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Formulation of Portland Composite Cement Using Waste Glass as a Supplementary Cementitious Material

Ria Julyana Manullang[1, a)], Tjokorde Walmiki Samadhi[2, b)] and Aprilina Purbasari [3]

[1]Center for Ceramics, Ministry of Industry of Republic of Indonesia, Indonesia
[2]Faculty of Industrial Technology, Institut Teknologi Bandung, Indonesia
[3]Faculty of Engineering, Universitas Diponegoro, Indonesia

[a)]ria_julyana@yahoo.com
[b)]Corresponding author: twsamadhi@che.itb.ac.id

Abstract. Utilization of waste glass in cement is an attractive options because of its pozzolanic behaviour and the market of glass-composite cement is potentially available. The objective of this research is to evaluate the formulation of waste glass as supplementary cementitious material (SCM) by an extreme vertices mixture experiment, in which clinker, waste glass and gypsum proportions are chosen as experimental variables. The composite cements were synthesized by mixing all of powder materials in jar mill. The compressive strength of the composite cement mortars after being cured for 28 days ranges between 229 to 268 kg/cm2. Composite cement mortars exhibit lower compressive strength than ordinary Portland cement (OPC) mortars but is still capable of meeting the SNI 15-7064-2004 standards. The highest compressive strength is obtained by shifting the cement blend composition to the direction of increasing clinker and gypsum proportions as well as reducing glass proportion. The lower compressive strength of composite cement is caused by expansion due to ettringite and ASR gel. Based on the experimental result, the composite cement containing 80% clinker, 15% glass and 5% gypsum has the highest compressive strength. As such, the preliminary technical feasibility of reuse of waste glass as SCM has been confirmed.

INTRODUCTION

The cement manufacturing sector is a major contributor to the global carbon dioxide (CO2) emission. CO2 is produced by the raw materials calcination process in clinker production, and also by fossil fuel combustion to generate heat and power. CO2 emissions from cement production currently contribute about 5% of anthropogenic global CO2 emissions [1]. Therefore, it is important to decrease CO2 emission by producing composite cement which has less content of clinker. Composite cement is produced by replacing some of clinker with supplementary cementitious materials (SCM) such as fly ash, metallurgical slag, silica fume, and lime. Most of these SCMs are waste with pozzolanic properties which improve cement performance.

Nowadays, there is a growing need for alternative materials that can be used as SCM. One of the promising materials for SCM application is waste glass., While the amount of waste glass is quite abundant and the pozzolanic behaviour of glass could improve cement performance, its use as SCM has not been applied on a commercial scale. In 2008, approximately 0.7 millions ton of waste glass were collected annually in Indonesian urban areas. This volume is produced by 26 major cities in Indonesia, and is considered as a major solid waste disposal problem in several municipalities [2]. Most of these waste glasses are sent to landfill and could not be recycled due to their impurities and mixed colour. Therefore, an alternative application for mixed waste glass needs to be developed.

Utilization of waste glass in cement is an attractive options because of the large quantity and low quality requirements. Studies which have been published on waste glass are more about its pozzolanic characteristics as aggregate. In general, the effect of glass aggregate depends on its fineness. The use of coarse glass was not

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satisfactory, resulting in marked strength regression and excessive expansion [3-5]. However, glass powders with a microscale size distribution produce an improvement in strength and transport properties of mortar and concrete [6-9]. Research on waste glass as SCM is still rare, whereas the market of glass-composite cement is potentially available.

Glass has amorphous atomic structure and high silica content which similar to other SCM. Finely ground glass shows pozzolanic behaviour. The pozzolanic properties of glass are first notable at particle sizes below approximately 300 μm [10-11]. Pozzolanic activity occurs when a mixture of aluminous siliceous materials and calcium hydroxide create a product which has similar cementitious properties to the cement hydration product (Calcium Silicate Hydrate (CSH)). However, the possibility of other reactions such as the alkali silica reaction (ASR) should also be concerned as it produce an ASR gel in cement. The ASR and pozzolanic reaction share the same initial materials and also have reaction products with similar chemical compositions but very different physical characteristics. The pozzolanic reaction provides high calcium and low alkali material with properties similar to CSH, while the ASR gel has high alkalis but low calcium and does not contribute to cement strength. ASR gel can absorb water and expand to create a pressure which can cause deterioration in cement matrix. The selectivity of both reactions is affected by several controlling factors including particle size of glass, pore solution of cement and chemical composition [12-15].

In this study, the characteristic of composite cement containing waste glass especially the compressive strength was analyzed statistically using analysis of variance (ANOVA). Statistical modelling approaches are commonly used to identify the relative significance of primary mixture parameters and their coupled effects on relevant properties of cement. Experiment was designed with an extreme vertices design mixture. Waste glass is directly mixed and contact with clinker and gypsum. Thus, the effect of each component as well as the interaction of all component could be investigated more briefly.

EXPERIMENTAL

Materials

Materials selected for this study are Portland cement clinker, waste glass, and gypsum. The clinker was produced by PT. Holcim cement manufacturer in Bogor area, with particle sizes between 1 to 3 cm in diameter. Waste glass was obtained by grinding broken soda lime silicate (SLS) window glasses from a testing laboratory at the Center for Ceramics in Bandung. Gypsum was purchased from local supplier. Clinker and waste glass were processed by crushing and grinding in a jar mill in the laboratory, followed by sieving the ground powders to the desired particle size. In this study, ground glass and clinker have particle sizes less than 150 μm. The chemical composition of all materials were measured by using X-Ray Fluorescence (XRF) spectrometer (ADVANT XP Thermo ARL9900) and are given in Table 1.

TABLE 1. Chemical composition of raw materials.

Oxide	Clinker (%)	Glass (%)	Gypsum (%)
SiO2	20.23	70.27	1.27
TiO2	0.259	0.0317	0.0222
Al2O3	4.96	1.47	0.543
Fe2O3	3.58	0.138	0.157
MnO	0.046	0.0066	-
CaO	66.33	8.66	46.29
MgO	1.96	4.69	0.169
Na2O	0.304	13.8	-
K2O	0.793	0.322	0.0954
P2O5	0.0716	0.0608	-
SO3	0.707	0.202	43.79
LOI	0.32	0.3	7.5

Specimen Preparation

The Portland composite cements were prepared by mixing of clinker, glass waste and gypsum in jar mill for one hour. The composite cement then were mixed with sand at a sand-cement ratio of 2.75 for the preparation of mortars. Water to cement mass ratio of 0.484 was maintained throughout the research. The composite cement mortar were then cast into cubes measuring 50 x 50 x 50 mm and demolded 24 hours after casting to be used in compressive strength measurement on a uniaxial load tester. The mortars were tested according to the SNI 15-2049-2004 standard method for Portland cement after being cured for 28 days. As reference, compressive strength of ordinary Portland cement (OPC) mortar was also measured.

Experimental Design

In this work, the Minitab 16.0 statistical software package was used to develop an extreme vertices mixture design to identify the relative significance effect of primary mixture parameters and their coupled effects on relevant properties of cement. The experimental factors are components of the mixture forming a ternary system: clinker, glass and gypsum. These components are not independent to each other and the proportions of a mixture must sum up to 100%. The composition of three components are constrained by upper or lower or both boundary conditions. The boundary conditions are set based on studies from published works which suggest that the optimum waste glass content is approximately 20% mass [11-12, 14]. The compositional boundary conditions for the composite cement system are 70-83% clinker, 15-25% waste glass, and 2-5% gypsum. Gypsum proportion is set in a narrow range , because of SO_3 limitation content according to SNI 15-7064-2004 that is than 4%. The experimental area is shown in **Fig. 1.**

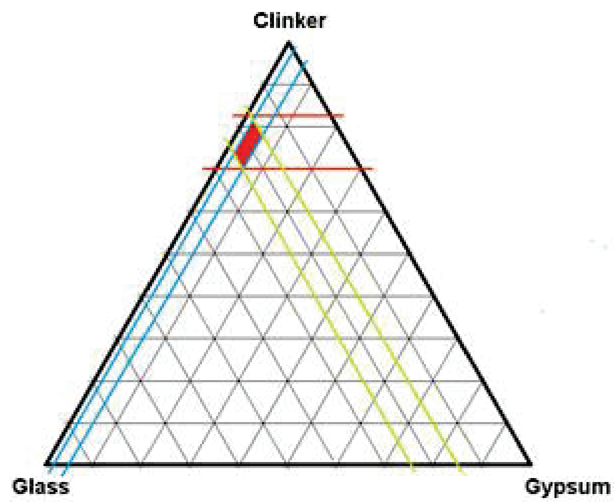

FIGURE 1. Mixture design field with boundary limitation for a three component system.

The Minitab software generated nine runs, consisting of four runs at each corner of the experimental area, and five runs in the interior of the area, where the compressive strength of mortars were measured. Each experimental run were repeated twice. The designed formulations of materials defined by the software and the related experimental results are given in Table 2. The mathematical relationship of the response with three significant independent variables can be approximated by the statistical ANOVA data analysis.

RESULTS AND DISCUSSION

The compressive strength is the most important property which defines the use of cementitious materials. Table 2 contains the compressive strength measurement results for all compositions included in this study. Letters 'A' and 'B' in the sample codes denote the first and second replicate of the run. The compressive strength of the OPC mortar is 323,7 kg/cm2 while the compressive strength of the glass-containing composite cement mortars after being cured for 28 days ranges between 229 to 268 kg/cm2. The composite cement containing 80% clinker, 15% glass and 5%

gypsum has the highest compressive strength among the nine compositions. According to SNI 15-2049-2004 national Indonesian standard, the minimum compressive strength for composite cement after cured for 28 day is 250 kg / cm2. The composite cement mortars exhibit lower compressive strength than OPC mortars, but at least a portion of glass-containing compositions in Table 2 still meets the requirement of SNI 15-7064-2004.

TABLE 2. Extreme vertices design for three-component mixture of clinker, glass and gypsum with the experimental results.

Run	Sample Code	Clinker, X_1 (%)	Glass, X_2 (%)	Gypsum, X_3 (%)	Compressive strength (Kg/cm2)
1	SK8315A	83	15	2	267.31
2	SK8315B	83	15	2	265.93
3	SK7325A	73	25	2	242.37
4	SK7325B	73	25	2	237.41
5	SK7025A	70	25	5	259.76
6	SK7025B	70	25	5	253.97
7	SK8017A	80	17.25	2.75	263.99
8	SK8017B	80	17.25	2.75	264.14
9	SK7475A	74.75	22.5	2.75	229.46
10	SK7475B	74.75	22.5	2.75	232.65
11	SK7650A	76.5	20	3.5	234.39
12	SK7650B	76.5	20	3.5	241.14
13	SK7825A	78.25	17.5	4.25	249.95
14	SK7825B	78.25	17.5	4.25	254.32
15	SK7322A	73	22.75	4.25	234.66
16	SK7322B	73	22.75	4.25	238.88
17	SK8015A	80	15	5	263.59
18	SK8015B	80	15	5	268.04

The lower compressive strength is caused by expansion due to ettringite formation. The scanning electron microscopy (SEM) observation on the microstructure of cement as shown in Fig. 2 support this phenomenon. At 28 days, OPC paste has less content and smaller ettringite than the composite cement paste. Ettringite could be a big problem when the formation process occurs after cement hardened. This ettringite is called secondary ettringite. Ettringite is formed due to glass present that have high alkali content, so that cement pore solution pH will increase. Thus cause small primary ettringete dissolved on pore solution and recrystalized forming secondary ettringite that have bigger size. The presence of secondary ettringite will enhance cement volume thereby increasing the internal stress on cement which cause microcrack and lower strength [16].

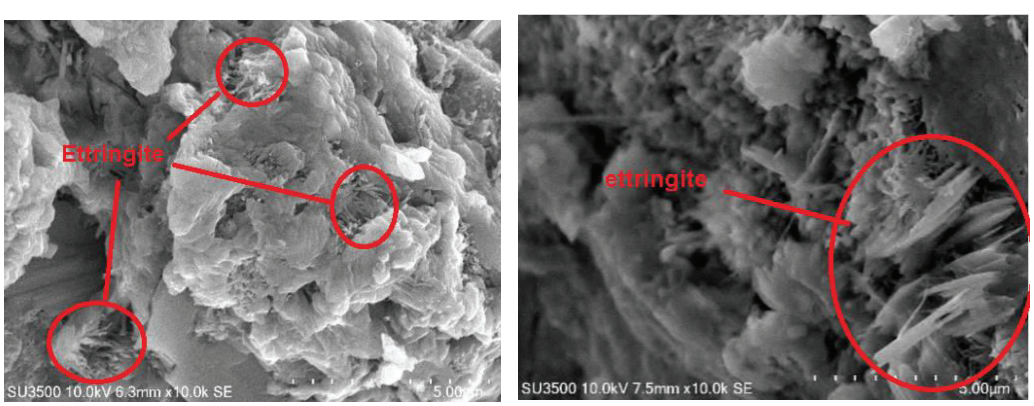

FIGURE 2. SEM observation on cement paste at 28 days (a) OPC; (b) Portland composite cement SK 8015

The decreased strength is also probably caused by ASR gels. ASR gels combine with the moisture of the media and expansion occurs. This expansion is followed by increase of porosity and would reduce the compressive strength. As argued by Shi and Khmiri [10-11], glass particle sizes under 300 μm does not promote ASR. However, if there is reactive aggregate in the mixture, the alkali oxide in glass could react with reactive forms of silica in the aggregate though the particle size is quite small. Silica minerals in aggregates are generally stable if they are crystalline and reactive if they are amorphous, but there are exceptions. Tridymite and cristobalite were defined as moderately reactive minerals [17]. These reactive minerals in aggregate affect the occurence of ASR. In this research, silica sand was used as aggregate. However, the potential alkali reactivity of this aggregate has not been studied. Laboratory tests should be done to evaluate the potential alkali reactivity of aggregate according to ASTM C1260 From this test, we could verify whether the aggregate is considered potentially reactive to ASR based on the expansion of aggregate-containing mortar.

Table 3 shows the ANOVA data analysis results as regression coefficients and p-values (probability of finding an effect at least as extreme as the measured data, assuming true null hypothesis) of each mixture model component. Variables with p-values lower than the selected significance level (less than 0.05) were considered as factors of significance. It can be concluded that effects of linear terms and quadratic terms were statistically significant. From the results of ANOVA, it was found that the quadratic model is quite fitted with the experimentally data and also has good statistical characteristics, such as the R^2 and R^2 (pred) of 0.81 and 0.70 which allows us to use this model to present the results and make prediction.

Through regression fitting, with a 95% confidence, the quadratic models were summarized at Eq. (1) as follows :

$$Y = 6.06X_1 + 42.74X_2 - 6.1X_3 - 0.69X_1X_2 \quad (1)$$

where X_1, the amount of clinker (wt.%); X2, the amount of glass (wt.%); and X3, the amount of gypsum (wt.%). The model represents the relative significance of each component, X, on the studied response (compressive strength), Y. From this model, it can be noticed that the compressive strength is most heavily influenced by glass proportion, followed by gypsum proportion, then by clinker proportion, finally the quadratic mixture effects of clinker-glass, pairs.

TABLE 3. Model parameters estimated for the compressive strength of composite cement mortar

Parameter	Regression Coefficient	P-Value
Linear	-	0.001
X1	6.06	-
X2	42.74	-
X3	-6.1	-
Quadratic	-	0.000
X1.X2	-0.69	0.000

To check the adequacy of model, residual plots from the ANOVA analysis are shown in Fig. 3. The normal plot of residuals, Fig. 3.a., indicates that the ANOVA assumption of normally distributed residuals is met. The residuals vs. fitted data points, Fig. 3.b. does not indicate any obvious pattern (other than the mirroring of the residuals which are caused by marginal degree of freedom of the data set). This suggests that the variance in the error terms is constant and the model is valid.

On the quadratic model, there are two effects that determine experimental response that is linear effect and quadratic effect. Each experimental component could have these effects so the influence by the changes of amount each component to experimental response was not linear form. An influence of each component must be evaluated with all linear and quadratic coefficient. Based on positive value of clinker linear regression coefficient, increasing of clinker while keeping the other component constant should improves the compressive strength. However the presence of interaction effect between clinker and glass which resulted the antagonistic effect, so that increasing amount of clinker also decrease cement strength, depends on clinker changes amount. The same thing applied on the other components. Because of each component proportion in mixture is independent, the change of single component could change other component proportion on cement mixture. The estimated linear regression coefficient of glass are much higher than clinker and gypsum proportion. It means the effect of glass proportion is larger than gypsum proportion for the same magnitude of proportion change.

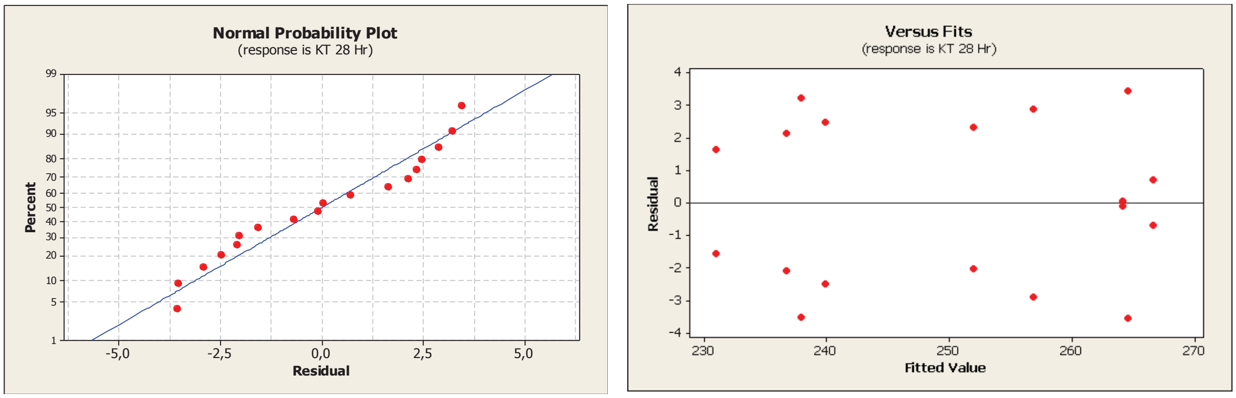

FIGURE 3. Residual plots for checking the validity of ANOVA treatment of the compressive strength data, (a) Normal probability plot; (b) Residual versus fits

To design the formulation of PCC which has the highest compressive strength, all of effects must be concerned. The highest compressive strength is obtained by shifting the cement blend composition to the direction of increasing clinker and gypsum proportions as well as reducing glass proportion. Further research is needed to confirm the optimum compressive strength based on the mathematical model obtained from this experiment.

CONCLUSIONS

The formulation of composite cement utilizing common SLS waste glass has been evaluated through an extreme vertices mixture experiment. The effect of three factors of clinker proportion, glass proportion and gypsum proportion on the compressive strength of composite cement mortars were investigated. In general, composite cement mortars incorporating waste SLS glass exhibit lower compressive strength than ordinary Portland cement (OPC) mortars, but is still capable of meeting the SNI 15-7064-2004 standards. Of the nine blend compositions tested in this work, 80% clinker, 15% glass and 5% gypsum has the highest compressive strength. The highest compressive strength is obtained by shifting the cement blend composition to the direction of increasing clinker and gypsum proportions as well as reducing glass proportion. The lower compressive strength of composite cement is caused by expansion due to ettringite and ASR gel. Further tests should be done to evaluate the potential alkali reactivity of aggregate in order to prevent the occurence of ASR.

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