Study on the leaching performance of chromium (Cr) and cadmium (Cd) from the utilization of solidified nickel slag as concrete floors

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Abstract. With the increasing demands on more metals extraction, the hazardous waste resulted from mining industry has also raised. In this paper, the treatment process of nickel slag containing hazardous metals is described. The treatment involved a solidification process, where nickel slag is used as fine aggregates substituting agent. This study aimed to determine the optimum dosage of nickel slag that met specification in the construction of concrete floors. A series of technical feasibility test were carried out by replacing the weight proportions of sand with nickel slag gradually from 0% to 100% to examine the compressive strength, absorption rate, durability and leaching performance. The results indicated that even though all mixture variations possessed high value of absorption rate indicating high permeability concrete mix, all mixtures, however, had good durability. Furthermore, based on the compressive strength test, a mixture with 60% substitution of nickel slag is considered as a viable replacement of sand in the concrete floors construction in conformance to American Concrete Institute. The leaching performance test showed that leachability of heavy metals content, particularly Cr and Cd from mortar specimens were below the standard according to Indonesian Government Regulation No 101 of 2014, therefore, in terms of environmental point of view, the utilization of solidified nickel is considered safe to be used as concrete floors.

1 Introduction

Mining is one of the potential sectors that contribute to the national income, due to wide range of uses of metals and growing of their demand. However, the operation of mining industry could not be separated with the waste or by-products resulting from its process, of which hazardous waste is included. Rapid growth of mining industry has obviously led to steep increase of hazardous waste that should be properly managed. Otherwise, serious negative impacts on human and environment may occur.

Slag is the most by-product left over in the mining industry, which resulted from a process separation between metals with its raw ore through heating process. Originally, the slag is produced in liquid form, but then as the temperature cools down it is naturally transformed to be a solid. In various mining industry, slag can be found in the form of steel slags, phosphorus slag, zinc slag, nickel slag, etc, depending on the metals that the industry produces.

One of the nickel mining industry in Indonesia, generates approximately 50 ton of nickel slag to produce one ton of pure nickel, this means an annual production of 40,000-60,000 ton of pure nickel leading to annual slag production equal to 2-3 million ton [1]. Moreover, slag is categorized as hazardous waste with code B403 due to its heavy metal content, in conformance to Indonesian Government Regulation No 101 of 2014. Therefore, the need of having treatment alternatives for slag becomes crucial, given that the huge amount of hazardous waste produced annually.

Solidification and stabilization process is an alternative treatment that may be able to convert slag to any others harmless product by way of immobilizing contaminants or waste within any other constituent materials in concrete production, hence, the migration of contaminant to human and environment is prevented. The contaminant immobilization can be achieved through a mixing process between a binding material and the contaminated material [2]. In addition, the incorporation slag into concrete volume would benefit construction industry as slag could be utilized as a replacement of constituent material like fine aggregates or cement [3].

This current study focuses on nickel slag generated from nickel mining industries. The objective of the study reported here was to investigate the possibility of nickel slag to substitute fine aggregates material in the

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production of concrete floors. Additionally, this study aims to determine the optimum of compositional variation between nickel slag and binder with respect to the required products specifications and lastly, to analyze the leaching performance on Cr and Cd from the solidified nickel slag.

2 Experimental Methods

2.1 Materials

Nickel slag sample taken from one of the largest nickel mining industry in eastern part of Indonesia was expected to be used as fine aggregates replacement in the construction of concrete floors. An Ordinary Portland Cement (OPC) was used as a binder in the solidification process. Fine aggregates used was a typical of natural sand found in Indonesia. Nickel slag, OPC and fine aggregates have specific gravity of 2.73, 3.15, and 2.53, respectively [4].

2.2 Analysis

Analysis on nickel slag, OPC, fine aggregates and water used in the experiment were carried out in order to determine the physics-chemical characteristics of each material. The analysis including water content, dry matter, absorption rate, ash content, volatile content, metals oxide and heavy metals were undertaken based on methods available in Indonesian National Standard (SNI) and American Standard Testing and Material (ASTM) [5-8]. The sieve analysis was also performed on the nickel slag samples and the sand in conformance to ASTM C136:2012 [9]. The main elements of nickel slag and the OPC used are shown in Table 1 and the heavy metals content of the nickel slag are shown in Table 2.

Table 1. Main elements of nickel slag and OPC.

	LOI	**Main elements (% w/w)**					
		CaO	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**Na_2O+K_2O**
Nickel slag	16.7	10.34	48	1.17	10.19	9.75	0.88
OPC		60-65	17-25	3-8	0.5-6	0.5-4	0.5-1

Table 2. Heavy metals content in nickel slag, OPC and fine aggregates.

Metal content (mg/kg)	**As**	**Ba**	**Cd**	**Cr**	**Co**	**Cu**	**Pb**
Nickel slag	0.432	0.1	0.25	25.4	4.1	1.25	0.025
Sand	1.25	279.75	8.5	1.25	3.25	50.75	31.75
OPC	3.75	251	5.5	51.25	3	46	65.25
Metal content (mg/kg)	**Hg**	**Mo**	**Ni**	**Sn**	**Se**	**Ag**	**Zn**
Nickel slag	0.012	0.025	310.5	0.025	0.205	0.025	2.45
Sand	0.007	<0.001	0.074	4.75	ND*	0.005	ND*
OPC	0.008	<0.001	0.182	8.75	ND*	0.004	109.5

* Not detected

2.3 Preparation of solidification solids

Based on the results of sieve analysis from the previous stage and the data of specific gravity, it is obtained that nickel slag has met the requirements of fine aggregates, as it has fineness modulus of 3 compared to the standard value for fine aggregates according to ASTM C 33-03, which is lied within the range of 2.3-3.1. Therefore, in this current study, a total of 10 concrete mixtures for each variation were prepared by varying the proportions of nickel slag and the sand, whereas the OPC was maintained constant. Here, where nickel slag was used to substitute fine aggregates in concrete floors construction, the required weight ratio between OPC and fine aggregates is within the range of 1:4 – 1:6 [1]. The proportion variations of nickel slag and sand are shown in Table 3.

Table 3. The mix variations of concrete specimens in percent weight.

Weight ratio of OPC:sand	NS:S*	NS:S	NS:S	NS:S	NS:S
1:4	0:100	55:45	65:35	75:25	100:0
1:5	0:100	35:65	45:55	55:45	100:0
1:6	0:100	15:85	25:75	35:65	100:0

*NS: nickel slag; S: sand

The amount of added water to each of the sample variations corresponded to the flow table test based on ASTM C1437-07, resulting in water-to-cement ratio within the range 0.7-1. According to the proportional variations, the mix concrete paste was placed into cubical molds (5 cm x 5 cm x 5 cm) and compacted. After 24 hours and naturally dried, the concrete specimens then demolded. To estimate the duration needed by the concrete specimens to completely dry, an analysis on setting time based on ASTM C191-04-a [10] was performed by dropping a Vicat needle to the mortar paste. Dried samples were ready to undergo a further test after being cured in water for certain period of curing days.

2.4 Technical feasibility test

To evaluate the mechanical properties of the concrete specimens, a series of testing in conformance to ASTM were carried out. The technical feasibility test includes compressive strength test following ASTM C 109-01 by using Universal Testing Machine (UTM) [11]. The test was undertaken to the mortar specimens that have been cured in water during period of 3, 7, 14, and 28 days. The absorption test was carried out on all the variation of 28 days old mortar specimens [12]. The durability test was done on similar number of specimens as in the absorption test, but following the procedure on ASTM D 4843-88 R04 for 13 cycles, which one cycle equals to 48 hours [13].

2.5 Leaching test

Leaching test includes the Toxicity Characteristics Leaching Procedure (TCLP) test, static and dynamic test were carried out on both nickel slag and concrete specimens. All the concrete specimens that met criteria required by previous technical feasibility tests were included in the leaching test. In the TCLP test, acetate acid was used according to US EPA SW-846 Test Method 1311 [14], where the selected mortar specimens were agitated in acid solution during ±18 hours.

The static and dynamic leaching test used a modified method based on ASTM D3987-12 [15]. In the present study, the observation of leaching test is focused on Cr and Cd since the predominant metals in nickel slag, such as Ni and Co have been examined in another study. In the static test, with regards to the procedure in USEPA Test Method 1311 [13], concrete specimens were contained and H_2SO_4 and CH_3COOH with pH 4.92 ± 0.05 were added to soak the specimens. The liquid-to-solid ratio (L/S) of 20:1 was used to quantify the volume of acid solution and the amount of solid sample. Cr and Cd contaminant in the leachate samples were observed during curing period of 1, 3, 6, and 9 days using Atomic Absorption Spectroscopy (AAS).

On the other hand, carbonate acid was used in the dynamic test to represent the condition of acid rain, in which samples of concrete specimens and nickel slag were placed in glass cylinders and acid solution was flown into the cylinder for 3 hours. The leachate produced then was underwent a heavy metals analysis [8]. The test was continued by drying the specimen samples and the nickel slag that have been flown by acid solution for 24 hours in the temperature of 60°C. The dried specimen samples and the nickel slag then for the second time were flown by the carbonate acid, while produced leachate were taken hourly to conduct the heavy metals analysis using AAS.

3 Results and Discussion

3.1 Compressive strength test

A concrete compressive strength is a maximum strength that concrete can hold for an area functional unit, of which it is one of the most necessary parameter in the building construction materials. Concrete compressive strength is highly affected by several factors like the water-to-cement ratio, aggregates type and characteristics, workability, maintenance and period of curing days. Figure 1 presents the results of compressive strength of concrete specimens for various composition as sand substitution agent at 7, 14, and 28 days curing periods.

In general, the results show a decreasing trend as more nickel slag in the concrete mixtures. This is probably due to the high value of water to cement ratio in the mortar specimens with nickel slag. According to the SNI 03-6468-2000 [16], the required water-to-cement ratio for high strength concrete should be within the range of 0.2-0.5, whereas the ratio value in this

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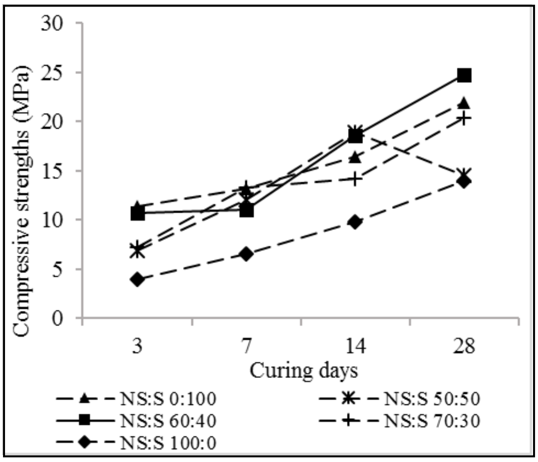
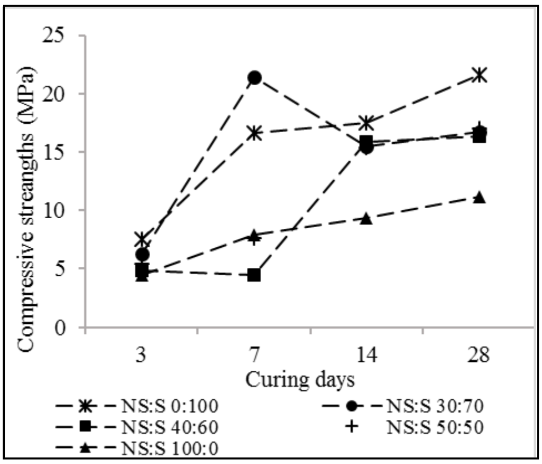
experiment reached 0.7-1. The high ratio of water to cement may be due to low water content in the nickel slag, which is 1.812%, that is quite lower than most aggregates value, which is lied between 3-8% [17].



(a)



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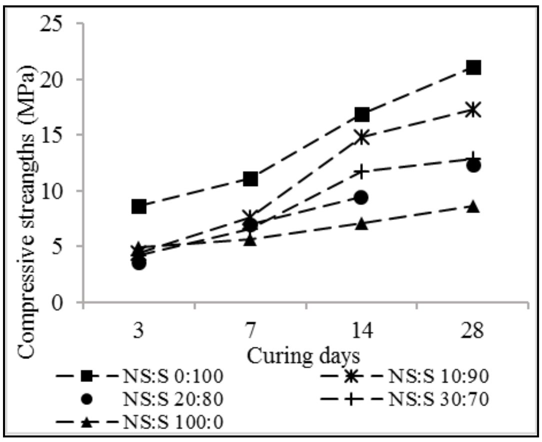

(c)

Fig. 1. The compressive strength performance of mortar specimens (a) cement:fine aggregates 1:4, (b) cement:fine aggregates 1:5. (c) cement:fine aggregates 1:6.

Concrete mix with cement-to-aggregates ratio of 1:4 presents the highest value of compressive strengths, whereas between 2 others ratio, the difference of compressive strength on the control specimen is pretty small. The value of compressive strength obtained was far below the value when copper slag is used as substituting agent for aggregates in building construction material, even for the control specimen as reported by Al-Jabri, et al [18]. In accordance with American Concrete Institute [19], only the mixture with 60% substitution of nickel slag that met the concrete strength requirements as concrete floors level 1,2, and 3 that require minimum strength of 21 MPa.

The compressive strength raises as the curing period was extended due to longer hydration duration allowing a more complete bond forms between concrete constituents and at the same time preventing the presence of excess water that may form internal voids in the concrete mix. The existence of porosity in the concrete mix is unexpected, as it may weaken the bond between the concrete components, which is one of determining factors for the strength of concrete [20].

The fineness modulus in the nickel slag is beyond the range of most aggregates commonly used in the construction. According to Wu et al. [20], this condition is beneficial as finer particles of nickel slag leading to the less porosity that may form in the concrete mix, but on the other hand, the property is naturally denser than most aggregates, hence to fill the same volume of space that sand occupies, more nickel slag is needed. Considering this fact, the concrete strength with more nickel slag is more likely weaker than those with less nickel slag due to larger surface area of nickel slag per unit volume exposed, resulting in inadequate cement content for binding the concrete matrix together. Furthermore, as the fineness level of aggregates increases, the shrinkage possibility increases as well. In some cases, the shrinkage that cause deep cracks does not appear in surface of concrete mix, but inside the concrete [21].

Based on the metal oxides and heavy metals estimation, it was obtained that nickel slag constitutes a relatively high content of ferric oxide and chromium. This may be another reason that as nickel slag content is higher, the compressive strength of concrete mix is lower. Previous study showed that the duration of cement hydration goes longer when heavy metals present. The delay of cement hydration becomes more serious with the addition of nickel slag that leaves more excess water in the concrete and forms more flaws or weakest links harm to the concrete structure [20].

3.2 Absorption test

Absorption test aims to determine the ability of concrete mix in absorbing water. The maximum limit of absorption rate of concrete mix in conformance with ARTO Brick and California Pavers is 12%. The absorption rate of concrete specimens was presented in Table 4. The results showed that all specimens have met the requirement of desired concrete mix with regards to absorption rate.

Table 4. Value of absorption rate of all mortar specimens.

Cement aggregates ratio	Proportional variations (% w/w)	Absorption rate (%)
1:4	NS:S 0:100	8.54
	NS:S 50:50	9.51
	NS:S 60:40	9.38
	NS:S 70:30	9.8
	NS:S 100:0	11.6
1:5	NS:S 0:100	11.3
	NS:S 30:70	9.73
	NS:S 40:60	8.75
	NS:S 50:50	10.9
	NS:S 100:0	12.2
1:6	NS:S 0:100	9.18
	NS:S 10:90	8.42
	NS:S 20:80	8.87
	NS:S 30:70	9.6
	NS:S 100:0	11.82

It can be seen from the results that there was an inverse relationship between compressive strength and absorption rate, of which this result is supported by Zhang [3], the specimens that show highest strength will have lowest absorption rate. However, the absorption rate that is evaluated in current study only represented a surface water absorption and did not take into account an internal water absorption, which is also one of determining factor of concrete strength.

Based on study done by Zhang [3], a linear correlation exists between absorption and permeability, where permeability is one of the main characteristics affecting the durability of concrete. It can be seen from the results that higher nickel slag content possessed higher absorption rate indicates higher permeability. This is primarily due to higher water cement ratio in the mortar specimen that comprise more nickel slag than that in the control concrete. The high level of water cement ratio can cause volume change, that eventually results in the development of micro-cracks and disintegration [22].

3.3 Durability test

The durability of concrete was evaluated to understand the effect of harsh environments that can result in failure of structures. Table 5 presents the results of durability test on all variations of concrete specimens. In conformance to ASTM D 4843-88 R 04 [13], the maximum percentage of mass loss after durability test for 13 cycles is 30%. The smallest mass loss from present study was shown by a mixture with 60% substitution of nickel slag. This value is even lower than those for three values of control mortar. This result reveals that even though the absorption rate on all mixtures are high, the mass loss percentage, however, still met the relevant criteria.

Table 5. The results of durability test of all compositional variations.

Cement aggregates ratio	Proportional variations	Durability (%)
1:4	NS:S 0:100	7.7
	NS:S 50:50	6.34
	NS:S 60:40	6.01
	NS:S 70:30	7.32
	NS:S 100:0	8.52
1:5	NS:S 0:100	9.36
	NS:S 30:70	7.54
	NS:S 40:60	6.2
	NS:S 50:50	8.24
	NS:S 100:0	10.97
1:6	NS:S 0:100	7.6
	NS:S 10:90	7.33
	NS:S 20:80	7.08
	NS:S 30:70	7.78
	NS:S 100:0	8.08

3.4 TCLP test

In current study, TCLP test was conducted to identify the effect of pozzolan characteristics in stabilizing heavy metals and to determine the heavy metals presence in the leachate. As it was expected, most of heavy metals level in all mix variations decrease after solidification was carried out (Figure 2). The pozzolan physical nature is very effective in the metals immobilization leading to reduced leachability, primarily because most of the compound is reacted into undissolved hydroxide [23].

Even though most of the metals level decline after solidification took place, several metals concentration like Ba, Cu, Ag and Zn raise. This is probably due to the contribution of heavy metal content in the OPC and sand themselves, in which Ba, Cu, and Zn content in OPC and sand were far greater than those in nickel slag.

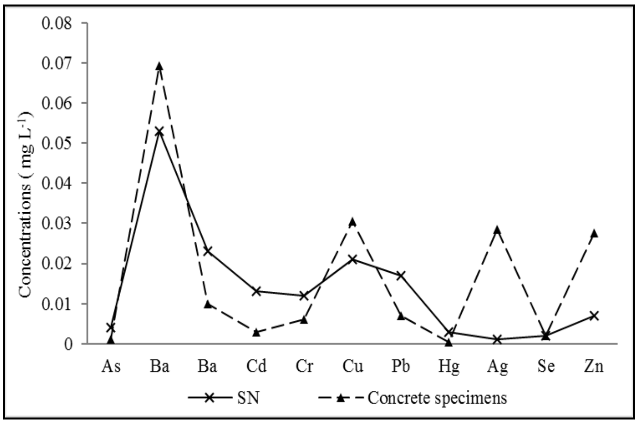

Fig. 2. Comparison of TCLP analysis of concrete specimen and nickel slag.

3.5 Static and dynamic leaching test

Within this test, the leaching behavior of Cr and Cd that present in the concrete mix was measured. This test differs from previous TCLP test, in which within this study, TCLP is a used method to estimate the leachability of heavy metals that consider severe environment condition that involve agitation within the procedure. On the other hand, both static and dynamic test were used as leaching test that represent natural environment condition, where agitation is not necessary.

Both static and dynamic test were carried out on the nickel slag and concrete mix with the highest compressive strength value and 28 days curing period, to compare the leaching performance prior and after the solidification took place. The result of leaching performance test showed that the concentration of Cr and Cd for both nickel slag and mortar specimens in all conditions were not detected in the AAS. This means that the Cr and Cd concentration was extremely low, even below the detection limit in the used AAS.

3 Conclusions

The results of this study have demonstrated the effectiveness of solidification process in immobilizing heavy metals in nickel slag Therefore, the cement-based solidification technique is proven can be an option to treat nickel slag when it is intended to be utilized as concrete floors. Through this study it is identified that a dosage of 60% nickel slag with cement aggregates ratio of 1:4 met the requirements of concrete floors construction in terms of compressive strength, absorption rate, and durability. The TCLP test also indicates that heavy metals content were below the standard and in particular, leaching behavior of Cr and Cd in mortar specimens are also found still within tolerable concentration criteria in accordance with Government Regulation No 101 of 2014.

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