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Cement-based solidification for the safe disposal of blasted copper slag

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Abstract

This paper describes an investigation of cement-based solidification/stabilization process for the safe disposal of blasted copper slag. The treatments evaluated were based on ordinary Portland cement (OPC). Mortar specimens with ground copper slag ranging from 0% to 10% by weight of cement were tested for whole block and crushed block leachability, compressive strength and hydration. The results indicated that the leaching of selected heavy metal ions from the cement matrix was low and did not exceed the Malaysian Environmental Quality Act. Addition of copper slag to cement increased initial and final setting times. The primary hydration process was the OPC hydration. The strength of the copper slag mortar was generally lower than that of the control mortar and the amount of ground copper slag to replace cement for optimum strength was about 5%.

Keywords: Copper slag; Solidification; Leachability; Hydration; Mortar

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1. Introduction

Copper slag is used as an abrasive in shot blasting to prepare steel surfaces for painting. The widespread use of lead and other heavy metals in protective paints [1] increases heavy metals in used slag, which is classified as a solid/hazardous waste. Landfill disposal of copper slag is not feasible since a few hundred tonnes are produced per year per factory; leaching of heavy metals into ground water is of concern. Solidification/stabilization (S/S) is an increasingly attractive alternative to the remediation of improperly discarded hazardous or toxic materials, and is particularly effective when these toxic compounds are bound into a form immune to leaching. S/S basically involves waste containment within a solid matrix using different binder materials such as cement, pozzolans, clay and polymer. It is a treatment process that produces a solid monolithic or soil-like mass from a waste and leads to a product with improved structural integrity and physical characteristics [2]. It is a relatively new treatment process that has the potential to reduce leachability of hazardous constituents from the disposed waste.

Investigations relating to the disposal of industrial by-products in concrete have been actively pursued [3]. The disposal of these materials in concrete conserves natural resources and energy, and reduces pollution. However, the research work on copper slag has not been extensive. Copper slag has been used as an aggregate and backfilling material [4–7]. A few studies [2,8,9] have been performed to investigate the stabilization of heavy metals present in copper slag within the cement matrix. It is noticed, however, that most studies were conducted on non-ground slag. In cases where ground slags were used, the slags were normally not contaminated with other waste. Therefore, it is felt that further studies need to be performed to justify cement-based solidification/stabilization for the safe disposal of ground copper slag.

The present studies embrace the safe disposal of the copper slag using cement-based solidification/stabilization as well as the potential reuse of the end product as construction material. The leachability of heavy metals, compressive strength of copper slag mortar and the effects of the heavy metals on the hydration of the copper slag mortar are reported.

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2. Materials and experimental procedures

2.1. Materials

Copper slag from a metal fabricating company at Pasir Gudang in Johor (Malaysia) was used; its chemical composition and physical properties are listed in Table 1. Physically it is angular, black, glassy and shiny with sharp edges (Fig. 1). The copper slag passing 2.36 mm sieve was ground to a fineness of 20% retention on 45 μm wet sieve and this fineness was the same as that of the cement used (Table 1). This fineness was achieved also to conform to the maximum retention limit of 34% stated in ASTM C618-92a [10] and 20% in ASTM C989-89 [11]. Ordinary Portland cement (OPC) complying with MS 522: Part 1:1989 [12] was used. The chemical composition and physical properties of cement are also shown in Table 1. The fine aggregate was washed mining sand. The aggregates typically fall into Grade C with 51.6% passing through 600 mm sieve according to MS 29:1995 [13] and BS 882:1991 [14].

2.2. Preparation of specimens

The water–binder ratio of the mortar was fixed at 0.5 and the sand–binder ratio at 2.75 (according to ASTM C109-92 [15]). All mortars were prepared using hand-mixed method. During dry mixing, the materials were divided into four parts with each part thoroughly mixed before mixing into one homogeneous paste. Mortars were cast in two layers into molds: three-gang molds, steel or Perspex, either 50 × 50 × 50 mm (steel, for compressive strength and dynamic leaching test) or 25 × 25 × 25 mm (Perspex, for static leaching test). The mortar was compacted by a vibration table operating at 12000 ± 400 rpm. The specimens were covered with damp cloth for the first 24 h. After demolding at one day, the specimens meant for compressive strength were cured under lime-saturated water; specimens for the leaching test were air cured in a 70 ± 5% R.H. environment to prevent loss of heavy metal ions.

Table 1
Chemical composition and physical properties of cement and copper slag

Item	Materials	
	Cement	Copper slag
Chemical composition (%)		
Silica, SiO_2	20.0–22.5	31 ± 2
Calcium oxide, CaO	Min 62.0	4 ± 0.5
Alumina, Al_2O_3	4.8–6.0	6 ± 0.5
Iron oxide, Fe_2O_3	2.4–4.5	36 ± 1
Magnesium oxide, MgO	Max 3.5	–
Sulfuric anhydrite, SO_3	2.1–2.4	–
Cu as CuO	–	0.33–0.80
Ni as NiO	–	0.05
Pb as PbO	–	0.28
Zn as ZnO	–	0.7–1.3
Loss on ignition	Max 2.0	<1
Physical properties		
Specific gravity at 25 °C	3.12–3.16	3.4–3.6
Fineness:		
45 μm sieve, % retained	15–20	15–20
Setting time (min)		
Initial	90–180	210[a]
Final	180–270	450[a]

[a] Value for 10% replacement.

Fig. 1. SEM photograph of copper slag (magnification: 50×).

2.3. Test of mortar specimens

Consistency and setting time tests were carried out according to MS 522: Part 2:1989 [16]. Compressive strength was tested using a hydraulic type Tonipact 3000 testing machine according to ASTM C109-92 [15] from age one day to one year. Loading rate was 0.6 kN/s and the average strength of three cubes was taken as the result.

For the whole block leachability (WBL) test, 25 mm cubes were subjected to extraction for 24 h using acetic acid (pH = 2.88 ± 0.05). The solid:liquid ratio was 1:10 by weight. The leachates were filtered through 0.6 μm borosilicate glass-fiber filter and the aliquots were preserved for flame atomic absorption spectrometry (AAS). The crushed block leachability (CBL) test was similar to the toxicity characteristic leaching procedure (TCLP) recommended by the United States Environmental Protection Agency (USEPA). 50 mm cubes were crushed discarding the near-surface fraction. The core fraction was further crushed to a particle size of less than 9.5 mm and 40 g portions were transferred to extraction vessels. The extractant, acetic acid, was added at a solid:liquid ratio of 1:20 by weight. The vessels were agitated using a rotary tumbler at 30 ± 2 rpm for 18 h. The leachates were filtered as in the WBL test and analyzed using AAS.

Thermogravimetry (TG) was carried out using a PL Thermal Sciences TGA 1500. All specimens were oven-dried at 105 °C for 24 h before the test. Oven-dried method was chosen over organic solvent drying methods due to the fact that major errors can arise in thermal methods from the use of specimen in contact with organic liquids [17]. The tests were conducted in a CO_2-free nitrogen gas atmosphere flowing at 5 ml/min. The heating rate used was 20 °C/min and the specimens were heated from ambient to 1000 °C. The amount of free calcium hydroxide (CH) was calculated using the equations of Bhatty and Reid [18] and Taylor [19].

3. Results and discussion

3.1. Trial mixes, water requirement and setting time

It was found that used copper slag retarded cement hydration adversely beyond 10% replacement [20]. As a result, a range of up to 10% replacement was selected for the tests. The consistency test [16] was used to evaluate the differences in the amount of water required for the copper slag incorporated paste to achieve the same consistency as the control paste. The water required by the paste with 10% replacement, by volume, was about 97% of that required by the control paste. This may be due to the fact that the copper slag paste does not absorb water. The initial and final setting times for the various levels of replacement are shown in Fig. 2. The setting time increased with the increase of copper slag. The presence of Cu, Pb and Zn compounds in the slag, which are set-inhibiting [8,21], is believed to contribute to the increased setting time.

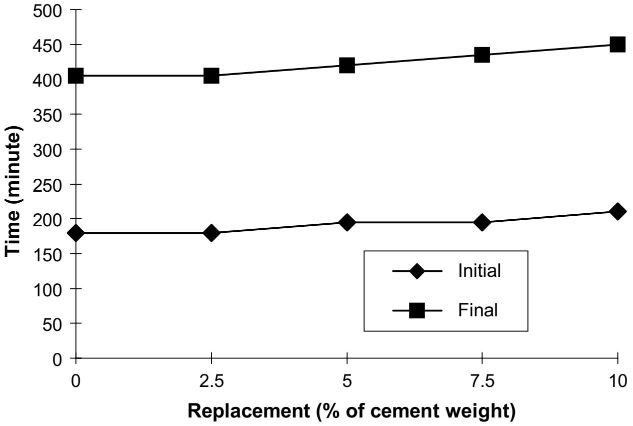

Fig. 2. Setting time of the slag mortars.

3.2. Leachability

The metal ions selected for the study were Cu, Ni, Pb and Zn. They were selected due to their presence in the copper slag and also their toxic nature that required proper handling under the Malaysian Environmental Quality Orders [22]. The method used in determining the concentration of the respective ions in leachability test was direct air-acetylene flame AAS. The use of acetic acid as an extractant provides a severe test for the samples and is expected to predict the metal released over many years in landfill conditions [23]. Table 2 shows the leachability limits imposed by the Malaysian Environmental Quality Orders [22]. Standard A is the limit allowed for effluent to be safely released into any catchment area whereas Standard B is for effluent to be released into any terrestrial water system.

The WBL test intends to simulate the leachability of an intact structure of the copper slag mortar subject to an acidic environment. Table 3 shows the WBL test results where 'ND' denotes 'Not Detected', which means that the concentration of the particular ion being tested is well below the sensitivity limits of AAS. Cu was not detected in all replacement levels from one day to one year of curing age. This indicates that the concentration of Cu ion in the test leachates was below 0.1 mg/l and, therefore, fulfills even the most stringent limit of 0.2 mg/l (i.e., Standard A). The leachability of Cu, Ni and Zn was below the Standard A limits and that of Pb was below the Standard B limits. The low leachability of the ions is expected, as the content of copper slag was relatively low in the mortar cubes. It was noted that the concentration of Zn increased with curing age for all samples. However, the concentration was 0.803 mg/l at one year for 10% replacement level that did not exceed the stipulated limits. The higher concentration of Zn with age may be attributed to the solubility of Zn compounds at different pH environment. Possibly insoluble Zn substances were converted to a more soluble one during the hydration process. Table 4 shows the initial leachability of the respective ions in the raw copper slag and cement determined according to the Standard Methods for the Examination of Water and Wastewater [24]. The content of the heavy metals in slag was considerably higher than that in cement. Table 4 also shows that the heavy metals were largely contained

Table 2
Regulatory limits for various heavy metals [22]

Element (mg/l)	Standard A	Standard B
Cu	0.20	1.00
Ni	0.20	1.00
Pb	0.10	0.50
Zn	1.00	1.00

Table 3
WBL leachability of different heavy metals

Replacement (%)	Curing (day)							
	3	7	14	28	56	180	270	365
Element: Cu (sensitivity = 0.1 mg/l)								
0	ND	ND	ND	ND	ND	ND	ND	ND
2.5	ND	ND	ND	ND	ND	ND	ND	ND
5.0	ND	ND	ND	ND	ND	ND	ND	ND
7.5	ND	ND	ND	ND	ND	ND	ND	ND
10.0	ND	ND	ND	ND	ND	ND	ND	ND
Element: Ni (sensitivity = 0.15 mg/l)								
0	ND	ND	ND	ND	ND	ND	ND	ND
2.5	ND	ND	ND	ND	ND	ND	ND	ND
5.0	ND	ND	ND	ND	ND	ND	ND	ND
7.5	ND	ND	ND	ND	ND	ND	ND	ND
10.0	ND	ND	ND	ND	ND	ND	ND	ND
Element: Pb (sensitivity = 0.5 mg/l)								
0	ND	ND	ND	ND	ND	ND	ND	ND
2.5	ND	ND	ND	ND	ND	ND	ND	ND
5.0	ND	ND	ND	ND	ND	ND	ND	ND
7.5	ND	ND	ND	ND	ND	ND	ND	ND
10.0	ND	ND	ND	ND	ND	ND	ND	ND
Element: Zn (sensitivity = 0.02 mg/l)								
0	ND	ND	0.026	0.038	0.068	0.235	0.325	0.399
2.5	0.100	0.056	0.094	0.108	0.117	0.527	0.497	0.525
5.0	0.070	0.066	0.086	0.103	0.124	0.462	0.589	0.618
7.5	0.080	0.063	0.074	0.112	0.189	0.453	0.620	0.671
10.0	0.056	0.057	0.037	0.109	0.139	0.500	0.715	0.803

Note. ND = not detected.

Table 4
Initial leachability of heavy metal ions from raw materials

Element	Initial leachability from cement (mg/l)	Initial leachability from copper slag (mg/l), a	Max leachability from slag mortar (mg/l), b	$(b/a) \times 100$ (%)
Cu	0.207	15.498	0.1[a]	0.65
Ni	0.396	1.218	0.15[a]	12.32
Pb	0.233	8.793	0.5[a]	5.69
Zn	0.636	12.073	0.803	6.65

[a] Value taken as sensitivity limits.

within the mortar matrix with the leachability well below the regulatory limits (Table 2).

The CBL test intends to simulate the worst-case scenario whereby the matrix may be crushed/smashed during handling or after disposal. Table 5 shows the results of the CBL test. The leachability of Zn ion was high initially but apparently decreased with age. All concentrations were below the stipulated limits; the leaching concentrations were even lower than those in the WBL test. This contradicts with the general perception that CBL test should produce higher leachability since the surface area of crushed sample in CBL test is higher than that of the sample in WBL test. In determining the pH of the final leachates, it was noticed that the pH of the leachates between the two tests differed considerably. The pH of leachates in WBL test ranged from 4.40 to 4.48 for all replacement levels, while the pH of leachates in CBL test ranged from 10.78 to 11.28. This may be due to the quicker rate of dissolution of calcium hydroxide into the leachate in the CBL test. The CBL test used crushed pieces of the specimens that passed 9 mm sieve. In using crushed pieces, the areas of contact of the specimen with the extraction fluid, acetic acid in this case, increased substantially. As a result, the calcium hydroxide from the mortar dissolved quickly into the extraction fluid and neutralized it. Thus the extraction condition was less severe than the WBL test and hence the low leachability. However, this is certainly not the case in natural environment, as fresh leachant will continuously wash away the leachate. Therefore, authors realized that further study regarding a continuous flow extraction method needed to be devised to simulate actual leaching condition.

In general, the leaching of the selected heavy metals from the mortar did not exceed the requirements of the

Table 5
CBL leachability of different heavy metals

Replacement (%)	Curing (day)							
	3	7	14	28	56	180	270	365
Element: Cu (sensitivity = 0.1 mg/l)								
0	ND	ND	ND	ND	ND	ND	ND	ND
2.5	ND	ND	ND	ND	ND	ND	ND	ND
5.0	ND	ND	ND	ND	ND	ND	ND	ND
7.5	ND	ND	ND	ND	ND	ND	ND	ND
10.0	ND	ND	ND	ND	ND	ND	ND	ND
Element: Ni (sensitivity = 0.15 mg/l)								
0	ND	ND	ND	ND	ND	ND	ND	ND
2.5	ND	ND	ND	ND	ND	ND	ND	ND
5.0	ND	ND	ND	ND	ND	ND	ND	ND
7.5	ND	ND	ND	ND	ND	ND	ND	ND
10.0	ND	ND	ND	ND	ND	ND	ND	ND
Element: Pb (sensitivity = 0.5 mg/l)								
0	ND	ND	ND	ND	ND	ND	ND	ND
2.5	ND	ND	ND	ND	ND	ND	ND	ND
5.0	ND	ND	ND	ND	ND	ND	ND	ND
7.5	ND	ND	ND	ND	ND	ND	ND	ND
10.0	ND	ND	ND	ND	ND	ND	ND	ND
Element: Zn (sensitivity = 0.02 mg/l)								
0	0.037	ND	ND	ND	ND	0.039	0.057	0.052
2.5	0.031	ND	ND	ND	ND	ND	0.025	ND
5.0	0.058	0.051	0.050	0.045	0.039	0.038	0.047	0.041
7.5	0.072	0.067	0.065	0.065	0.043	0.027	0.032	0.028
10.0	0.088	0.071	0.037	ND	ND	ND	0.024	ND

Note. ND = not detected.

Malaysian Environmental Quality Orders [22]. The cement-based solidification/stabilization technique successfully contained the waste within the solidified matrix. Therefore, cement-based solidification/stabilization technique can be used for the safe disposal of blasted copper slag up to 10% by weight of cement.

3.3. Compressive strength

In order to study the feasibility of using solidified/stabilized copper slag as construction material, compressive strengths of mortar samples were determined. A plot of compressive strength against percentage replacement (Fig. 3) reveals that the strength of the copper slag mortar is generally lower than that of the control mortar. There is an optimum strength performance in the range of 5–7.5% for the copper slag mortar. The strength at this range is slightly lower but comparable to the control mortar. The lower strength could be attributed to the retardation of cement hydration due to the presence of heavy metals in copper slag. The lower strength could also be due to the fact that the very fine particles of the slag supplied a large amount of surface area per unit volume to be coated with cement [1]. This might have effectively reduced the amount of cement available for binding the fine and coarse aggregates required to provide adequate strength.

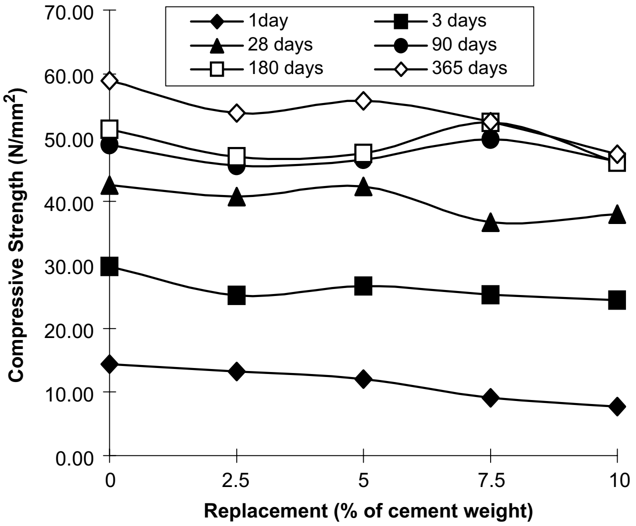

Fig. 3. Compressive strength of slag mortars as a function of replacement level.

3.4. Thermogravimetric analysis

Table 6 shows that the maximum CH content of the mortars (relative to control) are proportional to their cement content percentage for 2.5% and 5% replacement, suggesting a predominant OPC-like hydration.

Table 6
Maximum CH content for different mortars

Slag content (%)	Cement content (%)	Maximum CH content (% per ignited weight)	Maximum CH content relative to control (%)	Age at maximum CH content (days)
0 (Control)	100	6.94	100	285
2.5	97.5	6.78	97.7	75
5	95	6.60[a]	95.1	85
7.5	92.5	6.16	88.8	180
10	90	6.04[a]	87.0	180

[a] Taken as the second maximum value.

For 7.5% and 10% replacement, the maximum CH content is slightly lower than their respective cement content percentages. This may be due to the activation of slag that consumed part of the CH produced by cement hydration. It may be observed that the mortar reached the maximum CH content earlier as the slag content decreased except for the control mortar (Table 6). This may be due to the fact that Zn, Pb and a part of Cu compounds are set inhibiting while some Pb compounds are set accelerating in nature [8]. At low replacement level, the set inhibiting compounds were not sufficient to cause appreciable inhibiting effects and the set accelerating compounds promoted the cement hydration and resulted a maximum CH content at an early age. The reversal is thought to be true for the higher replacement levels. On the other hand, the CH content of the control continued to build up due to the unhindered-hydration and non-consumption of CH by the slag.

4. Conclusion

This study has shown that the waste copper slag from blasting operation can be safely solidified/stabilized in a cement-based S/S system. The leachability of copper, nickel, lead, and zinc ions presence in copper slag were lower than the regulatory limits. The mortar incorporating waste copper slag up to 10% replacement is, therefore, safe with respect to leachability of the above metal ions.

The compressive strength of copper slag mortar was found to be lower than that of OPC mortar. The safe disposal level of copper slag in mortar for optimum strength performance was about 5%. Heavy metals present in the blasted copper slag retarded the initial and final setting of cement by interfering with the normal hydration reactions. The lower strength of the waste slag mortar was attributed to the set-inhibiting properties of these heavy metals. The hydration in the slag mortar seemed to be OPC hydration.

Because of the good leaching properties, a cement-based system may be an effective medium for the embodiment of copper slag, which is a hazardous material, thus providing a safe disposal method. This, however, is only achieved at the cost of reduction in strength and works for only small quantities of the slag (about 5%).

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