IOP Conf. Series: Materials Science and Engineering **299** (2018) 012046 doi:10.1088/1757-899X/299/1/012046

Evaluation of the suitability of tin slag in cementitious materials: Mechanical properties and Leaching behaviour

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Abstract. Tin slag, a by-product of tin production has been used in cementitious application. The present investigation focuses on the suitability of tin slag as primary component in cement and as component that substitute some amount of Portland Cement. The tin slags studied were taken from Bangka, Indonesia. The main contents of the tin slag are SiO_2, Al_2O_3, and Fe_2O_3 according to the XRF investigation. The aim of this article was to study the mechanical behaviour (compressive strength), microstructure and leaching behaviour of tin slag blended cement.
This study used air-cooled tin slag that had been passed through 400# sieve to replace Portland Cement with ratio 0, 10, 20, 30, 40 by weight. Cement pastes and tin slag blended cement pastes were prepared by using water/cement ratio (W/C) of 0.40 by weight and hydrated for various curing ages of 3, 7, 14 days
The microstructure of the raw tin slag was investigated using Scanning Electron Microscope (SEM). The phase composition of each cement paste was investigated using X-ray Diffraction (XRD). The aim of the leachability test was to investigate the environmental impacts of tin slag blended cement product in the range 4-8 pH by using static pH-dependent leaching test.
The result show that the increase of the tin slag content decreasing the mortar compressive strength at early ages. The use of tin slag in cement provide economic benefits for all related industries.

1. Introduction

Portland cement has a big impact in the large CO_2 emissions in the world, that are generated during the production of Portland cement. This production also need big energy and natural resources. Considering the process of cement clinker production, half of the carbon emission originates from the dissociation of limestone during clinkering, whereas the other half is due to fuel combustion [3]. Utilization of metallurgical slags can be solution for energy and environmental problems, in the production of Portland cement.

An example of metallurgical slags is tin slag. Like other metallurgy slags, tin slag has the potential to be used in cementitious material, due to the similarity between the oxides that are present in both Portland clinker and Tin slag. The annual production of tin in Indonesia is between 70.000 and 96.000 tonnes (Kemenperin 2016). This big amount of production tin slag in Indonesia also generates big quantity of tin slag. At present the tin slag is stored at landfill, and no solution to utilize it.

Tin slags can be treated as a cementitious material due to its silicate calcium minerals. However, the hydration activity of tin slag is much lower than that of Portland cement due to their mineralogy properties and relatively high content of inert components.

In this study, Air cooled tin slag (ACTS) was used as component to replace Portland cement. Air cooled Tin Slag, is a by-product in tin smelter. Molten tin slag, which is discharged from the furnace, is cooled by air quenching. The slag was solidified slowly and forms slag lumps. Air cooled tin slag has partly glassy and partly crystalline phase. Air cooled tin slag composed primarily of SiO_2, Al_2O_3, Fe_2O_3 and CaO. The main objective of this research was to investigate the mechanical properties and leaching behaviour of tin slag as pozzolanic materials in Portland cement to form Portland pozzolan cement.

2. Materials and methods

This research used OPC and Air-cooled Tin Slag (ACTS). Commercially available ordinary Portland Cement (OPC) was used as the principal binder and ACTS as pozzolanic materials. This research used ACTS with particle size under 0.037 mm, coresponding to ASTM C 595 (Standard Specification for Blended Hydraulic Cement). Table 1 shows the chemical composition of OPC and tin slag which were evaluated by X-ray fluorescence (XRF).

The microstructure of the raw tin slag and hydrated cement paste was investigated using Scanning Electron Microscope (SEM). The phase composition of cement paste (OPC, S10, and S20) was investigated using X-ray Diffraction (XRD).

Table 1. OPC and Slag chemical composition

	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	TiO_2	P_2O_5	MgO	SnO_2	Na_2O
OPC	62.34	23.83	5.96	2.56	3.23	-	-	2.92	-	0.46
Slag	5.65	39.66	13.18	8.77	-	6.84	5.26	1.91	4.00	3.75

2.1 Compressive strength

The test used ASTM C109 as a standard. Specimens were cast in 50 mm cube molds with water/cement (W/B) ratio of 0.4. These samples were first cured in room temperature at 95% relative humidity for 24 h and later demolded. The cement cube was kept in a water until testing time (3, 7, and 14 days). Specimens were removed from the bath and tested at laboratory temperature.

2.2 Leaching test

The leaching test used CEN/TS 14429 pH dependence test standard. The test was carried out using deionised water at Liquid/solid ratio (L/S) = 20: 1 L/kg, with range of pH test $4 \leq pH \geq 8$ for 48 hours. Acid (1M HNO_3) or base (1M NaOH) was added to added to adjust the pH values [5]. An experiment at the natural pH was included in all cases without addition of acid or base. Leachates were filtered through a 0.45 μm pore size nitrocellulose filtration membrane and divided into subsamples for measuring Cr, Mn, and Pb concentrations. The leachate solutions was analysed with ICP to identify Cr, Mn, and Pb concentration

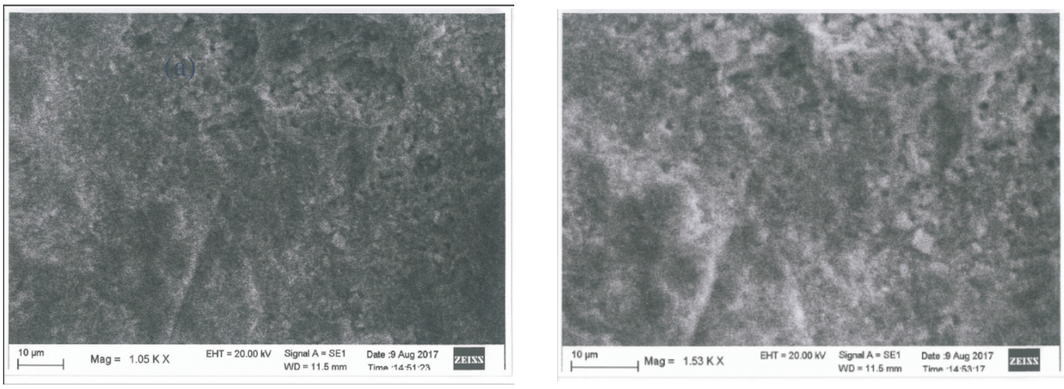
Table 2. Samples mix design

Samples	Cement (wt%)	Tin Slag (wt%)	W/B ratio
OPC	100	-	0.4
TS-10	90	10	0.4
TS-20	80	20	0.4
TS-30	70	30	0.4
TS-40	60	40	0.4

3. Result and Discussion

3.1 Air Cooled Tin Slag Characterization

The main constituents of ACTS determined by XRF are SiO_2, Al_2O_3, CaO, Fe_2O_3 and TiO_2. Figure 1 presents the microstructure of Air Cooled Tin Slag (ACTS) investigated with Scanning Electron Microscopy (SEM). Through the SEM investigation, is observed the presence of particle with rough surface texture, with smooth and very low porosity surfaces.



(a) (b)

Figure 1. SEM image of Air Cooled Tin Slag (a) magnification 1000 x (b) magnification 1500 x.

Figure 2 shows the XRD pattern of ACTS slag. ACTS slag has amorphous phase as dominant phase. Mineralogical phases that can be identified from this XRD pattern: Quartz (SiO_2), Hematite (Fe_2O_3), Cassiterite (SnO_2), and Corundum (Al_2O_3)

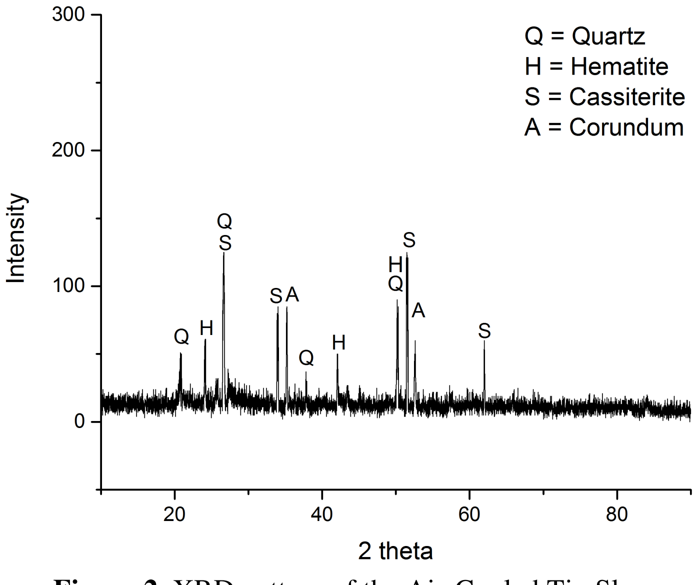


Figure 2. XRD pattern of the Air-Cooled Tin Slag

3.2 XRD Analysis

Figure 3 shows the XRD graphic of 7 days curing samples. According to the result shown in Figure 3, portlandite, calcite, ettringite, and CSH were observed in all the pastes products. Sample with replacement of 10% and 20% ACTS show lower portlandite and Calcium Silicate Hydrate (CSH) than in OPC. This was attributed to the fact that replacement of OPC with ACTS decreased the calcium oxide in slag-cement blended paste. The lower of calcium oxide also has impact in the lower amount of tricalcium silicate (C_3S) in the slag-cement blended paste. C_3S can react with water to form CSH and calcium hydroxide or portlandite according to the reaction:

$$2(3CaO.SiO_2) + 6H_2O = 3\,CaO.2SiO_2.3H_2O + 3Ca(OH)_2$$

Tricalcium Silicate   Calcium Silicate Hydrate   Calcium Hydroxide

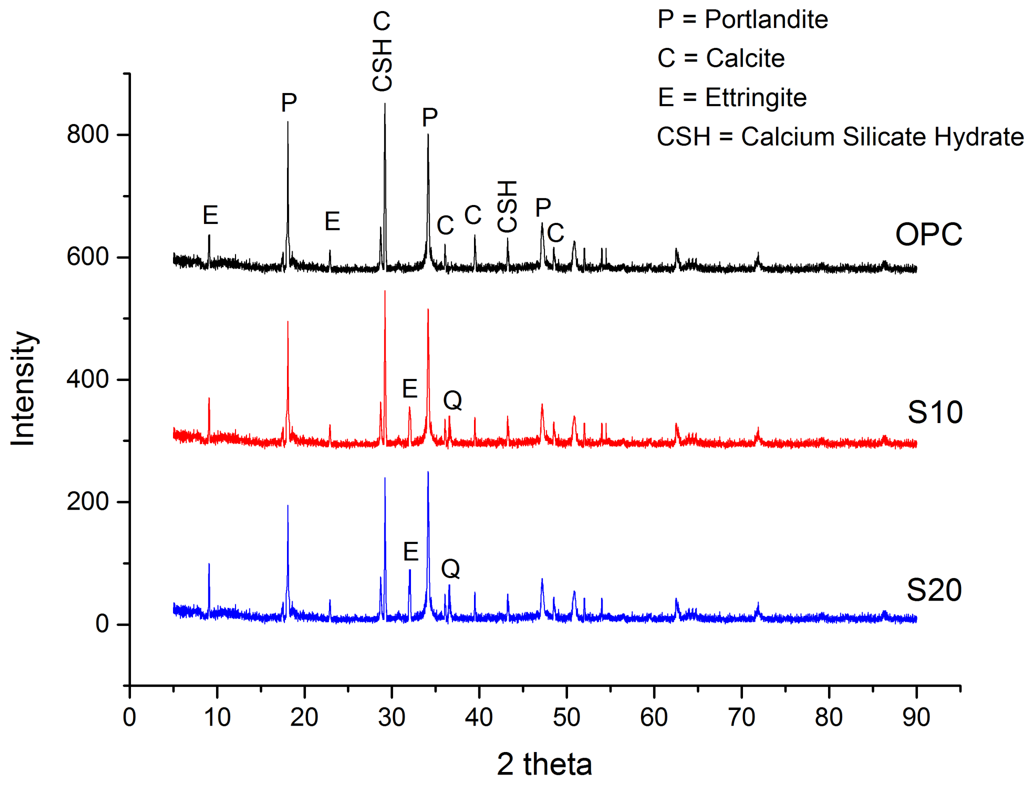


Figure 3. XRD pattern of cement hydrated for 7d

XRD patterns also show that samples S10 and S20 have higher ettringite peaks than OPC. Increasing amount of ACTS in cement blended paste can produced higher ettringite due to increasing ticalcium aluminate (C_4F) in cement paste. The ettringite (Calcium trisulfoaluminate hydrate) transformation from C_4F corresponds to the reaction:

$$3CaO.Al_2O_3 + 26H_2O + 3CaSO_4.2H_2O = 3CaO.Al_2O_3.3CaSO_4.32H_2O$$

Tricalcium aluminate   gypsum   Calcium trisulfoaluminate hydrate

The calcite content shows no difference with or without ACTS addition in cement paste. In contrast, the characteristic peak of quartz phase shows a clear difference with or without ACTS addition. The quartz's peak was higher with the increasing ACTS in cement blended paste, which is probably due to higher amount of quartz in ACTS than in OPC

3.3 Compressive Strength

Figure 4 presents the compressive strength of mortar with different ACTS replacement ratio at W/B ratio 0.4. The early compressive strength of mortar containing ACTS is significantly lower than OPC. The compressive strength of mortar, decrease with the increasing of ACTS replacement. At 3 days curing, comparing to the reference mortar (OPC), mixtures with the lowest replacement (TS10), presented a decrease 42% of compressive strength. The largest decrease of compressive strength occurred in sample with the most replacement content (TS40), reaching 68.9% of OPC compressive strength. OPC compressive strength can reached 19.79 MPa at 3 days curing, while slag-cement paste just only reach 11.44, 8.81, 7.59 and 6.15 MPa for 10, 20, 30, and 40 of ACTS replacement in OPC, respectively. At 7 days, the difference value of compressive strength between PC and slag-cement composite decrease. The lowest replacement (S10) gave a decrease 40.7% and the largest replacement (S40) gave a decrease 68.5%. The 14 days curing samples show the lowest difference value of compressive strength of OPC and slag-cement paste, with 37.1% difference for 10% ACTS replacement in OPC.

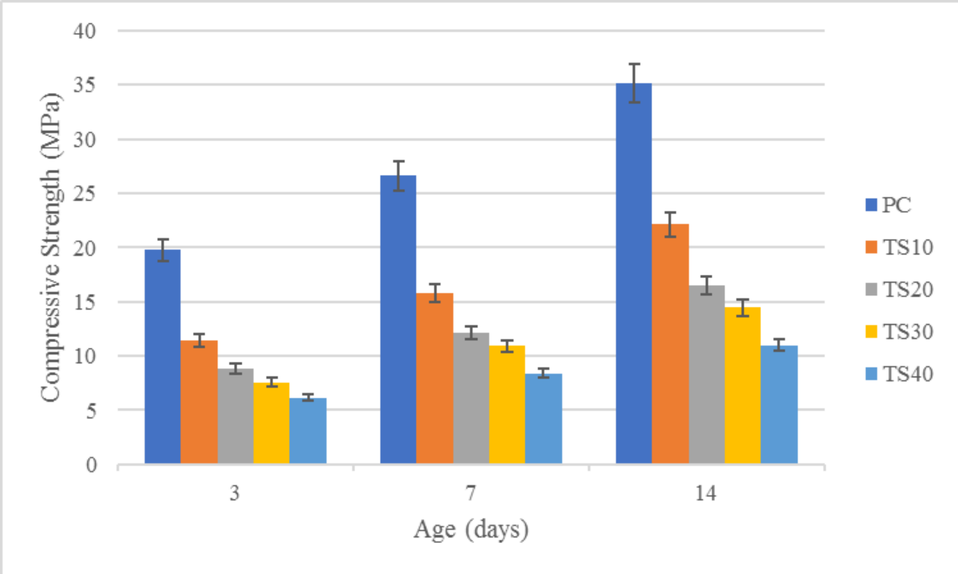
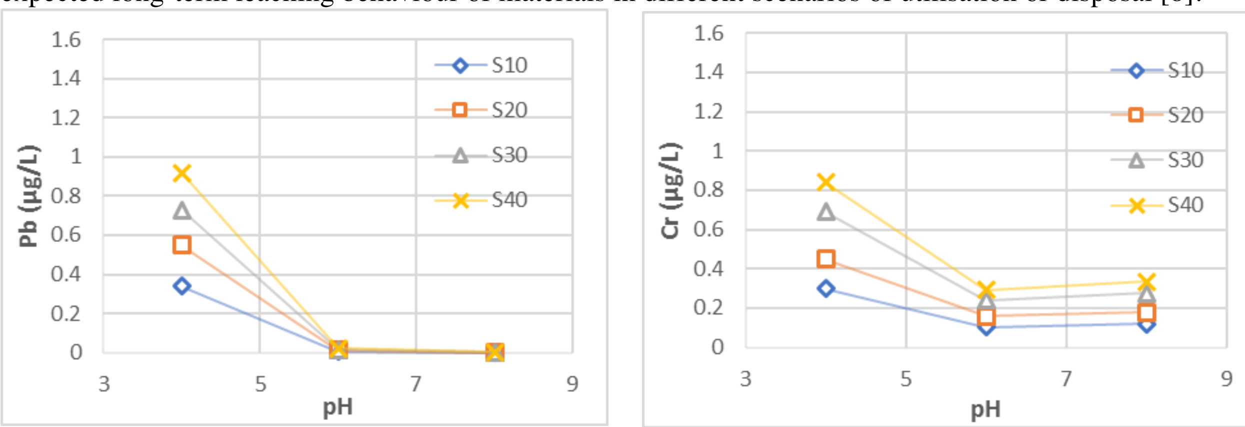


Figure 4. Compressive Strength of cement mortar

Decrease of compressive strength of mortar samples, with the increase of tin slag content is due to several reasons: 1). Cement dilution by less active component. 2). Increase of water demand (due to less water absorption of tin slag) and easily workable mixtures (less viscous mixtures than OPC), 3). The content of calcium hydroxide ($Ca(OH)_2$) and chemically bounded water ($W_{c.bw}$) in hardened cement paste decrease with increasing slag content. The lower compressive strength of slag-cement also corresponding to the lower amount of CSH and Portlandite as a hydration product as detected by XRD. Portlandite or calcium hydroxide give slightly strength to cement paste. Decrease of mechanical properties also attributed to higher levels of iron oxides, zinc oxides, and traces of sulphur in the chemical composition of the slag.

3.4 Leaching Behaviour

The pH dependence test CEN/TS 14429, can assess the metal matter release at different pH values [5]. The evaluation of pH dependence of leaching test is one of the important tools in the assessment of the expected long-term leaching behaviour of materials in different scenarios of utilisation or disposal [8].



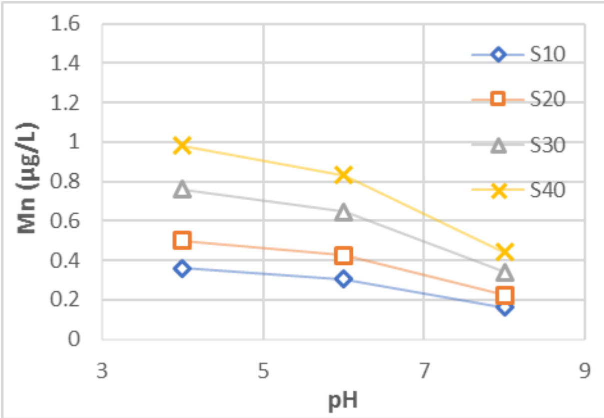


Figure 5. Pb, Cr, and Mn concentration in leachates solution

Figure 5 shows the concentration of Pb, Cr, and Mn in leachate solution. Concentration of Pb, Cr, and Mn increasing with the increasing amount of ACTS replacement in cement paste, due to higher amount of Pb, Cr and Mn, than in OPC. Concentration of Cr, Pb, and Mn in aqueous leachates of cement composite increased with decreasing pH. The highest Cr concentration occurred in S40 leachate samples with 0.84 µg/L in pH = 4. Pb and Mn also show same leaching behaviour with Cr. The highest concentration of Pb and Mn in leachate solution occurred in S40 leachate sample with pH test = 4 (0.92 µg/L and 0.98 µg/L). The trace elements Pb, Cr, and Mn in slag-cement composite tend to soluble in acid solution. This characteristic due to dissolving of some $Ca(OH)_2$ and C-S-H in acidic solution [15, 16].

4. Conclusions

ACTS is a by-product of tin production that has major constituent SiO_2, Al_2O_3, CaO, Fe_2O_3, and TiO_2. Portlandite, C-S-H, Calcite, and Ettringite are the major phase that detected in both OPC and slag-cement composite according to the XRD evaluation. Slag-cement composite also shows quartz phase that not detected in OPC. Replacement of OPC with ACTS decreasing the compressive strength of the cement mortar. The trace elements Pb, Cr, and Mn in slag-cement composite tend to soluble in acid environment, due to dissolving of $Ca(OH)_2$ C-S-H.

Acknowledgment
This research was supported by DRPM Universitas Indonesia with the PITTA program.

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