determine the amount of Pb that can be leached from the stabilized sludge with the optimum percent of pozzolanic materials to waste. The obtained results revealed that, Pb leaching concentrations were decreased from 18.5 mg/L to 3.26 and 1.62 mg/L for fly ash-stabilized sludge and CCD-stabilized sludge, respectively. These results agree to some extent with observation, which have been achieved by several authors [71,72]. Also, the results revealed that, Pb was well fixed by applying pozzolanic materials as binders and the average leachate concentration of Pb did not exceed (5 mg/L) the limit specified by USEPA [36].

After MEP, the results showed that, the cumulative percentages of Pb leached decreased with increasing leaching time, it reduced from 1.367 wt.% in the Balaqus sludge sample to 0.21 and 0.145 wt.% for fly ash-stabilized sludge and CCD-stabilized sludge, respectively. This should be attributed to these pozzolanic materials that are typically appropriate for immobilization of heavy metals in well-stabilized matrices [62].

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) was 1.37 and 3.32 MPa for S/S Balaqus sludge using fly ash-stabilized sludge and CCD-stabilized sludge, respectively. These results agree to some extent with observation, which have been achieved by several authors [68,73].

4. Conclusion

This paper describes the potential use of pozzolanic-based materials for immobilization of hazardous heavy metal-contaminated sludge, where only 5% of fly ash and CCD to waste is the required percent to produce a waste form with high physical stability. The leachability of cadmium, chromium, copper, lead, nickel, and zinc of the stabilized sludge did not exceed the limit specified by the USA. Environmental Protection Agency which is the same thresholds set by Egyptian Regulations law 4/1994 for hazardous waste management. The unconfined compressive strength of the solidified/stabilized (S/S) sludge, by using optimum ratio of pozzolanic-based materials, was 1.55 and 4.57 MPa for fly ash and CCD, respectively, which was greater than the recommended minimal compressive strength required for solid waste disposal at landfills by about 3- and 12-fold, respectively.

Case study, by applying the optimum percent of the different pozzolanic-based as binders for immobilization of Pb-contaminated sludge from Balaqus WWTP, it could reduced Pb leaching concentration from 18.5 mg/L to 3.26 and 1.62 mg/L for fly ash and CCD, respectively. Also, it was found that the average leachate concentration of Pb did not exceed (5 mg/L) the limit specified by Egyptian Regulations law 4/1994 for hazardous waste management. The compressive strength test of the solidified/stabilized Balaqus WWTP sludge, stabilized with the optimum percent of fly ash, CCD, was 1.37 and 3.32 MPa which indicated that the remediate sludge was well solidified and safe to be used in a wide variety of applications, such as a raw material used in concrete blocks or to be sold as pavement blocks or used in roadbeds and/or parking lots.

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