Eco-cement production with alternative resources: recycling solution for shells ashes, organic husk ashes, organic waste ashes, and industrial sludge waste

N Citrasari, N G Pratiwi, S Hariyanto and L S Octavia
Environmental Science and Technology, Department of Biology, Faculty of Science and Technology, Airlangga University, Indonesia

Email: nita-c@fst.unair.ac.id

Abstract. This study aimed to determine the ratio of samples A, B, C, and D containing the combination from shells ashes, rice husk ashes, organic waste ashes, Lapindo mud, and industrial sludge waste as the chosen ecocement according to the closest value of compressive strength to SNI 15 2049 2004 on Portland Cement. Semen Gresik type OPC was used for blank sample. Data analysis was divided into two parts. Raw material analysis was done to determine CaO contained in shells ashes and SiO₂ and Al₂O₃ contained in rice husk ashes, organic waste ashes, Lapindo mud, and industrial sludge waste using AAS. Product analysis was done to determine the powder density and compressive strength value in 3 days cubic mortar sample with the length of each side of 50 mm. The result of CaO contained in shell ashes was 81.57%. The highest, SiO₂ and Al₂O₃, were 68.06% in rice husk ashes and 39.01% in industrial sludge waste. Sample A was chosen as ecocement according to the density and compressive strength values of 2.2 g/mL and 28.20 kg/cm², respectively. Based on SNI 15 2049 2004 on Portland Cement, the compressive strength of Sample A complies with the compressive strength of Portland Cement type IV.

1. Introduction
Indonesia's national cement consumption has shown an increase with the average growth rising up to 6.79%. By the end of 2012, the growth had dipped to 2.330 million, though this was later followed by consistent increases [1]. Cement is an important commodity for the national development. Thus, the use of alternative cement raw materials is a challenge for this industry. In spite of the raw resources that are available in nature, industrial waste also has an opportunity to be recycled as an alternative source for cement materials [2].

The eco-cement is a new type of cement that is not included in the five types of Portland cement (Types I, II, III, and IV, and V). Through recycling household waste ashes as an additional material in the cement, Japan has become one of the countries that use eco-cement [3]. Eco-cement can easily be found in pedestrian pavement blocks. Materials that can be recycled as the resources of eco-cement include: shells, organic waste, rice husk, Lapindo mud (the Sidoarjo mud), and industrial sludge. With a 98.7% CaO content, shells have a high potential to be recycled as an alternative resource [4]. Another type of waste that can be recycled is organic waste such as leaves. After being burned, the ashes of organic waste contain 46% SiO₂ [3] and rice husks with their high silica level that reaches 73.7% [5]. Other raw materials that are recyclable as the substitutes for adhesive are the Lapindo mud and industrial sludge wastes that are currently abundant in quantity. Lapindo mud has a high Al, 2O₃,
and FeO content. However, the CaO content is still considered to be low. To recycle it, an additional element, which is CaO in this research, is required [6]. Therefore, this research aimed to determine the required ratio of selected materials. Eco-cement is expected to be an alternative for waste processing and raw resources for cement manufacture in Indonesia, so that it may fulfill the required needs for national development.

2. Research Methods

The materials used were shells obtained from Kenjeran Beach, Surabaya, East Java; organic waste such as leaves collected from the yard of Faculty of Science and Technology Universitas Airlangga; rice husk from Benjeng, Gresik, East Java; mud from the Sidoarjo mudflow (Lapindo), industrial waste from PT. Petrobidada, Gresik, East Java; sand, and water. The tools used were barrels, stoves, gas tanks, gunny sacks, mortar and pestle, 200 mesh sieve, plastic clips, digital scales, Le Chatelier vessels, mixers, mortar cast, digital thermometers, and compressive strength analysis tool.

2.1. Preparation of materials

Seashells, leaf litter, and rice husk were burned for 8 hours at 550°C and then crushed by using pounders. Lapindo mud and industrial sludge were dried in an oven at 105°C for 24 hours. All the materials were then filtered using 200 mesh sieve.

2.2. Analysis of raw materials

The CaO content in shell ashes was then analyzed. As for rice husk ashes, Lapindo mud, and factory waste sludge, the SiO2 and Al2O3 content were analyzed using the Atomic Absorption Spectrophotometry (AAS) method.

2.3. Sampling

The sample variation was done as follows:
1. Blank sample: OPC cement from Semen Gresik
2. Code A: 49.1% shell ashes; 49.1% organic waste ashes; 1.8% Lapindo mud.
3. Code B: 49.1% shell ashes; 49.1% organic waste ashes; 1.8% industrial sludge.
4. Code C: 49.1% shell ashes; 49.1% rice husk ashes; 1.8% Lapindo mud.
5. Code D: 49.1% shell ashes; 49.1% rice husk ashes; 1.8% industrial sludge waste.

2.4. Product analysis

There were two physical parameters tested in order to analyze the product:

a. Powder density

The sample taken weighed 60 g. Firstly, kerosene was inserted into the Le Chatelier vessel and the initial volume is measured. Kerosene had been settled for two days before measuring the final volume. The density equation is as follows:

\[ \rho = \frac{m}{(V_a - V_o)} \]  

Description:
- \( \rho \) is the density (g/mL)
- \( m \) is the sample powder mass (g)
- \( V_a \) is the volume of powder + kerosene sample (mL)
- \( V_o \) is the initial volume of kerosene (mL)

b. Pressure strength

The mortar dough was made from 740 g of sample mixture, 2,035 g of sand, and 360 mL of purified water. The dough was casted on a 50 mm cube molds. The mortar used in this research fulfills the national standard (SNI 15 2049 2004) on Portland cement. The tested mortar was 3 days old.

3. Result and Discussion

3.1. Characteristics of raw materials

The results of the chemical characteristics analysis can be seen in Table 1. It can be seen in table 1 that rice husk ashes had the highest SiO2 content (68.06%). The high percentage of SiO2 can be optimized up to 88.92% by performing combustion for one day [7]. On the other hand, industrial sludge waste had the lowest SiO2 with only 17.83%, while Lapindo mud contained 42.56% SiO2. The SiO2 content in the materials above can be optimized by drying and other
chemical treatments. These content values can be improved because they were still lower than the values obtained from Fadli et al. [8], with 46.7%.

| Material            | Unit | Compound Content |
|---------------------|------|------------------|
| Shells ashes        | %    | 81.57            |
| Rice husk ashes     | %    | 68.06 34.70      |
| Organic waste ashes | %    | 21.05 23.81      |
| Lapindo mud         | %    | 42.56 28.90      |
| Industrial sludge   | %    | 17.83 39.01      |

SiO$_2$ plays a pivotal role in the formation of dicalcium silicate (C$_2$S) and tricalcium silicate (C$_3$S), necessary for increasing cement strength value, with cements containing up to 30% SiO$_2$ content [9]. Based on the minimum percentage of SiO$_2$ (20%) in Portland II cement, rice husk ashes, organic waste ashes, and Lapindo mud had already met the required main chemical conditions of the eco-cement, while other types of cement do not require SiO$_2$ in the making. The average content required is usually between 18.6 up to 23.4% [10].

In type II cement, the maximum Al$_2$O$_3$ in the compound is 6%, other types of cement do not require the same amount (SNI 15 2049 2004). Alumina is an important component in a cement compound. With the right quantity during the cement setting time, alumina is able to decrease the clinkering temperature, contributing to the formation of calcium aluminate. Excess quantity of calcium aluminate will weaken the cement [9]. As for the aluminate content, according to Kosmatka et al. [10], the required amount is 2.4 - 6.3%: based on the analysis result, industrial sludge waste had the highest aluminate value (39.01%) while the leaf litter ashes had the lowest value.

Shell ashes were used as the main alternative component to replace limestone. The CaO content of shell ashes was 81.57%. This value has met the required CaO content for cement; 61.1% for eco-cement, and 64.6% for Portland cement [11]. The CaO content in a material can be optimized by increasing the calcination temperature to 700ºC for 2 hours. By using this method, the value of CaO will be able to increase up to 95.62% [12]. In addition to temperature, the size of the combusted particles also affects the CaO content. The calcined shells in this study were still intact, while particles of 0.125 - 0.25 mm had the highest decomposition rate [13].

### 3.2. Product characteristics

There were 2 parameters analyzed: powder density and mortar compressive strength.

1. **Powder Density**

   The powder density values can be seen in Table 2.

   | Sample     | Density (g/mL) |
   |------------|----------------|
   | Blank sample | 3.17           |
   | A          | 2.20           |
   | B          | 2.08           |
   | C          | 2.15           |
   | D          | 2.05           |

2. **Mortar compressive strength**

   The values of mortar compressive strength can be seen in Table 3.

   Based on the research results, it is known that sample A had the highest density and compressive strength of 3.17 g/mL and 28.20 kg/cm$^2$ respectively. Sample D scored the lowest for each parameter with the value of 2.05 g/mL and 24.20 kg/cm$^2$. This suggests that the greater the density, the greater the value of the compressive strength [14]. However, the density value of A is still lower compared to the Blank sample sample.
In this study, the powder used as the sample was 0.074, however, it still needs to be reduced to 45μm (SNI 15 2049 2004). This is because the larger the size of the powder, the less tight the bond of the particles will be, resulting in weak particle contact and the formation of air pores that might reduce sample density [15]. Based on Table 3, no sample ratio exceeded the compressive strength value of the blank sample that consists of clinker and gypsum. However, all four samples had met the minimum requirement of compressive strength of Portland Cement type IV, which does not require a minimum value. Table 3 also explains that sample A had the highest compressive strength value. Sample A had the lowest Al₂O₃ content (52.71%), while sample D has the highest content (73.71%). This shows that the higher the content of Al₂O₃, the lower the compressive strength value due to excess alumina [9].

In addition to the oxide content, the combustion temperature of the clinker should also be considered. Clinker is a slag of calcium silicate minerals that is formed in high temperature combustion of limestone [16]. Clinker combustion temperature reaches 1,425°C on average [17]. Each temperature change produces a different impact on each kiln feed due to chemical and physical processes.

This study used 1,200°C, a solid-state reaction zone in the range between 900° -1,300°C. In this temperature range, the compound C₃S had not yet been formed since it requires higher temperature and greater energy consumption [18]. C₃S is the most abundant mineral in Portland cement and is a major source of mechanical strength. However, this research did not analyze the content of C₃S in the samples combusted at 1,200°C.

3.3. Sample selected as eco-cement

Although all four samples were able to fulfill the requirements for Portland IV cement, this study selected sample A to be used as the alternative material for eco-cement. This choice is based on its highest value in both parameters, powder density, and compressive strength. The eco-cement produced is equivalent to Portland IV cement that can be applied to large structured buildings such as dams. However, this type is rarely used because its content is similar to blended cement [19].

4. Conclusion

It can be concluded that the content of CaO in shell ashes is as much as 81.57%; SiO₂ and Al₂O₃ content in were 21.05% and 23.81% in leaf litter waste; 69.06% and 34.70% in rice husk ashes; 42.56% and 28.90% in Lapindo mud, and 17.83% and 39.01% in industrial sludge. The compressive strength values of samples A, B, C, and D had complied with the national standard (SNI 15 2049 2004) on Portland cement. The density values of the four samples were relatively small. The sample ratio chosen as an eco-cement is based on SNI 15 2049 2004 is sample A. However, it is necessary to engineer the sample both physically and chemically in order to increase the value of its compressive strength so that it may fulfill the further requirements of the national standards.

Reference
[1] Sulistyorini, D. T., Putri, R. W. Y. E., and Indrayani, R. 2013. Kajian Aspek Teknis dan Aspek Ekonomis Proyek Packing Plant PT Semen Indonesia di Banjarmasin. Jurnal Teknik POMITS. Vol. 1, No. 1

[2] Imbabi, M. S., Carrigan, C., and McKenna, S. 2013. Trends and Developments In Green Cement and Concrete Technology. International Journal of Sustainable Built Environment 1
[3] Shinoda, T. and Yokoyama, S. 1999. *Eco-Cement: A New Portland Cement To Solve Municipal and Industrial Waste Problems*. Proceedings of The International Conference of Modern Concrete Materials: Binders, Additions, and Admixtures, Dundee, 1999 (Ed Dhir RK and Dyer TD). Thomas Telford, London, Pp. 17-30

[4] Fachry, R. A., Sari, T. I., and Sthevanie, S. S. 2014. Pengaruh Filler Campuran Silica dan Kulit Kerang Darah Terhadap Sifat Mekanis Kompon Sol Sepatu dari Karet Alam. *Jurnal Teknik Kimia* Vol. 20, No. 3-1-1

[5] Coniwati, P., Srikandhy, R., and Apriliyanti. 2008. Pengaruh Proses Pengerinan, Normalitas HCl, dan Temperatur Pembakaran pada Pembuatan Silika dari Sekam Padi. *Jurnal Teknik Kimia* Vol. 15, No. 1

[6] Mustopa, R. S., and Risanti, D. 2013 Karakterisrik Sifat Fisis Lumpur Panas Sidoarjo dengan Aktivasi Kimia dan Fisika. *Jurnal Teknik POMITS* Vol. 2, No. 2

[7] Ningsih, T., Chairunnisa, R., and Miskah, S. 2012. Pemanfaatan Bahan Additive Abu Sekam Padi Pada Cemeng Portland PT Semen Baturaja (Persero), *Jurnal Teknik Kimia* Vol. 18, No. 4

[8] Fadli, A.F., Tjahjanto, R. T., and Darjito. 2013. Ekstraksi Silika dalam Lumpur Lapindo Menggunakan Metode Kontinyu. *Kimia Student Journal* Vol. 1. No. 2. 182-187

[9] Anonymous. 2014. 8 Main Cement Ingredients & Their Functions. http://civiltoday.com/civil-engineering-materials/cement/10-cement-ingredients-with-function. accessed on April 21st 2016

[10] Kosmatka, S.H., Kerkhoff, B., and Panarese, W.C. 2002 *Design and Control of Concrete Mixtures 14th Edition*. Portland Cement Association, Skokie, IL

[11] Tanaka, S. 2013. Properties of Eco-cement Manufactured Using Large Amount of Municipal Waste Incinerator Ash – A Contribution of Cement Industry in Establishing a Sustainable and Recycling-Based Society. *Third International Conference on Sustainable Construction Materials and Technologies*

[12] Nurdin, N., Zainab, H., Hashim, O., Kasim, F. H., and Abdullah, R. 2015. Effect of Temperature in Calcination Process of Seashells. *Malaysian Journal of Analytical Sciences*. Vol. 19. No. 1. 65-70

[13] Mohamed, M., Yusup, S., and Maitra, S. 2012 Decomposision Study of Calcium Carbonate in Cockle Shell. *Journal of Engineering Science and Technology*. Vol. 7 . No. 1. 1-10

[14] Erakhrumen, A. A., Areghan, S. E., Ogunleye M.B., Larinde S. L., and Odeyale. 2008. Selected Physico-Mechanical Properties of Cementbonded Particleboard Made from Pine (Pinus caribea M.) Sawdust-corr (Cocos nucifera L). Mixture. *Scientific Research Essay.*, Vol 3

[15] Mujatahid. 2010. *Skripsi*, Pengaruh Ukuran Serbuk Aren Terhadap Kekuatan Bending, Densitas, dan Hambatan Panas Komposit semen-Serbuk Aren (Arenga pinnata), Jurusan Teknik Mesin, Fakultas Teknik, Universitas Sebelas Maret, Surakarta

[16] Van Oss, H. G. and Pandovani, A. C. 2003. Cement Manufacture and Environment. *Journal of Industrial Ecology*. Vol. 7. No. 1. 93-126

[17] Moore, D. 2015 Cement Kilns. http://www.cementkilns.co.uk/ck_clinker.html. accessed on April 21st 2016

[18] Guihua, H., Xiaodong, S., and Zhongzi, Xu. 2007. Composition Design for High C3S Cement Clinker and Its Mineral Formation. *Journal of Wuhan University of Technology-Mater. Sci. Ed.* Vol 22. No. 1. 56-60

[19] Thomas, J., and Jennings, H. 2014. *The Science of Concrete*. http://iti.northwestern.edu/cement/index.html. accessed on April 21st 2014