Statistical Analyses of Optimum Partial Replacement of Cement by Rice Husk Ash Based on Complete Consumption of Calcium Hydroxide

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Abstract

The objectives of this technical paper were to propose the optimum partial replacement of cement by rice husk ash based on the complete consumption of calcium hydroxide from hydration reactions of cement and the long-term strength activity index based on equivalent calcium silicate hydrate as well as the propagation of uncertainty due to randomness inherent in main chemical compositions in cement and rice husk ash. Firstly the hydration- and pozzolanic reactions as well as stoichiometry were reviewed. Then the optimum partial replacement of cement by rice husk ash was formulated. After that the propagation of uncertainty of main chemical compositions in cement and rice husk ash was discussed and the reliability analyses for applying the suitable replacement were reviewed. An applicability of the concepts mentioned above based on statistical data of materials available was demonstrated. The results from analyses were consistent with the testing results by other researchers. The results of this study provided guidelines of suitable utilization of rice husk ash for partial replacement of cement. It was interesting to note that these concepts could be extended to optimize partial replacement of cement by other types of pozzolan which were described in the other papers of the authors.

Keywords: *Stoichiometry, Rice Husk Ash, Strength Activity Index, Propagation of Uncertainty, Statistical Analysis, Reliability Analysis*

บทคัดย่อ

บทความนี้มีวัตถุประสงค์เพื่อนำเสนอ การแทนที่ซีเมนต์ด้วยเถ้าแกลบอย่างเหมาะสุด โดยอาศัยการใช้แคลเซียมไฮดรอกไซด์ที่เกิดจากปฏิกิริยาไฮเดรชันของซีเมนต์หมดสมบูรณ์ และนำเสนอดัชนีกิจกรรมกำลังระยะยาว โดยอาศัยหลักการแคลเซียมซิลิเกตไฮเดรตเทียบเท่า เช่นเดียวกับการแพร่กระจายความไม่แน่นอนที่เกิดตามธรรมชาติในองค์ประกอบหลักทางเคมีของซีเมนต์และเถ้าแกลบ ดำเนินการวิจัย โดยในเบื้องต้นจะทบทวนปฏิกิริยาไฮเดรชันของสารประกอบหลักในซีเมนต์ และปฏิกิริยาปอซโซลานิกของสารประกอบหลักในเถ้าแกลบ หลังจากนั้นจะแสดงวิธีกำหนดสูตรหาการแทนที่ซีเมนต์บางส่วนด้วยเถ้าแกลบอย่างเหมาะสุด ตามด้วยการอภิปรายการแพร่กระจายความไม่แน่นอนของสัดส่วนสารเคมีหลักในซีเมนต์และเถ้าแกลบ และการทบทวนการวิเคราะห์ความน่าเชื่อถือสำหรับการนำสัดส่วนการแทนที่ซีเมนต์ด้วยเถ้าแกลบที่เหมาะสมไปใช้งาน นอกจากนั้น ยังสาธิตการนำหลักการดังกล่าวมาแล้วทั้งหมดไปใช้โดยอาศัยข้อมูลทางสถิติของวัสดุที่มีอยู่ ผลการวิเคราะห์สอดคล้องเป็นอย่างดีกับผลการทดสอบโดยนักวิจัยรายอื่นๆ ผลการศึกษาให้แนวทางการนำเถ้าแกลบไปใช้แทนที่ซีเมนต์บางส่วนได้อย่างเหมาะสม ประเด็นที่น่าสนใจ คือ เราสามารถขยายแนวคิดนี้ไปใช้กับการแทนที่ซีเมนต์ด้วยสารปอซโซลานอื่นๆ ซึ่งได้แสดงไว้ในผลงานอื่นของผู้เขียน

คำสำคัญ: *ปริมาณสารสัมพันธ์ เถ้าแกลบ ดัชนีกิจกรรมกำลัง การแพร่กระจายความไม่แน่นอน การวิเคราะห์สถิติ การวิเคราะห์ความน่าเชื่อถือ*

1. Introduction

Cement contents in concrete is the main cost for the concrete production. The reduction of cement content in concrete mix proportion would lower the cost of concrete and would increase the competitiveness in marketing. Therefore the probabilistic concrete mix design for mass production of concrete has been commercially applied (Kamollertvara and Ouypornprasert, 2015). Dumrongsil, Chatveera and Ouypornprasert (2000) studied the suitable partial replacement of cement by rice husk ash (RHA). In this study the optimum replacement of cement by RHA was derived by the concept of calcium oxide equivalent. Results showed that the values of compressive strength of concrete mixed with RHA of the age less than 28 days tend to be lower than those of concrete mixed with Ordinary Portland Cement (OPC).

However with suitable replacements of cement by RHA the values of compressive strength of concrete can be higher than those of ordinary concrete even at the early age (Habeeb and Mahmud, 2010). The major reason might be the heat of hydration of cement mixed with pozzolan could surpass that of OPC (Langan, Weng and Ward, 2002).

In this technical paper the optimum replacement of cement by RHA based on stoichiometry of complete consumption of calcium hydroxide from hydration of cement and pozzolanic reactions of pozzolan substances as well as the long-term strength activity index based on Equivalent Strength of Calcium Silicate Hydrates (C-S-H) is proposed. Guidelines of suitable utilization of rice husk ash for partial replacement of cement should be discussed in light of cost reduction. Since the chemical compositions of cement and RHA are varied in the production process, propagation of uncertainty with respect to main chemical compositions will also be discussed. To assure the quality of concrete mixed with RHA the suitable replacement of cement by RHA should be determined with the target confidence interval. Once the particular replacement is selected the distribution of the long-term strength activity index could be obtained. Then reliability of the selected replacement could be determined accurately by Monte-Carlo simulations or approximately by the advanced First-Order Second-Moment (FOSM) method. The applicability of the proposed formulations could be demonstrated by a set of data available in hand.

2. Objectives

The objectives of this study were to:
1) Formulate the optimum replacement of cement by rice husk ash based on the complete consumption of calcium hydroxide from hydration of cement.
2) Propose the long-term strength activity index based on equivalent calcium silicate hydrate.
3) Analyze the propagation of uncertainty of the optimum replacement of cement by rice husk ash in terms of variation of main chemical compositions in cement and rice husk ash.
4) Review the reliability analyses for utilizing the optimum replacement of cement by rice husk ash.
5) Provide guidelines of suitable utilization of rice husk ash for partial replacement of cement in light of cost reduction.
6) Demonstrate the applicability of the proposed concepts.

3. Materials and methods

3.1 General Remarks

It is usual for the cement chemist to use the abbreviations as listed Table 1 for discussions about hydration of cement and pozzolanic reactions (Neville, 1995).

Table 1 Abbreviations for hydration of cement and pozzolanic reactions.

Abbreviation	Technical Term (Chemical Formula)
C	calcium oxide (CaO)
S	silicon dioxide (SiO_2)
H	water (H_2O)
A	aluminium oxide (Al_2O_3)
F	ferric oxide (Fe_2O_3)
CH	calcium hydroxide ($Ca(OH)_2$)
C_3S	tricalcium silicate ($3CaO \cdot SiO_2$)
C_2S	dicalcium silicate ($2CaO \cdot SiO_2$)
C_3A	tricalcium aluminate ($3CaO \cdot Al_2O_3$)
C_4AF	tetracalcium alumino ferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$)

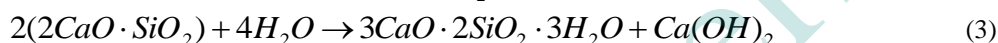| Abbreviation	Technical Term (Chemical Formula)
$C_3S_2H_3$ or $C-S-H$	calcium silicate hydrate ($3CaO \cdot 2SiO_2.3H_2O$)
C_3AH_6	calcium aluminate hydrate ($3CaO \cdot Al_2O_3.6H_2O$)
C_3FH_6	calcium ferrite hydrate ($3CaO \cdot Al_2O_3.6H_2O$)

3.2 Hydration Reactions, Pozzolanic Reactions and Stoichiometry
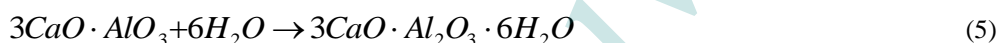
3.2.1 Hydration Reactions

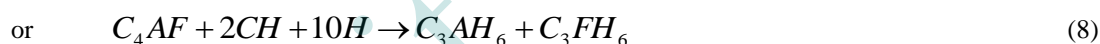*3.2.1.1 Hydration reaction of Tricalcium Silicate (C_3S)*

$$2(3CaO \cdot SiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \qquad (1)$$

or $\qquad 2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \qquad (2)$

3.2.1.2 Hydration reaction of Dicalcium Silicate (C_2S)

$$2(2CaO \cdot SiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \qquad (3)$$

or $\qquad 2C_2S + 4H \rightarrow C_3S_2H_3 + CH \qquad (4)$

3.2.1.3 Hydration reaction of Tricalcium Aluminate (C_3A)

$$3CaO \cdot AlO_3 + 6H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O \qquad (5)$$

or $\qquad C_3A + 6H \rightarrow C_3AH_6 \qquad (6)$

3.2.1.4 Hydration reaction of Tetra calcium Alumino Ferrite (C_4AF)

$$4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 2(Ca(OH)_2) + 10H_2O \rightarrow$$
$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3CaO \cdot Fe_2O_3 \cdot 6H_2O \qquad (7)$$

or $\qquad C_4AF + 2CH + 10H \rightarrow C_3AH_6 + C_3FH_6 \qquad (8)$

3.2.2 Pozzolanic Reactions

3.2.2.1 Additional Calcium Hydroxide from Calcium Oxide (CaO) in Pozzolan

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (9)$$

or $\qquad C + H \rightarrow CH \qquad (10)$

3.2.2.2 Pozzolanic Reaction of Silicon Dioxide (SiO_2)

$$3Ca(OH)_2 + 2SiO_2 \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O \qquad (11)$$

or $\qquad 3CH + 2S \rightarrow C_3S_2H_3 \qquad (12)$
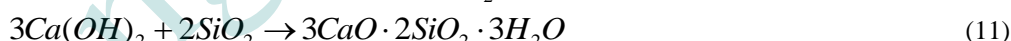
3.2.2.3 Pozzolanic Reaction of Aluminium Oxide (Al_2O_3)

$$3Ca(OH)_2 + 2Al_2O_3 \rightarrow 3CaO \cdot 2Al_2O_3 \cdot 3H_2O \qquad (13)$$

or $\qquad 3CH + 2A \rightarrow C_3A_2H_3 \qquad (14)$
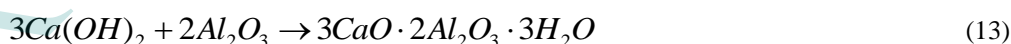
3.3 Stoichiometry

Atomic and molecular weights of all substances related in stoichiometry of hydration and pozzolanic reactions are summarized in Table 2 – 4.

Table 2 Atomic weight of elements related in hydration- and pozzolanic reactions.

Element	H	O	Al	Si	Ca	Fe
Atomic Weight	1	16.00	26.98	28.09	40.08	55.85

Table 3 Molecular weight of main chemical components in cement and rice husk ash.

Compound	C_3S	C_2S	C_3A	C_4AF	CaO	SiO_2	Al_2O_3	Fe_2O_3
Molecular Weight (g/mol)	228.2	172.2	270.0	483.1	56.1	60.1	102.0	156.7

Table 4 Molecular weight of chemical components related in hydration- and pozzolanic reactions.

Chemical Components	H_2O	$Ca(OH)_2$	$C_3S_2H_3$	C_3AH_6	C_3FH_6
Molecular Weight (g/mol)	18.0	74.1	228.2	378.1	432.8

3.4 Optimum replacement of Cement by Rice Husk Ash and Long Term Strength Activity Index
3.4.1 Optimum replacement of Cement by Rice Husk Ash

        In this technical paper the optimum replacement of cement by rice husk ash (RHA) will be considered by the complete consumption of calcium hydroxide (CH) from hydration of main minerals in cement by the main chemical compositions in RHA.

        Let fC_r, fS_r and fA_r be the fraction of C, S and A in RHA, respectively and r_r be the fractional replacement of cement by RHA, then the fractional calcium hydroxide (fCH) from hydration of cement in unit weight replaced by RHA with the ratio r_r would be $fCH \cdot (1 - r_r)$.

$$fCH = fC_3S \cdot r_{CH-C_3S} + fC_2S \cdot r_{CH-C_2S} - fC_4AF \cdot r_{CH-C_4AF} \tag{15}$$

Where fC_3S, fC_2S and fC_4AF are the fraction of C_3S, C_2S and C_4AF in cement per unit weight, respectively. r_{CH-C_3S}, r_{CH-C_2S} and r_{CH-C_4AF} are the ratios of CH from the hydration reactions of C_3S, C_2S and fC_4AF, respectively. Their values are:

$$r_{CH-C_3S} = \frac{3 \cdot w_{CH}}{2 \cdot w_{C_3S}} = 0.48678 \tag{16}$$

$$r_{CH-C_2S} = \frac{w_{CH}}{2 \cdot w_{C_2S}} = 0.21509 \tag{17}$$

$$r_{CH-C_4AF} = \frac{2 \cdot w_{CH}}{w_{C_4AF}} = 0.30677 \tag{18}$$

Where w_{CH}, w_{C_3S}, w_{C_2S} and w_{C_4AF} are molecular weight of CH, C_3S, C_2S and C_4AF, respectively (See Table 3 and 4).

        Since calcium oxide (CaO) can be soluble in water and yield calcium hydroxide as shown in Eq. (9) and (10) and the SiO_2 content in RHA is usually much more than CaO, it might be assumed that amount of SiO_2 in RHA is always more than the amount required for the pozzolanic reaction with CaO in RHA itself, there will be adequate residual amount of SiO_2 to react with the residual calcium hydroxide from hydration of cement (see Eq. (11) and (12)). Aluminium oxide (Al_2O_3) in RHA can also react with the residual calcium hydroxide from hydration of cement (see Eq. (13) and (14)).

        The residual CH from Eq. (15) can be completely consumed in pozzolanic reactions with SiO_2 and Al_2O_3 as shown in Eq. (21).

$$(1 - r_r) \cdot fCH = (fS_r - fC_r \cdot r_{CS}) \cdot r_{SCH} + fA_r \cdot r_r \cdot r_{ACH} \tag{19}$$

where $r_{SCH} = \dfrac{3w_{CH}}{2w_S} = 1.84986$ and $r_{ACH} = \dfrac{3w_{CH}}{2w_A} = 1.09003$ are the ratio of SiO_2 and Al_2O_3 to

react with $Ca(OH)_2$, respectively.

Let

$$fS'_r = fS_r - fC_r \cdot r_{CS} \qquad (20)$$

Where r_{CS} is the ratio by weight of C to S for complete pozzolanic reactions of SiO_2 whose value is given in Eq. (23).

$$r_{CS} = \frac{3 \cdot w_C}{2 \cdot w_S} = 1.40063 \qquad (21)$$

Where w_C and w_S are the molecular weights of C and S, respectively (see Table 3).

Then Eq. (19) reduces to:

$$r_r = \frac{fCH}{fCH + fS'_r \cdot r_{SCH} + fA_r \cdot r_{ACH}} \qquad (22)$$

3.4.2 Long Term Strength Activity Index
3.4.2.1 Complete Consumption of Calcium Hydroxide

Strength of cement paste is mainly contributed by C-S-H from C_3S and C_2S. Additional contributions are from C_3AH_6, the product of C_3A and C_4AF. With rice husk ash and fly ash in binder C-S-H and C_3AH_6 from pozzolanic reactions have not been clearly understood in terms of rate of reactions as well as the strength development. It was concluded that C-S-H from pozzolanic reactions had the same structure as C-S-H from hydration of cement (Taylor, 1997). However the rate of hydration of C_2S as well as the strength development is much slower at the early age of cement paste than that of C_3S. Fortunately the long-term strength of C-S-H developed from C_2S is insignificantly lower than that from C_3S, the long-term strength of C-S-H from the pozzolanic reaction could be assumed as the average strength of C-S-H from C_3S and C_2S without significant errors. Furthermore the contribution of C_3AH_6 from the hydration of cement and pozzolanic reactions take minor contribution to the overall strength of binder. Therefore the strength of C_3AH_6 can be assumed equal for both type of reactions. Based on the reasons mentioned above and the given values of strength for the age of 360 days (Bogue, 1955) the long-term strength activity index (SAI) can be defined as the ratio of the strength of binder paste over the strength of cement paste at the age of 360 days as shown below:

$$SAI = \frac{(fa + fb) \cdot (1 - r_r) - \left(\dfrac{fA_r \cdot r_r}{2 \cdot wAl_2O_3}\right) \cdot (\alpha\beta - \gamma s) + \left(\dfrac{fC_r \cdot r_r}{3wCaO}\right) \cdot \alpha\beta}{fa} \qquad (23)$$

$$fa = \frac{1}{2}\left(\frac{fC_3S}{wC_3S} \cdot \alpha s + \frac{fC_2S}{wC_2S} \cdot \beta s\right) + \left(\frac{fC_3A}{wC_3A}\right) \cdot \gamma s + \left(\frac{fC_4AF}{wC_4AF}\right) \cdot \delta s \qquad (24)$$

$$fb = \left(\frac{1 \cdot fC_3S}{2 \cdot wC_3S} + \frac{fC_2S}{6 \cdot wC_2S} - \frac{2 \cdot fC_4AF}{3 \cdot wC_4AF}\right) \cdot \alpha\beta \qquad (25)$$

Where $\alpha s = 72.0$, $\beta s = 71.265$, $\gamma s = 8.082$, $\delta s = 5.143$ and $\alpha\beta = 71.6325$. It should be noted that $\alpha\beta$ could be taken as the average of αs and βs without significant error because of a small difference between the two values.

The long-term strength activity index can be extended for predicting strength activity index for different ages and different surface areas. The coefficients can be obtained by curve fitting of data. Data from tests were carried out by many investigators such as Habeeb and Mahmud (2010), Le and Ludwig (2016), Khalil et al (2014), Nawaz et al (2016) and Chatveera and Nimityongskul (1994). The more elaborated tests and details will be out of the scope of this technical paper and will be discussed in the authors' complete research project (2016).

3.4.2.2 Suitable Partial Replacement of cement by Rice Husk Ash

Suitable replacement of cement by rice husk ash should be considered carefully. The proper utilization of rice husk ash might be applied by the concept shown in Figure 1.
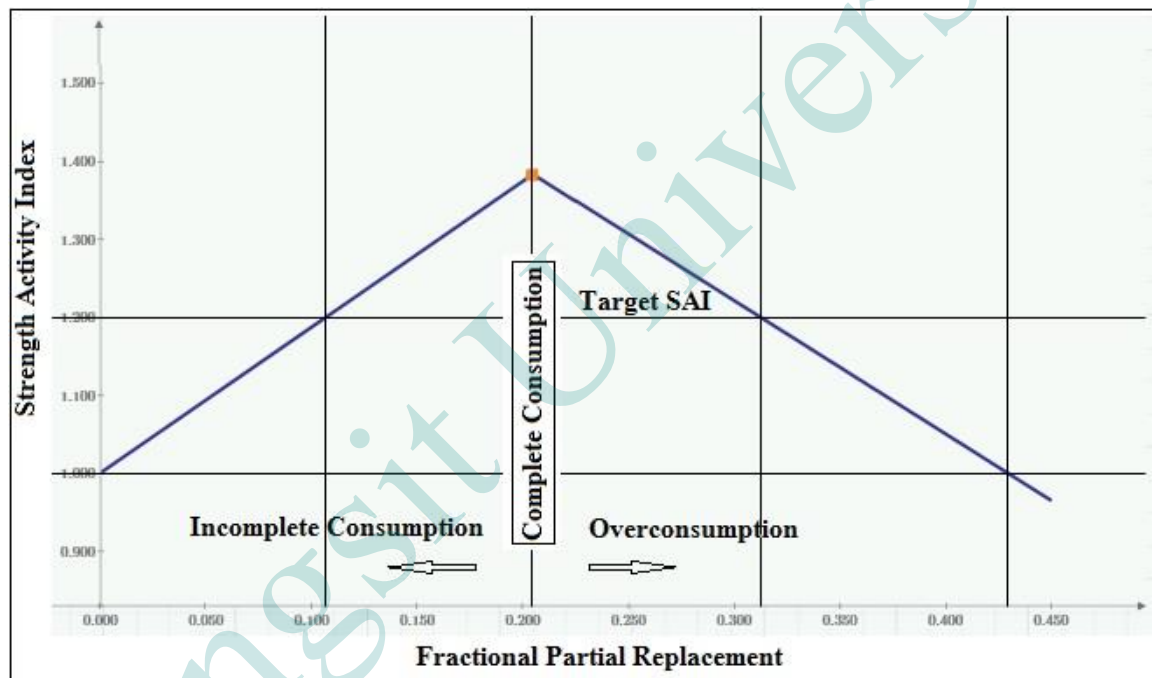

Figure 1 Suitable range of partial replacement of cement by rice husk ash.

Actually the value of strength activity index (SAI) for the partial replacement of cement by rice husk ash at the complete consumption should be very high. This value of replacement could be considered as the boundary between incomplete consumption and overconsumption. The values of SAI could be obtained by slight modification of fa in Eq. (24). The SAI curve is bilinear. The SAI is zero for the point of zero replacement and increases linearly to the maximum SAI. Then SAI decreases linearly with respect to the increase of replacement. There will be a limit of replacement that $SAI = 1$.

However for the mass production the target $SAI > 1$ should be selected in order to take into account of the variation in chemical compositions of cement and rice husk ash. This target SAI will determine the range of application of the partial replacement of cement by rice husk ash. Theoretically the higher the replacement, the lower to cost of production. In reality the increasing replacement by rice husk ash will lower the workability of mortar and/or concrete. In this case the cost of additional admixtures has to be considered.

3.4.2.3 Strength Activity Index for Any Age

For the strength activity index at the other ages the values of strength of C-S-H from C_3S and C_2S are rather different at early ages. However the difference in values would decrease with the increasing age. Since the development of strength of C-S-H products from pozzolanic reactions of pozzolan is still not clear, it should be studied extensively so that we can use rice husk ash in partial replacement of cement more appropriately and with more confidence. To demonstrate how the strength activity index at the other ages could be extended, again the values strength of main minerals in cement were measured directly from Bogue's curve (Bogue, 1955). For example at the age of 28 days $\alpha s = 47.76$, $\beta s = 5.89$, $\gamma s = 4.58$, $\delta s = 2.77$ and $\alpha\beta = (47.76 + 5.89)/2 = 26.825$. The predicted values strength activity index at the age of 28 days were consistent with the tested results of concrete mixed with rice husk ash carried out by Habeeb and Mahmud (2010) as shown in Figure 2. It should be noted that the surface areas of grounded rice husk ash of the data points marked by solid triangles, solid circles and solid asterisks were higher, respectively. The consistency was also verified for the concrete at the other ages for the same group of researchers as well as the other groups of researchers mentioned in section 3.4.2.2.
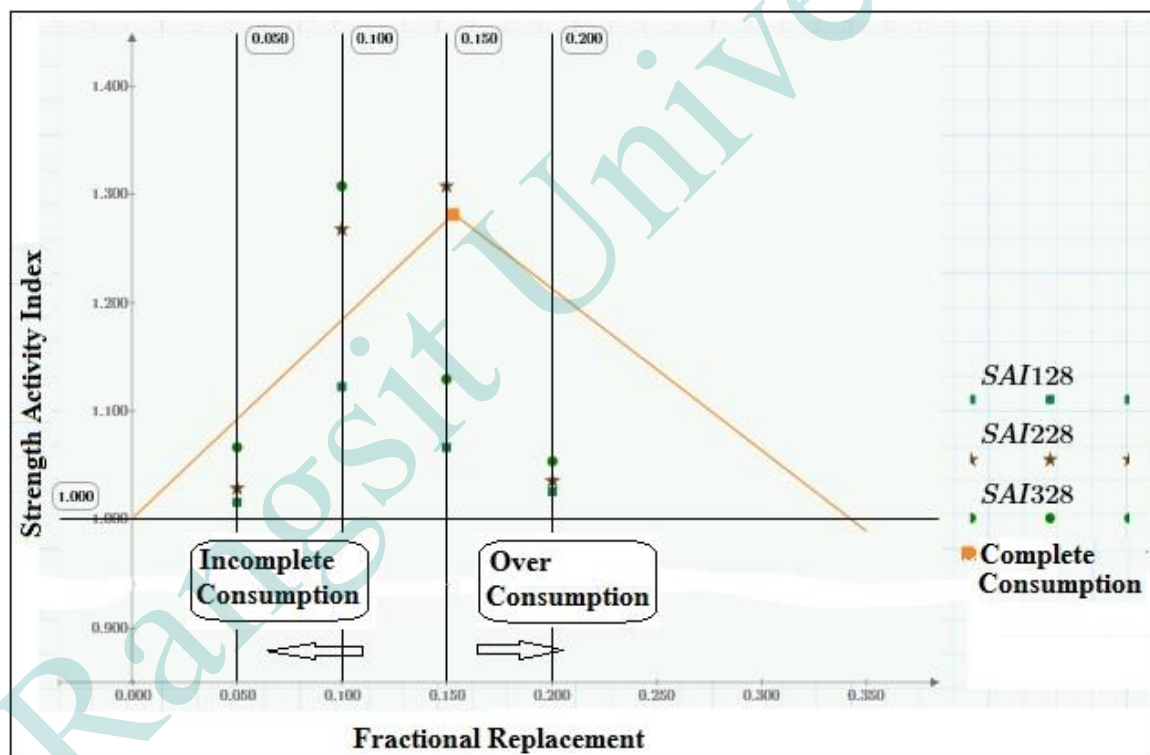

Figure 2 Comparison of strength activity index with tested data (concrete at the age of 28 days).

3.5 Propagation of Uncertainty
3.5.1 Linear Functions

For a linear function of n random variables in form of:

$$g(\underline{X}) = a_0 + \sum_{i=1}^{n} a_i \cdot X_i \qquad (26)$$

The correlation matrix of $\underline{X}$ is symmetric in form of:

$$[C] = \begin{bmatrix} 1 & \rho_{12} & \cdot & \rho_{1n} \\ \rho_{12} & 1 & \cdot & \rho_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ \rho_{1n} & \rho_{2n} & \cdot & 1 \end{bmatrix} \tag{27}$$

Where ρ_{ij} is the correlation coefficient between X_i and X_j. The covariance term σ_{ij} can be expressed in terms of the correlation coefficients:

$$\sigma_{ij} = \rho_{ij} \cdot \sigma_i \cdot \sigma_j \tag{28}$$

Where σ_i and σ_j are standard deviations of variables X_i and X_j respectively. Thus σ_i^2 and σ_j^2 are variance of variables X_i and X_j, respectively.

Then the variance of $g(\underline{X})$ is:

$$\sigma_g^2 = \sum_{i=1}^{n} a_i \cdot \sigma_i^2 + \sum_{i=1}^{n} \sum_{j=1(j \neq i)}^{n} a_i \cdot a_j \cdot \rho_{ij} \cdot \sigma_i \cdot \sigma_j \tag{29}$$

In the case that variables $\underline{X}$ are uncorrelated variables the variance and the standard variation of $g(\underline{X})$ are reduced to:

$$\sigma_g^2 = \sum_{i=1}^{n} a_i \cdot \sigma_i^2 \tag{30}$$

$$\sigma_g = \sqrt{\sum_{i=1}^{n} a_i^2 \cdot \sigma_i^2} \tag{31}$$

3.5.2 Nonlinear Functions and Monte-Carlo Simulations

For a nonlinear function of n uncorrelated random variables, the standard deviation of $g(\underline{X})$ (σ_g) to calculate error propagation, the variance formula (Ku, 1966):

$$\sigma_g = \sqrt{\sum_{i=1}^{n} \left(\frac{\partial g}{\partial x_i}\right)^2 \cdot \sigma_{x_i}^2} \tag{32}$$

For other cases Monte-Carlo simulations may be applied. Then the suitable distributions for $g(\underline{X})$ can be obtained by Goodness-Of-Fit Tests e.g. Chi-Square Errors Test and K-S Test (Ouypornprasert, 2002).

3.5.3 Optimum Replacement of Rice Husk Ash for Cement

For the sake of further discussions: Let the value of a reduced variable y_i of a random variable X_i with mean (μ_{X_i}) and standard deviation (σ_{X_i}) be:

$$y_i = \frac{x_i - \mu_{X_i}}{\sigma_{X_i}} \tag{33}$$

The partial derivative of a function $g(\underline{X})$ with respect to a reduced variable y_i is $\frac{\partial g(x)}{\partial y_i}$. By applying the chain rule this term may be rewritten as:

$$\frac{\partial g(x)}{\partial y_i} = \frac{\partial g(x)}{\partial x_i} \cdot \frac{dx_i}{dy_i} = \frac{\partial g(x)}{\partial x_i} \cdot \sigma_{X_i} \tag{34}$$

From Eq. (22):

$$\frac{\partial r_r}{\partial yfC_3S} = \frac{r_{CH-C_3S} \cdot \left(fS_r' \cdot r_{SCH} + fA_r \cdot r_{ACH}\right)}{\left[fCH + fS_r' \cdot r_{SCH} + fA_r \cdot r_{ACH}\right]^2} \cdot \sigma_{fC_3S} \tag{35}$$

$$\frac{\partial r_r}{\partial yfC_2S} = \frac{r_{CH-C_2S} \cdot \left(fS_r' \cdot r_{SCH} + fA_r \cdot r_{ACH}\right)}{\left[fCH + fS_r' \cdot r_{SCH} + fA_r \cdot r_{ACH}\right]^2} \cdot \sigma_{fC_2S} \tag{36}$$

$$\frac{\partial r_r}{\partial yfC_4AF} = \frac{- r_{CH-C_3AF} \cdot \left(fS_r' \cdot r_{SCH} + fA_r \cdot r_{ACH}\right)}{\left[fCH + fS_r' \cdot r_{SCH} + fA_r \cdot r_{ACH}\right]^2} \cdot \sigma_{fC_4AF} \tag{37}$$

$$\frac{\partial r_r}{\partial yfC_r} = \frac{fCH \cdot r_{SCH} \cdot r_{CS}}{\left[fCH + fS_r' \cdot r_{SCH} + fA_r \cdot r_{ACH}\right]^2} \cdot \sigma_{fC_r} \tag{38}$$

$$\frac{\partial r_r}{\partial yfS_r} = \frac{- fCH \cdot r_{SCH}}{\left[fCH + fS_r' \cdot r_{SCH} + fA_r \cdot r_{ACH}\right]^2} \cdot \sigma_{fS_r} \tag{39}$$

$$\frac{\partial r_r}{\partial yfA_r} = \frac{- fCH \cdot r_{ACH}}{\left[fCH + fS_r' \cdot r_{SCH} + fA_r \cdot r_{ACH}\right]^2} \cdot \sigma_{fC_r} \tag{40}$$

Thus:

$$\sigma_{r_r} = \sqrt{\left(\frac{\partial r_r}{\partial yfC_3S}\right)^2 + \left(\frac{\partial r_r}{\partial yfC_2S}\right)^2 + \left(\frac{\partial r_r}{\partial yfC_4AF}\right)^2 + \left(\frac{\partial r_r}{\partial yfC_r}\right)^2 + \left(\frac{\partial r_r}{\partial yfS_r}\right)^2 + \left(\frac{\partial r_r}{\partial yfA_r}\right)^2} \tag{41}$$

3.6 Reliability Analyses

3.6.1 Linear Limit-State Functions

For a linear function of n random variables $g(\underline{X})$ as in form of Eq. (36), the mean (μ_g) and the standard deviation (σ_g) of a vector of normal variables X can be calculated from the equations below:

$$\mu_g = a_0 + \sum_{i=1}^{n} a_i \cdot \mu_{X_i} \tag{42}$$

$$\sigma_g = \sqrt{\sum_{i=1}^{n} a_i^2 \cdot \sigma_{X_i}^2} \tag{43}$$

Then the reliability index (β) may be defined as:

$$\beta = \frac{\mu_g}{\sigma_g} \tag{44}$$

Thus the failure probability (p_f) can be calculated from the equation below:

$$p_f = \Phi(-\beta) \tag{45}$$

Where $\Phi(z)$ is the cumulative probability of the standard normal variable of a z-score. For more details about reliability analyses it is referred to Ouypornprasert (1988).

3.6.2 Nonlinear Limit-State Functions and Monte-Carlo Simulations

For general applications where the functions $g(\underline{X})$ are nonlinear and/or random variables are non-normal, then the statistical representation of a limit-state function may be obtained by Monte-Carlo simulations as discussed earlier in section 3.5.2. However the failure probability may be estimated efficiently by Monte-Carlo simulations together with an advanced variance reduction technique such as Importance Sampling Technique as shown below:

$$p_f \cong \frac{1}{N}\sum_{j=1}^{N} I\big(g\big(\underline{x}_j\big)\big)\cdot \frac{f_{\underline{X}}\big(\underline{x}_j\big)}{h_{\underline{Y}}\big(\underline{x}_j\big)} \tag{46}$$

Where N is the number of simulations, $f_{\underline{X}}(\underline{x})$ is the joint probability density function, $h_{\underline{Y}}(\underline{x})$ is an importance sampling density function, $I\big(g(\underline{x})\big)$ is an indicator function whose value equals 1 when $g(\underline{x}) \leq 0$ and equals 0 otherwise.

4. Mass Production of Precast Concrete

The statistical data of cement, rice husk ash and fly ash available in hands showed significant variation. On one hand the mass production of precast products should be of optimum cost. On the other hand the products should be qualified for all specifications with pre-specified criteria. Therefore the statistical data should be analyzed in advance. For a concrete cast of cement mixed with rice husk ash, the statistical data available of the materials are summarized in Table 5.

Table 5 Statistical properties of main chemical oxide compositions in cement and rice husk ash.

Chemical Components	fractional		coefficient of variation
	mean	standard deviation	(stand.dev./mean)
C_3S	0.60877	0.01170	0.0192
C_2S	0.14857	0.01169	0.0787
C_3A	0.08473	0.00283	0.0334
C_4AF	0.10293	0.00064	0.0062
CaO (RHA)	0.00773	0.00283	0.3661
SiO_2 (RHA)*	0.62738	0.08844	0.1410
Al_2O_3 (RHA)	0.00255	0.00173	0.6784

Remarks *reactive silica, rice husk ash from western part of Thailand

5. Discussion

For preliminary analyses all related variables are assumed uncorrelated and normally distributed. The optimum fractional replacement of cement by rice husk ash was 0.2047.

The long-term strength activity index of the optimum replacement of cement by rice hush ash was 1.3829. The uncertainty of the long-term strength activity index can be obtained by simple Monte-Carlo simulations. Goodness-Of-Fit tests revealed that the long-term strength activity index can be represented well by normal distribution. For optimum replacement of cement by rice husk ash the long-term strength activity index based on 8192 simulations can be represented well by normal distribution with mean value and standard deviation = 1.178 and 0.0816, respectively. The goodness of fit is shown in Figure 3.
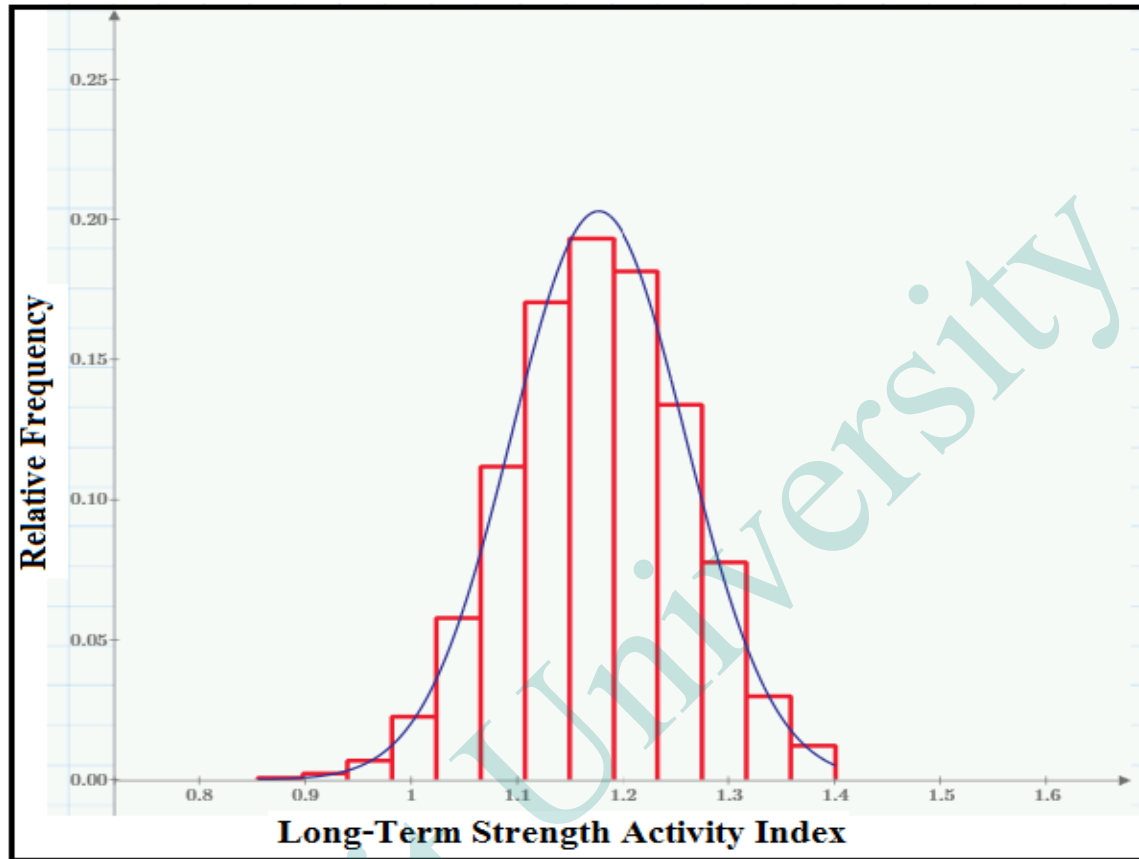
Figure 3 Goodness-Of-Fit test (Chi-Square Error) for the optimum replacement of cement by rice husk ash.

For the decision based on strength of the concrete the values of failure probability may play an important role. If the failure of the binder paste is defined as the value of the long-term strength activity index less than 1, then the value of failure probability can be estimated. It can be seen from Eq. (23) that the cross multiplication for $SAI = 1$, forming the limit-state function from the difference of both sides of the equation, then the limit-state function is linear in terms of related random variables. Since all these variables are assumed normally distributed, then the reliability index and the corresponding value of failure probability can be obtained easily by using Eq. (44) and Eq. (45), respectively. In other cases the Monte-Carlo simulations together with an Important Sampling Technique may be applied.

For this particular case the reliability index and the value of failure probability for the optimum replacement of cement by rice husk ash were 2.176 and $\Phi(-2.176) = 1.48 \times 10^{-2}$, respectively. Theoretically SAI of the optimum replacement should yield the maximum SAI. Since the failure probability in terms of SAI was very low for this particular case, a higher or lower value of replacement of cement by rich husk ash might be possible so that products could be qualified for all specifications.

Once this optimum replacement of cement by rice husk ash = 0.2047 was selected, then the propagation of uncertainty in terms of optimum ratio should be also considered. The corresponding standard deviation of this ratio was 0.0234. Again if the ratio was assumed normally distributed, then the interval of the applied ratio should be [0.1589,0.2505] with 95% confidence interval $(0.2047 \pm 1.96 \cdot 0.0234)$. More precise conclusion may be, again, estimated from Monte-Carlo Simulations and Goodness-Of-Fit tests.

From sensitivity analyses as concluded in Table 6 the optimum replacement of cement by rice ash was most sensitive to the fractional quantity of C_3S and C_2S in cement and SiO_2 in rice husk ash, respectively. The optimum replacement was insignificantly sensitive to C_4AF, CaO and Al_2O_3 because of low quantities in the binder.

Table 6 Sensitivity of optimum replacement of cement by rice husk ash with respect to uncertainty.

Chemical Components	error propagation		error propagation
	partial derivative	standard deviation	(part. deriv.×stand.dev.)
C_3S	0.2397	0.01170	0.0028
C_2S	0.1059	0.01169	0.0012
C_4AF	-0.1510	0.00064	-0.0001
CaO (RHA)	0.1405	0.00283	0.0004
SiO_2 (RHA)*	-0.1968	0.08844	-0.0017
Al_2O_3 (RHA)	-0.1160	0.00173	-0.0002

<u>Remarks</u> *reactive silica, rice husk ash from western part of Thailand

The range of the fractional replacement of cement by rice husk ash is shown in Figure 4. The maximum $SAI = 1.38286$ occurs at the point of complete consumption of calcium hydroxide. The upper limit of replacement should be 0.430 because for higher value of replacement $SAI < 1.0$. Since the cost of grounded rice husk ash is much lower than the cost of cement, the higher the replacement of cement by rice husk ash, the lower the is cost of concrete production. However, the higher the quantity of rice husk ash in the binder, the lower is the workability and SAI. If the target $SAI = 1.2$ is selected, the range of replacement is [0.107,0.313]. In practical all relevant specifications should be considered. Too high replacement of cement by rice husk ash may require additional admixtures. The additional cost due to admixtures may limit the maximum value of replacement.
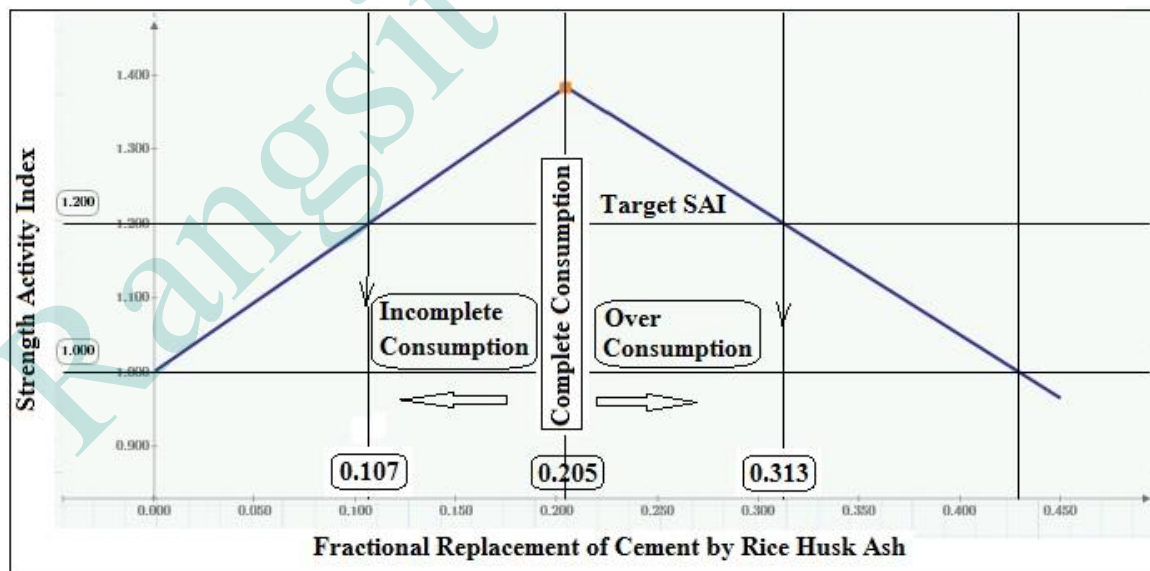

Figure 4 Range of suitable fractional replacement of cement by rice husk ash.

6. Conclusions

1) Hydration of main chemical compositions of cement and pozzolanic reactions of minerals in rice husk ash were reviewed. Data necessary for stoichiometry of hydration- and pozzolanic reactions were also given.

2) Formula for the optimum replacement of cement by rice husk ash based on the complete consumption of calcium hydroxide from hydration of cement was derived,

3) The long-term strength activity index for the age of 360 days based on equivalent calcium silicate hydrate was proposed.

4) The suitable replacement of cement by rice husk ash in light of strength activity index was proposed. Once the target strength activity index was selected, the range of suitable replacement of cement by rice husk ash could be determined. The higher the replacement, the lower the cost of production.

5) The extension of strength activity index at any age was possible, but the extensive series of tests should be carried out so that the coefficients of in the formulas can be obtained with an acceptable level of confidence.

6) The propagation of uncertainty of the partial replacement of cement by rice husk ash in terms of variation of main chemical compositions in cement and rice husk ash were formulated.

7) Reliability analyses for utilizing the optimum replacement of cement by rice husk ash were reviewed.

8) The applicability of the proposed concepts was demonstrated based on statistical data of materials available in hand. Results from analyses agreed very well with the tests carried out by other investigators.

9) All the concepts mentioned above could be extended to one other type of pozzolan as well as mixed pozzolan.

7. Acknowledgements

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