AJChE 2005, Vol. 5, No. 2, 169–175

# Kinetic Consideration of Clinker Formation in Portland Cement Production Using Demolition Rubbles (Concrete, mortar and plaster) Part I : Burning Ability of Raw Mixes

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In general, the main raw materials in Portland cement production are limestone, clay, and corrective materials such as iron sand and silica sand. These raw material come from natural deposits, which are very hard to find in some countries. In this research, Portland cement was made by utilizing the demolition rubble of office and housing buildings. The rubble consists of concrete wastes (mixtures of hydrated Portland cement minerals and some aggregates) and some building bricks as well as mortar/plaster of Portland cement. To meet the cement modulus, which is generally used in Portland cement industries, corrective materials such as limestone (source of CaO) and disposed building bricks are used. The term *burning ability* is used for Portland cement to measure the CaO free content in the cement clinker produced from specified raw material mixes at a specific operating condition of clinkering. The cement modulus used is Lime Saturation Factor (LSF) and Silica Modulus (SM). The minimum CaO free content was found by using LSF: 0.86, SM: 2.14, and clinkering temperature 1400°C for 30 minutes. The cement modulus was made from concrete waste, limestone, and disposed red brick with a weight ratio of 1: 3.489: 0.677.

***Keywords:*** Burning ability, demolition rubble of buildings, Portland cement, *and* raw mixes.

## INTRODUCTION

Portland cement is mainly used in building construction. The raw materials used for Portland cement are limestone and some corrective materials, such as clay, silica sand, and iron sand. All these materials come from natural deposits as nonrenewable resources. The development and renovation of buildings (e.g., offices and houses) disposes off waste materials. Most of these demolition rubble consist of concrete, mortar cement, and building bricks. Physically, concrete and mortar wastes consist of coarse and fine aggregates and hydrated Portland cement. Chemically, hydrated Portland cement in the waste could be dehydrated to convert them into mineral cement compounds again. If all these demolition rubble were collected, they would have the potential to serve as alternative raw material in Portland cement production and as alternative for limestone or for the recovery process of Portland cement minerals ($C_3S$, $C_2S$, and $C_3A$). Using these wastes as raw materials to make Portland cement clinker requires controlling the CaO free in the cement clinker.

CaO free in the clinker should be no more than 2%. The CaO free comes from unreacted CaO (from lime stone, rubbles raw material) and the dissociation $C_3S$ at high temperature. The measure of the CaO free content in the clinker that was produced by burning raw materials mixed for clinker is called *burning ability*. The burning ability of raw material mixes was studied.

Some of the variables used in this research are composition of raw material mixes and clinkering temperature. The composition of the raw material mixes was denoted as lime saturation factor (LSF) and Silica Modulus (SM).

## LITERATURE STUDY

The main mineral constituents for cement clinker are $C_3S$ (alite), $C_2S$ (belite), $C_3A$ (aluminates), and $C_4AF$ (ferrites/brown milerite). The deteriorate constituent is CaO free (Duda 1985, Singh 1997). These minerals, which were formed by the reaction of the main oxides in the raw minerals, were used at high temperatures, from 1,400 to 1,450°C.

The main oxides are: CaO, $Al_2O_3$, $SiO_2$, and $Fe_2O_3$. The others oxides, which are impurities in the Portland cement clinker, are $Na_2O$ and $K_2O$ (as alkali total < 0.60 %), as well as MgO (mineral periclase < 2–2.5 %). The main reaction that occured during the clinkering at around 800°C were as follows (Kohlhaas 1983):

$$\underset{\text{(Clay/ kaolin)}}{Al_2O_3.2SiO_2.2H_2O} \rightarrow \underset{\text{(meta kaolin)}}{Al_2O_3.2SiO_2} + 2H_2O$$

$$Al_2O_3.2SiO_2 \rightarrow Al_2O_3 + O_2$$

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + SiO_2 \rightarrow CaOSiO_2$$

$$CaOSiO_2 + CaO \rightarrow 2\ CaOSiO_2$$

$$CaO + Al_2O_3 \rightarrow CaO\ Al_2O$$

$$CaO + Fe_2O_3 \rightarrow CaO\ Fe_2O_3$$

According to Ghosh (1983), the solid state reaction occured at around 1,200°C:

$$CaO\ Al_2O_3 + 2\ CaO \rightarrow 3\ CaO\ Al_2O_3$$

$$2CaO\ Fe_2O_3 + 2\ CaO + Al_2O_3 \rightarrow 4\ CaO\ Al_2O_3\ Fe_2O_3$$

$$2\ CaO\ Al_2O_3 + 3\ CaO + Fe_2O_3 \rightarrow 4\ CaO\ Al_2O_3Fe_2O_3$$

The mineral alite, $C_3S$ ($3CaOSiO_2$), is formed by the reaction that takes place in the liquid phase of aluminates and ferrates (Ahluwalia et al. 1997). At around 1,400–1,450°C, the reaction can be written as:

$$2\ CaOSiO_2 + CaO \underset{\text{(melt)}}{\rightarrow} 3\ CaOSiO_2$$

The hydration process, which occurs during the concrete or cement paste formation, can be written as follows:

$$2(3\ CaOSiO_2) + 6\ H_2O \rightarrow 3\ CaO_2SiO_2\ 3H_2O + 3\ Ca\ (OH)_2$$

$$2\ (2\ CaOSiO_2) + 4\ H_2O \rightarrow \underset{\text{(tobermorite)}}{3\ CaO_2SiO_2\ 3H_2O} + \underset{\text{(portlandite)}}{Ca\ (OH)_2}$$

$$3CaO\ Al_2O_33CaSO_4 + 32\ H_2O \rightarrow \underset{\text{(ettringgite)}}{3\ CaOAl_2O_33CaSO_4\ 32\ H_2O}$$

Historically, the aggregates used in concrete construction are gravel and sand (river sand). These aggregates consist mostly of feldspar minerals (Anorthite: $CaOAl_2O_3\ SiO_2$ and Albite: $Na_2O\ Al_2O_3\ SiO_2$).

Ghosh (1983) stated that feldspar minerals could be used as sources of $Al_2O_3$ and $SiO_2$. During the burning of feldspar minerals, the decomposition occurs at around 1,150°C (Sumardi 1999) and can be written as follows:

$$(CaO / Na_2O)\ Al_2O_3\ SiO_2 \rightarrow CaO + Na_2O + Al_2O_3 + SiO_2$$

The dehydration process, or the *thermal decomposition*, of concrete and plaster (hydrated cement minerals), according to Sumardi (1999), produces belite, $2CaOSiO_2$, at around 1,100°C.

There are four types of Portland cement, according to the American Society of Testing and Materials (ASTM) classification. The ordinary Portland cement type is widely produced. This type requires a certain mineral cement composition with a typical range of $C_3S$ : 46 %, $C_2S$ : 28%, $C_3A$ 10%, and $C_4AF$ : 10% (Duda 1985).

To use demolition rubble (concrete waste and mortar/plaster waste) as a raw material in clinker cement formation, the cement modulus would have to be used to limit the occurence of CaO free in the clinker. The CaO free in the clinker was characterized by varying the LSF modulus and the SM modulus.

$$LSF = \frac{CaO - (1.65\ Al_2O_3 + 0.35\ Fe_2O_3)}{2.8\ SiO_2}$$

$$SM = \frac{SiO_2}{Al_2O_3 + Fe_2O_3}$$

Christensen (1979) wrote that to get the minimum amount of CaO free, a lower value of SM had to be used in order to produce more melt phase. To meet the LSF and SM moduli, corrective materials had to be used. These corrective materials were limestone (for correcting the CaO requirement) and pulverized red brick disposal (for correcting for $Al_2O_3$ and $SiO_2$ requirements).

## RESEARCH METHODOLOGY

### *Raw materials and corrective materials*

The chemical composition of these materials was determined by using Atomic Absorption Spectrum (AAS) Analyzer. The composition can be seen in Table 1.

Mineralogy composition was determined by using XRD Analyzer, the typical mineral content of these materials can be seen in Table 2.

### *Raw mixed design*

The raw material (concrete waste) and the corrective materials (red/building brick disposal and limestone) were mixed to form raw mixes. The amount of each material to meet the LSF and SM moduli are found in Table 3.

### *Sample preparation*

Each material was crushed in a jaw crusher, milled by using a ball mill equipment, and screened to get pulverized material that has a size of –200 mesh. Each pulverized material was weighed in order to meet the LSF or SM modulus cited in Table 3, and then mixed thoroughly by using a ball mill.

***Table1. Chemical Composition of Raw and Corrective Materials***

| The Main Oxides | Concrete Waste (% by weight ) | Limestone (% by weight) | Red Brick Disposal (% by weight) |
|---|---|---|---|
| $SiO_2$ | 30. | 1.42 | 68.00 |
| $Al_2O_3$ | 13.10 | 0.48 | 12.60 |
| $Fe_2O_3$ | 6.90 | 2.70 | 2.95 |
| CaO | 50.00 | 50.40 | 5.70 |

***Table 2. Mineral Content in Raw and Corrective Materials***

| Materials Used | Mineralogy Content |
|---|---|
| Concrete waste | Calcium aluminates mono carbonate, portlandite , feldspars, calcite, tobermorite, hematite ($Fe_2O_3$), No Quartz |
| Clayish brick disposal | Mullite ($3Al_2O_3\ 2\ SiO_2$), trace of hematite |
| Lime stone | Calcite ($CaCO_3$), trace of hematite |

***Table 3. Weight Ratio of Raw and Corrective Materials***

| Codes of Samples | Concrete : Limestone : Clayish Brick | LSF (target) | SM (target) |
|---|---|---|---|
| J | 1 : 2.309 : 0.358 | 0.86 | 1.89 |
| I | 1 : 1.830 : 0.23 | 0.86 | 1.95 |
| F | 1 : 2.637 : 0.451 | 0.86 | 1.98 |
| E | 1 : 3.489 : 0.677 | 0.86 | 2.14 |
| G | 1 : 4.872 : 1.075 | 0.86 | 2.33 |
| H | 1 : 7.540 : 1.758 | 0.86 | 2.55 |
| B | 1 : 3.788 : 0.768 | 0.85 | 2.2 |
| D | 1 : 4.18 : 0.788 | 0.87 | 2.2 |
| C | 1 : 4.18 : 0.805 | 0.0.9 | 2.2 |
| A | 1 : 4.34 : 0.820 | 0.92 | 2.2 |

The homogenous raw mixed samples, which are called *raw mixes,* were formed into cylindrical shape by using hydraulic press, sundried, and held at 120°C in an electrical drier until constant weight was achieved. Samples were burnt in a programmable electrical furnace.

## RESULTS AND CONCLUSIONS

### *Concrete waste and raw mixed characterization*

Characterization of raw material (concrete waste) and raw mixes were carried out by using XRD.

Figure 1 shows that during clinker formation feldspar minerals still remained and the minerals of Portland cement clinker ($C_3S$, $C_2S$, $C_3A$, and $C_4AF$) were formed. The remaining mineral feldspars were caused by the incomplete dissociation/calcination of feldspars that came from aggregates in concrete waste.

Figure 2 represents typical raw mixes burned at 1,400°C, which shows that the feldspar minerals had disappeared. This can be explained by the by the complete dissociation of feldspar minerals from their oxides and then combination by ceramic bonding with existing oxides to produce clinker minerals. The characterization of a typical clinker produced by the Indonesian Portland cement industry was carried out and showed that there were no feldspar minerals at all.

### *Burning ability of raw mixes*

The burning ability of raw mixes were analyzed qualitatively by comparing the total count of X-ray beam diffracted by a mineral corresponding to its specific peaks. The specific peaks of $CaO_{free}$ were identified according to their 2θ value, which were 37.98° and 53.71°. These corresponded to the *d* value: 2.39 A and 1.69 A. The CaO free content in each sample which was burnt at 1,450°C can be seen in Table 4.

The burning ability of raw mixes was characterized by measuring the *CaO free content*, or the remaining/uncombined CaO, in clinker produced by burning raw mixes at various temperatures and various cement moduli. These correlations are shown graphically in Figure 4 and Figure 5. As indicated in Figure 3, the burning ability of raw mixes decrease with increase in silica modulus. Increasing the silica modulus means that the $SiO_2$ content in raw mixes will also increase, so that the CaO particles will have more probable contact with the providing $SiO_2$ to form calcium silicate compound (clinker cement minerals). More CaO reacted with $SiO_2$ caused the remaining CaO to be less.

***Table 4. The Total Count of CaO Mineral (Burnt at 1,400°C)***

| Sample Code | SM | LSF | CaO Total Count | |
|---|---|---|---|---|
| | | | 0 min burning | 30 min burning |
| J | 1.89 | 0.98 | 100 | 61 |
| I | 1.95 | 0.98 | 67 | 62 |
| F | 1.98 | 0.98 | 75 | 57 |
| E | 2.14 | 0.98 | 42 | 37 |
| G | 2.33 | 0.98 | 72 | 52 |
| H | 2.55 | 0.98 | 56 | 45 |

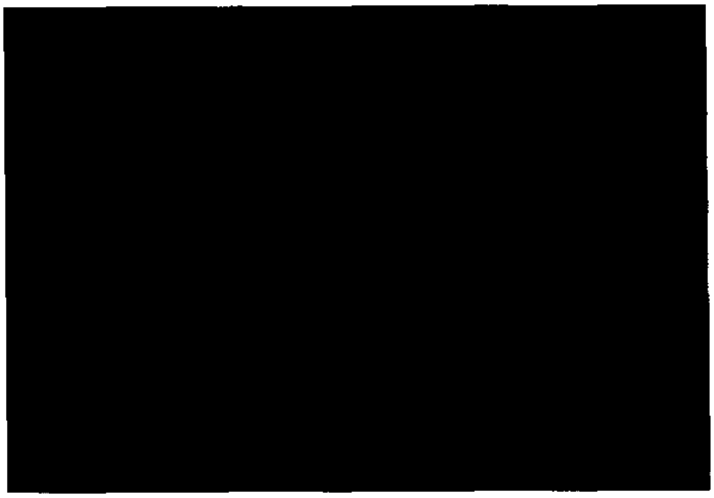

*Figure 1. Characterization of Early Burnt Raw Mix at 1100°C*

*Figure 2. Characterization of Early Burnt Raw Mix at 1400°C*

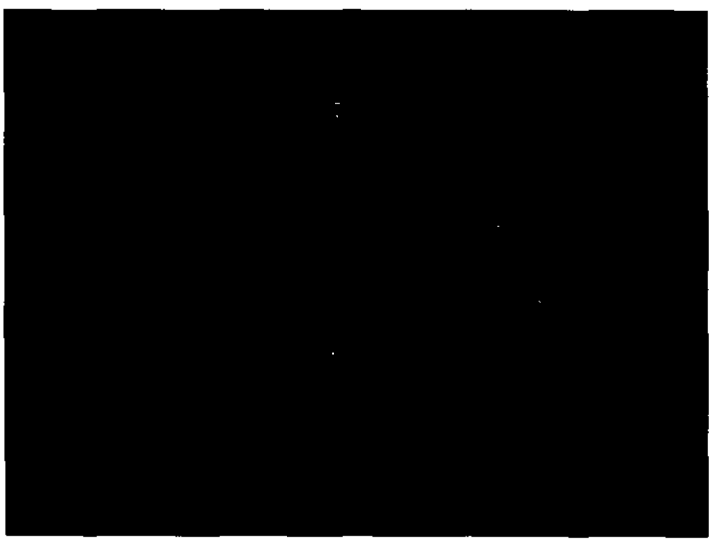

*Figure 3. Characterization of Early Burnt Raw Mix at 1450°C*

*Table 5. Total Count of CaO Mineral (Burnt at 1,450°C)*

| Sample Code | SM | LSF | CaO Total Count | |
|---|---|---|---|---|
| | | | 0 min burning | 30 min burning |
| J | 1.89 | 0.98 | 84.8 | 57 |
| I | 1.95 | 0.98 | 80 | 67 |
| F | 1.98 | 0.98 | 114 | 56 |
| E | 2.14 | 0.98 | 84 | 49 |
| G | 2.33 | 0.98 | 62 | 76 |
| H | 2.55 | 0.98 | 54 | 43.3 |
| B | 2.2 | 0.85 | 72 | 31.3 |
| D | 2.2 | 0.87 | 63 | 44 |
| C | 2.2 | 0.90 | 78 | 35 |
| A | 2.2 | 0.92 | 77 | 63 |

Increasing the temperature from 1,400 to 1,450°C, means that the available energy provided for CaO to diffuse through the melt phase of aluminates and ferrites would be higher. So the probability of particles CaO contacted / combined with particles $SiO_2$ would be higher too, so the CaO free would be decreased. In other words, the burning ability of raw mixes would be easier.

Increasing the LSF, means that the amount of CaO particles in the raw mixes also increased. If clinkerization was carried out at constant SM modulus, it meant that the $SiO_2$ content in raw mixes had been held constant too, so that there were not enough $SiO_2$ particles to react with CaO particles. This would yield CaO free increase with increasing LSF.

## CONCLUSIONS

1. Raw mixes for clinker cement production can be made by mixing of demolition rubbles (concrete waste and mortar/plaster waste) and corrective materials, which provide oxides requirement to meet the cement modulus.
2. Burning of raw mixes under specified LSF and SM moduli can produce clinker that contains minerals, which compose clinker of Portland cement.
3. Burning ability of raw mixes was influenced by the LSF, SM, and burning temperature.
4. Increasing the SM and increasing the burning temperature can lower the burning ability of raw mixes. It means that the raw mixes that can easily be burnt which produce lower CaO free can enhance the quality of the clinker produced.
5. Increasing the LSF modulus produces higher CaO free in the clinker produced.

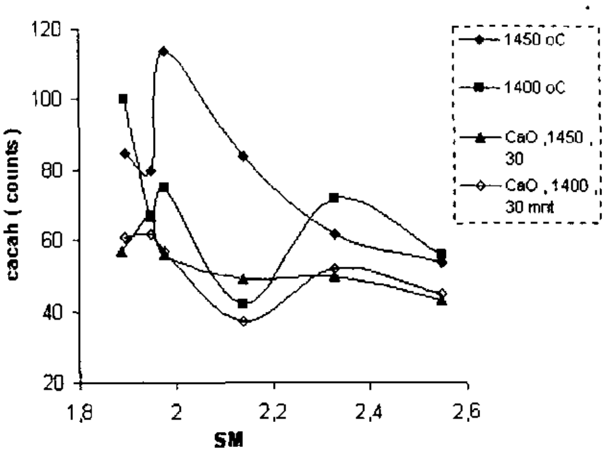


*Figure 5: Counts of $CaO_{free}$ at 1400 °C & 1450 °C, Burning Duration 0 and 30 minutes, LSF = 0,86*

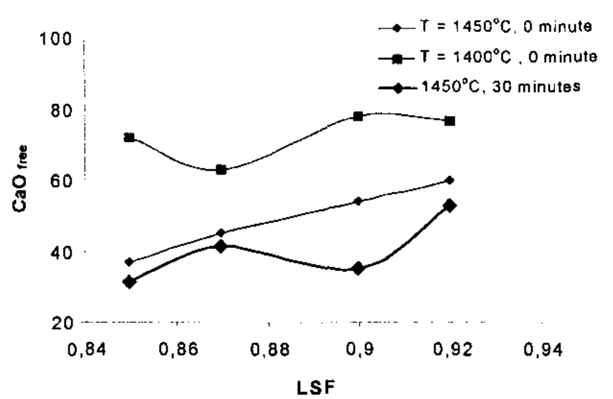


*Figure 6. Total Counts of $CaO_{free}$ at 1400°C and 1450°C, Burning Duration, t= 0 and 30 minutes, SM = 2.20*

**Figure 7. Housing Demolition Rubble (Source of Raw Mixes Constituents)**

**Figure 8. View of Stock Piles of Demolition Rubble**

**Figure 9. Picking Out Burning Clinker from Electrical Furnace for Quenching**

6. To select the optimum operating LSF or SM, the quality of minerals formed in the clinker should be considered also and not just the CaO free.

## REFERENCES

Ahluwalia,S.C., Goswaani, R. K., and Harsh, S. (1997). "Modeling the kinetics of clinkerization," *Clinker and Cement Production, Proceedings of the 10th International Congress on Chemistry of cement, Plenary Lectures*, vol. 1, Gothenburg, Sweden.

Christensen, N. H. (1979). "Burning ability of cement raw mixes at 1400°C : The effect of fineness," *An International Journal, Cement and Concrete Research, 9*, 2, 285–294, Pergamon Press, New York.

Duda, W. H. (1985). *Cement data book, International process engineering in the cement industry*, 2nd ed., completely revised and enlarged new ed., Bauverlag Gmbh–Wiesbaden.

Ghosh, S. N. (1983). *Advances in cement technology*, Cement Research Institute of India, Pergamon Press, New York. 39–177.

Sumardi, P. (1999). *Heat treatment on hydrated cement*, Ceramic Technology Laboratory, Chemical Engineering Department, Engineering Faculty, Gadjah Mada University.

## ABBREVIATIONS

| | |
|---|---|
| $C_3S$ | $3CaOSiO_2$ |
| $C_2S$ | $2CaOSiO_2$ |
| $C_4AF$ | $4CaOAl_2O_3Fe_2O_3$ |
| $C_3A$ | $3CaO\ Al_2O_3$ |
| *LSF* | Lime Saturation Factor |
| *SM* | Silica Modulus |

Symbols on refracto graph: For example: 3.01/ $C_3S$/268 it means for mineral $C_3S$ which having d- value of 3.01 A° and the mineral counts at this d- value : 268