# Evaluating Reactivity of Supplementary Cementitious Materials in Low-Carbon Triple-Blended Systems: Assessment Using Calorimetry and Strength Activity Index

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**Abstract**: The increasing demand for sustainable construction materials has driven the development of low-carbon cementitious systems incorporating supplementary cementitious materials (SCMs) such as fly ash and slag. This study investigates the reactivity of SCMs in paste samples using isothermal calorimetry and mortar samples using the Strength Activity Index (SAI). Paste samples with varying fly ash and slag proportions were prepared to evaluate hydration kinetics, phase development, and mechanical performance. The results demonstrate that mixes with higher slag content exhibit enhanced early-age reactivity due to slag's latent hydraulic properties, promoting early C-S-H formation. Conversely, fly ash-rich mixes displayed prolonged pozzolanic activity, improving long-term strength development. The integration of calorimetry and SAI results highlights the combined influence of hydration kinetics and phase formation on mechanical performance. These findings contribute to optimizing SCM combinations for improved early-age strength, long-term durability, and sustainability in low-carbon concrete applications.

**Keywords**: Reactivity, Hydration kinetic, Triple blend, Strength Activity Index, Isothermal calorimetry

## 1. INTRODUCTION

The increasing demand for sustainable construction materials has accelerated the development of low-carbon concrete incorporating supplementary cementitious materials (SCMs) such as fly ash and slag. These materials are essential in modern concrete design due to their ability to reduce the environmental impact of cement production while enhancing the mechanical and durability properties of concrete. Understanding the reactivity of SCMs is critical for optimizing their performance in blended cement systems and ensuring long-term durability in concrete structures.

Fly ash and slag are widely used SCMs that play complementary roles in enhancing concrete performance. While both materials contribute to hydration reactions, their reactivity is influenced by distinct physical and chemical characteristics. Combining fly ash and slag in blended cement systems leverages their strengths to optimize hydration, strength development, and durability.

The reactivity of fly ash and slag is governed by several factors, including fineness, particle size distribution (PSD), particle shape, and amorphous phase content.

Fineness - Finer particles provide greater surface area, accelerating hydration reactions. Research by Paya et al. (1) showed that fly ash particles smaller than 10 μm significantly improved the strength of mortar. Similarly, Aydin et al. (2) demonstrated that increasing the Blaine fineness of fly ash from 290 $m^2/kg$ to 907 $m^2/kg$ using a ball mill, resulted in enhanced compressive strength under steam curing conditions. Similarly, increasing the fineness of slag enhances its reactivity and promotes greater strength development at later ages by improving hydration. Unlike fly ash, Finer slag particles promote strength development at later ages due to improved hydration, though they have a limited effect on early strength because slag generally hydrates more slowly (3). However, economic and energy considerations often constrain further increasing slag fineness, which must be balanced with the desired reactivity improvements. Thus, optimising slag's fineness within practical limits is essential for achieving both reactivity and cost efficiency in concrete applications.

Particle Shape - The spherical nature of fly ash particles improves workability by enhancing packing density and reducing friction. Conversely, the angular structure of slag may increase surface area, promoting enhanced early-age reactivity (4).

Amorphous Phase Content - The amorphous (vitreous) phase content significantly dictates the reactivity of both materials. Research by Ward and French (5) demonstrated that higher glass content in fly ash enhanced pozzolanic activity, while Babu and Kumar (6) and Gruskovnjak et al. (7) confirmed that slag with a higher vitreous phase content promoted faster hydration and improved long-term durability.

Assessing the reactivity of SCMs requires reliable experimental techniques that capture their complex hydration behaviour. Among these methods, Isothermal calorimetry and the Strength Activity Index (SAI) are particularly effective in evaluating SCM performance at both early and later stages.

Isothermal calorimetry measures the heat flow during hydration, offering valuable insights into hydration kinetics and the degree of SCM reaction. Studies by Ramanathan (8) and Snellings (9) demonstrated that calorimetry effectively distinguishes between SCMs with varying reactivity, correlating early heat release with strength development. Furthermore, calorimetry provides valuable data on the synergistic effects of SCM combinations, where ternary blends containing fly ash and slag often exhibit prolonged hydration with sustained heat release (10).

The Strength Activity Index (SAI) is a well-established method for assessing SCM reactivity by measuring compressive strength relative to a control cement mix. By analysing early-age and long-term strength data, SAI provides insights into the contribution of both slag's early hydration and fly ash's sustained pozzolanic reactions.

By integrating calorimetry and SAI, researchers can comprehensively evaluate SCM behaviour, identify optimal SCM proportions, and develop improved mix designs for enhanced concrete performance and sustainability. This study investigates the reactivity of various combinations of fly ash and slag in triple-blended paste systems using calorimetry and SAI. The insights gained from this research will contribute to optimizing SCM proportions for improved hydration kinetics, strength development, and long-term durability in low-carbon concrete formulations.

In cementitious paste systems, SCM reactivity directly influences the formation of hydration products, which impact mechanical strength, durability, and microstructural stability. While binary systems have been widely studied, research on triple-blended paste systems remains limited.

## 2. MATERIALS AND METHODS

### 2.1 Binder

The binders used in this study include Ordinary Portland Cement, fly ash (FA), and Ground Granulated Blast Furnace Slag (GGBFS).

### 2.2 Mix Proportions

The paste mixes were designed to evaluate SCM reactivity in triple blends. All mixes replaced 50% of cement with SCMs by volume.

**Table 2. Mix the proportion of binders**

| MIX ID | OPC (%v) | FA (%v) | GGBFS (%v) |
|---|---|---|---|
| OPC | 100 | 0 | 0 |
| F0S5 | 50 | 0 | 50 |
| F1S4 | 50 | 10 | 40 |
| F2S3 | 50 | 20 | 30 |
| F3S2 | 50 | 30 | 20 |
| F4S1 | 50 | 40 | 10 |
| F5S0 | 50 | 50 | 0 |

2.3 Method

**Table 3. The method used to measure reactivity**

| Method | Equipment | Standard | Description |
|---|---|---|---|
| Isothermal calorimetry | I -Cal 4000 | ASTM C1702 | Conduct at 23˚C for 7 days to assess early age hydration kinetics, heat flow was continuously recorded. |
| Strength activity index | | ASTM C311 | Compressive strength was measured at 7 and 28 days. Results were normalized against the control cement mix. |

## 3. RESULTS AND DISCUSSION

### 3.1 Strength Activity Index

The Strength Activity Index (SAI) results provide valuable insights into the reactivity and performance of supplementary cementitious materials (SCMs) in comparison to the reference Ordinary Portland Cement (OPC) mix.

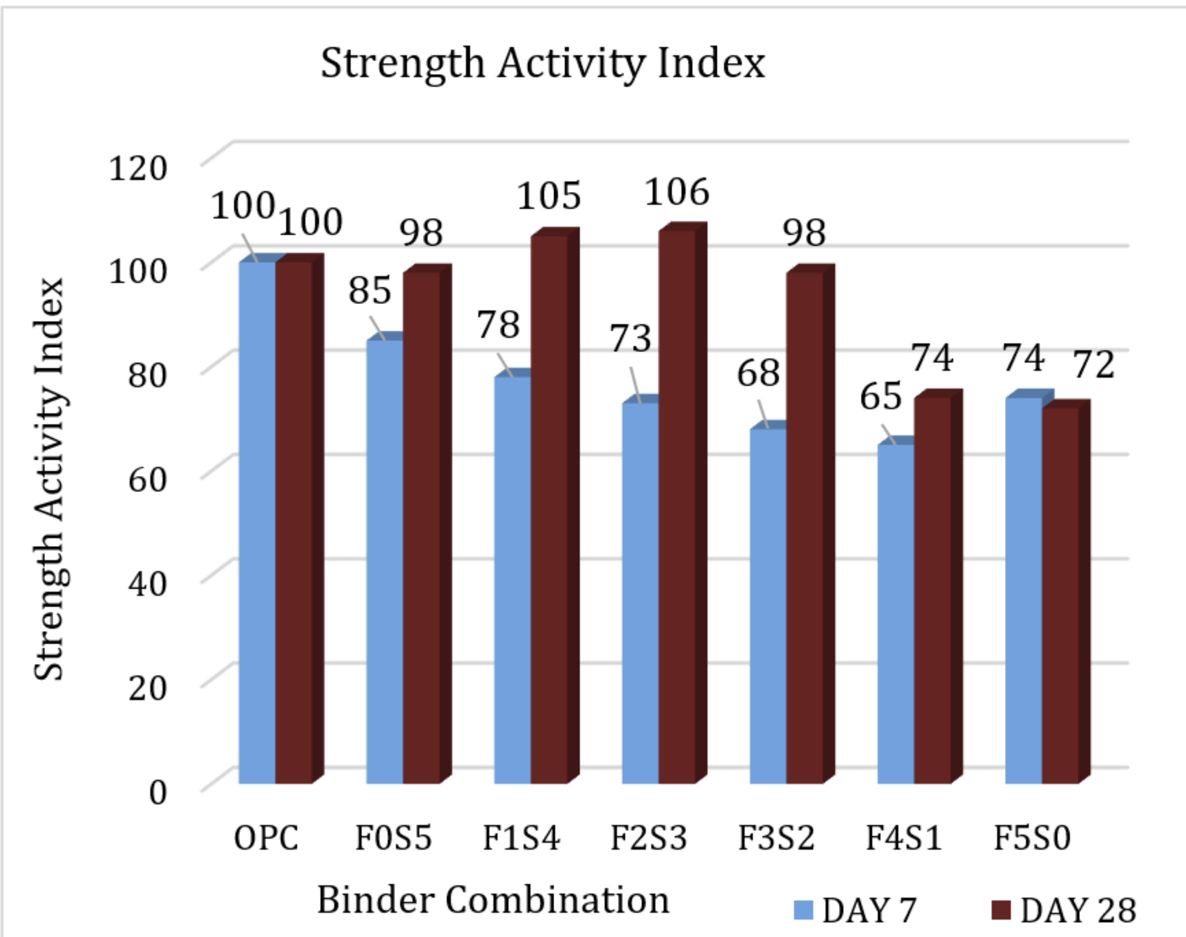


**Figure 1 – Strength Activity Index of mortar for 50% SCM**

At 7 days, Ordinary Portland Cement (OPC) achieved the highest SAI of 100%, reflecting rapid early-age hydration. Mixes incorporating supplementary cementitious materials (SCMs) showed reduced early-age strength, attributed to slower hydration kinetics. Among these, the blend containing 50% slag (F0S5) exhibited relatively higher early strength (SAI=85), followed by balanced blends such as F1S4 (SAI=78) and F2S3 (SAI=73). Fly ash-rich blends, including F3S2 (SAI=72), F4S1 (SAI=68), and F5S0 (SAI=68), displayed the lowest early-age strengths, consistent with the delayed pozzolanic activity of fly ash.

**Table 3. Strength activity index on the 7th and 28th day**

| Strength Activity Index | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mix Id | OPC | F0S5 | F1S4 | F2S3 | F3S2 | F4S1 | F5S0 |
| Day 7 | 100 | 85 | 78 | 73 | 68 | 65 | 74 |
| Day 28 | 100 | 98 | 105 | 106 | 98 | 74 | 72 |

By 28 days, significant improvements in the mechanical performance of SCM mixes were observed, with all blends surpassing the industry standard threshold of 75% SAI, indicating their high quality and suitability for intended construction applications. The F2S3 blend demonstrated the highest strength gain (SAI=106), closely followed by F1S4 (SAI=105), confirming that balanced combinations of fly ash and slag provided optimal reactivity and strength development. Blends richer in fly ash, such as F3S2, F4S1, and F5S0, continued to show relatively lower strength values (SAI between 75-85), indicative of the inherently slower pozzolanic reaction of fly ash.

3.2 Isothermal Calorimetry

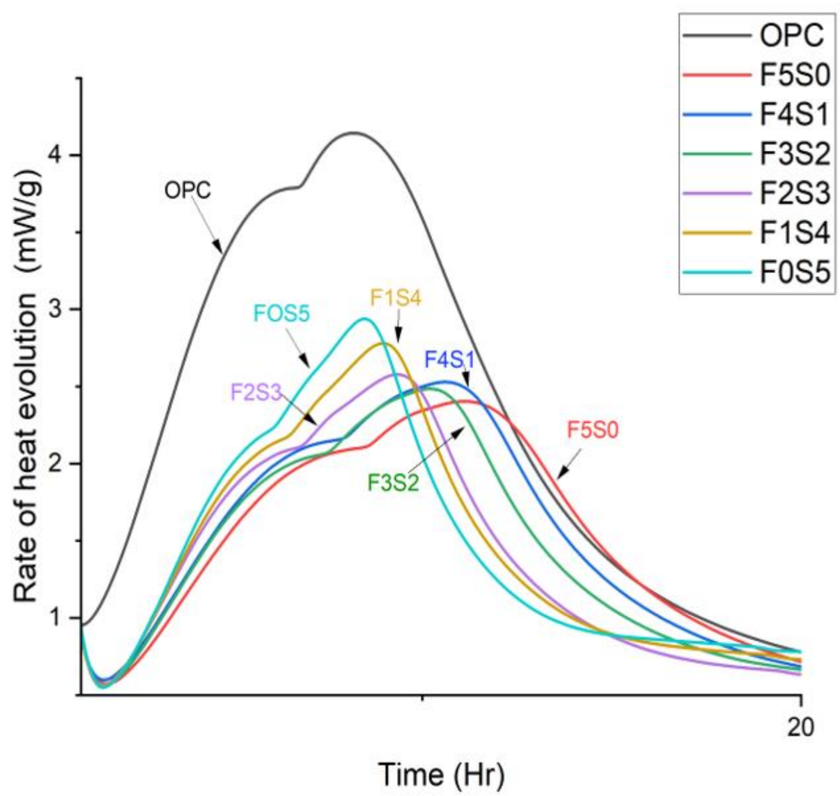


**Figure 2 – Rate of heat evolution curve for 50 % SCM**

The calorimetry results illustrate distinct hydration characteristics across the tested paste systems, reflecting the influence of varying fly ash (FA) and slag (S) proportions. The OPC mix exhibited the highest and sharpest early-age heat peak, indicative of rapid cement hydration without SCM replacement. In contrast, the F5S0 mix, containing a high proportion of fly ash and no slag, displayed the lowest initial heat evolution, confirming the well-known delayed pozzolanic reactivity of fly ash. Conversely, the F0S5 mix, which incorporated 50% slag without fly ash, demonstrated an accelerated and pronounced heat release peak, reinforcing the slag's ability to enhance early hydration through its latent hydraulic properties.

Blended systems such as F1S4, F2S3, and F3S2 exhibited intermediate hydration behaviour, with their peaks appearing later than OPC but earlier than the fly ash-dominant system, indicating a balanced hydration process. The combined presence of slag (promoting early heat release) and fly ash (supporting sustained hydration) suggests that these blends may provide improved long-term performance.

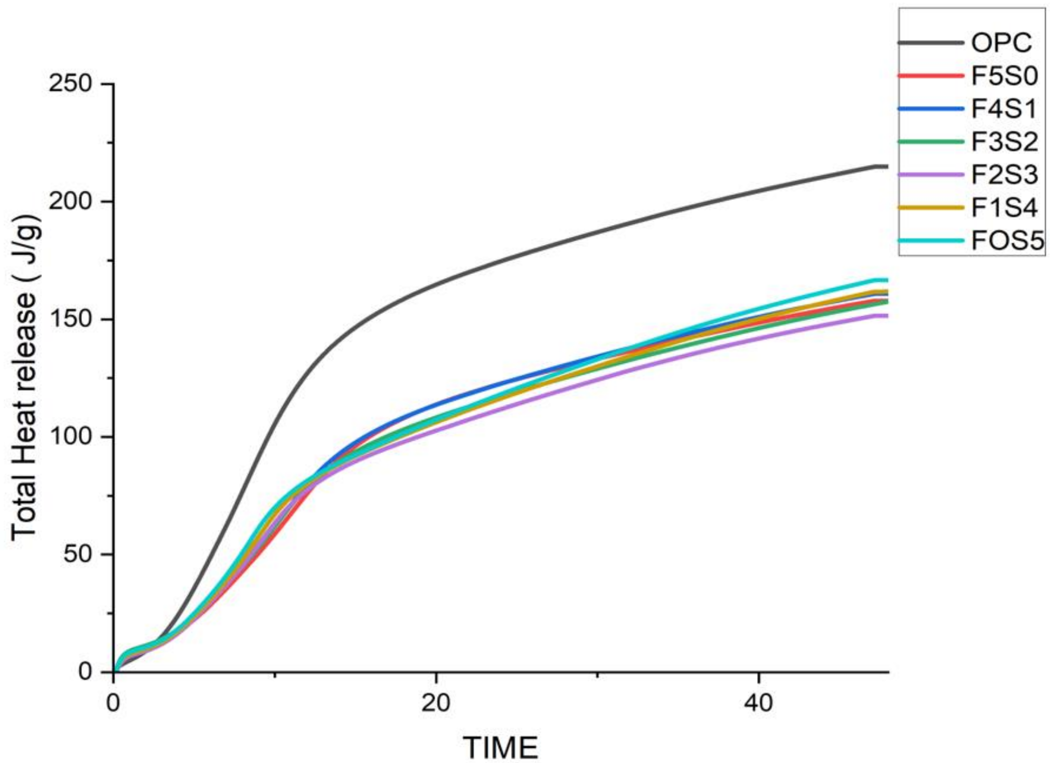


**Figure 3. Total heat release curve for 50% SCM**

The cumulative heat release profile of binder combinations offers key insights into the hydration mechanisms influenced by dilution and filler effects. These effects significantly impact the hydration kinetics, microstructural development, and performance of SCM-rich systems.

The dilution effect refers to the reduction in cement content when SCMs partially replace Portland cement, resulting in lower early heat evolution. As OPC contains a higher clinker content, it exhibited the highest cumulative heat release across all time points, attributed to the rapid hydration of $C_3S$ and $C_3A$ phases. This accelerated heat release promotes early C-S-H and calcium hydroxide (CH) formation, enhancing initial strength development.

In SCM-rich mixes, such as F5S0 (50% FA) and F4S1 (40% FA, 10% GGBFS), the reduced clinker content led to slower initial heat evolution. The delayed hydration in these blends is characteristic of fly ash, which requires calcium hydroxide from cement hydration to trigger secondary pozzolanic reactions.

Consequently, these mixes exhibited lower early-age heat release due to reduced immediate cement dissolution and slower SCM activation.

Conversely, ternary blends like F2S3 (20% FA, 30% GGBFS) and F3S2 (30% FA, 20% GGBFS) displayed improved heat evolution due to the synergistic interaction between slag's latent hydraulic properties and fly ash's pozzolanic contribution. The inclusion of slag in these mixes facilitated earlier C-S-H formation, partially offsetting the dilution effect by accelerating hydration kinetics.

The filler effect describes the role of fine, inert SCM particles in enhancing particle packing, nucleation, and hydration product formation. Although FA and GGBFS may not contribute immediately to hydration reactions, their fine particles provide nucleation sites for C-S-H growth, promoting microstructural refinement.

This effect was evident in blends like F4S1 and F3S2, which demonstrated sustained heat evolution beyond 24 hours. The presence of fine SCM particles improved the microstructural densification by filling voids and enhancing the connectivity of hydration products. This synergy resulted in higher cumulative heat release in these balanced mixes compared to those dominated by fly ash or slag alone.

The observed heat release trends confirm that the dilution effect delays early hydration in SCM-rich systems with reduced clinker content, whereas the filler effect enhances particle packing and long-term hydration performance. Blends like F4S1, F2S3 and F3S2 successfully balance these effects, achieving improved early hydration while maintaining sustained pozzolanic reactivity. These findings emphasise the need for optimised SCM proportions to maximise both early-age performance and long-term durability in low-carbon concrete systems.

**Table 4. Heat release of paste samples over time**

| Time | Heat Release (J g-1) | | | | | | |
|---|---|---|---|---|---|---|---|
| | OPC | F5S0 | F4S1 | F3S2 | F2S3 | F1S4 | F0S5 |
| 24 | 175 | 123 | 123 | 117 | 112 | 116 | 118 |
| 48 | 215 | 158 | 161 | 157 | 152 | 162 | 167 |
| 72 | 234 | 176 | 183 | 183 | 154 | 165 | 170 |
| 96 | 255 | 192 | 198 | 200 | 156 | 168 | 173 |
| 120 | 268 | 203 | 211 | 214 | 159 | 170 | 176 |
| 143 | 276 | 212 | 221 | 225 | 161 | 173 | 178 |
| 168 | 283 | 220 | 223 | 227 | 163 | 175 | 184 |

The OPC mix exhibited the highest cumulative heat release (283 J/g at 168 hours) due to its rapid hydration driven by high clinker content. Among SCM-based mixes, F5S0 (50% FA, 0% GGBFS) showed the lowest heat release (220 J/g), reflecting fly ash's slower pozzolanic reaction.

The ternary blend F3S2 (30% FA, 20% GGBFS) recorded the highest heat release among SCM mixes (227 J/g), demonstrating fly ash's delayed and sustained reactivity. F4S1 (40% FA, 10% GGBFS) achieved 223 J/g, reinforcing the benefits of balanced SCM proportions. Mixes with dominant slag content, such as F0S5 (0% FA, 50% GGBFS), showed improved early hydration but lower long-term reactivity (184 J/g).

Overall, the data suggest that while OPC delivers the best standalone performance, certain slag-dominant blends offer competitive results with significantly reduced clinker content, supporting their suitability for low-carbon concrete applications.

The early-age Strength Activity Index (SAI) values varied across the different mixes. Some mixes exhibited relatively high strength at early ages, while others showed moderate performance. These differences may be influenced by improved particle packing, reduced porosity, and enhanced microstructural development, which contribute to strength gain. For instance, denser binder matrices can result from optimised packing of the supplementary cementitious materials, leading to improved load-bearing capacity. Additionally, early formation of hydration products like calcium silicate hydrate (C–S–H) in a more refined microstructure may also enhance early strength. These mechanisms collectively highlight the multifaceted nature of strength development beyond just chemical reactivity.

## 4. CONCLUSION

The results of this study demonstrate that both isothermal calorimetry and the Strength Activity Index (SAI) are valuable tools for characterising the reactivity and performance of supplementary cementitious materials (SCMS) in triple-blended paste systems. Mixes with higher slag content exhibited enhanced early-age reactivity, as evidenced by greater cumulative heat release, reflecting slag's latent hydraulic behaviour and its ability to accelerate early hydration. On the other hand, fly ash-dominant blends showed slower heat evolution but exhibited steady strength development over time, likely due to ongoing pozzolanic activity.

Mixes such as F2S3 and F3S2 showed favourable performance in terms of both heat release and compressive strength, indicating that balanced combinations of fly ash and slag can support both early hydration and long-term strength gain.

To further explore the mechanisms influencing these outcomes, advanced characterisation techniques such as X-ray diffraction (XRD), thermogravimetric analysis (TGA), and pH tracking are being conducted. These analyses will provide deeper insights into phase development, microstructural evolution, and chemical interactions, ultimately contributing to the understanding and optimisation of durable, low-carbon cementitious systems.

## 5. ACKNOWLEDGEMENT

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