

# 無機質再生可能資源に対する各種ポゾラン反応性試験の適用性評価

## Applicability Assessment of Various Pozzolanic Reactivity Tests for Inorganic Recycled Resources

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### ABSTRACT

To produce cement and concrete with lower CO<sub>2</sub> emissions, it is necessary to partially replace cement clinker with other reactive materials. In this study, the pozzolanic reactivity of six types of inorganic recyclable resources, including conventionally used fly ash, was evaluated using various test methods, and their potential as novel clinker-substituting materials was investigated. The experimental results showed that the R<sup>3</sup> test exhibited a very high correlation with compressive strength, which is the most important performance indicator of cement. In particular, calcined clay with a thermal treatment history demonstrated the highest pozzolanic reactivity, exhibiting a compressive strength activity of approximately 97% or higher.

### 1. Introduction

Recently, there has been growing interest in using supplementary cementitious materials (SCMs) to partially replace clinker to achieve eco-friendly and sustainable cement production [1]. These materials can be inorganic natural mineral materials, inorganic mineral materials derived from the clinker production process, and inorganic recycled resources (IRR) derived from other industries. Traditionally, SCMs such as blast furnace slag from the steel industry and fly ash from the power generation industry have been used. However, the net-zero strategies being adopted by various industries are anticipated to cause significant changes in the availability, chemical composition, and mineral characteristics of these materials [1]. Consequently, in the long term, the development and research of new SCMs to replace them are essential.

SCMs have been studied widely since their introduction. Depending on the environment in which

they form, IRR possess some amorphous characteristics and may contain clay minerals as well as less reactive or inert minerals. Additionally, since they primarily consist of silica and alumina, IRR can exhibit pozzolanic reactions, forming insoluble calcium silicate hydrate (C-S-H) through reactions with portlandite. Recent studies have found that IRR such as calcined clay, circulating fluidized bed combustion fly ash, dry bottom ash, waste glass powder, and silica fume are being discussed as new SCMs [2-4]. However, unlike clinker, which maintains a certain level of quality consistency, the homogeneity of IRR can vary due to various external factors such as the country of origin, source, and raw materials used. This variability directly impacts the reactivity of the material. Although several studies have demonstrated that pozzolanic materials are effective, their reactivity is not as high as clinker, making it crucial to understand the quality characteristics of each material and evaluate their reactivity before utilization.

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The aim of this study is to investigate the relative pozzolanic reactivity of various IRR derived from other industries in Korea, including fly ash, which is traditionally used as a pozzolanic material. This study was conducted using various test methods capable of assessing pozzolanic reactivity. Furthermore, this research examined the feasibility of using IRR as new SCMs. Based on the evaluated results, this investigation sheds new light on the correlations between different pozzolanic reactivity methods.

## 2. Materials and methods

### 2.1 Materials

Firstly, in this study, six types of raw materials were adopted. Furthermore, pure Portland cement (RC; Asia Cement Co., Ltd., KR) was intentionally manufactured by grinding only clinker and gypsum, excluding SCMs such as limestone and blast furnace slag, to evaluate pozzolanic reactivity without their influence. The IRR materials included pulverized coal combustion fly ash (FA; KOMIPO, KR), calcined clay (CC; Lakwoo Co., Ltd., KR), circulating fluidized bed combustion fly ash (CFBC; KOSPO, KR), dry bottom ash (dBA; KOEN, KR), waste glass powder (WG; KR), and silica fume (SF; Taiwang International, KR). These materials are either inorganic natural minerals or IRR derived from other industries and produced through additional processing. The physical properties and chemical compositions, identified using X-ray fluorescence

(XRF; ZSX PrimusII, Rigaku) and particle size analysis (PSA; Mastersizer 3000, Malvern), are represented in Table 1.

### 2.2 Pozzolanic reactivity test methods

Firstly, in this study, four methods were adopted: (a) the Frattini test, (b) the saturated lime test, (c) the strength activity index, and (d) the  $R^3$  test. The Frattini test, a standardized method recognized by the European Union, measures the pozzolanic reactivity of pozzolanic cement in accordance with EN 197-1 and is specified in EN 196-5 [5, 6]. Briefly, this test involves preparing a paste sample by mixing a binder composed of RC and IRR with deionized water. The concentration of  $Ca^{2+}$  and  $OH^-$  dissolved in the filtrate is then determined through chemical titration. The results are plotted as points on a saturation curve of  $Ca^{2+}$  concentration versus  $OH^-$  concentration at 40°C. If the results plotted below the curve, it indicates pozzolanic reactivity; if plotted above the curve, it indicates no pozzolanic reactivity.

The saturated lime test (SLT) is similar in concept and methodology to the Frattini test for evaluating pozzolanic reactivity. However, instead of inducing a pozzolanic reaction with portlandite formed from the hydration of cement, the SLT evaluates pozzolanic reactivity through the direct reaction of IRRs with a lime solution, which is prepared by dissolving reagent portlandite in deionized water. This method is simpler than the Frattini test and allows for a more quantitative approach, as the initial concentration of

**Table 1 Physical properties and chemical composition of inorganic recycled resources**

| Classification           |                                | Inorganic recycled resources |       |       |       |       |         |
|--------------------------|--------------------------------|------------------------------|-------|-------|-------|-------|---------|
|                          |                                | CC                           | FA    | CFBC  | dBA   | WG    | SF      |
| Physical properties      | Density(g/cm <sup>3</sup> )    | 2.5                          | 2.3   | 2.8   | 2.0   | 2.5   | 2.2     |
|                          | Blaine(cm <sup>2</sup> /g)     | 3,616                        | 3,810 | 6,023 | 3,616 | 3,834 | 200,000 |
|                          | Mean( $\mu$ m)                 | 38.84                        | 30.22 | 25.61 | 23.41 | 28.34 | -       |
| Chemical composition (%) | CaO                            | 3.4                          | 7.9   | 19.9  | 4.8   | 11.3  | 0.1     |
|                          | SiO <sub>2</sub>               | 51.6                         | 53.3  | 35.3  | 65.1  | 69.1  | 98.5    |
|                          | Al <sub>2</sub> O <sub>3</sub> | 39.1                         | 20.8  | 13.5  | 18.8  | 2.2   | 0.8     |
|                          | Fe <sub>2</sub> O <sub>3</sub> | 3.2                          | 8.8   | 17.3  | 5.7   | 0.5   | 0.2     |
|                          | SO <sub>3</sub>                | 0.1                          | 0.9   | 5.7   | 0.2   | 0.2   | 0.03    |
|                          | MgO                            | 0.5                          | 2.2   | 4.8   | 1.9   | 1.6   | 0.03    |
|                          | K <sub>2</sub> O               | 0.8                          | 1.7   | 0.9   | 0.8   | 0.8   | 0.01    |
|                          | Na <sub>2</sub> O              | 0.7                          | 0.9   | 0.5   | 0.7   | 13.2  | 0.02    |

$\text{Ca}^{2+}$  ions in the lime solution is precisely known [7, 8].

The Strength Activity Index (SAI) was examined according to the methods specified in KS L 5405 and KS F 2567, with samples prepared in accordance with KS L ISO 679. In Korea, there are no established standards for evaluating the reactivity of IRRs other than FA and SF. Therefore, following the standards KS L 5405 and KS F 2567, all materials except SF were examined by replacing 25% of RC with the respective IRR, while SF was examined by replacing 10% of RC to measure the SAI [9-11].

The  $\text{R}^3$  test is the most recently proposed method for evaluating the pozzolanic reactivity of IRR. Initially introduced to evaluate the pozzolanic reactivity of calcined clay in [12], it was later established as ASTM C1897. The  $\text{R}^3$  test quantitatively evaluates pozzolanic reactivity by measuring the bound water content in a paste composed of portlandite and SCMs, allowing for the separation of pozzolanic reactions from the hydration reactions of clinker.

### 3. Results and Discussion

#### 3.1 Frattini test

The results of the Frattini test for ages 3, 8, and 15 days are provided in Figure 1. Despite being conducted at 40°C to accelerate pozzolanic reactivity as per the standard, all samples plotted above the

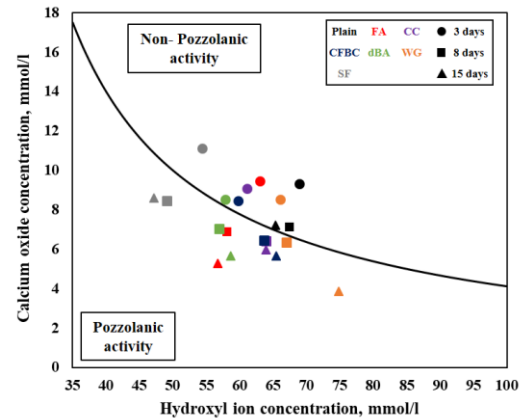


**Figure 1 Results of the Frattini test**

indicating the presence of pozzolanic reactivity. This suggests that the pozzolans reacted with the portlandite formed from the hydration of clinker, resulting in the fixation of CaO.

The Frattini test qualitatively evaluates the pozzolanic reactivity of pozzolanic cement. However, quantitative evaluation is necessary to compare the pozzolanic reactivity differences among materials. EN 196-5 provides the solubility curve of portlandite at 40°C, allowing for the calculation of theoretical CaO concentration. Table 2 shows the CaO fixation calculated from the theoretical CaO concentrations at 8 and 15 days. At 8 days, FA, dBA, and SF fixed 15.0%, 15.8%, and 17.6% of CaO, respectively, with SF fixing more CaO than FA. CC and CFBC showed similar fixation of about 10%, while WG had the

**Table 2 Quantitative Frattini test results at the 8 and 15 days**

| Inorganic recycled resources | 8 days         |                 |                        | 15 days        |                 |                        |
|------------------------------|----------------|-----------------|------------------------|----------------|-----------------|------------------------|
|                              | [OH]<br>mmol/l | [CaO]<br>mmol/l | [CaO]<br>reduction (%) | [OH]<br>mmol/l | [CaO]<br>mmol/l | [CaO]<br>reduction (%) |
| FA                           | 58.1           | 6.9             | 15.0                   | 56.7           | 5.3             | 36.9                   |
| CC                           | 64.0           | 6.4             | 10.3                   | 64.0           | 6.0             | 16.4                   |
| CBFA                         | 63.6           | 6.5             | 10.1                   | 65.5           | 5.7             | 18.3                   |
| dBA                          | 56.9           | 7.0             | 15.8                   | 58.6           | 5.7             | 29.4                   |
| WG                           | 67.0           | 6.3             | 5.6                    | 74.9           | 3.9             | 34.0                   |
| SF                           | 49.4           | 8.5             | 17.6                   | 47.2           | 8.6             | 21.1                   |

curve at 3 days, indicating no pozzolanic reactivity. However, at 8 and 15 days, the results for five samples, including FA, plotted below the curve,

lowest rate at 5.6%. At 15 days, FA and dBA showed significant CaO fixation rates of 36.9% and 29.4%, respectively. WG, which had the lowest CaO fixation

at 8 days, exhibited an additional 28% CaO fixation over the next 7 days, reaching a similar level to FA at 34%. However, CC, CFBC, and SF did not show much progress in reaction during the additional curing period. In conclusion, while there are differences in pozzolanic reactivity depending on the type of IRR and the reaction period, all materials exhibited pozzolanic reactivity within the EN 196-5 standard.

### 3.2 Saturated lime test

Figure 2 presents the SLT results for ages 1, 3, 8, and 15 days. The plain sample ( $\text{Ca}^{2+}$  concentration of 10.3 mmol/l) represents the lime solution without IRR. All IRR exhibited CaO fixation, indicating pozzolanic reactivity. While there were slight differences among IRR at the early age, CaO fixation increased continuously with age due to ongoing reactions.

SF showed the highest CaO fixation of 62.7% at 1 day, but its reactivity significantly slowed, resulting in a minor increase to 69.3% at 15 days. WG demonstrated the highest pozzolanic reactivity, with 47% CaO fixation at 1 day, and further increased to 87.3%, 94%, and 95.2% at 3, 8, and 15 days, respectively. CC and FA exhibited similar pozzolanic reactivity, ultimately fixing 64.5% and 74% of CaO, respectively. dBA showed the lowest CaO fixation (21.1%) among the tested IRR and had a similar pozzolanic reactivity trend to SF.

CFBC showed a different trend at the early age

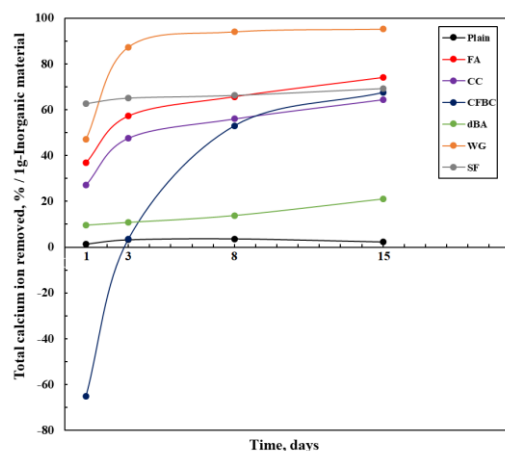


Figure 2 Results of the saturated lime test

compared to another IRR. Unlike other samples, which showed CaO fixation from 1 day, CFBC initially showed negative results, indicating an increase in CaO concentration in the solution. This suggests that while the lime solution used in the experiment contained 10.3 mmol/l of  $\text{Ca}^{2+}$ , the theoretical saturation concentration at 40°C is 20.5 mmol/l, indicating the solution was not saturated. The negative result for CFBC is likely due to the dissolution of free-CaO, which is inevitably formed during its production process. Despite this, CFBC showed significant pozzolanic reactivity, fixing 53% and 67.5% of CaO at 8 and 15 days, respectively, similar to CC and FA.

### 3.3 Strength Activity Index (SAI) Test

The SAI evaluated through compressive strength is presented in Figure 3. According to KS L 5405, the activity index must meet or exceed 80% at 28 days, while KS F 2567 requires it to meet or exceed 105% at 28 days. FA, CC, CFA, and dBA satisfied the activity index of 80%, with CC showing the highest activity index of 97.3% at 28 days, nearly equivalent to the plain sample. Continuous pozzolanic reactivity influenced strength development, with FA, CC, and CFA all exhibiting activity indices above 90% at 91 days, while dBA showed an index of 86%. In contrast, WG maintained an initial activity index of about 50%, which persisted up to 91 days, unlike other IRRs whose activity indices increased with age. Meanwhile, SF, despite being used in high-strength concrete

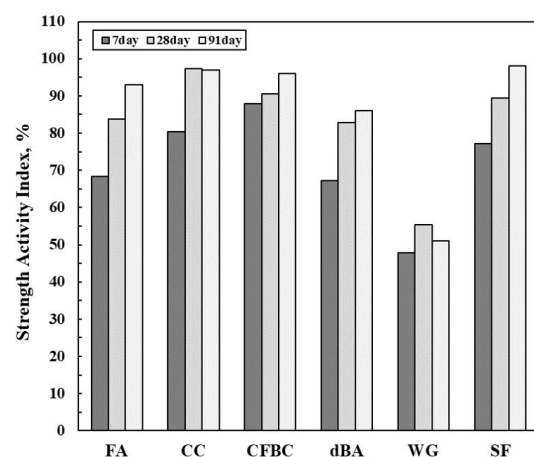


Figure 3 Results of the strength activity index

where high mechanical properties are required, did not meet the activity index threshold in this experiment. However, it showed an activity index of 98%, which is nearly equivalent to the plain.

### 3.4 R<sup>3</sup> test – bound water

Figure 4 presents the bound water content at 7 days as measured by the R<sup>3</sup> test. The results, expressed as the amount of water bound per 100g of dried paste, range from approximately 3.7 to 7.9 g/100g dried paste. An inert quartz reference sample was used to validate the experiment's reliability. The interpretation of the results indicates that higher

bound water content signifies higher pozzolanic reactivity, meaning more hydration products were formed. According to RILEM TC 267, the R<sup>3</sup> test results can be used to assess whether various SCMs contribute to strength development through chemical reactions. Based on statistical analysis, a critical

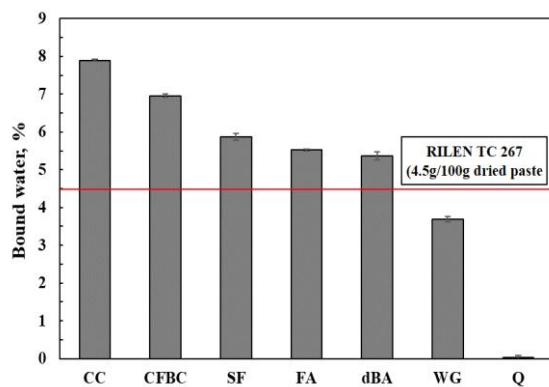


Figure 4 Results of the R<sup>3</sup> test

value of 4.5 g/100g dried paste at a 90% confidence level was suggested for bound water content [15]. When evaluating the results of this experiment against this benchmark, WG did not meet the threshold with 3.7 g/100g dried paste. In contrast, all IRR met the threshold, with CC exhibiting the highest pozzolanic reactivity at 7.9 g/100g dried paste. Consequently, based on the RILEM TC 267 criteria, all materials except WG demonstrated pozzolanic reactivity.

### 3.5 Comprehensive results of pozzolanic reactivity using various methods

Table 3 provides a comprehensive ranking of the pozzolanic reactivity of IRR as determined by various methods, and Table 4 presents the correlation coefficients between each method. Differences in reactivity ranking were observed depending on the test method and the type of IRR. Higher pozzolanic reactivity indicates the formation of more C-S-H, which directly impacts compressive strength. Comparing the methods used in this study with the SAI test, it was found that the Frattini test and SLT sometimes overestimated or underestimated the reactivity of IRR. For instance, WG showed a SAI of less than 50%, yet exhibited the highest reactivity (over 95% CaO fixation) in the SLT. In contrast, the R<sup>3</sup> test showed good correlation coefficients with the SAI. Notably, the reactivity rankings of IRR as shown by the 91 days of SAI and the R<sup>3</sup> test were consistent. These results indicate that the R<sup>3</sup> test is an

Table 3 The order of pozzolanic reactivity of the IRR obtained using various methods

| Test methods   |         | Pozzolanic reactivity |                 |                 |                 |                 |                 |
|----------------|---------|-----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                |         | 1 <sup>st</sup>       | 2 <sup>nd</sup> | 3 <sup>rd</sup> | 4 <sup>th</sup> | 5 <sup>th</sup> | 6 <sup>th</sup> |
| Frattini test  | 8 days  | SF                    | dBA             | FA              | CC              | CFBC            | WG              |
|                | 15 days | FA                    | WG              | dBA             | SF              | CFBC            | CC              |
| SLT            | 3 days  | WG                    | SF              | FA              | CC              | dBA             | CFBC            |
|                | 8 days  | WG                    | SF              | FA              | CC              | CFBC            | dBA             |
|                | 15 days | WG                    | FA              | SF              | CFBC            | CC              | dBA             |
| SAI            | 7 days  | CFBC                  | SF              | CC              | dBA             | FA              | WG              |
|                | 28 days | CFBC                  | CC              | SF              | FA              | dBA             | WG              |
|                | 91 days | CC                    | CFBC            | SF              | FA              | dBA             | WG              |
| R <sup>3</sup> | 7 days  | CC                    | CFBC            | SF              | FA              | dBA             | WG              |

**Table 4 The correlation coefficients of pozzolanic reactivity of the IRR obtained using various methods**

| Test methods   |         | SAI     | Frattini |         | SLT    |        |        | R <sup>3</sup> |        |
|----------------|---------|---------|----------|---------|--------|--------|--------|----------------|--------|
|                |         | 28 days | 8 days   | 15 days | 1 days | 3 days | 8 days | 15 days        | 7 days |
| SAI            | 28 days | 1.00    | 0.53     | -0.70   | -0.30  | -0.55  | -0.52  | -0.44          | 0.92   |
| Frattini       | 8 days  |         | 1.00     | -0.01   | 0.22   | -0.25  | -0.54  | -0.57          | 0.17   |
|                | 15 days |         |          | 1.00    | 0.38   | 0.40   | 0.21   | 0.15           | -0.82  |
| SLT            | 1 days  |         |          |         | 1.00   | 0.83   | 0.39   | 0.25           | -0.42  |
|                | 3 days  |         |          |         |        | 1.00   | 0.83   | 0.73           | -0.51  |
|                | 8 days  |         |          |         |        |        | 1.00   | 0.99           | -0.36  |
|                | 15 days |         |          |         |        |        |        | 1.00           | -0.26  |
| R <sup>3</sup> | 7 days  |         |          |         |        |        |        |                | 1.00   |

efficient and reliable method for quantitatively confirming the pozzolanic reaction, which typically progresses slowly over the long term, within a short period.

#### 4. Conclusions

In this study, the pozzolanic reactivity of six IRR was evaluated using the Frattini test, SLT, SAI, and R<sup>3</sup> test. Among these methods, the R<sup>3</sup> test exhibited the best correlation with compressive strength. Additionally, based on the R<sup>3</sup> test results, CC demonstrated higher reactivity than both the traditionally used FA and SF. Therefore, CC is considered a strong candidate for use as a new SCM, potentially replacing conventional materials such as blast furnace slag and fly ash.

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