

화산회 가루를 사용함에 의한 CO₂-저방출 포트랜드-혼합 시멘트 제조

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(접수 2011. 2. 17; 수정 2011. 2. 25; 게재확정 2011. 2. 25)

Portland-Blended Cement with Reduced CO₂ using Trass Pozzolan

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(Received February 17, 2011; Revised February 25, 2011; Accepted February 25, 2011)

요약. 이산화탄소 방출을 줄이기 위해 포트랜드 시멘트 성분 일부를 시멘트 보충재를 혼합해준 시멘트의 제조에 대해 연구하였다. 이산화탄소를 0.18 kg CO₂/kg 정도 줄이기 위해 포트랜드 시멘트에 보충재를 20 wt% 정도 혼합하였다. 이 혼합시멘트의 압축 강도는 포트랜드 시멘트 ASTM C-150의 표준치를 초과하며, 28일간의 굳는 과정에서 37 MPa의 압축 강도를 가졌다. 혼합시멘트의 미세구조는 포트랜드 시멘트와 유사하였다.

주제어: 포트랜드 용재괴, 보충 시멘트 재료, 이산화탄소 방출, 포트랜드-혼합 시멘트, 기계 강도

ABSTRACT: This paper reports the use of supplementary cementing materials (SCMs) derived from local resources, for the partial replacement of Portland cement to reduce CO₂ emission during cement production. Replacement of Portland clinkers up to 20 wt.% with SCMs in normal cements reduced CO₂ emission by 0.18 kg CO₂/kg. The compressive strength exceeded the standard specification for Portland cement ASTM C-150. Blended cement samples containing 20% Portland clinker replacement had compressive strengths of 37 MPa after 28 days of curing time. The microstructure evolution of blended cement at a composition of 80:20 was similar to that of the 100% Portland cement, where the structure between days 28 and 56 reached a steady state. Blended cements with compositions of 70:30 and 60:40 still showed progress of CSH plate formation and the lack of massive structure development. It is shown that the use of supplementary cementing materials could be as one of alternative ways to reduce CO₂ emissions during cement production.

Keywords: Portland clinkers, SCMs, CO₂ emission, Portland-blended cement, Mechanical strength

INTRODUCTION

Since the 19th century, Portland cement has been commonly used in concrete production. Its performance in terms of mechanical strength and durability is still the best available. Unfortunately, the sintering process of Portland cement has become a major contributor to environmental problems because of resulting CO₂ emission. Burning the main materials, including limestone, and fossil fuels, such as coal, oil or petroleum cokes, has the potential to release approximately 0.8 tons of CO₂ per ton of clinkers¹. As sustainability becomes a global goal, as outlined by the inter-governmental Panel Group for Climate Change, the current standard technology used in the cement industry must be redesigned in such a way as to achieve a reduction target that is in line with reducing emissions by 50%

by 2050.²

Supplementary Cementing Materials (SCMs) have been introduced and are commonly used to partially replace Portland cement. These materials have been standardised, and the results are reported in the European Cement Standard EN 197-1:2000, *Composition, specification and conformity criteria for common cements*. Blended cement is produced by mixing Portland clinkers with Supplementary Cementing Materials (SCMs), which could be natural or artificial and include slag, fly ash, silica fume, metakaolin, and rice husk ash.^{3,4} Research on Indian clays has demonstrated that the burning of clays to form metakaolin produces a pozzolan with good reactivity. Replacement of 10% of the Portland cement with metakaolin resulted in a better strength than 100% Portland cement.⁵ Because the utilisation of non-renewable

resources like Portland clinkers is reduced in blended cements, the negative impact of cement use on the environment is reduced, and primary raw materials are conserved. Moreover, the durability of concrete structures constructed using blended cement must be assessed. Since the mid-1990s, the production of blended cement has been increased with the use of two or three SCMs. The development of ternary and quaternary blended cement systems has motivated considerable research in this field because of the advantages of the blended cement systems. Therefore, combinations of various SCMs, such as fly ash-silica fume and fly ash-slag, have been developed and are commonly used in several countries.⁶ The optimum amount of pozzolan used in blended cement to obtain the maximum strength is approximately 0.28/1 pozzolan/cement. The efficiency decreases with increases in the pozzolan-to-cement ratio.^{7,8}

In this paper, we report the possibility of using natural pozzolan trass, which is abundantly available in Indonesia. The results of replacing up to 40% Portland cement with trass are reported. The main objective was to study the mechanical strength over a wide range of trass percentages. The durability properties were investigated through micro-structure and mechanical strength properties.

EXPERIMENT

Trass samples from different sources were characterised by XRF (ARL 8480) and XRD (Bruker D4 with TOPAS software) to identify their chemical and mineral compositions. However, in the current research, samples from only one source were used in the experiments. Trass materials were ground together with Portland clinkers and gypsum to produce blended cement. Cement samples in which 20, 30 or 40% of the Portland clinkers were replaced were prepared. The compressive strengths of the resulting cements mortar were measured in accordance with ASTM standard C-109, and the measured mechanical strengths were then compared with the standard cement specification for Portland cement ASTM C-150. The microstructures of the cement pastes were investigated using a Jeol Scanning Electron Microscope, JSM-5310LV. Prior to observation, a fractured surface of a sample was coated with Au using a JFC-1200 Fine Coater to increase the conductivity. Phase identification was performed by XRD to support the microstructure data. The water-to-cement ratio (W/C) used to prepare the mortar and paste was 0.485

RESULTS AND DISCUSSION

Performance of trass in blended cement

The chemical and mineral compositions of trass are listed in *Table 1*. The main content of trass is aluminium silicates, which exist in crystalline and non-crystalline (amorphous) phases. Mineral analysis by XRD showed that the dominant minerals were andesine (group of feldspar) and quartz, which constituted 36.13% and 15.55% of the trass, respectively. The non-crystalline phase, which could be made up of silicon oxides or aluminium silicates, was found to be the main component, accounting for 47.60%. Quartz is crystalline silicon oxide, and this mineral is considered to be inert because no chemical reaction with cement is expected. Both andesine and the amorphous phase in trass play important roles in the reaction with Portland cement. Compared with metakaolin and fly ash, trass has higher silica content and lower alumina content.⁹ On the other hand, blast furnace slag has a high calcium oxide content, approximately 35%, and contains silicon and aluminium oxides, which have self-cementing properties.⁴

As cement mainly contains calcium silicates and aluminates, trass material is suitable for use as an SCM to partially replace Portland clinkers. The role of trass in cement is not as a filler but as a material that reacts with Ca(OH)₂ resulting from Portland cement hydration. The reaction of Portland clinkers with Ca(OH)₂ produces calcium silicate hydrates, which are responsible for the mechanical strength of cement. It is expected that reactive trass will contribute to the mechanical strength of blended cement.

Microstructure evolution of blended cement

Cement acts as a binder when it reacts with water to form a massive structure of hydration products. This massive structure is made up of calcium silicate hydrate

Table 1. Chemical and mineral composition of the sample of trass used in these experiments

Chemical Composition	Wt %	Mineral Composition	Wt %
SiO ₂	67.41	Quartz	15.55
Al ₂ O ₃	15.81	Andesine	36.13
Fe ₂ O ₃	2.99	Muscovite	0.14
CaO	2.14	Kaolinite	0.23
MgO	0.53	Montmorillonite	0.35
LOI	4.95	Amorphous phase	47.60
Na ₂ O	2.55		
K ₂ O	3.01		

(CSH), which grows as plate-like structures. At an early point in the hydration process, the structure is still not dense, as demonstrated by the presence of pores or voids. The hydration mechanism can be investigated through the development of the microstructure of the cement paste at different time points during the hydration process. Porosity decreases with hydration time, as more CSH is formed.^{10,11} In the following section, the microstructure evolution of blended cement made from Portland cement and trass at days 7, 28 and 56 of hydration is presented.

The microstructures of CSH in cement pastes at days 7, 28 and 56 days for the 100% Portland cement and blended cements are represented in *Fig. 1*. Micrographs of the 100% Portland cement show that it has a very dense structure because the CSH starts to develop at early time points and continues to develop until a dense structure is present at late time points (*Fig. 1(a)*). Denser structures make concrete more durable because it is resistant to environmental attack. A structure similar to that shown in *Fig. 1(b)* was observed in a blended 80:20 cement sample, indicating that Portland cement hydration is still dominant at 20% substitution. When the substitution of Portland cement with trass increased, different structures were observed. *Fig. 1(c)* and (d) show blended cement samples with ratios of 70:30 and 60:40; these images show that the reaction between trass and $\text{Ca}(\text{OH})_2$ had not started yet, as indicated the abundance of hexagonal crystals of $\text{Ca}(\text{OH})_2$ or Portlandite. This result implies that the formation of CSH plates was not well developed and that voids or pores were still dominant.

The microstructure of 28-day paste showed a more developed structure for all pastes, especially for 100% Portland cement and blended 80:20 cement, as shown by *Fig. 1(a)* and (b). CSH plates were massive at this time point and were well ordered, though voids were still clearly present. As the hydration of blended 70:30 and 60:40 cements occurred at a later time point, after 28 days of hydration, the microstructures were not well developed, and voids were still dominant (*Fig. 1(c)* & (d)).

In concrete manufacturing, 28 days is considered to be the age at which the concrete has achieved a dense structure and after which no more significant development is expected. The microstructures at hydration times of 28 to 56 days for Portland cement show that this material had already achieved steady state, as shown in *Fig. 1(a)*. The microstructures of blended 80:20 cement were similar to that for the 100% Portland cement, as the 28- to 56-day structures had reached steady state (*Fig. 1(b)*). On the other hand, the blended cements with compositions of

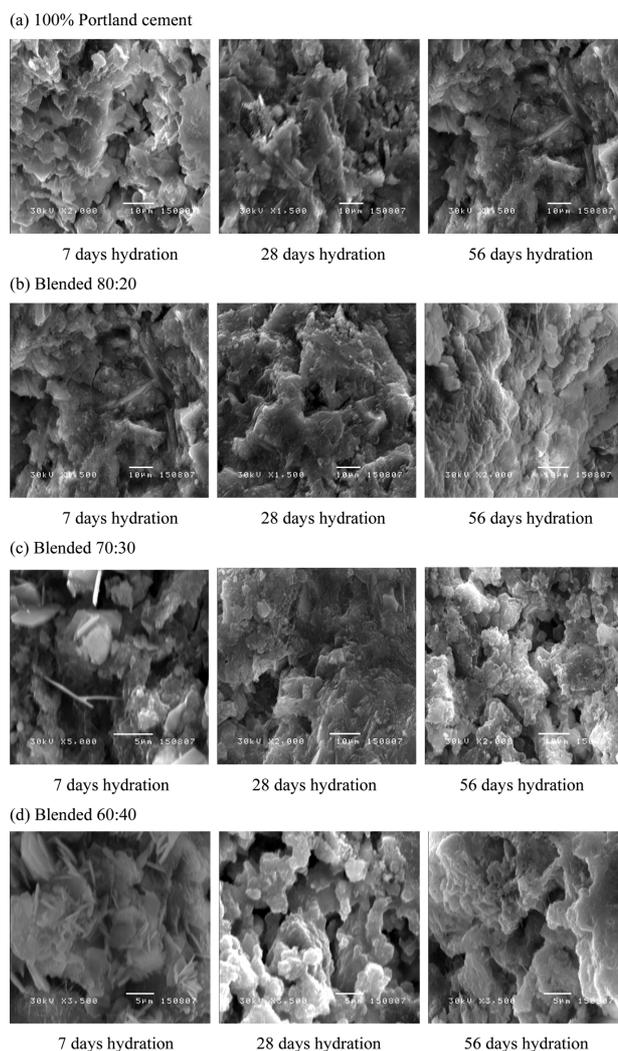


Fig. 1. Micrographs of blended cement pastes after 7, 28 and 56 days of hydration. (a). 100% Portland cement, (b). Blended 80:20, (c). Blended 70:30 and (d) Blended 60:40.

70:30 and 60:40 still showed progress in CSH plate formation, and massive structure had not yet developed at an age of 56 days (*Fig. 1(c)*, and (d)).

Referring to the observation of microstructures as highlighted above, samples of 100% Portland and blended cements had different densifications. In all cases, the evolution of the microstructure with hydration time indicated that the differences in densification were due to a retardation of CSH formation in blended cements. Partial substitution of Portland clinkers with trass, up to 20%, had no significant effect on the speed of densification; however, this was not the case for blended cements containing more than 20% trass, for which the retardation of the CSH reaction was obvious. Samples of blended cements with com-

positions of 80:20, 70:30 and 60:40 still showed progress of CSH plate formation at 56 days of hydration time, and massive structure had not formed at this time point. Considering that the reaction of trass and Ca(OH)₂ should take place, it is possible that this reaction occurs at hydration times greater than 56 days. This hypothesis is in line with the statement that ternary mixtures undergo more balanced reactions, resulting in better performance and higher ultimate strength.³

Observation of the microstructures of the blended cement made from Portland clinkers and trass showed that replacement of up to 20% of the Portland clinkers with trass did not negatively affect the development of a massive structure in cement pastes. This statement was later confirmed with mechanical strength testing.

Phase identification was carried out for powder cement and pastes after 56 days of hydration time. Fig. 2 compares the diffraction profiles of Portland cement and blended cements at 56 days. A new phase of Portlandite, Ca(OH)₂, was identified in both Portland and blended cements. As the hydration time increased, the fraction of Portland cement decreased, and new phases of CSH and Ca(OH)₂ were formed.^{8,12}

Portlandite, which is a phase resulting from cement hydration, remained in the pores. In the blended cement, Ca(OH)₂ will react with the silicates present in trass. If this reaction takes place effectively, it should contribute directly to an increase in the ultimate strength of the cement. The intensity of the Portlandite phase at 2 theta 18 degrees was still quite high, indicating that the pozzolanic reaction between Ca(OH)₂ and trass still occurred at time points after 56 days of hydration.

Mechanical Strength of Blended Cement

Fig. 3 shows the compressive strength of 100% Portland cements compared with that of blended cements con-

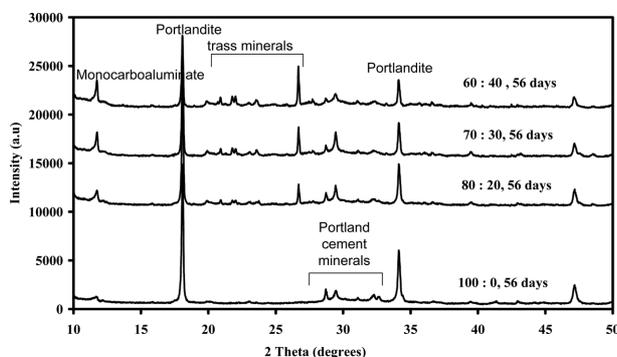


Fig. 2. Diffraction profiles of Portland and blended cement pastes after 56 days of hydration.

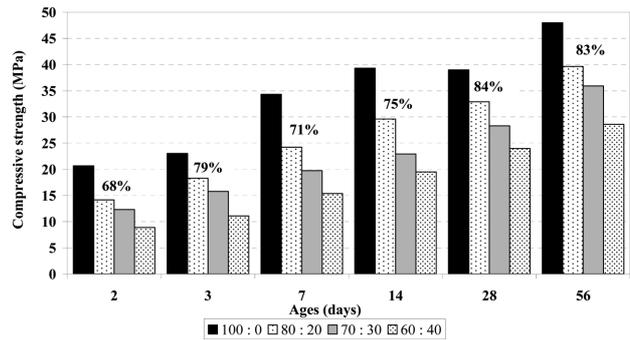


Fig. 3. Strength development of blended cements.

taining 20, 30 or 40% trass. Fig. 3 shows that compressive strengths of the blended cements decreased as the clinker content decreased. This decrease was almost proportional to the percentage of clinker replaced by trass. Replacement of 20% Portland cement reduced the compressive strength by 16% at 28 days. However, the compressive strength at 28 days still met the minimum requirement of 25 Mpa set by ASTM.

The results of this experiment show that replacement of 20% Portland cement with trass resulted in compressive strength 24, 31, and 37 MPa at 3, 7 and 28 days, respectively. These values comply with ASTM C 150: Standard Cement Specification for Portland Cement. Replacement of 30 and 40% of clinkers resulted in lower compressive strengths compared with that of the 20% blend; these blends are considered to be inadequate because of the low compressive strengths. Ternary blended cements must be investigated to improve the mechanical strength for replacements higher than 20%.

Blended cement with reduced CO₂

Production of Portland clinkers produces CO₂, both from the raw materials and from the fuel used. During the sintering process, limestone is the main raw material, and CaCO₃ produces 0.53 kg CO₂/kg clinker. The fuel used produces between 0.37 and 0.6 kg CO₂/kg clinker.^{1,2} Such variation in the amount of CO₂ produced by fuels is the result of the type and efficiency of the process. The modern system of clinker processing has a specific heat consumption of 3.1 GJ/t clinker and is based on burning carbon-based fuels such as oil, coal or petroleum coke. According to the above data, the total CO₂ emission from clinker processing is in the range of 0.9 to 1.1 kg CO₂/kg clinkers.^{1,2}

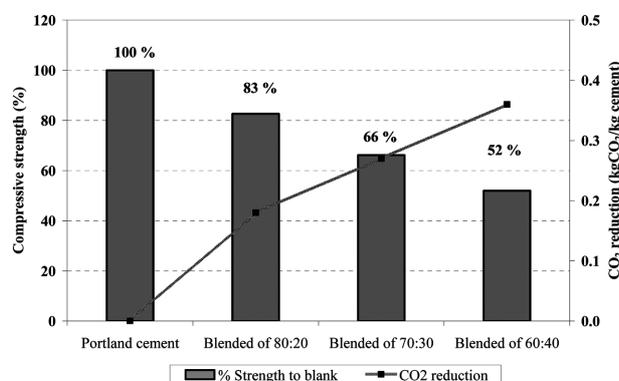
The cement plant that produced the clinkers used in this experiment had a specific consumption of 3.0 GJ/t clinker

Table 2. Data on CO₂ emission in the cement plant used in this study

Item	Amount
CO ₂ in limestone raw material	42%
CO ₂ if 82% limestone used	0.3444 kg/kg material
Clinker-to-raw material ratio	0.66
CO ₂ produced from raw materials	0.53 kg/kg clinker
Plant specific heat consumption	3 GJ/ton
CO ₂ derived from fuels	0.37 kg/kg clinker approx.
Total CO ₂ emission	0.90 kg/kg cement

using coal as the main fuel. The calculation of the amount of CO₂ produced by clinker processing is presented in Table 2. Because the cement production process still emitted 0.9 kg CO₂/kg cement, technological and scientific advances must be made to reduce CO₂ emissions while producing cement that meets international quality standards.

One way to reduce CO₂ emission in cement production is to use a suitable SCM to partially replace Portland clinkers. In this experiment, trass was used to replace Portland clinkers. Based the CO₂ emission data in Table 2, it follows that CO₂ reductions of 0.18, 0.27 and 0.36 T/T cement would result from using 20, 30 and 40% clinker replacement, respectively. The CO₂ emission reduction and the corresponding reduction in ultimate compressive strength for partially trass-substituted Portland cements are shown in Fig. 4. The results indicate that replacement of 20% clinkers by trass results in a product with 83% of the compressive strength of Portland cement with an associated CO₂ reduction of 0.18 kg/kg cement. Replacement of 30% and 40% of clinkers with trass resulted in higher CO₂ reduction values, but their respective compressive strengths were only 66% and 52% of that of the original Portland cement, respectively, which are considered too low.

**Fig. 4.** Percent ultimate strength of blended cement relative to Portland cement and CO₂ reduction.

CONCLUSIONS

The current example of blended cement made of Portland cement and trass clearly demonstrates that reductions in CO₂ emissions during cement production could be achieved through the use of supplementary cementing materials. The total CO₂ emitted associated with the clinker samples used in this experiment was 0.9 kg/kg, and replacement of 20, 30 and 40% of clinkers would result in reductions in CO₂ emissions of 0.18 to 0.36 kg/kg cement. The effectiveness of the replacement depends on the reactivity of the alternative material used. In this experiment, replacement of 20% Portland clinkers with trass was considered optimal, with the cement still having a good mechanical strength of 37 Mpa after 28 days of curing time.

Acknowledgements. I gratefully acknowledge the support of the Postgraduate program of Materials Science, Universitas Indonesia, for research facilities. I would also like to thank PT. Indocement Tunggal Prakarsa for the use of laboratory facilities and for the data provided for this paper.

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