REACTIVITY ASSESSMENT OF POZZOLANIC MATERIALS FOR PARTIAL REPLACEMENT OF CEMENT IN CONCRETE

by

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ABSTRACT

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Under the Supervision of Professor Habib Tabatabai

Reductions in portland cement use have important benefits in reducing the embodied energy in concrete and controlling CO_2 emissions. Developing new, sustainable, and low-carbon construction materials is critical in addressing climate change. Many industrial by-products are disposed of in landfills as waste materials. It is imperative to assess the pozzolanic reactivity of industrial by-products and other waste materials to develop alternative supplementary cementitious materials (SCMs) such as pozzolanic materials. This study evaluates the pozzolanic reactivity of seven different powdered materials: pottery cull, brick powder, lightweight aggregate fines, class C fly ash, silica fume, glass powder, and dolostone. Seven different pozzolanic reactivity test methods were employed: the Frattini test, strength activity index (SAI), ultrasound pulse velocity index, thermogravimetric analysis, calorimetry, electrical conductivity, and pH. A comparative study was performed to evaluate the efficiency and efficacy of various pozzolanic reactivity test methods through robust correlation analyses and a ranking method. The degree of pozzolanic reactivity of the tested materials was also compared. An analytical approach for calculating the amount of consumed portlandite is proposed for the electrical conductivity and pH test methods, and the results are then correlated with the Frattini and TGA results. Electrical conductivity and pH tests are rapid, effective, and direct methods for assessing pozzolanic reactivity. Finally, this study

proposes an equation to predict the SAI of any potential pozzolan using its chemical and physical properties, thus providing more efficient and timely assessments.

I dedicate this dissertation to my parents who have been an unwavering source of support, love, and inspiration throughout my life.

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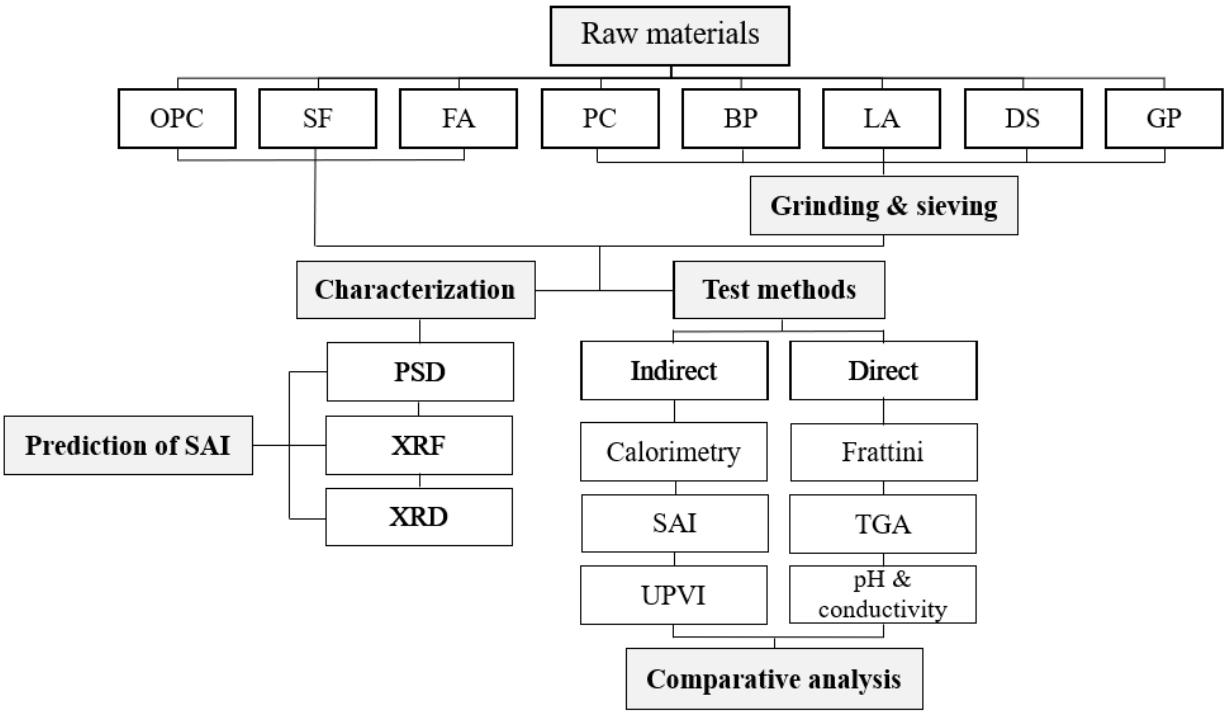
Research framework

The research framework is reported in the following diagram.



Chapter 1: History and background

1-1. Introduction

1-1-1. Scope

cement and concrete and discusses opportunities associated with alternative pozzolanic materials for beneficial use in concrete as sustainable partial replacement for portland cement. The background, statement of problem, objectives, structure, and scope of this thesis are briefly summarized.

1-1-2. Background

Concrete is the most widely used construction material worldwide. It is commonly produced by mixing portland cement, water, sand (fine aggregate), and gravel (coarse aggregate). The beneficial factors that have contributed to its widespread usage are as follows [1]:

- Formability into a variety of shapes and sizes.
- Economical to produce with readily available materials.
- Reduced maintenance requirements for corrosion when compared to steel.
- Fire resistance

Portland cement is a finely pulverized material that develops its binding properties due to hydration (chemical reaction between water and cement). Portland cement is the most widely used hydraulic cement for producing concrete. The binding characteristics of portland cement are due to the formation of calcium silicate hydrates (C-S-H) (among other products). During hydration, C-S-H reaction products are stable in aqueous environments [1].

To reduce the economic and environmental costs of portland cement production and to improve the durability of concrete, supplementary cementitious materials (SCMs) are commonly used to

partially replace cement in concrete. In a recent study, SCMs were classified into three major types depending on their generated reaction products: fillers, active non-pozzolanic additions, and active pozzolanic additions [2]. In this study, SCMs are classified as fillers, latent hydraulic materials, and pozzolans with some examples of each type provided in fig 1.1 based on the literature. Prior to the invention of portland cement, pozzolans had been used for making concrete and mortars. Greeks, Romans, and other ancient civilizations made concretes and mortars using various cementitious binders consisting of natural pozzolans such as volcanic ash, pulverized pumice, and diatomaceous earth [3]. Pozzolans were mixed with water and burnt limestone to form cementitious materials. In general, pozzolans are siliceous or siliceous alumina materials that react with calcium hydroxide to form cementitious materials. The term pozzolan comes from pozzolana, the name given to a deposit of volcanic materials located near Pozzuoli, Italy including pumice ash and trachyte [3]. Trachyte is a volcanic rock that is mainly feldspar crystals in a matrix of silica [3]. Some of the oldest natural pozzolans were reported in the Mediterranean region, which were produced from two volcanic eruptions that occurred between 1600 and 1500 BC in Greece and in 79 AD in Italy[3]. Both materials contained almost 80% volcanic glass (pumice and obsidian) [3]. The Greek masons found pozzolan-lime mixtures between 700 and 600 BC and passed the knowledge to Romans in 150 BC. Then, the Romans explored and developed a variety of pozzolans during the 600 years of their domination [3]. The structures that Greeks and Romans built such as aqueducts, sea walls and marine structures demonstrate the durability of pozzolan-lime mortars under mild weather conditions [3]. According to Thorstensen and Fidjestol [4], pozzolans are natural or industrial by-products that reduce cement consumption in concrete mixtures by increasing the mechanical strength of

cement matrices leading to reductions in final economic and environmental costs. Since, some of the pozzolans are industrial by-products (e.g., fly ash and silica fume), their use can offer a beneficial solution for some by-products that would otherwise be disposed of as waste [5].

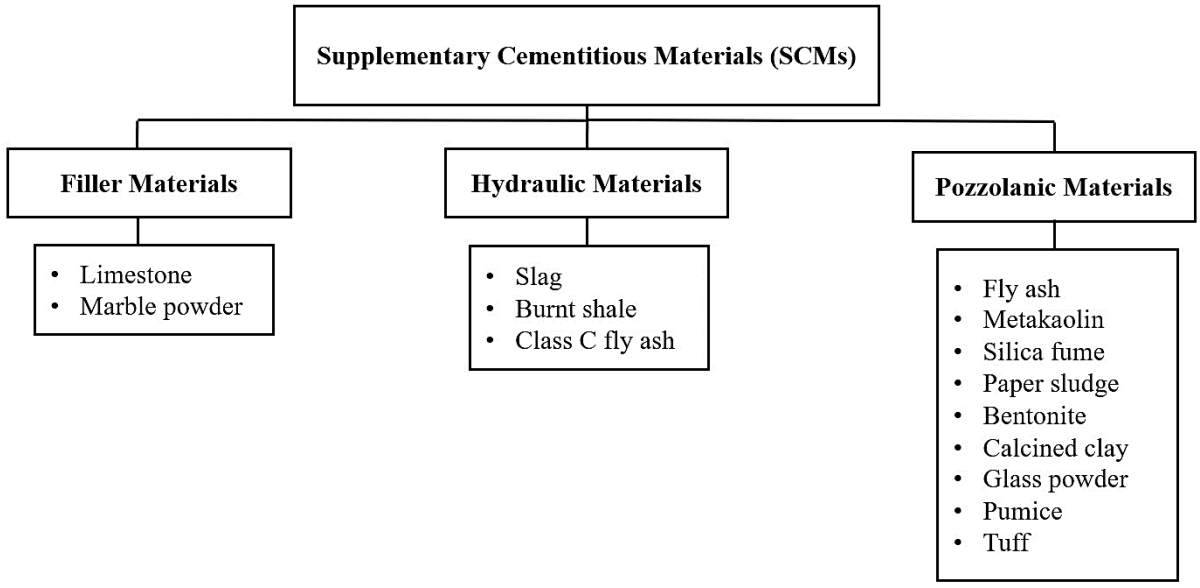


Figure 1-1: Classification of SCMs.

1-1-3. Pozzolans

1-1-3-1. Natural pozzolans

All nature pozzolanic materials except diatomaceous earth are derived from volcanic rocks [6]. Natural pozzolans are in the category of SCMs that may require grinding or calcination processing. Natural pozzolans had a significant role in the development of mortars and concrete leading to the improved mortars and concretes of today. According to ASTM C618, the sum of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3) in natural pozzolans and fly ash must be more than 70% and 50%, respectively [7].

1-1-3-2. Zeolites

Zeolites are hydrated crystalline aluminosilicates composed of a three-dimensional framework of SiO_4 and AlO_4 tetrahedra [8]. Over the past 200 years, 40 natural zeolites have been identified [9]. The most well-known include analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite and phillipsite. Zeolites may also be synthetic as well[9]. According to Virta Virta (2002), one hundred and fifty synthetic zeolites have been produced. Zeolites have pozzolanic properties due to the presence of reactive silica (SiO_2) and alumina (Al_2O_3) which can react with $Ca(OH)_2$ to produce C-S-H gel and hydrate aluminate phases. Therefore, Zeolites can be used as a cement replacement material [3,10].

1-1-3-3. Calcined clays

The most abundant raw materials for calcined pozzolans are clay minerals [11]. According to ASTM C618, raw or calcined natural pozzolans including clays and shales are classified as class N that require calcination to achieve the necessary properties [7]. Calcined clays are an excellent source of SCMs [12]. Due to production of highly reactive amorphous metakaolin phase after calcination, kaolinitic clays exhibit the highest pozzolanic reactivity among all types of clays [13]. Metakaolin is a calcined kaolinite clay that is commonly used as SCM in concrete. During calcination of clays some clay minerals like illite and hectorite are dehydroxylated and stay inert in cementitious mix. However, other minerals such as calcined smectite, bentonite and montmorillonite clays can be pozzolanic reactive [12].

1-1-3-4. Fly ash

Fly ash is a by-product from coal burning power production and is a common SCM used in concrete [14]. There are two types of fly ash: siliceous fly ash (also known as class F fly ash) and calcareous fly ash (also known as class C fly ash) [15]. Both types of fly ash are fine powders with

mostly spherical particles having pozzolanic properties. Siliceous fly ash mostly consists of reactive silica (SiO_2) and alumina (AL_2O_3) while calcareous fly ash consists of reactive calcium oxide as well as silica and alumina providing both hydraulic and pozzolanic properties for this type of fly ash [15]. One of the reasons for using fly ash in concrete is to reduce early heat generation in concrete that can lead to thermal cracking, enhance durability, and decrease expansion due to alkali silica reaction (ASR) [14].

1-1-3-5. Silica fume

Silica fume is a by-product derived from the production of silicon and ferrosilicon alloys in electric arc furnaces [16]. It is made up of very fine amorphous spherical particles. Silica fume is a more reactive pozzolan compared to natural pozzolan and fly ash and can significantly enhance the compressive strength of concrete [17].

1-1-4. Problem statement

Approximately 7% of the anthropogenic emissions worldwide (e.g., CO_2) is related to the production of portland cement [18]. Production of one ton of portland cement can be attributed to 0.9 tons of carbon dioxide emissions. In addition, moderate quantities of NO_x, SO_x and particulates are emitted into the atmosphere during cement production [19]. Therefore, the concrete industry is under growing pressure to decrease the greenhouse gas emissions and embodied energy in portland cement production [14]. The global construction industry can potentially reduce the environmental footprint of its activities through reductions in the production of portland cement [20]. On the other hand, by increasing production of construction materials like cement, mining industry is also under pressure for extraction of natural resources and generating a great deal of waste [21]. In this respect, finding highly reactive materials (e.g.,

pozzolans) that are suitable for partial or full replacement of portland cement in concrete not only helps to reduce the negative environmental and economic impacts of concrete but can also provide a way to minimize landfilling of industrial waste materials. Currently, fly ash, a by-product from coal combustion, is commonly used in concrete [14]. According to the American Coal Ash Association (ACAA), and the American Road and Transportation Builders Association (ARTBA) estimates, concrete production is expected to increase by more than 50% by 2033. This means that the production of common SCMs (like fly ash) would have to increase substantially to meet demand. All fly ash produced in coal-burning power plants cannot be used in concrete and the overall supply of fly ash is expected to decline with the reduction in coal-burning power plants. Hence, there would be an expected gap between supply and demand of fly ash in the future [14]. There have been recent acute shortages of fly ash in several markets. Therefore, exploring alternative SCMs and pozzolanic materials for partial replacement of cement in concrete is required.

1-1-5. Pozzolanic behavior and reactivity

Pozzolanic reactivity is the main beneficial function of supplementary cementitious materials. Pozzolans can stabilize calcium hydroxide ($Ca(OH)_2$) or portlandite (produced during cement hydration reactions) and form hydrated phases including calcium silicate hydrates (C-S-H), calcium aluminate hydrates (C-A-H), or calcium aluminosilicate hydrates (C-A-S-H). Pozzolanic activity can be measured by means of $Ca(OH)_2$ reduction or the formation of hydrated phases [5]. These factors are related to the nature of pozzolan, quantity, quality, size of active phases as well as the amount of water that is available for the reaction [5]. Reactive pozzolanic materials have

high oxide contents (specifically silicon dioxide, aluminum oxide and iron oxide) that should exceed 70% of the mass of the pozzolan as specified in ASTM C618 [7].

1-2. Research significance

This research explores avenues for extending the use of the waste materials and industrial by-products that have the potential to partially replace portland cement in concrete especially in the context of current and expected shortages of conventional SCMs such as fly ash.

1-3. Research objectives

The primary objectives of this research are:

- Finding new pozzolanic materials from industrial waste products such as pottery cull and lightweight aggregate fines.
- Using physical and chemical characteristics of materials to predict the strength activity index.
- Using comparative analyses to categorize and rank various reactivity test methods and pozzolans.
- Exploring electrical conductivity and pH tests as direct methods for assessing the amount of lime consumed by pozzolans.

1-4. References for chapter 1

[1] P.K. Mehta, P.J.M. Monteiro, Concrete microstructure, properties, and materials, 4th ed., McGrew Hill Education, New Delhi, 2016.

[2] C.M. Martinez, I.S. del Bosque, M.F. G. Medina, M.S. de Rojas, Fillers and additions from industrial waste for recycled aggregate concrete, 2022. https://doi.org/10.1016/b978-0-12-824105-9.00012-3.

[3] ACI 232.1R, ACI 232.1R-12 Report on the Use of Raw or Processed Natural Pozzolans in Concrete, (2012).

[4] R.T. Thorstensen, P. Fidjestol, Inconsistencies in the pozzolanic strength activity index (SAI) for silica fume according to EN and ASTM, Materials and Structures/Materiaux et Constructions. 48 (2015) 3979–3990. https://doi.org/10.1617/s11527-014-0457-6.

[5] O. Mendoza, J.I. Tobo, An alternative thermal method for identification of pozzolanic activity in Ca $(OH)_2$/pozzolan pastes, (2013) 589–596. https://doi.org/10.1007/s10973-013-2973-y.

[6] V.M. Malhotra, P.K. (Povindar K. Mehta, Pozzolanic and cementitious materials, Gordon and Breach, 1996.

[7] ASTM C618: Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, (2019).

[8] S. Liu, X. Cao, L. Li, C. Li, Y. Ji, F.S. Xiao, Preformed zeolite precursor route for synthesis of mesoporous X zeolite, Colloids Surf A Physicochem Eng Asp. 318 (2008) 269–274. https://doi.org/10.1016/J.COLSURFA.2008.01.002.

[9] R. Virta, Zeolites, U.S. Geological Survey Minerals Yearbook, 2002.

[10] T. Perraki, G. Kakali, E. Kontori, Characterization and pozzolanic activity of thermally treated zeolite, J Therm Anal Calorim. 82 (2005) 109–113. https://doi.org/10.1007/S10973-005-0849-5.

[11] E.F. Irassar, A. Tironi, V.L. Bonavetti, M.A. Trezza, C.C. Castellano, V.F. Rahhal, H.A. Donza, A.N. Scian, Thermal Treatment and Pozzolanic Activity of Calcined Clay and Shale, ACI Mater J. 116 (2019) 133–143. https://doi.org/10.14359/51716717.

[12] M.C.G. Juenger, R. Snellings, S.A. Bernal, Supplementary cementitious materials: New sources, characterization, and performance insights, Cem Concr Res. 122 (2019) 257–273. https://doi.org/10.1016/j.cemconres.2019.05.008.

[13] F. Avet, X. Li, K. Scrivener, Determination of the amount of reacted metakaolin in calcined clay blends, Cem Concr Res. 106 (2018) 40–48. https://doi.org/10.1016/j.cemconres.2018.01.009.

[14] I. Diaz-Loya, M. Juenger, S. Seraj, R. Minkara, Extending supplementary cementitious material resources: Reclaimed and remediated fly ash and natural pozzolans, Cem Concr Compos. 101 (2019) 44–51. https://doi.org/10.1016/j.cemconcomp.2017.06.011.

[15] British Standard Institution BSI, Methods of testingComposition, Specifications and Conformity Criteria for Common Cements, Bs En 197. (2011) 50.

[16] L. Black, Low clinker cement as a sustainable construction material, Sustainability of Construction Materials. (2016) 415–457. https://doi.org/10.1016/B978-0-08-100370-1.00017-2.

[17] J. Fink, Cement additives, Petroleum Engineer’s Guide to Oil Field Chemicals and Fluids. (2021) 441–492. https://doi.org/10.1016/B978-0-323-85438-2.00010-4.

[18] K. Robalo, H. Costa, R. Do Carmo, E. Júlio, Enhanced Mechanical and Durability Performances of Low Cement Concrete with Natural Pozzolan Addition, Journal of Advanced Concrete Technology. 19 (2021) 519–535. https://doi.org/10.3151/jact.19.519.

[19] G.M.S. Islam, M.H. Rahman, N. Kazi, Waste glass powder as partial replacement of cement for sustainable concrete practice, International Journal of Sustainable Built Environment. 6 (2017) 37–44. https://doi.org/10.1016/J.IJSBE.2016.10.005.

[20] J.L. Provis, S.A. Bernal, Geopolymers and Related Alkali-Activated Materials, Annual Review of Materials Research. 44 (2014) 299–327. https://doi.org/10.1146/ANNUREV-MATSCI-070813-113515.

[21] S.C.L. Lima, L.C.B. Costa, K.C.S. Defáveri, J.M.F. de Carvalho, R.A.F. Peixoto, G.J. Brigolini, Study on Assessment of Pozzolanic Activity: Slate Cutting Waste, ACI Mater J. (2020). https://doi.org/10.14359/51724611.

Chapter 2: Pozzolanic reactivity test methods: A review of direct and indirect methods

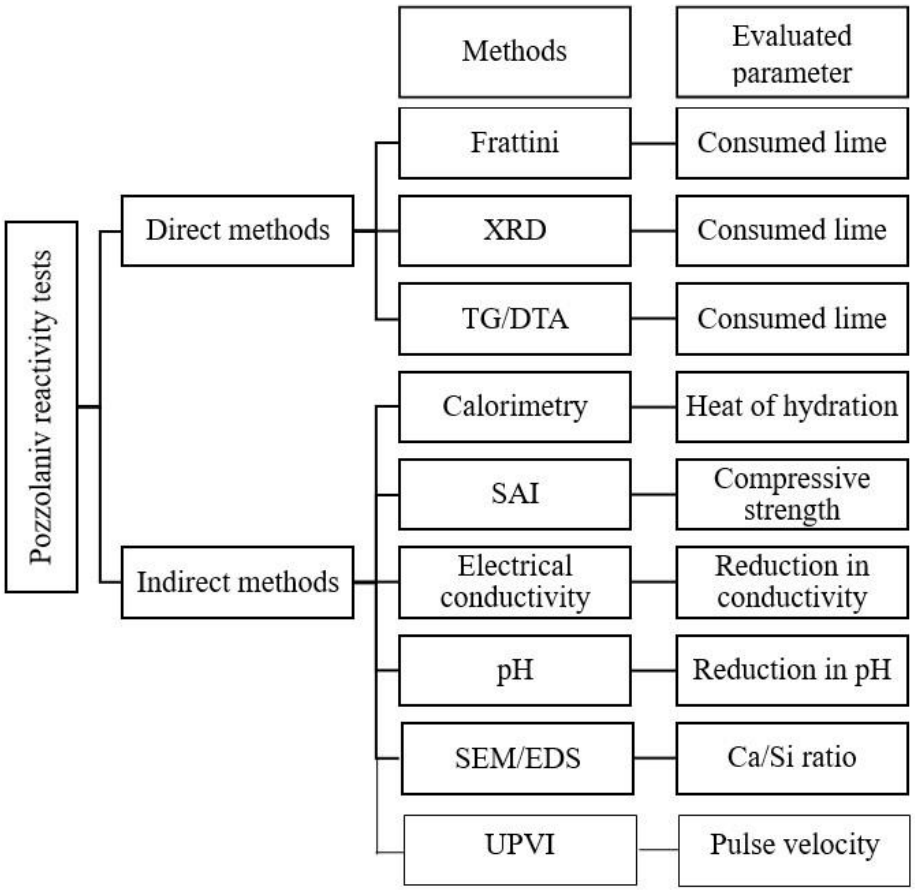
2-1. Abstract

The production of portland cement is associated with adverse effects on the environment. It is crucial to identify sustainable alternatives, such as supplementary cementitious materials (SCMs), to address this issue. As a form of SCM, pozzolanic materials play a significant role in reducing the economic and environmental impacts of portland cement used in concrete. These materials mainly consist of silica and alumina that react with the available calcium hydroxide to form strength-bearing phases such as calcium silicate hydrates. Hence, it is important to detect potential pozzolanic materials using efficient reactivity test methods. There are several test methods to assess the pozzolanic reactivity of materials. This chapter reviews the available literature related to direct and indirect pozzolanic reactivity test methods. Direct methods quantify the amount of consumed calcium hydroxide, whereas indirect methods assess changes in the physical properties of the specimen due to pozzolanic reactions.

2-2. Keywords

Pozzolanic reactivity tests, Pozzolanic materials, portland cement, SCMs, Sustainability

2-3. Graphical abstract



2-4. Introduction

Approximately 7% of the anthropogenic emissions worldwide (i.e., CO_2) are related to the production of ordinary portland cement [1]. Alternative binders based on pozzolanic materials are therefore being developed. Pozzolans are primarily siliceous in nature and contribute to the densification of the microstructure of concrete by reacting with water and hydrated cement paste to form additional strength-bearing phases [2]. According to ASTM C618 [3], the sum of SiO_2, Al_2O_3, and Fe_2O_3 must be more than 70% for the material to be considered a pozzolan. Pozzolans stabilize portlandite ($Ca(OH)_2$), which is produced during cement hydration reactions, to form calcium silicate hydrates (C-S-H), calcium aluminate hydrates (C-A-H), or calcium

aluminosilicate hydrates (CASH). Pozzolanic reactivity can be directly measured based on $Ca(OH)_2$ reduction and the formation of hydrated phases [4].

Three stages express the progression of a pozzolanic reaction. The first stage is the dissolution of lime in water (Eq. 2-1) which provides a strongly basic medium (pH > 12). Typically, $Ca(OH)_2$ forms during the hydration of the main cement phases (alite and belite). The second stage is the dissolution of amorphous silica from the pozzolan (Eq. 2-2), and the third stage is the reaction of $H_2SiO_4^{2-}$ with calcium ions to form C-S-H ($CaO.SiO_2.H_2O$) (Eq. 2-3) [5].

$$Ca(OH)_2 \rightleftarrows Ca^{2+} + 2OH^- \quad (2\text{-}1)$$

$$SiO_2 + 2OH^- \rightleftarrows H_2SiO_4^{2-} \quad (2\text{-}2)$$

$$H_2SiO_4^{2-} + Ca^{2+} \rightleftarrows CaO.SiO_2.\ H_2O \quad (2\text{-}3)$$

The cement hydration process predominates over the pozzolanic reaction at younger ages of concrete. However, at higher ages, say 90 days, the pozzolanic reaction would outweigh the cement hydration with a gradual reduction in the portlandite content within the paste and the formation of additional C-S-H [5].

It is important to note that different methods are utilized to evaluate the reactivity of SCMs, and using only one method may lead to misleading results [6]. The pozzolanic reactivity tests consist of direct and indirect methods. In general, direct methods (e.g., Frattini and thermogravimetric analysis) employ analytical means to assess the ability of pozzolans to consume free lime and form hydration compounds [7]. In contrast, indirect methods (e.g., the strength activity index (SAI) and calorimetry) demonstrate the extent of pozzolanic reactivity by measuring a physical property of a test specimen [8–10]. For instance, SAI is an indirect indication of the effect of pozzolanic reactivity on compressive strength, whereas Frattini and thermogravimetric analysis

(TG/DTA) provide direct insight into the amount of portlandite consumed for the formation of the hydrates [9]. This chapter reviews several direct and indirect test methods for evaluating the reactivity of pozzolanic materials in concrete. These methods are Frattini, X-ray diffraction, TG/DTA, calorimetry, SAI, UPVI, electrical conductivity, and pH. In this chapter, other less effective test methods, such as the Chapelle test, saturated lime test, Raman spectroscopy, and Fourier-transform infrared spectroscopy (FTIR), have not been discussed.

2-5. Direct methods

2-5-1. Frattini

This test was first developed by N. Frattini and was later adopted by the EN 196-5 standard [11]. Using this standard procedure, it is possible to quantify the lime released during the hydration process in an aqueous solution containing a sample at a temperature of 40°C [12]. The pozzolanic reactivity can be measured by contrasting the number of calcium ions (Ca^{2+}) in the aqueous solution in contact with the hydrated cement with time (e.g., 8 or 15 days) [13]. Figure 2-1 shows a diagram for assessing pozzolanic activity provided in EN 169-5. Results of test samples that fall below the lime solubility curve show pozzolanic reactivity, as indicated by the removal of Ca^{2+} from the solution [14]. Decreasing hydroxyl content results in increasing C-S-H and C-A-S-H nuclei [15]. The lime solubility curve represents the maximum Ca^{2+} concentration as a function of OH^- at 40°C using Eq. 2-4 [8], where Ca^{2+}, equivalent to CaO in mmol/l, is linked to OH^- in mmol/l [13].

$$\text{Max [CaO]} = \frac{350}{[OH^-]-15} \quad (2\text{-}4)$$

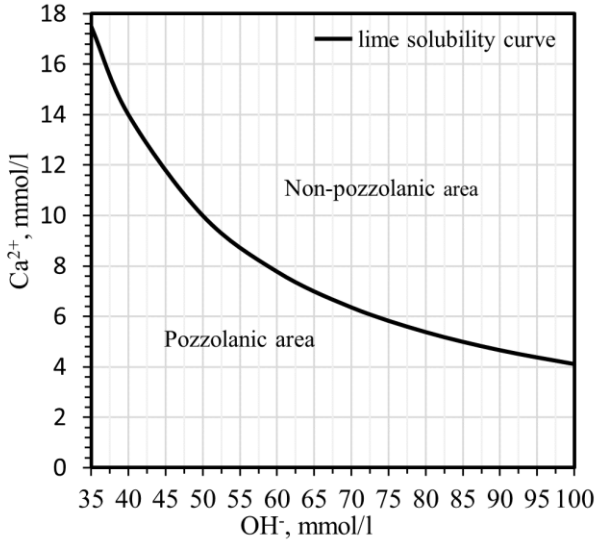


Figure 2-1: Pozzolanic assessment diagram adapted from [34].

According to the BS EN 196-5 standard [13], the Frattini test sample weighs 20 grams and is prepared by mixing 80% cement, and 20% finely ground pozzolan in 100 ml of distilled or deionized water. After preparation, the sample is placed in an oven at 40°C for a period of between 8 and 15 days. After the specified test period, the sample is vacuum filtered using a dry double filter paper with a pore size of 2 µm and allowed to cool down at room temperature. The filtered solution is then analyzed for the $OH^-$and Ca^{2+}concentrations using titration. The OH^- concentration can be found by titration against a 0.1 mol/l diluted hydrochloric acid solution using a methyl orange indicator. After adjusting the pH of the titrated solution to 12.5± 0.2 with the addition of sodium hydroxide, the Ca^{2+} concentration can be analyzed by titration against a 0.03 mol/l EDTA solution using one of the suggested indicators (murexide, calcon, or Patton and Reeder's).

Studies have shown that there is a good correlation between the Frattini test results and some other pozzolanic reactivity test methods. For instance, Donatello et al. [8] compared three different pozzolanic activity test methods, including the Frattini, SAI, and the saturated lime test.

Using these methods, they evaluated the reactivity of metakaolin, silica fume, coal fly ash, incinerated sewage sludge ash (ISSA), and sand as inert material. The authors concluded that the Frattini test and the SAI were significantly correlated and were closely controlled methods. In contrast, the saturated lime test results did not correlate with the other results. Also, the saturated lime test showed positive pozzolanic reactivity for sand and ISSA. In the Frattini test, however, these materials did not exhibit pozzolanic reactivity. Likewise, a study by Kramar and Ducman [9] indicated that the Frattini and SAI results indicated similar trends for the various ash samples tested. Several other pozzolan assessment studies have been performed using the Frattini test. Trusilewicz et al. [12] observed that higher metakaolin content showed higher pozzolanic reactivity at older ages as more Ca^{2+} and OH^- ions were consumed. Similarly, Rahhal et al. [16] observed that the pozzolanic reactivity of waste brick powder as partial cement replacement improved at the later age of hydration and a higher cement replacement level [17,18].

In another study using the Frattini test, the pozzolanic reactivity of volcanic tuffs and fly ash was investigated at the age of 15 days with different cement replacement ratios. Since the levels of hydroxyl and calcium ions were below the lime saturation curve, all tested materials demonstrated pozzolanic reactivity [19]. The authors also reported that lime consumption increased with increasing pozzolan replacement ratios, which is consistent with the findings of other studies [12,16]. It is worth mentioning that, in an earlier study on pozzolanic reactivity of rice husk ash, amorphous silica, and particle fineness were mentioned as the main factors affecting reactivity in an alkaline environment [20]. Kramar and Ducman [9] also observed that ashes with a higher proportion of amorphous phase showed more reactivity by means of higher

free lime removal. A recent study on wood biomass fly ash concluded that the highest reduction of calcium ions was related to higher pozzolanic oxide contents (SiO_2+ Al_2O_3+ Fe_2O_3) [21].

In general, the Frattini test helps to assess the ability of a pozzolan (that is partially replacing cement) with respect to reducing portlandite content in a solution. However, it does not provide any information on the potential presence of portlandite in hardened pastes [22].

2-5-2. X-ray diffraction (XRD)

X-ray diffraction spectroscopy is a powerful technique for the quantification of crystalline and amorphous phases [23]. This technique can not only detect and characterize the main phases such as quartz, muscovite, albite, chlorite, and calcite in pozzolan powders [10] but is also a direct method to quantify consumption of $Ca(OH)_2$ in hydrated samples [24]. Figure 2-2 demonstrates XRD peaks of the hydrated products, CH and CASH, for a hydrated cement sample partially replaced with brick powder.

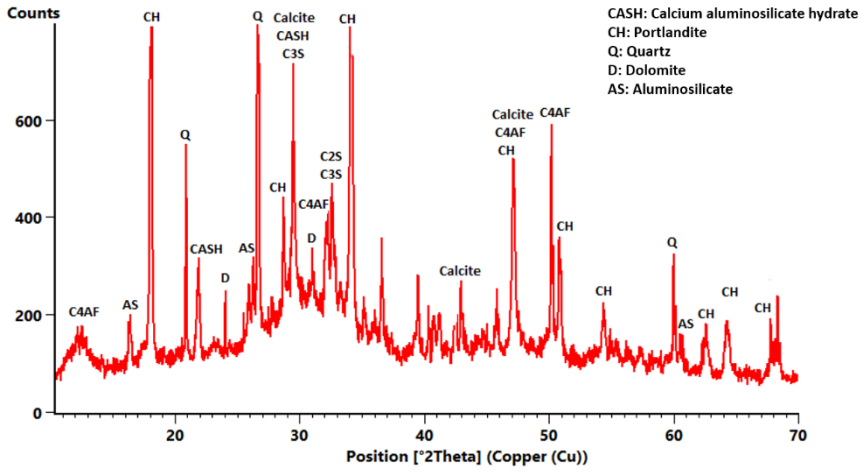


Figure 2-2: XRD patterns for the hydrated cement sample containing 20% brick powder after 28 days of curing.

Belie et al. [25] noted that the coexistence of an amorphous SCM and the C-S-H phase in hydrated blended cement presents an issue since the C-S-H contribution may overlap with the SCM signal

either partially (e.g., metakaolin) or completely (e.g., blast furnace slag). So, for correct quantification, the proper selection and calibration of a fingerprint model of C-S-H are required [25].

Du and Tan [26] used XRD patterns for cement paste with 30% and 60% glass powder replacement at curing ages of 7, 28, and 91 days. Their results showed that the principal peaks associated with $Ca(OH)_2$ were weakened in samples with higher glass powder and higher curing age. For example, the $Ca(OH)_2$ peak was relatively small for the paste with 60% glass powder at 91 days, indicating that most $Ca(OH)_2$ had been consumed to form the additional C-S-H phase. At later ages, lime was not sufficiently available to fully react with the dissolved silicates of the glass powder [26]. In a study by Snellings et al. [27], it was observed that the XRD peaks associated with the main clinker phases (e.g., alite, belite, celite) decreased for the blended cement pastes with partial fly ash replacement. On the other hand, the number of peaks associated with the hydration products increased [27]. The reduction of the main clinker phases is related to an increase in the formation of hydration products such as ettringite (AFt), portlandite, and C-S-H during the hydration process [5]. In a study by Tognonvi et al. [5], hydrated lime samples containing 70% glass powder showed high carbonation (calcite peaks) at ages up to 28 days. However, samples that were cured for 91 days showed the absence of calcite and the appearance of C-S-H peaks because of the pozzolanic reaction of the glass powder with lime over time [5].

In another study [28], the effect of quartz powder and silica fume was investigated using XRD. It showed that after 28 days, portlandite was only found in the portland cement reference sample and the sample with 20% cement replacement with quartz powder. In contrast, in the blended silica fume-cement sample, no portlandite was detected due to the consumption of portlandite

and enhancement of C-S-H nuclei. That is an indication of the high pozzolanic reactivity of silica fume and the low pozzolanic reactivity of quartz powder [28].

Martins Torres et al. [24] measured the amount of portlandite in the calcined and non-calcined sugarcane bagasse ash (SBA)- pastes with lime (CH-pozzolan) through assessment of relative decrease in peak intensities (RDPIs), relative intensity ratio (RIR) and Rietveld refinement. Relative estimation is only acquired by comparing CH peaks of the control (only CH) and CH-pozzolan samples. The CH consumption from the pozzolanic reaction for the CH-pozzolan paste was quantified by studying the main CH peak intensities using the RDPI method (Eq. 2-5).

$$\text{Relative consumed CH} = \frac{\text{CH peak intensity of (CH}-\text{pozzolan) paste}}{\text{CH peak intensity of control}} \quad (2\text{-}5)$$

XRD analyses demonstrated that the portlandite peak intensity reduced due to the pozzolanic reactivity of fine SBA. Moreover, SBA with finer particle size and the calcined SBA demonstrated an additional reduction in the peak intensity of portlandite [24].

2-5-3. Thermal gravimetric and differential thermal analyses (TG/DTA)

Thermogravimetry (TG) and differential thermal analyses (DTA) have been widely used for the characterization of pozzolanic reactivity [9]. TG/DTA is one of the direct methods to measure the amount of portlandite consumption [10,19,29]. This is an analytical method that records the relationship between mass and temperature (TGA curve) on a thermal balance [30]. A TGA test measures the change in mass of a sample as a function of temperature or heating time [19]. The tangent method is used to calculate the percent weight change of calcium hydroxide in the samples [30]. An indicator of pozzolanic reactivity is the amount of consumed portlandite in the lime-pozzolan pastes measured with TG/DTA [31]. Typically, the content of remaining portlandite

increases with age in samples that consist of plain portland cement due to the formation of additional hydration products with time. In contrast, the amount of portlandite in pastes containing SCMs is less than that in plain cement samples because of a combination of the dilution effect and pozzolanic reaction [32]. Therefore, by determining the consumption of portlandite, the extent of reactivity of SCMs in the cement pasts can be evaluated [33]. The four main weight loss ranges typically identified by the TGA curve are as follows (Fig. 2-3):

I. Evaporable water decomposition between 25°C and 105°C (related to the loss of free water).

II. Dehydration reaction between 105°C and 400°C (represents the decomposition of hydrates).

III. Dehydroxylation of portlandite between 400°C and 500°C.

IV. Decarbonation between 600°C and 800°C (corresponds to calcite ($CaCO_3$) decomposition) [34].

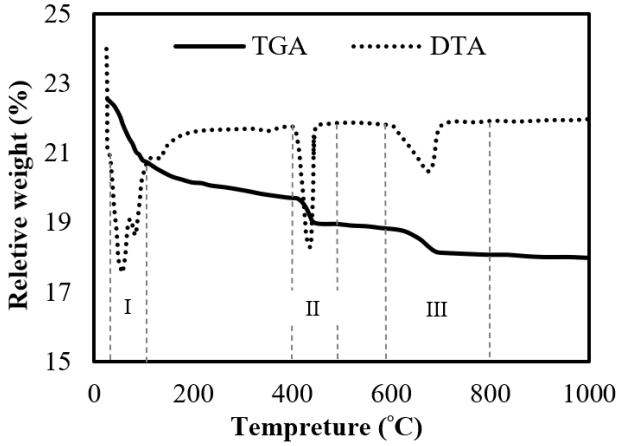


Figure 2-3: TG/DTA of cement paste containing 10% limestone filler at 28 days, adapted from [55].

It is worth mentioning that proper sample preparation and interpretation of the TG/DTA are required for accurate determination of $Ca(OH)_2$ [35]. The $Ca(OH)_2$ content can be overestimated due to the carbonation effect when using traditional methods that only measure weight changes resulting from $Ca(OH)_2$ decomposition at a fixed range of temperature. The temperature range for the decomposition of $Ca(OH)_2$ depends on several factors, like particle fineness and the amount of sample, the crystallinity of the material, and gas pressure in the thermogravimetry analysis instrument [35].

The remaining $Ca(OH)_2$ can be calculated by considering the effect of carbonation using Eq. 2-6 [10].

$$CH_r = 4.11\ (m_{CH}) + 1.68\ (m_{CC}) \quad (2\text{-}6)$$

Where CH_r is the mass of remaining $Ca(OH)_2$ in the sample, 4.11 is the molar mass ratio of $Ca(OH)_2/H_2O$, and 1.68 is the molar mass ratio of $Ca(OH)_2/CO_2$. m_{CH} is the mass loss due to the decomposition of $Ca(OH)_2$ (dehydroxylation) and, m_{CC} is the mass loss due to the decomposition of $CaCO_3$ (decarbonation) [10].

The percentage of the consumed or fixed lime of the blended samples with respect to the control sample can also be calculated using Eq. 2-7 [36].

$$\text{Fixed lime (\%)} = \left[\frac{(CH_{r,c} \times C) - CH_{r,b}}{(CH_{r,c} \times C)}\right] \times 100 \quad (2\text{-}7)$$

Where $CH_{r,c}$ and $CH_{r,b}$ are the mass of remaining $Ca(OH)_2$ in the control and blended cement samples, respectively. C is the proportion of cement in the blended samples (e.g., for a blended cement sample with 80% cement and 20% pozzolan, C is 0.8).

Various methods have been developed for preparing TGA mixtures. For example, Uzal et al. [29] prepared different mixtures of lime-pozzolan pastes to monitor lime depletion using TGA. They

used $Ca(OH)_2$, with a 1:1 lime: pozzolan ratio and a water-to-solid ratio of 0.55. Fresh pastes were kept in plastic syringes to avoid moisture loss and carbonation, and the samples were held at 50±1°C to accelerate the pozzolanic reaction. Then the amount of consumed lime in the hardened pastes (for each lime–pozzolan paste) was calculated by performing the TGA test at 3, 7, and 28 days. Results were reported as a percentage of the total weight of the components. The authors studied pozzolanic activity of a natural zeolite (clinoptilolite) in comparison with silica fume, fly ash, and a non-zeolitic natural pozzolan. From the TGA results, the portlandite depletion of silica fume was higher than all other tested pozzolans for all tested ages [29].

In other studies by Pacewska et al. [37] and Kramar and Ducman [9], samples were prepared by mixing 30% ash (fly ash and pulverized combusted brown coal) and 70% $Ca(OH)_2$. Pastes were enclosed in hermetic plastic bags and stored at room temperature for the given time periods. Samples were pulverized, and powders were tested through TG/DTA after 7, 28, and 90 days [9,37]. Kramar and Ducman [9] reported that samples containing ash with higher surface area showed considerable portlandite consumption. On the other hand, Lima et al. [10] tested slate cutting waste (SCW) as a partial (25%) replacement of portland cement with water to binder ratio of 0.55. Pastes were cast in plastic molds to prevent carbonation and were kept in sealed plastic bags in a wet chamber at 40°C. After 28 and 56 days, dried pastes were ground and sieved using a No. 200 sieve and tested using TG/DTA. SCW showed no pozzolanic reactivity since it did not significantly reduce $Ca(OH)_2$. Its filler effect and specific surface area reportedly played a significant role in enhancing the degree of hydration and compressive strength [10,38]. Table 2-1 is a summary of studies using the TGA method to assess the pozzolanic reactivity of common pozzolans.

Table 2-1. A summary of the TGA method for common pozzolans, test conditions, and results

Assessed pozzolans	Mixture	w/b or l/s*	Age	Results	Reference
Five types of fly ash	30% ash+ 70% lime	0.5, 0.41, 0.35, 0.60 & 0.81	7,28 &90 days	Two ash types with the high surface area showed considerable consumption of portlandite	[9]
Earth of Milos (a natural pozzolan) ceramic powder from handmade ground brick, metakaolin	Lime/pozzolan with ratios of 1/0.5,1/1,1/2, 1/3, 1/2	0.54-1	0, 3, 7, 14 & 28 days	Lime/metakaolin pastes presented the highest activity with higher portlandite consumption	[31]
Reclaimed fly ash types and natural pozzolan	20% fly ash+ 80% portland cement type I	0.40	7, 28 & 90	All pozzolans showed a reduction in portlandite	[39]
Waste glass powder (WGP)	30% glass powder+ 70% portland cement type I	0.4	3 & 28	The total molar amount of portlandite reduced from 3 - 28 days because of active silicas in WGP mortars	[30]
Slate-cutting waste (SCW)	25% SCW +75% portland cement type III	0.55	28 & 56	The total molar amount of portlandite didn't reduce significantly by partial replacement of SCW	[10]
Four types of fly ashes, four slags, two calcined clays, two silica fumes, a quartz, a limestone	Calcium hydroxide and SCMs in a mass ratio of 3:1 + 0.5 M potassium hydroxide	0.9	240 h	The order of calcium hydroxide consumption from the greatest to the lowest: silica fume > calcined clay >fly ash> quartz> slag> limestone	[33]
Waste glass powder	Glass powder with 30% and 60% replacement of ordinary portland cement type I	0.485	7,28 & 91 days	The content of consumed $Ca(OH)_2$ decreased by increasing glass powder content and curing age.	[26]
Densified silica fume, nano silica and metakaolin	$Ca(OH)_2$/50% pozzolan paste	1	1,3,7,14 & 28 days	Lime fixation was more at the long age. Order of reduction in calcium hydroxide from greatest to the lowest: nano silica > metakaolin > silica fume	[4]

2-6. Indirect methods

2-6-1. Isothermal calorimetry

Due to cement's exothermic hydration reaction, the hydration kinetics of the clinker could be evaluated by measuring its heat of hydration. It is possible to characterize the effect of different additives and admixtures on the mixture's hydration kinetics through measurement of the heat of hydration versus time [40]. The most widely used equipment for studying cement hydration are isothermal and semi-adiabatic calorimeters. Isothermal calorimeters directly measure the heat of hydration (heat evolution) of small samples of cement paste or mortars. A semi-adiabatic calorimeter measures the temperature change of the mortar or concrete samples that are insulated [41].

In general, the heat generation at the early age of hydration is related to highly reactive cement phases such as alite, ferrite, and brownmillerite. Belite is less reactive but contributes to the hydration products and strength gain at later ages, approximately after ten days [42].

Typically, an isothermal calorimetry curve consists of four peaks and stages [42] (Fig. 4).

- Stage I is related to rapid dissolution and the early reaction period. Rapid and overall exothermic dissolution of free lime, alkalis, gypsum, ferrite, and brownmillerite with some alites occurs in this stage, which lasts only a few minutes. Ions such as Ca^{2+}, SO_4^{2-}, $Al(OH)_4$, SiO_4^{4-}, K^+, Na^+ and OH^- are released into the solution.
- Stage II is an induction period that happens after the initial highly exothermic reactions. This stage is a period of deceleration of cement hydration in which heat evolution is relatively low.

- Stage III is an acceleration period that is due to nucleation and growth of the C-S-H.
- Stage IV is a deceleration period with a slow and continued reaction. This is a result of diffusion control and space-filling. Diffusion control is a mechanism in which a thick layer of C-S-H slows the diffusion of water ions, resulting in a slower reaction. Also, space-filling occurs when there is a reduction in the available surface area and pore volume to grow C-S-H [42].

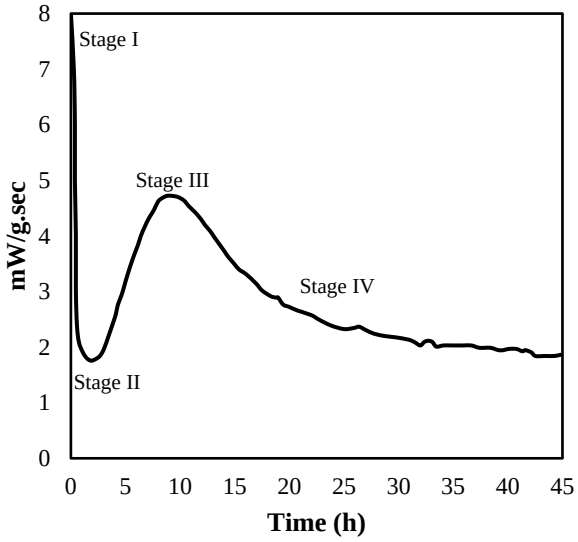


Figure 2-4: A typical calorimetry plot for cement's heat of hydration at 25 °C adapted from [43]

Several studies have assessed pozzolanic reactivity using calorimetry [27,44–46]. Bobrowicz and Chyliński [47] compared the pozzolanic activity of R-Mud waste with other pozzolans, such as silica fume, fly ash, and trass, using an isothermal calorimeter. The calorimetry tests were conducted using 8 grams of cement and 4 grams of water inserted in syringes at 20 ˚C and monitored for a minimum of 140 hours in a customized measurement equipment. Each tested pozzolan replaced 15% of Type I portland cement. The waste R-Mud generated the highest heat after the control sample, demonstrating that R-Mud was a highly reactive pozzolan, not much less than silica fume, after 24 hours of hydration. Higher specific surface area and very fine grains of colloidal silica

present in R-Mud were mentioned as the main reasons for its high pozzolanic reactivity. In contrast, samples containing fly ash and trass showed the lowest heat of hydration compared to R-Mud and silica fume. In an earlier study by Siler et al. [48], the effect of silica fume, granulated blast furnace slag, and fly ash on cement hydration (with 10% and 50% replacement levels) was assessed at seven days. The authors found that the maximum heat for the fly ash sample was lower than the heat from the plain cement paste. A dilution effect due to the replacement of reactive cement with a less reactive additive (fly ash) and a slower reaction rate (pozzolanic reaction) was noted as the reasons for the observed reduction in the heat of hydration.

Suraneni and Weiss [33] proposed a slightly modified method for determining the pozzolanic reactivity through isothermal calorimetry. They examined the heat evolution of fly ash, slag, calcined clay, silica fume, quartz, and limestone mixed with calcium hydroxide (3 to 1 mass ratio of calcium hydroxide to SCM mixed with a solution of 0.5 molar potassium hydroxide with a liquid-to-solid ratio of 0.9). The initial temperature of the calorimeter was set at 50°C to shorten the time of the test from 12 to 10 days and to improve calorimetric stability. After ten days, the heat release was in the following order, from highest to lowest: calcined clay> silica fume> slag> fly ash> quartz> limestone.

2-6-2. Strength activity index (SAI)

SAI is the most widely used indirect approach for measuring pozzolanic reactivity. This method assesses how pozzolanic reaction affects the cementitious matrix densification and packing effect, which results in the enhancement of compressive strength [49,50]. In other words, the SAI test establishes the actual contribution of microstructure densification brought on by the pozzolanic reaction [51]. The SAI approach demonstrates the direct impact of the pozzolanic activity on the

mixture's mechanical properties [52]. To determine SAI, two sets of test specimens are made using a standard mix design; one with 100% portland cement (control sample) and the other with a portland cement-pozzolan blend based on Table 2-2. Both sets of specimens are examined for compressive strength after a specific number of days of curing [53]. The US standard for assessing pozzolans' reactivity is ASTM C311, which compares the compressive strength of mortar with pozzolans replacing 20% of the portland cement binder [54].

Table 2-2. SAI mixture designation [54]

Specimens	Water (ml)	portland cement (g)	Tested material (g)	Graded standard sand (g)
Control mix	242	500	0	1375
Blended mix	Required for flow ±5 of control mix	400	100	1375

The SAI is a measure of the pozzolanic material's impact, which is calculated using Eq. (2-8) [53]:

$$SAI = S_1/S_2 \quad (2\text{-}8)$$

S_1 and S_2 denote the compressive strengths of the sample with pozzolan replacement and the control sample, respectively [53]. According to ASTM C618, fly ash, and natural pozzolans must have an SAI greater than 0.75 at 7 and 28 days (at a 20% cement substitution) to be considered a pozzolan [3].

Pozzolanic materials can fill the micropore structure of cement mortar and concrete. In cement-based materials, highly reactive pozzolans such as metakaolin can contribute to early hydration and also promote secondary hydration processes, which can improve mechanical properties such as compressive strength [53,55]. By replacing cement with pozzolanic materials, extra C-S-H is generated, which increases the strength at later ages.

Due to the slower activity rate of some pozzolanic materials and the absence of significant amounts of portlandite at the early stages of cement hydration, the strength gain in pozzolanic mixes is

usually slower than in the control samples [52]. However, some pozzolanic materials, such as metakaolin and silica fume, exhibit enhanced compressive strength even at early ages (in comparison to the control sample) due to their high pozzolanic activity and high specific surface area [52].

Another factor that influences compressive strength is the condition of the interfacial transition zone (ITZ). Replacing cement with reactive pozzolans such as metakaolin, silica fume, and slag improves the ITZ, pore structure, and pore size distribution of concrete. Therefore, the concrete will have a greater compressive strength compared to the control sample, which results in a greater SAI [56]. Other factors that affect the SAI are fineness and active silica content of the pozzolan. The small silica fume particles have a higher surface area and contain more active silica than the control sample [57]. Consequently, the finer silica fume is more reactive and produces stronger concrete and mortar. It should be noted that $Ca(OH)_2$ regulates the pozzolanic process, so additional silica fume beyond the optimum level only serves as an inert filler in the mixture [57].

A major disadvantage of the SAI test is that it may not be able to differentiate between an active and an inert pozzolan in some cases under the ASTM requirements [3,7,58]. First, according to ASTM C618, a target mortar flow requirement must be met for the mix rather than a fixed water to binder requirement. Consequently, fluctuation in the w/b ratio (to meet the flow requirement) may result in a false impression of pozzolanic reactivity [59]. Second, when the pozzolan content is low, the filler effect would likely dominate the reactivity effect [2,60]. Third, in most cases, fly ash may exhibit a minor degree of reactivity at seven days, and frequently pozzolanic materials could not be distinguished from inert fillers at this stage [61,62].

There is also a criticism of the SAI in that the threshold value of 75% may be too low. If the additive did not contribute at all, the strength could be approximately 80% of the control (with 20% replacement of cement) at the same w/b ratio [63,64]. In other words, if the tested pozzolans were fully inert, the dilution effect may cause a 20% decrease in strength development. The cement content, however, is not the only factor that affects strength. There are other factors that influence strength development, including permeability, porosity, and hydration reaction kinetics [8]. Therefore, results from an indirect pozzolanic activity test are commonly confirmed by direct methods to ensure that pozzolanic reactions are truly happening [65,66].

2-6-3. Electrical conductivity and pH

Electrical conductivity and pH measurements are relatively easy and rapid tests to assess pozzolanic reactivity in comparison to the common reactivity tests that are time-demanding and slow [67]. In these methods, a chemical reaction occurs between the pozzolan and calcium hydroxide that is dissolved in water [36]. Through the reaction of silica and alumina from the pozzolan with dissolved Ca^{2+} and OH^-ions in an aqueous suspension, insoluble and non-conductive products (e.g., C-S-H) form, which decrease the solution's conductivity [36,67,68]. The reduction of these ions in an unsaturated lime solution leads to declining electrical conductivity. A decrease in pH also occurs since the concentration of OH^- ions decrease due to the pozzolanic reaction [36]. Thus, changes in conductivity and pH are related to the removal of calcium hydroxide due to pozzolanic reactivity. Several researchers refer to these as indirect methods for the pozzolanic reactivity assessment [7,36,69].

Luxan et al. [70] first proposed an electrical conductivity method for assessing natural pozzolans such as opaline rocks and volcanic tuff. Later, other researchers used these methods for the

evaluation of the reactivity of artificial pozzolans, such as sewage sludge ash [11]. According to Luxán et al. [70], a material's pozzolanic reactivity can be determined based on the measurement of the electrical conductivity of a blended material with a lime-saturated solution at a minimum time (e.g., 2 minutes) (Table 2-3). The authors monitored the loss of electrical conductivity of 100 different pozzolans using 5 g of pozzolan in 200 ml of saturated calcium hydroxide at 40 ±1˚C for 120 sec. [71].

Table 2-3. Reduction in the electrical conductivity for determination of pozzolanic reactivity [70]

Non-Pozzolanic	Variable pozzolanic reactivity	Good pozzolanic reactivity
<0.4 mS/cm	Between 0.4 and 1.2 mS/cm	>1.2 mS/cm

In other studies, Uzal et al. [29] and Payá et al. [72] determined the contribution of pozzolanic materials to conductivity and then subtracted the results from the measured conductivity of the lime-pozzolan water suspension. Pozzolanic materials such as fly ash could contain several soluble ions that may contribute to conductivity in the aqueous solution [29]. Thus, the adjusted loss of electrical conductivity is calculated using Eqs. 2-9 and 2-10 [67].

$$LC\ (\%) = \frac{C_0 - C_{t,c}}{C_0} \times 100 \tag{2-9}$$

$$C_{t,c} = C_t - C_{t,pozzolan} \tag{2-10}$$

Where LC is the relative loss of electrical conductivity of lime-pozzolan suspensions at time t, C_0 is the electrical conductivity of lime suspension before adding pozzolanic material, C_t is the measured electrical conductivity of lime-pozzolan suspensions at time t, $C_{t,pozzolan}$ is the measured electrical conductivity of pozzolan-deionized water suspension at time t, and $C_{t,c}$ is the corrected electrical conductivity at time t [67].

According to Tashima et al. [67], increasing temperature positively affects the reduction of electrical conductivity and pH due to increasing pozzolanic reaction. This finding was also confirmed in prior research conducted by Sinthaworn and Nimityongskul [73] and Velázquez et al. [36]. Tashima et al. [67] also reported that LC > 30% and variation of pH > 0.15 units are the thresholds for characterization of the pozzolanic reactivity.

In the method proposed by Uzal et al. [29], a lime-water suspension (200 mg $Ca(OH)_2$ in 250 ml water) was mixed using an electric mixer at a constant temperature of 40 ±1˚C. The initial pH and conductivity measurements were recorded for the lime-water suspension using digital pH and electrical conductivity meters. After stabilization of the conductivity and pH, 5 g of pozzolan was added to the suspension, and the conductivity/pH parameters were continuously measured. The authors reported that the pH and electrical conductivity results provided consistent results in their experiment. In addition, the specific surface area and the reactive SiO_2 content of the pozzolan were noted as important factors affecting conductivity and pH [29].

Borges et al. [7] used a similar method based on electrical conductivity to evaluate the pozzolanic reactivity of glass powders with different particle sizes (150 μm, 75 μm, and 45 μm). In their approach, the lime solution was first homogenized at 80˚C for 1 hour, then the temperature was reduced to 60˚C, and 5 g of glass powder was added to the solution to measure the relative loss of electrical conductivity for about 100,000 s. Their results indicated that the highest percentage of LC was related to the smallest particle size of glass powder (<45 μm) [7].

2-6-4. Scanning electron microscopy (SEM)

Although scanning electron microscopy is a recognized and useful method for analyzing the microstructure and characteristics of hardened concrete, its use for pozzolanic reactivity

assessments is not widely understood. However, several researchers have used SEM for pozzolanic reactivity assessments[74–77] . SEM illustrates how variations in pozzolans lead to varying microstructures in concrete [78]. SEM provides images of particles' dimensions, shape, composition, crystallography, and other physical and chemical characteristics [79].

An SEM image is an indirect method to look at changes in the cement's hydrated microstructure and hydrate formations as it relates to pozzolanic reactivity, as depicted in Figure 2-5 [28,80,81]. SEM can also be used to analyze ITZ between cement matrix and aggregates. This analysis is important since reactive pozzolans can fill the pores of ITZ, and this development can be observable through SEM images [82].

Another technique in SEM analysis is known as backscattered scanning electron (BSE) imaging, which has several benefits including reproducible contrast (depending on atomic number) and the ability to visualize representative cross-sections at a variety of magnifications [83,84]. The BSE imaging analysis provides an accurate indication of the microstructure. In this respect, BSE images can assess the degree of hydration and reactivity [85]. Pozzolanic reactivity can result in a more refined and denser microstructure that can be observed through BSE images [85]. The shape of hydrated phases such as C-S-H may be seen in the highest magnifications of BSE images [84]. Typically, $Ca(OH)_2$ and C-S-H are quite distinctive through BSE images since $Ca(OH)_2$ precipitates in pores filled with water, whereas C-S-H deposits mostly around cement grains [84]. While BSE distinguishes between different phases in the reacted materials, it is not possible to measure these phases with precision due to the difficulty in determining their boundaries [84].

To solve the inaccuracy problem of the BSE method, SEM and energy-dispersive X-ray spectroscopy (SEM/EDS) are introduced. To be more precise, the findings of the SEM imaging and

SEM/BSE are qualitative, while SEM/EDS can quantify the mineral phases of the mixtures [83]. Hydrated phases in a pozzolan blended cement (e.g., blended cement-fly ash) can be quickly and easily identified quantitatively using SEM/EDS [86]. Furthermore, SEM/EDS quantitatively analyzes the distribution of components and microstructural changes caused by the reaction of $Ca(OH)_2$ with the pozzolanic materials [87,88]. SEM/EDS can promptly reveal details on the chemical composition of the components in the sample as well as microstructural aspects such as morphology [78]. The pozzolanic reaction can also be determined by the Ca/Si ratio in EDS analysis [87]. Generally, Ca/Si ratios are low in C-S-H that is produced during the pozzolanic reaction [89]. It should be noted that at the early ages of the reaction, the Ca/Si ratio is often high, while this ratio stabilizes at the end of the pozzolanic reaction due to portlandite depletion [87]. For instance, a decrease in the Ca/Si ratio was observed in a study by Maraghechi et al. [87] (using glass powder) from 28 to 60 days, indicating an ongoing pozzolanic reaction. Another ratio that is detectable by SEM/EDS is Si/Al, which conveys significant information related to the type of reaction products created during the pozzolanic reaction. It is known that a higher Si/Al indicates faster reactivity of a pozzolan [90]. Phase detection in SEM images can also be validated by the XRD analysis [91].

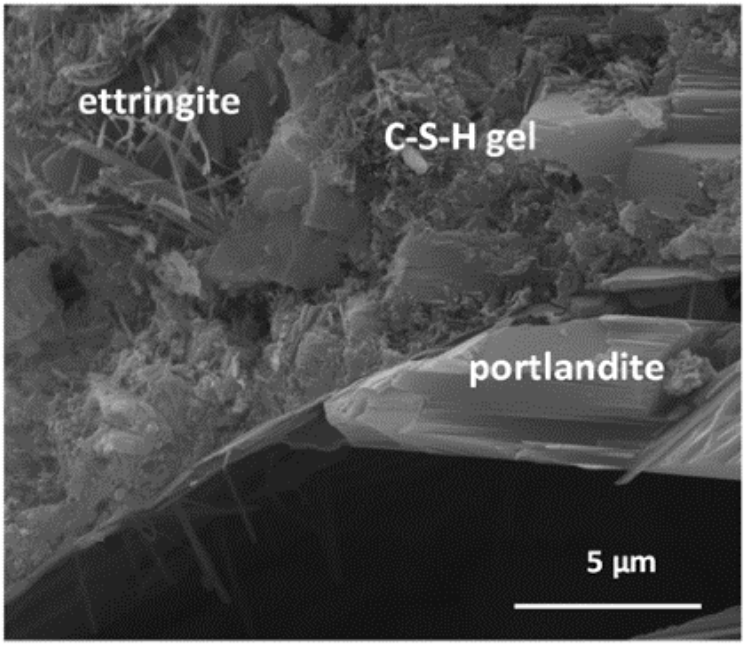


Figure 2-5: C-S-H gels, portlandite, and ettringite filling cracks [81]

2-6-5. Ultrasonic pulse velocity (UPV)

Ultrasonic pulse velocity is a test method to determine the uniformity and relative quality of concrete, as well as to detect voids and cracks and to assess the success of crack repairs [92]. UPV also serves as an indirect measure of durability and strength. With concrete materials, UPV has been successfully utilized to qualitatively evaluate property improvements/degradation, such as growth in compressive strength and degree of cracking [93]. UPV is calculated using Eq. 2-11.

$$V = \frac{d}{t} \tag{2-11}$$

Where V is the pulse velocity, d is the distance between the center of transducer faces, and t is the transit time. Figure 2-6 illustrates the different approaches of UPV tests. In UPV, it is important to mark the test locations on the structure to ensure repeatability over time [92].

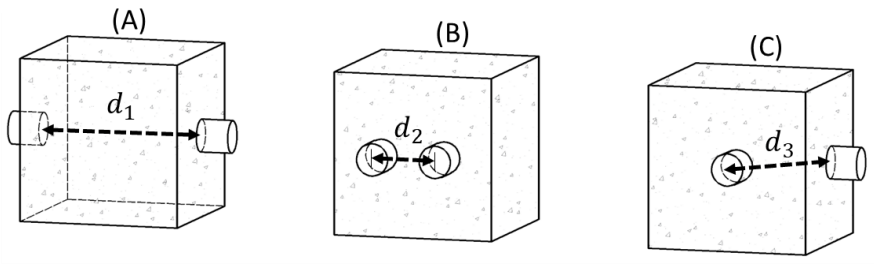


Figure 2-6: Schematic view of UPV test: (A) direct, (B) indirect, and (C) semi-direct approach

Variations in ultrasonic velocity are caused by factors such as anisotropy and the presence of water [94]. In general, the UPV is a function of porosity, and it decreases as porosity increases, meaning that UPV increases as the density increases [95]. Therefore, densification is correlated with UPV [96].

The quality of cement-based materials can also be evaluated via UPV measurements. Whitehurst [97] suggests a broad scheme for categorizing the quality of concrete. Concrete UPV measurements greater than 4500 m/s, 3500 m/s, 3000 m/s, 2000 m/s, and below are categorized as excellent, good, doubtful, poor, and very poor, respectively [97,98]. UPV values associated with concrete mixtures are strongly influenced by mix proportions, materials properties, pore structure, and characteristics of the ITZ [99]. Considering pozzolanic reactivity, UPV can be utilized to monitor the interaction between the pozzolanic material and $Ca(OH)_2$ in cement composites [100]. UPV increases when additional C-S-H gel is formed due to the pozzolanic reaction, filling up the pores and refining them [101–103]. Therefore, UPV may be considered an indirect method for assessing pozzolanic reactivity.

In terms of pozzolanic reactivity, UPV is significantly influenced by the type of pozzolan, replacement level, curing temperature, and curing period [104]. Jiang et al. [105] studied the impact of fly ash replacement levels (10, 50, and 80%) on pozzolanic reactivity using UPV. UPV

measurements were lower for samples with higher cement replacement levels compared to the lower cement replacement levels. This can be attributed to a reduction in the hydrated products in samples with higher fly ash content and more pores. It also appears that pozzolanic materials refine the pores in the ITZ and in the matrix, depending on their fineness and reactivity. The curing condition for the cement-pozzolan mixtures can also affect the UPV results. In comparison to air-cured samples, water-cured samples have higher UPV results [103,106]. It is important to note that replacing cement with pozzolanic materials can slow the hydration process, thus delaying the stabilization of the UPV values. Therefore, UPV needs to be monitored at different stages over time [105].

It should be noted that pozzolanic materials, due to their different rates of reactivity, have different UPV measurements. For instance, UPV results of fly ash are lower at early ages due to its slow pozzolanic reactivity [103]. Mardani-Aghabaglou et al. [52] replaced cement with silica fume, metakaolin, and fly ash by 10% and conducted UPV after 7, 28-, 90-, 180-, and 300-days following mixing. Silica fume showed the highest UPV at all tested ages due to its higher surface area and rate of reactivity. Table 2-4 summarizes the derived relationships (based on regression analyses) between UPV and compressive strength values reported by several researchers. Results from previous studies illustrate a high degree of correlation between UPV and compressive strength for some common pozzolans indicating the potential of the UPV method for indirect reactivity assessment.

Table 2-4. Relationship between UPV (V_c) and compressive strength

Tested Pozzolan	Cement Rep. level (%)	w/b	Prediction Eq.	R^2	Reference
Silica Fume	10	0.485	$f_c' = 32.565V_c - 101.35$	0.99	[52]
Fly ash	10	0.485	$f_c' = 33.42V_c - 104.92$	0.989	[52]
Metakaolin	10	0.485	$f_c' = 28.312V_c - 81.228$	0.976	[52]
Blast Furnace Slag	50, 60, 70	0.35	$f_c' = 0.0049e^{0.0021V_c}$	0.96	[107]
Fly ash	25	0.39	$f_c' = 0.0003e^{2.4329V_c}$	0.99	[108]
Metakaolin	20	0.38	$f_c' = 0.0723V_c - 249.67$	0.9982	[109]

$f_c' = compressive\ strength\ (MPa), V_c = \frac{x}{t}, where\ x\ is\ the\ propagated\ path\ and\ t\ is\ the\ transmitted\ time\ (UPV)$

2-7. Summary and conclusions

Cement production has adverse effects on the environment by emitting CO_2 into the atmosphere. Consequently, pozzolans are considered economical and efficient materials to partially substitute cement in concrete and thus reduce the environmental impact of portland cement. Pozzolanic reactivity tests are utilized to find suitable potential pozzolanic materials and assess their characteristics. These tests are categorized into direct and indirect test methods. Direct test methods evaluate the ability of pozzolans to consume free lime and form hydration products. Indirect test methods assess the reactivity of pozzolans by evaluating changes in the physical properties of concrete /mortar that can be attributed to the pozzolan.

The following conclusions can be drawn based on this review of prior research:

- Pozzolanic reactivity is best assessed using more than one method.
- It is important to assess pozzolanic reaction by a combination of direct and indirect methods to assess the effect of pozzolanic reaction in concrete both physically and chemically to find a potential replacement material for cement in concrete.

- It is possible to accurately estimate the amount of portlandite to be consumed by a pozzolan using the available direct methods. However, the current direct methods are relatively complicated to perform and are time-consuming.
- Indirect methods are less conclusive since it is possible to misidentify pozzolanic materials due to the filler effect instead of the pozzolanic effect.
- The Frattini test is the most widely used direct method to quantify portlandite's consumption due to pozzolanic reaction. However, this method is based on titration on liquid suspension and cannot be used to determine the consumption of calcium hydroxide in the hardened paste.
- SEM provides visual evidence of the development of hydrated products of cement paste in the presence of pozzolan at different curing ages.
- Electrical conductivity and pH can assess the reactivity of the materials easily and quickly in comparison to other methods. With further development, these methods can become rapid, effective, and direct methods for assessing pozzolanic reactivity.

2-8. References for chapter 2

[1] K. Robalo, H. Costa, R. do Carmo, E. Júlio, Enhanced Mechanical and Durability Performances of Low Cement Concrete with Natural Pozzolan Addition, Journal of Advanced Concrete Technology. 19 (2021) 519–535. https://doi.org/10.3151/jact.19.519.

[2] S. Ramanathan, M. Kasaniya, M. Tuen, M.D.A. Thomas, P. Suraneni, Linking reactivity test outputs to properties of cementitious pastes made with supplementary cementitious materials, Cem Concr Compos. 114 (2020) 103742. https://doi.org/10.1016/j.cemconcomp.2020.103742.

[3] ASTM C618-19, Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete, ASTM International: West Conshohocken, PA, USA. (2019).

[4] O. Mendoza, J.I. Tobón, An alternative thermal method for identification of pozzolanic activity in Ca(OH)2/pozzolan pastes, J Therm Anal Calorim. 114 (2013) 589–596. https://doi.org/10.1007/s10973-013-2973-y.

[5] M.T. Tognonvi, A. Tagnit-Hamou, L.K. Konan, A. Zidol, W.C. N'Cho, Reactivity of Recycled Glass Powder in a Cementitious Medium, New Journal of Glass and Ceramics. 10 (2020) 29.

[6] Y. Wang, P. Suraneni, Experimental methods to determine the feasibility of steel slags as supplementary cementitious materials, Constr Build Mater. 204 (2019) 458–467. https://doi.org/10.1016/j.conbuildmat.2019.01.196.

[7] A.L. Borges, S.M. Soares, T.O.G. Freitas, A. de Oliveira Júnior, E.B. Ferreira, F.G. da S. Ferreira, Evaluation of the Pozzolanic Activity of Glass Powder in Three Maximum Grain Sizes, Materials Research. 24 (2021). https://doi.org/10.1590/1980-5373-mr-2020-0496.

[8] S. Donatello, M. Tyrer, C.R. Cheeseman, Comparison of test methods to assess pozzolanic activity, Cem Concr Compos. 32 (2010) 121–127. https://doi.org/10.1016/j.cemconcomp.2009.10.008.

[9] S. Kramar, V. Ducman, Evaluation of Ash Pozzolanic Activity by Means of the Strength Activity Index Test, Frattini Test and DTA/TG Analysis, Tehnicki Vjesnik - Technical Gazette. 25 (2018). https://doi.org/10.17559/TV-20171203193229.

[10] S.C.L. Lima, L.C.B. Costa, K.C.S. Defáveri, J.M.F. de Carvalho, R.A.F. Peixoto, G.J. Brigolini, Study on assessment of pozzolanic activity: Slate cutting waste, ACI Mater J. 117 (2020) 3–10.

[11] O. Alayish, T. Çelik, Extending disposal route of dewatered sewage sludge produced from the new wastewater treatment plant in Nicosia toward sustainable building materials, Environ Earth Sci. 80 (2021) 146. https://doi.org/10.1007/s12665-021-09439-3.

[12] L. Trusilewicz, F. Fernández-Martínez, V. Rahhal, R. Talero, TEM and SAED Characterization of Metakaolin. Pozzolanic Activity, Journal of the American Ceramic Society. 95 (2012) 2989–2996. https://doi.org/10.1111/j.1551-2916.2012.05325.x.

[13] E. Standrads, Methods of Testing Cement-Part 5: Pozzolanicity Test for Pozzolanic Cements, NSAI: Dublin, Ireland. (2011) 195–196.

[14] I. Sanou, M. Seynou, L. Zerbo, Y. Millogo, R. Ouedraogo, A. Sana, Evaluation of Pozzolanic activity of illitic and lateritic raw materials from Burkina Faso, Chemical Science International Journal. 18 (2017) 1–13.

[15] S. Mohammed, Processing, effect and reactivity assessment of artificial pozzolans obtained from clays and clay wastes: A review, Constr Build Mater. 140 (2017) 10–19. https://doi.org/10.1016/j.conbuildmat.2017.02.078.

[16] V.F. Rahhal, M.A. Trezza, A. Tironi, C.C. Castellano, M. Pavlíková, J. Pokorný, E.F. Irassar, O. Jankovský, Z. Pavlík, Complex Characterization and Behavior of Waste Fired Brick Powder-Portland Cement System, Materials. 12 (2019) 1650. https://doi.org/10.3390/ma12101650.

[17] A.E. Lavat, M.A. Trezza, M. Poggi, Characterization of ceramic roof tile wastes as pozzolanic admixture, Waste Management. 29 (2009) 1666–1674. https://doi.org/10.1016/j.wasman.2008.10.019.

[18] A.R. Pourkhorshidi, M. Najimi, T. Parhizkar, F. Jafarpour, B. Hillemeier, Applicability of the standard specifications of ASTM C618 for evaluation of natural pozzolans, Cem Concr Compos. 32 (2010) 794–800. https://doi.org/10.1016/j.cemconcomp.2010.08.007.

[19] V.A. Baki, S. Nayır, Ş. Erdoğdu, İ. Ustabaş, Determination of the Pozzolanic Activities of Trachyte and Rhyolite and Comparison of the Test Methods Implemented, International Journal of Civil Engineering. 18 (2020) 1053–1066. https://doi.org/10.1007/s40999-020-00516-5.

[20] S.K. Antiohos, V.G. Papadakis, S. Tsimas, Rice husk ash (RHA) effectiveness in cement and concrete as a function of reactive silica and fineness, Cem Concr Res. 61–62 (2014) 20–27. https://doi.org/10.1016/j.cemconres.2014.04.001.

[21] K.K. Jurić, I. Carević, M. Serdar, N. Štirmer, Feasibility of using pozzolanicity tests to assess reactivity of wood biomass fly ashes, Journal of the Croatian Association of Civil Engineers. 72 (2021) 1145–1153. https://doi.org/10.14256/JCE.2950.2020.

[22] D. Caputo, B. Liguori, C. Colella, Some advances in understanding the pozzolanic activity of zeolites: The effect of zeolite structure, Cem Concr Compos. 30 (2008) 455–462. https://doi.org/10.1016/j.cemconcomp.2007.08.004.

[23] K.C. Reddy, K.V.L. Subramaniam, X-ray Diffraction-Based Quantification of Amorphous Phase in Alkali-Activated Blast Furnace Slag, Adv Civ Eng Mater. 10 (2021) 20200167. https://doi.org/10.1520/ACEM20200167.

[24] S. Martins Torres, V. Estolano de Lima, P. de Azevedo Basto, N.T. de Araújo Júnior, A.A. de Melo Neto, Assessing the pozzolanic activity of sugarcane bagasse ash using X-ray diffraction, Constr Build Mater. 264 (2020) 120684. https://doi.org/10.1016/j.conbuildmat.2020.120684.

[25] N. de Belie, K. Scrivener, B. Lothenbach, E. Gruyaert, J. Skibsted, R. Snellings, A. Vollpracht, Y. Villagrán, Determination of the degree of reaction of fly ash in blended cement pastes, in: 14th International Congress on the Chemistry of Cement (ICCC2015), 2015: pp. 1–12.

[26] H. Du, K.H. Tan, Waste Glass Powder as Cement Replacement in Concrete, Journal of Advanced Concrete Technology. 12 (2014) 468–477. https://doi.org/10.3151/jact.12.468.

[27] R. Snellings, H. Kazemi-Kamyab, P. Nielsen, L. van den Abeele, Classification and Milling Increase Fly Ash Pozzolanic Reactivity, Front Built Environ. 7 (2021). https://doi.org/10.3389/fbuil.2021.670996.

[28] L.R.C. Tavares, J.F.T. Junior, L.M. Costa, A.C. da Silva Bezerra, P.R. Cetlin, M.T.P. Aguilar, Influence of quartz powder and silica fume on the performance of Portland cement, Sci Rep. 10 (2020) 21461. https://doi.org/10.1038/s41598-020-78567-w.

[29] B. Uzal, L. Turanlı, H. Yücel, M.C. Göncüoğlu, A. Çulfaz, Pozzolanic activity of clinoptilolite: A comparative study with silica fume, fly ash and a non-zeolitic natural pozzolan, Cem Concr Res. 40 (2010) 398–404. https://doi.org/10.1016/j.cemconres.2009.10.016.

[30] Y. Wang, Y. Cao, P. Zhang, Y. Ma, Effective Utilization of Waste Glass as Cementitious Powder and Construction Sand in Mortar, Materials. 13 (2020) 707. https://doi.org/10.3390/ma13030707.

[31] A. Moropoulou, A. Bakolas, E. Aggelakopoulou, Evaluation of pozzolanic activity of natural and artificial pozzolans by thermal analysis, Thermochim Acta. 420 (2004) 135–140. https://doi.org/10.1016/j.tca.2003.11.059.

[32] P. Suraneni, V.J. Azad, B.O. Isgor, W.J. Weiss, Calcium oxychloride formation in pastes containing supplementary cementitious materials: Thoughts on the role of cement and supplementary cementitious materials reactivity, RILEM Technical Letters. 1 (2016) 24–30. https://doi.org/10.21809/rilemtechlett.2016.7.

[33] P. Suraneni, J. Weiss, Examining the pozzolanicity of supplementary cementitious materials using isothermal calorimetry and thermogravimetric analysis, Cem Concr Compos. 83 (2017) 273–278. https://doi.org/10.1016/j.cemconcomp.2017.07.009.

[34] W. Deboucha, N. Leklou, A. Khelidj, M.N. Oudjit, Hydration development of mineral additives blended cement using thermogravimetric analysis (TGA): Methodology of calculating the degree of hydration, Constr Build Mater. 146 (2017) 687–701. https://doi.org/10.1016/j.conbuildmat.2017.04.132.

[35] T. Kim, J. Olek, Effects of sample preparation and interpretation of thermogravimetric curves on calcium hydroxide in hydrated pastes and mortars, Transp Res Rec. 2290 (2012) 10–18.

[36] S. Velázquez, J. Monzó, M. Borrachero, J. Payá, Assessment of Pozzolanic Activity Using Methods Based on the Measurement of Electrical Conductivity of Suspensions of

Portland Cement and Pozzolan, Materials. 7 (2014) 7533–7547. https://doi.org/10.3390/ma7117533.

[37] B. Pacewska, G. Blonkowski, I. Wilińska, Studies on the pozzolanic and hydraulic properties of fly ashes in model systems, J Therm Anal Calorim. 94 (2008) 469–476. https://doi.org/10.1007/s10973-008-9179-8.

[38] T. Oey, A. Kumar, J.W. Bullard, N. Neithalath, G. Sant, The Filler Effect: The Influence of Filler Content and Surface Area on Cementitious Reaction Rates, Journal of the American Ceramic Society. 96 (2013) 1978–1990. https://doi.org/10.1111/jace.12264.

[39] I. Diaz-Loya, M. Juenger, S. Seraj, R. Minkara, Extending supplementary cementitious material resources: Reclaimed and remediated fly ash and natural pozzolans, Cem Concr Compos. 101 (2019) 44–51. https://doi.org/10.1016/j.cemconcomp.2017.06.011.

[40] M. Matysík, T. Vymazal, I. Plšková, Effect of Superplasticizers on the Cement Hydration Process, Adv Mat Res. 1100 (2015) 3–6. https://doi.org/10.4028/www.scientific.net/AMR.1100.3.

[41] Q.T. Phung, E. Ferreira, S. Seetharam, V.T. Nguyen, J. Govaerts, E. Valcke, Understanding hydration heat of mortars containing supplementary cementitious materials with potential to immobilize heavy metal containing waste, Cem Concr Compos. 115 (2021) 103859. https://doi.org/10.1016/j.cemconcomp.2020.103859.

[42] B. Pandel, Understanding the retardation of cement hydration caused by zinc, (2018).

[43] N.Y. Mostafa, P.W. Brown, Heat of hydration of high reactive pozzolans in blended cements: Isothermal conduction calorimetry, Thermochim Acta. 435 (2005) 162–167. https://doi.org/10.1016/j.tca.2005.05.014.

[44] P. Suraneni, T. Fu, V. Jafari Azad, O.B. Isgor, J. Weiss, Pozzolanicity of finely ground lightweight aggregates, Cem Concr Compos. 88 (2018) 115–120. https://doi.org/10.1016/j.cemconcomp.2018.01.005.

[45] S. Seraj, Evaluating natural pozzolans for use as alternative supplementary cementitious materials in concrete, (2014). https://repositories.lib.utexas.edu/handle/2152/28052 (accessed February 7, 2023).

[46] X. Li, R. Snellings, M. Antoni, N.M. Alderete, M. ben Haha, S. Bishnoi, Ö. Cizer, M. Cyr, K. de Weerdt, Y. Dhandapani, J. Duchesne, J. Haufe, D. Hooton, M. Juenger, S. Kamali-Bernard, S. Kramar, M. Marroccoli, A.M. Joseph, A. Parashar, C. Patapy, J.L. Provis, S. Sabio, M. Santhanam, L. Steger, T. Sui, A. Telesca, A. Vollpracht, F. Vargas, B. Walkley, F. Winnefeld, G. Ye, M. Zajac, S. Zhang, K.L. Scrivener, Reactivity tests for supplementary cementitious materials: RILEM TC 267-TRM phase 1, Mater Struct. 51 (2018) 151. https://doi.org/10.1617/s11527-018-1269-x.

[47] J. Bobrowicz, F. Chyliński, Comparison of pozzolanic activity of ilmenite MUD waste to other pozzolans used as an additive for concrete production, J Therm Anal Calorim. 143 (2021) 2901–2909. https://doi.org/10.1007/s10973-020-09740-6.

[48] P. Siler, J. Kratky, N. de Belie, Isothermal and solution calorimetry to assess the effect of superplasticizers and mineral admixtures on cement hydration, J Therm Anal Calorim. 107 (2012) 313–320. https://doi.org/10.1007/s10973-011-1479-8.

[49] H. Jang, Y.-T. Lim, J.-H. Kang, S. So, H. So, Influence of calcination and cooling conditions on pozzolanic reactivity of paper mill sludge, Constr Build Mater. 166 (2018) 257–270. https://doi.org/10.1016/j.conbuildmat.2018.01.119.

[50] L. Black, Low clinker cement as a sustainable construction material, in: Sustainability of Construction Materials, Elsevier, 2016: pp. 415–457. https://doi.org/10.1016/B978-0-08-100370-1.00017-2.

[51] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Assessment of pozzolanic activity of different calcined clays, Cem Concr Compos. 37 (2013) 319–327. https://doi.org/10.1016/j.cemconcomp.2013.01.002.

[52] A. Mardani-Aghabaglou, G. İnan Sezer, K. Ramyar, Comparison of fly ash, silica fume and metakaolin from mechanical properties and durability performance of mortar mixtures view point, Constr Build Mater. 70 (2014) 17–25. https://doi.org/10.1016/j.conbuildmat.2014.07.089.

[53] R.T. Thorstensen, P. Fidjestol, Inconsistencies in the pozzolanic strength activity index (SAI) for silica fume according to EN and ASTM, Mater Struct. 48 (2015) 3979–3990. https://doi.org/10.1617/s11527-014-0457-6.

[54] ASTM C311-18, C311/C311M-18 Standard test methods for sampling and testing fly ash or natural pozzolans for use in Portland-cement concrete, (2018).

[55] J. Xie, H. Zhang, L. Duan, Y. Yang, J. Yan, D. Shan, X. Liu, J. Pang, Y. Chen, X. Li, Y. Zhang, Effect of nano metakaolin on compressive strength of recycled concrete, Constr Build Mater. 256 (2020) 119393. https://doi.org/10.1016/j.conbuildmat.2020.119393.

[56] P. Duan, Z. Shui, W. Chen, C. Shen, Effects of metakaolin, silica fume and slag on pore structure, interfacial transition zone and compressive strength of concrete, Constr Build Mater. 44 (2013) 1–6. https://doi.org/10.1016/j.conbuildmat.2013.02.075.

[57] M.Á. Sanjuán, C. Argiz, J.C. Gálvez, A. Moragues, Effect of silica fume fineness on the improvement of Portland cement strength performance, Constr Build Mater. 96 (2015) 55–64. https://doi.org/10.1016/j.conbuildmat.2015.07.092.

[58] M. Kasaniya, M.D.A. Thomas, E.G. Moffatt, Pozzolanic reactivity of natural pozzolans, ground glasses and coal bottom ashes and implication of their incorporation on the chloride permeability of concrete, Cem Concr Res. 139 (2021) 106259. https://doi.org/10.1016/j.cemconres.2020.106259.

[59] M. Kasaniya, M.D.A. Thomas, E.G. Moffatt, Development of rapid and reliable pozzolanic reactivity test method, ACI Mater J. 116 (2019) 145–154.

[60] R.D. Kalina, S. Al-Shmaisani, R.D. Ferron, M.C.G. Juenger, False positives in ASTM C618 specifications for natural pozzolans, ACI Mater J. 116 (2019) 165–172.

[61] A. Benli, Mechanical and durability properties of self-compacting mortars containing binary and ternary mixes of fly ash and silica fume, Structural Concrete. 20 (2019) 1096–1108. https://doi.org/10.1002/suco.201800302.

[62] P. Suraneni, L. Burris, C.R. Shearer, R.D. Hooton, ASTM C618 fly ash specification: Comparison with other specifications, shortcomings, and solutions, ACI Mater. J. 118 (2021) 157–167.

[63] G.C. Cordeiro, R.D. Toledo Filho, L.M. Tavares, E.M.R. Fairbairn, Pozzolanic activity and filler effect of sugar cane bagasse ash in Portland cement and lime mortars, Cem Concr Compos. 30 (2008) 410–418. https://doi.org/10.1016/j.cemconcomp.2008.01.001.

[64] F. Deschner, F. Winnefeld, B. Lothenbach, S. Seufert, P. Schwesig, S. Dittrich, F. Goetz-Neunhoeffer, J. Neubauer, Hydration of Portland cement with high replacement by siliceous

fly ash, Cem Concr Res. 42 (2012) 1389–1400. https://doi.org/10.1016/j.cemconres.2012.06.009.

[65] C. Shi, P.E. Grattan-Bellew, J.A. Stegemann, Conversion of a waste mud into a pozzolanic material, Constr Build Mater. 13 (1999) 279–284. https://doi.org/10.1016/S0950-0618(99)00026-4.

[66] Y.-S. Tseng, C.-L. Huang, K.-C. Hsu, The pozzolanic activity of a calcined waste FCC catalyst and its effect on the compressive strength of cementitious materials, Cem Concr Res. 35 (2005) 782–787. https://doi.org/10.1016/j.cemconres.2004.04.026.

[67] M.M. Tashima, L. Soriano, J. Monzó, M. v. Borrachero, J.L. Akasaki, J. Payá, New method to assess the pozzolanic reactivity of mineral admixtures by means of pH and electrical conductivity measurements in lime:pozzolan suspensions, Materiales de Construcción. 64 (2014) e032. https://doi.org/10.3989/mc.2014.00914.

[68] L.R.S. Carneiro, D.C.S. Garcia, M.C.F. Costa, M. Houmard, R.B. Figueiredo, Evaluation of the pozzolanicity of nanostructured sol-gel silica and silica fume by electrical conductivity measurement, Constr Build Mater. 160 (2018) 252–257. https://doi.org/10.1016/j.conbuildmat.2017.11.042.

[69] P. de Azevedo Basto, H. Savastano Junior, A.A. de Melo Neto, Characterization and pozzolanic properties of sewage sludge ashes (SSA) by electrical conductivity, Cem Concr Compos. 104 (2019) 103410. https://doi.org/10.1016/j.cemconcomp.2019.103410.

[70] M.P. Luxán, F. Madruga, J. Saavedra, Rapid evaluation of pozzolanic activity of natural products by conductivity measurement, Cem Concr Res. 19 (1989) 63–68. https://doi.org/10.1016/0008-8846(89)90066-5.

[71] M. Amar, M. Benzerzour, N.-E. Abriak, Y. Mamindy-Pajany, Study of the pozzolanic activity of a dredged sediment from Dunkirk harbour, Powder Technol. 320 (2017) 748–764. https://doi.org/10.1016/j.powtec.2017.07.055.

[72] J. Payá, M.V. Borrachero, J. Monzó, E. Peris-Mora, F. Amahjour, Enhanced conductivity measurement techniques for evaluation of fly ash pozzolanic activity, Cem Concr Res. 31 (2001) 41–49. https://doi.org/10.1016/S0008-8846(00)00434-8.

[73] S. Sinthaworn, P. Nimityongskul, Effects of temperature and alkaline solution on electrical conductivity measurements of pozzolanic activity, Cem Concr Compos. 33 (2011) 622–627. https://doi.org/10.1016/j.cemconcomp.2011.02.012.

[74] J. Shao, J. Gao, Y. Zhao, X. Chen, Study on the pozzolanic reaction of clay brick powder in blended cement pastes, Constr Build Mater. 213 (2019) 209–215. https://doi.org/10.1016/J.CONBUILDMAT.2019.03.307.

[75] A. Cuesta, I. Santacruz, A.G. De la Torre, M. Dapiaggi, J.D. Zea-Garcia, M.A.G. Aranda, Local structure and Ca/Si ratio in C-S-H gels from hydration of blends of tricalcium silicate and silica fume, Cem Concr Res. 143 (2021) 106405. https://doi.org/10.1016/J.CEMCONRES.2021.106405.

[76] R. García-Giménez, M. Frias, R. Vigil de la Villa, S. Martínez-Ramírez, Ca/Si and Si/Al Ratios of Metakaolinite-Based Wastes: Their Influence on Mineralogy and Mechanical Strengths, (n.d.). https://doi.org/10.3390/app8040480.

[77] S.K. Kim, S.T. Kang, J.K. Kim, I.Y. Jang, Effects of particle size and cement replacement of LCD glass powder in concrete, Advances in Materials Science and Engineering. 2017 (2017). https://doi.org/10.1155/2017/3928047.

[78] H. Paiva, A.S. Silva, A. Velosa, P. Cachim, V.M. Ferreira, Microstructure and hardened state properties on pozzolan-containing concrete, Constr Build Mater. 140 (2017) 374–384. https://doi.org/10.1016/j.conbuildmat.2017.02.120.

[79] N. Ural, The significance of scanning electron microscopy (SEM) analysis on the microstructure of improved clay: An overview, Open Geosciences. 13 (2021) 197–218.

[80] G. Xu, X. Shi, Characteristics and applications of fly ash as a sustainable construction material: A state-of-the-art review, Resour Conserv Recycl. 136 (2018) 95–109. https://doi.org/10.1016/j.resconrec.2018.04.010.

[81] R. Vigil de la Villa Mencía, M. Frías, S.M. Ramírez, L.F. Carrasco, R.G. Giménez, Concrete/Glass Construction and Demolition Waste (CDW) Synergies in Ternary Eco-Cement-Paste Mineralogy, Materials. 15 (2022) 4661. https://doi.org/10.3390/ma15134661.

[82] S. Diamond, J. Huang, The ITZ in concrete – a different view based on image analysis and SEM observations, Cem Concr Compos. 23 (2001) 179–188. https://doi.org/10.1016/S0958-9465(00)00065-2.

[83] R.L. Figueiredo, S. Pavía, A study of the parameters that determine the reactivity of sugarcane bagasse ashes (SCBA) for use as a binder in construction, SN Appl Sci. 2 (2020) 1515. https://doi.org/10.1007/s42452-020-03224-w.

[84] K.L. Scrivener, Backscattered electron imaging of cementitious microstructures: understanding and quantification, Cem Concr Compos. 26 (2004) 935–945. https://doi.org/10.1016/j.cemconcomp.2004.02.029.

[85] A.M. Said, M.S. Zeidan, M.T. Bassuoni, Y. Tian, Properties of concrete incorporating nano-silica, Constr Build Mater. 36 (2012) 838–844. https://doi.org/10.1016/j.conbuildmat.2012.06.044.

[86] P.T. Durdziński, C.F. Dunant, M. ben Haha, K.L. Scrivener, A new quantification method based on SEM-EDS to assess fly ash composition and study the reaction of its individual components in hydrating cement paste, Cem Concr Res. 73 (2015) 111–122. https://doi.org/10.1016/j.cemconres.2015.02.008.

[87] H. Maraghechi, M. Maraghechi, F. Rajabipour, C.G. Pantano, Pozzolanic reactivity of recycled glass powder at elevated temperatures: Reaction stoichiometry, reaction products and effect of alkali activation, Cem Concr Compos. 53 (2014) 105–114. https://doi.org/10.1016/j.cemconcomp.2014.06.015.

[88] C.M. Belfiore, G.V. Fichera, G. Ortolano, A. Pezzino, R. Visalli, L. Zappalà, Image processing of the pozzolanic reactions in Roman mortars via X-Ray Map Analyser, Microchemical Journal. 125 (2016) 242–253. https://doi.org/10.1016/j.microc.2015.11.022.

[89] H. Siad, M. Lachemi, M. Sahmaran, K.M.A. Hossain, Effect of glass powder on sulfuric acid resistance of cementitious materials, Constr Build Mater. 113 (2016) 163–173. https://doi.org/10.1016/j.conbuildmat.2016.03.049.

[90] G. Mertens, R. Snellings, K. van Balen, B. Bicer-Simsir, P. Verlooy, J. Elsen, Pozzolanic reactions of common natural zeolites with lime and parameters affecting their reactivity, Cem Concr Res. 39 (2009) 233–240. https://doi.org/10.1016/j.cemconres.2008.11.008.

[91] N. Lemonis, P.E. Tsakiridis, N.S. Katsiotis, S. Antiohos, D. Papageorgiou, M.S. Katsiotis, M. Beazi-Katsioti, Hydration study of ternary blended cements containing ferronickel slag and

natural pozzolan, Constr Build Mater. 81 (2015) 130–139. https://doi.org/10.1016/j.conbuildmat.2015.02.046.

[92] ASTM, 597-16 (2016) Standard test method for pulse velocity through concrete, Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA. (2016).

[93] M. Kamath, S. Prashant, M. Kumar, Micro-characterisation of alkali activated paste with fly ash-GGBS-metakaolin binder system with ambient setting characteristics, Constr Build Mater. 277 (2021) 122323. https://doi.org/10.1016/j.conbuildmat.2021.122323.

[94] S. Hong, S. Yoon, J. Kim, C. Lee, S. Kim, Y. Lee, Evaluation of Condition of Concrete Structures Using Ultrasonic Pulse Velocity Method, Applied Sciences. 10 (2020) 706. https://doi.org/10.3390/app10020706.

[95] H. Sasanipour, F. Aslani, Effect of specimen shape, silica fume, and curing age on durability properties of self-compacting concrete incorporating coarse recycled concrete aggregates, Constr Build Mater. 228 (2019) 117054. https://doi.org/10.1016/j.conbuildmat.2019.117054.

[96] İ. Özkan, Z. Yayla, Evaluation of correlation between physical properties and ultrasonic pulse velocity of fired clay samples, Ultrasonics. 66 (2016) 4–10. https://doi.org/10.1016/j.ultras.2015.12.008.

[97] E.A. Whitehurst, Soniscope tests concrete structures, in: Journal Proceedings, 1951: pp. 433–444.

[98] R. Madandoust, S.Y. Mousavi, Fresh and hardened properties of self-compacting concrete containing metakaolin, Constr Build Mater. 35 (2012) 752–760. https://doi.org/10.1016/j.conbuildmat.2012.04.109.

[99] R. Chihaoui, H. Siad, Y. Senhadji, M. Mouli, A.M. Nefoussi, M. Lachemi, Efficiency of natural pozzolan and natural perlite in controlling the alkali-silica reaction of cementitious materials, Case Studies in Construction Materials. 17 (2022) e01246. https://doi.org/10.1016/j.cscm.2022.e01246.

[100] I. Shooshpasha, A. Hasanzadeh, M. Kharun, Effect of silica fume on the ultrasonic pulse velocity of cemented sand, in: J Phys Conf Ser, IOP Publishing, 2020: p. 012017.

[101] M. Ashraf, A. Naeem Khan, Q. Ali, J. Mirza, A. Goyal, A.M. Anwar, Physico-chemical, morphological and thermal analysis for the combined pozzolanic activities of minerals additives, Constr Build Mater. 23 (2009) 2207–2213. https://doi.org/10.1016/j.conbuildmat.2008.12.008.

[102] F. Althoey, A.K.A. El-Aal, H. Shoukry, I. Hakeem, Performance of Cement Mortars Containing Clay Exposed to High Temperature, Arab J Sci Eng. 47 (2022) 591–599. https://doi.org/10.1007/s13369-021-05583-x.

[103] P.-T. Bui, T.-P. Huynh, Performance and Microstructural Evaluation of Rice Husk Ash–Ground Granulated Blast Furnace Slag–CFBC Fly Ash Mixtures Produced as an Eco-Cement, Journal of Materials in Civil Engineering. 34 (2022) 04021485.

[104] B. Demirel, O. Keleştemur, Effect of elevated temperature on the mechanical properties of concrete produced with finely ground pumice and silica fume, Fire Saf J. 45 (2010) 385–391. https://doi.org/10.1016/j.firesaf.2010.08.002.

[105] H. Jiang, H. Yi, E. Yilmaz, S. Liu, J. Qiu, Ultrasonic evaluation of strength properties of cemented paste backfill: Effects of mineral admixture and curing temperature, Ultrasonics. 100 (2020) 105983. https://doi.org/10.1016/j.ultras.2019.105983.

[106] M.A. Khalaf, C.C. Ban, M. Ramli, The constituents, properties and application of heavyweight concrete: A review, Constr Build Mater. 215 (2019) 73–89. https://doi.org/10.1016/j.conbuildmat.2019.04.146.

[107] R. Demirboğa, İ. Türkmen, M.B. Karakoç, Relationship between ultrasonic velocity and compressive strength for high-volume mineral-admixtured concrete, Cem Concr Res. 34 (2004) 2329–2336. https://doi.org/10.1016/j.cemconres.2004.04.017.

[108] Z.Ç. Ulucan, K. Türk, M. Karataş, Effect of mineral admixtures on the correlation between ultrasonic velocity and compressive strength for self-compacting concrete., Russian Journal of Nondestructive Testing. 44 (2008).

[109] M.A. Chandak, P. Pawade, Compressive Strength and Ultrasonic Pulse Velocity of Concrete with Metakaolin, Civ. Eng. Archit. 8 (2020) 1277–1282.

Chapter 3: Electrical conductivity and pH measurement as direct and rapid methods to assess pozzolanic reactivity.

3-1. Abstract

Reducing cement use is critical for minimizing embodied energy in concrete and reducing carbon dioxide emissions. Hence, the assessment of the reactivity of pozzolanic materials is crucial in identifying their potential as alternative supplementary cementitious materials (SCMs) for concrete production. This experimental study investigates the feasibility of using pH and electrical conductivity measurements as direct methods for evaluating the pozzolanic reactivity of materials. Other commonly used direct reactivity test methods include the Frattini and thermogravimetric analysis (TGA) tests. Direct methods rely on measuring the consumption of lime or portlandite in a lime-pozzolan or cement-pozzolan blended sample to assess pozzolanic reactivity. The waste materials evaluated in this research include industrial by-products that could potentially be transformed into high-value SCMs. The tested materials were pottery cull (PC), brick powder (BP), lightweight aggregate fines (LA), waste glass powder (GP), class C fly ash (FA), dolostone powder (DS), and silica fume (SF). This paper presents an analytical method to calculate the consumed portlandite due to pozzolanic reactivity using electrical conductivity and pH measurements. Results are then compared with the Frattini and TGA methods.

3-2. Keywords

Pozzolanic reactivity, SCMs, electrical conductivity, pH, Frattini, TGA, Direct methods

3-3. Introduction

There is growing worldwide interest in reducing greenhouse gas emissions from portland cement production to address significant climate change concerns [1]. Consequently, the global construction industry seeks to reduce the environmental impact of its activities, especially portland cement usage, by developing new and sustainable materials with lower carbon footprints and embodied energy [2]. Therefore, pozzolanic materials are being developed as alternative binders in concrete [3]. The principal chemical reactions involved in portland cement hydration result in the conversion of tricalcium silicate (C_3S) and dicalcium silicate (C_2S) into calcium silicate hydrates (C-S-H) and calcium hydroxide (CH) or portlandite (Eq. 1-2) [3]. A pozzolanic material added to the concrete mix can utilize this CH in the presence of water (H), resulting in additional strength-bearing phases such as C-S-H, calcium aluminates hydrate (C-A-H), or calcium aluminosilicate hydrates (C-A-S-H) (Eq. 3) [3].

$$C_3S + H \rightleftarrows C\text{-}S\text{-}H + CH \quad (1)$$

$$C_2S + H \rightleftarrows C\text{-}S\text{-}H + CH \quad (2)$$

$$\text{Pozzolan} + CH + H \rightleftarrows C\text{-}S\text{-}H \quad (3)$$

Pozzolanic reactivity can be assessed using various direct and indirect methods. Direct methods detect the extent of pozzolanic reaction by monitoring the consumption of portlandite with time using experimental techniques such as X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), or classical chemical titration methods (e.g., Frattini) [4]. The Frattini test represents a widely used direct method that involves chemical titration to determine the concentrations of dissolved calcium and hydroxyl ions present in a solution that contains both portland cement and a pozzolan [4]. An indirect method measures a physical property of a test sample that is influenced

by pozzolanic reactions, such as compressive strength using the strength activity index (SAI) or heat evolution using calorimetry [4–6]. Test methods such as pH and electrical conductivity are easy and rapid test methods when compared to the more time-consuming reactivity test methods (either sample preparation or the test itself) [7].

The pH and conductivity methods were first proposed by Luxan et al. [8] in 1989 for the rapid evaluation of pozzolanic reactivity. In these tests, the pozzolan reacts directly with calcium hydroxide that is dissolved in water [9]. Silica and alumina from the pozzolan react with dissolved calcium and hydroxyl ions in an aqueous suspension and produce insoluble and non-conductive products such as C-S-H and C-A-S-H. The formation of these products coincides with a reduction in ions in the solution, which then reduces the electrical conductivity of the solution [7,9,10]. More specifically, when the pozzolanic reaction occurs, the concentration of hydroxyl ions decreases, resulting in a decrease in pH [9]. Therefore, changes in electrical conductivity and pH of the solution would occur due to the removal of calcium hydroxide through pozzolanic reactions. These tests have historically been regarded as indirect methods to assess pozzolanic reactivity [4,7,9,11–13]. It is, however, possible to quantify the consumption of portlandite using these methods by developing a set of equations that relate the variables to pozzolanic reactivity. This would allow the electrical conductivity and pH tests to be considered as direct methods for evaluating pozzolanic reactions.

The objective of this work is to determine whether the pH and conductivity tests can serve as direct tests of pozzolanic reactivity. A set of equations to calculate the consumption of portlandite is proposed. Test results based on pH and conductivity using seven different materials are compared with results from the two commonly used direct methods (Frattini and TGA).

3-4. Materials and methods

Seven different materials were tested. Two different types of calcined clay waste materials (pottery cull and fired clay brick) were used in this study. Pottery cull (PC) is a waste material from the production of ceramic sanitary ware, which is discarded due to manufacturing defects. The pottery cull for this research was provided by the Kohler Company in Kohler, Wisconsin. Clay bricks (brick powder - BP) are common waste material from construction demolition projects. Lightweight aggregate fines (LA) are fine particles produced during the manufacturing process of rotary kiln-expanded shale and lightweight clay aggregates. Samples of Stalite lightweight aggregate fines were provided by Arcosa, Inc. Silica fume (SF) is a by-product of the production of silicon and ferrosilicon alloys in electric arc furnaces. Other tested materials, including waste glass powder (GP), class C fly ash (FA), and dolostone (DS) (from an aggregate quarry in Wisconsin), were used in the tests. A Type I ordinary portland cement (OPC) produced by St. Mary's Cement was used as the binder in this study. When applicable, the materials were first air-dried at room temperature. PC, BP, LA, GP, and DS were ground using a ball mill, and fine powders passing through a 75µm sieve were collected. Fly ash and silica fume were used directly without grinding and sieving. Figure 3-1 shows the seven fine-powder materials and OPC used in this study.

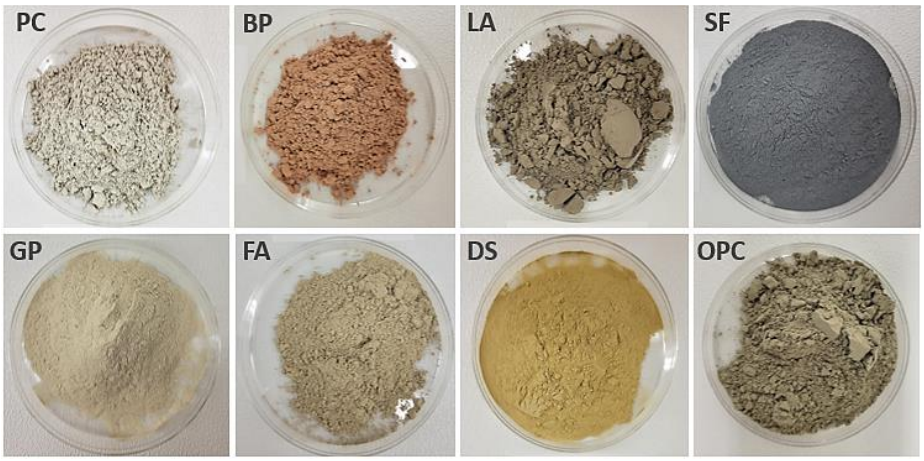


Figure 3-1: Materials used to investigate pozzolanic activity in this study

3-4-1. Physical and chemical characterization

The particle size distribution (PSD) test was performed using a laser diffraction particle size analyzer (Malvern Mastersizer 3000). X-ray Fluorescence Spectrometry (XRF) was performed with a Bruker S4 Pioneer to measure the oxide compositions of all tested materials. Powders were dried overnight at 105°C to evaporate extra water, and then a portion of the powders was ignited at 1050°C for 20 minutes to measure loss on ignition (LOI). The mineralogical phases of the materials were determined using XRD (Bruker D8 Discover) with Copper K-Alpha radiation.

3-4-2. Pozzolanic reactivity methods

3-4-2-1. Frattini

The Frattini test was performed according to EN 196-5 [14] by preparing 20 g samples consisting of 80% OPC and 20% of each tested material mixed with 100 ml of distilled water. The test samples were kept at 40°C for 15 or 28 days. After each test period, the samples were vacuum filtered and cooled at room temperature in sealed Buchner funnels. The acquired solutions were analyzed for [OH^-] by titrating against 0.1 mol/L HCl using a methyl orange indicator until a color change (from light yellow to light orange) was detected. After the determination of hydroxyl ions,

the same solution was examined for [Ca^{2+}] by titrating against a 0.03 mol/L EDTA using a murexide indicator until a color transition from pink to purple was noticed. The pH of the solution was adjusted to 12 ± 0.5 before titration against the EDTA solution. Three samples were prepared and tested for each material. Three parallel measurements were taken for each sample's reactivity assessment, and the average values were plotted on the lime solubility curve provided in the standard.

3-4-2-2. TGA

Blended cement-pozzolan pastes were prepared by replacing 20% of cement with the tested materials and a water-to-cement ratio of 0.484 before conducting the TGA test. Fresh pastes were cast in cube molds (2 in × 2 in), de-molded after 24 h, and kept in a sealed lime-water container at 23°C for 28 and 90 days of curing. Table 3-1 shows the TGA sample mixture information. After 28 and 90 days, mortar samples were finely ground by pestle and mortars and sieved through a #200 sieve. Powder samples retained on the pan were oven-dried at 50±1°C for 48 h and quickly employed for thermogravimetric analysis. A small sample (between 20-23) mg was placed in a platinum crucible and kept at an isothermal condition for 10 minutes. Thermal analysis was carried out using a TA Instruments SDT 650 at a constant heating rate of 10°C/min with temperature ranges of 23-1000°C in argon gas.

Table 3-1. TGA sample mixtures [15]

Specimens	w/c	OPC (g)	Tested material (g)	Graded standard sand (g)
Control mix	0.484	500	0	1375
Cement-pozzolan mix	0.484	400	100	1375

3-4-2-3. Electrical conductivity and pH

Electrical conductivity and pH were performed following the procedures described by Uzal et al. [16]. In this method, lime-pozzolan aqueous suspensions were prepared for pozzolanic reactivity assessment by electrical conductivity. Calcium hydroxide solutions were prepared by dissolving 200 mg of lime powder ($Ca(OH)_2$) in 250 ml of deionized water. The required amount of lime (200 mg) was based on the saturation point, which was determined through the gradual addition of lime in 250 ml of water to reach a saturation plateau at a constant pH of 12 (Fig. 3-2).

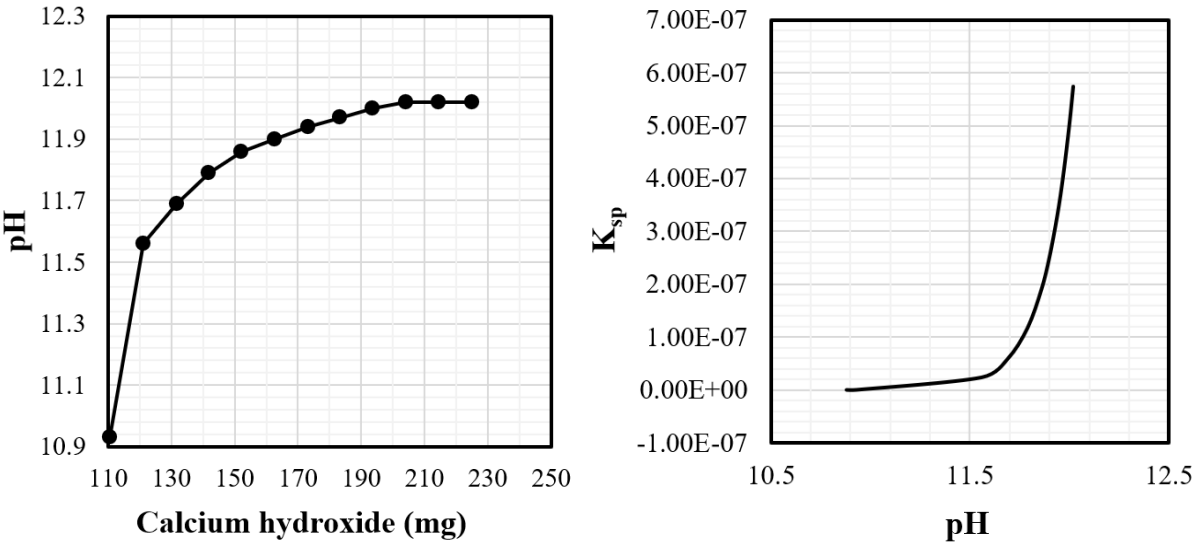


Figure 3-2. Required lime powder and solution solubility product constant (Ksp).

This study used a Fisher Scientific Accumet® BASIC conductivity meter and a pH meter to measure pozzolanic reaction by monitoring the electrical conductivity and pH of the lime-pozzolan suspensions using the procedures proposed by Uzal et al. [16]. An electrical water bath with a thermostatic magnetic stirrer was used to keep the suspensions' temperature at 40±1°C. Initially, a beaker with 250 ml of deionized water was placed in the water bath to reach a constant temperature of 40±1°C. Then, 200 mg of $Ca(OH)_2$ was added to water, and the solution

was allowed to reach a constant pH and conductivity (pH_0 and EC_0) in approximately 15 minutes. After recording the pH_0 and EC_0 values, 5 gr of each tested material was added to the solution, and conductivity and pH values were recorded every 15 minutes for 6 hours. Figure 3-3 illustrates the test setup.

Figure 3-3: Electrical conductivity and pH test setup.

3-5. Results and discussion

3-5-1. Characterization results

Figure 3-4 shows the PSD curves for all tested materials, including OPC. The order of size from smallest to largest is SF < FA < LA < OPC< BP< PC < DS <GP.

The results of oxide composition measured by XRF are summarized in Table 3-2. Chemical analysis indicated that PC and BP (calcined clay) were similar in their oxide composition and were mainly composed of silica and alumina. LA had more than 50% silica and 17% alumina. GP and SF

were primarily composed of silica, with 70% and 92.17%, respectively. In contrast, FA and DS had a considerable amount of lime. The Class C FA has both pozzolanic and hydraulic properties, with 37.5% silica and 25.2% lime. DS and SF had the lowest and highest silica content, respectively. Table 3-3 shows the major phases of OPC following a new Bogue model proposed by Shim et al. [17].

Figure 3-5 presents the mineralogical phases of the materials by XRD. The XRD pattern of SF showed a broad diffuse scattering associated with amorphous silica and some distinct peaks of crystalline silica. The major peaks in PC and BP are quartz (SiO_2) and mullite ($2AL_2O_3SiO_2$), which are crystalline compounds of silica. The major peaks in LA are associated with quartz, gypsum ($CaSO_4$), and some olivine $(Mg,Fe)_2SiO_4$). XRD pattern of GP presented an amorphous phase of silica with some distinct peaks related to quartz and calcite. The major peaks in FA are associated with quartz, C_3A, C_3S, periclase (MgO), gypsum, and CaO. The major peaks of DS are dolomite ($CaMg(CO_3)_2$), orthoclase ($KALSi_3O_8$), and quartz. The major peaks in OPC are the main cement phases, including C_3S, C_2S, C_3A, C_4AF, and gypsum.

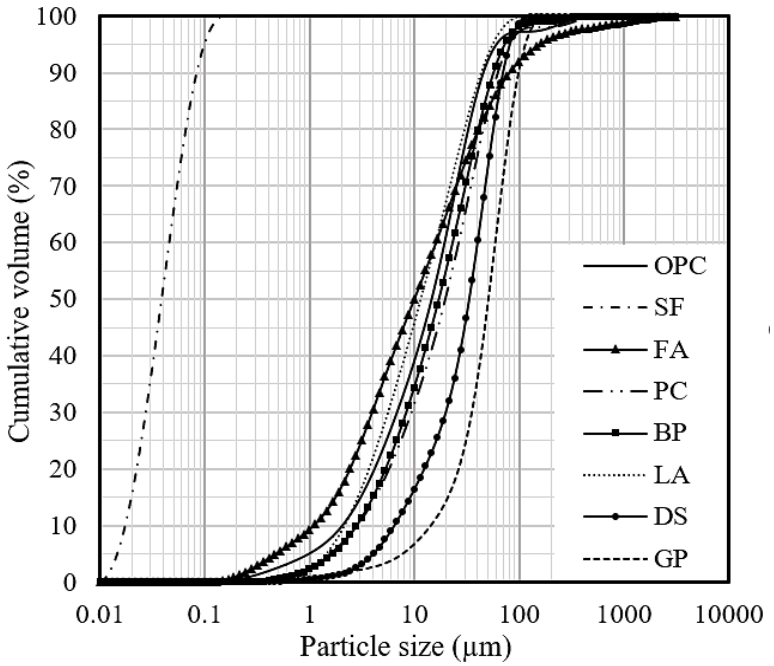


Figure 3-4: PSD of OPC, SF, PC, BP, LA, DS, and GP by laser diffraction method.

Table 3-2. Oxide composition (mass %) of the raw materials as measured by XRF.

Oxides	Materials							
	BP	PC	LA	OPC	FA	GP	SF	DS
SiO_2	68.88	67.09	51.81	22.86	37.47	70.03	92.17	15.52
Al_2O_3	21.44	18.62	17.72	5.09	19.18	2.23	0.82	3.64
Fe_2O_3	5.28	1.27	7.24	2.61	5.95	0.35	0.72	1.47
CaO	0.22	3.04	6.39	68.04	25.22	8.95	0.53	24.92
MgO	0.87	1.18	2.03	3.47	5.33	1.79	1.67	16.62
Na_2O	0.25	2.10	0.32	0.09	1.72	13.40	0.16	0.04
K_2O	1.44	1.72	2.06	0.98	0.63	0.58	0.77	2.28
TiO_2	1.17	0.69	0.71	0.45	1.41	0.05	0.01	0.14
P_2O_5	0.12	0.07	0.35	0.07	1.33	0.05	0.09	0.04
LOI	0.18	3.04	6.72	0.314	0.53	2.5	2.71	48.01

Table 3-3. Major phases of OPC (%)

C_3S (Alite)	C_2S (Blite)	C_3A (Aluminate)	C_4AF (Ferrite)	$CaSO_4$ (Gypsum)
63.75	18.89	4.39	6.06	6.67

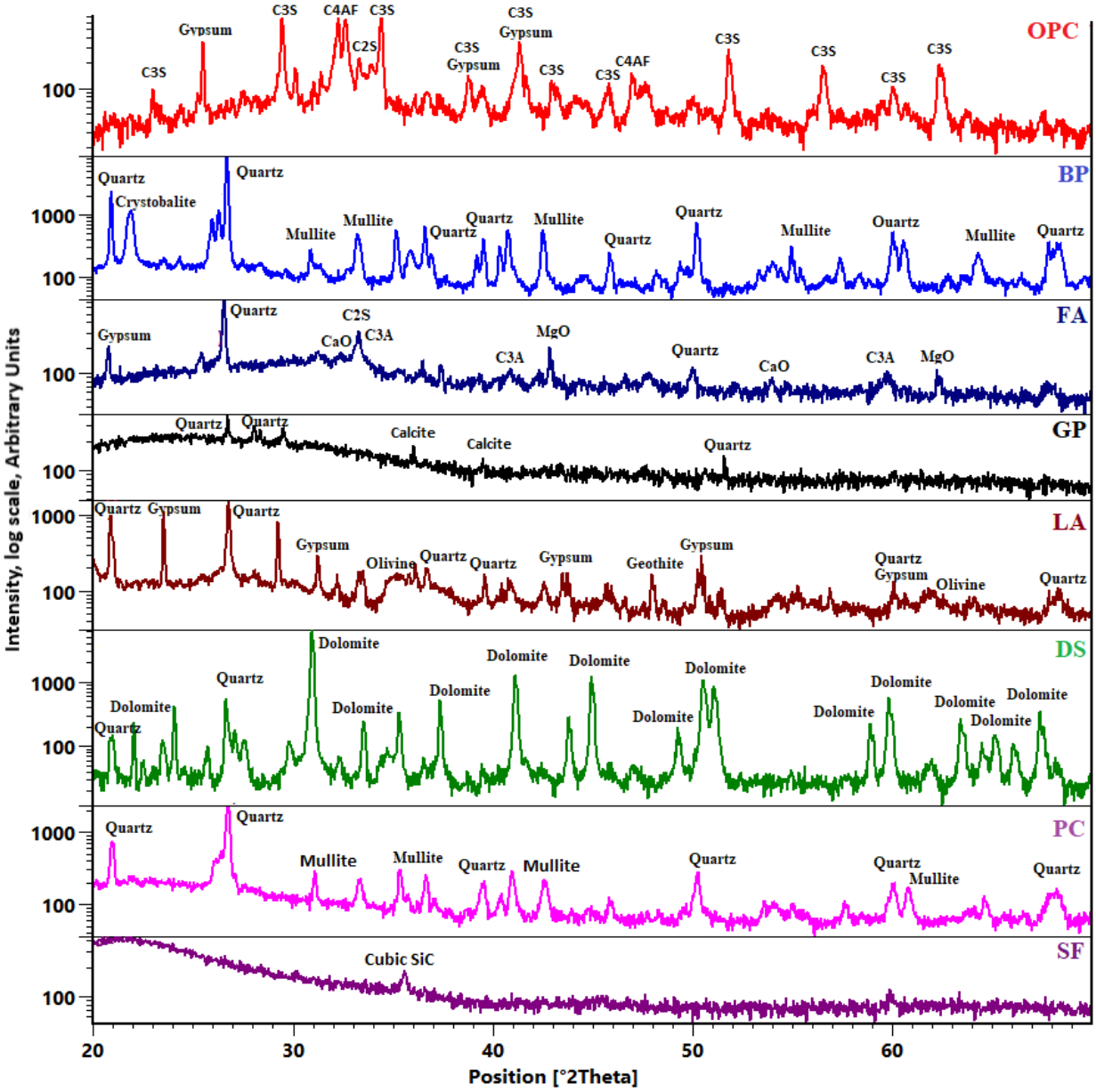


Figure 3-5: XRD patterns of OPC, BP, FA, GP, LA, DS, PC, and SF

3-5-2. Frattini

The lime solubility curve (the theoretical maximum lime concentration) is determined using a formula provided in EN 196–5 [14] (Eq. 4). To find the maximum lime consumption (for estimation of pozzolanic reactivity of each tested material), the vertical distance of data points

from the lime solubility curve was calculated according to the EN 196-5 [14] (Eq. 3-1). The lime consumption (in percent) can be computed using Eq. 3-2 [4].

$$\mathrm{Max}[CaO] = \frac{350}{[OH^-]-15} \quad (3\text{-}1)$$

$$Consumed\ lime\ (\%) = \frac{Max[CaO]-[CaO]}{Max[CaO]} \times 100 \quad (3\text{-}2)$$

Where $Max[CaO]$ is the maximum theoretical lime and $[CaO]$ is the lime consumed by each tested pozzolan. The test material is considered pozzolanic when the [CaO] and [OH^-] concentrations in the sample solution fall below the lime solubility curve (Fig. 3-6)[14]. At 15 days, only SF showed clear pozzolanic reactivity, whereas LA had some pozzolanic reactivity, and FA, PC, BP, GP, and DS were above the saturation curve and therefore considered inactive. At 28 days, however, PC, BP, GP, and FA also showed pozzolanic reactivity as their position shifted below the saturation curve. This indicates that these materials require more time to show pozzolanic reactivity and could be classified as slow-reactive pozzolans. At 15 days, SF had the highest reactivity among all the tested materials due to the presence of amorphous silica and smaller particle size (higher surface area). In fact, SF used the most lime at an early age of 15 days (34.5%). SF can therefore be classified as a quick reactive pozzolan. In contrast, GP with a high content of amorphous silica exhibited a lower reactivity (lime reduction) than other materials at 28 and 90 days. This could be attributed to larger particle sizes compared to the other tested materials. DS was inert and did not show pozzolanic reactivity with a slight rate of lime reduction (Table 3-4). The OPC values were also located above the curve, which is an indication that cement is not a pozzolanic material (it is hydraulic).

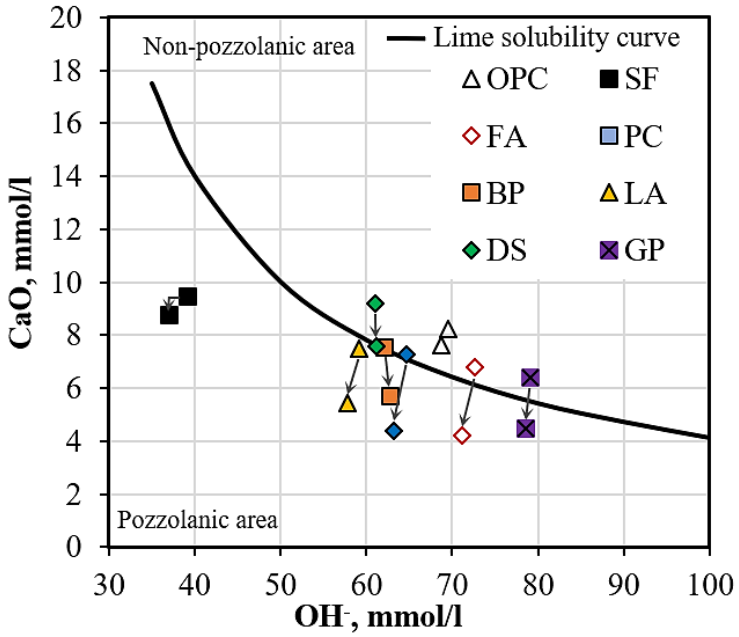


Figure 3-6. Results of Frattini at 15 and 28 days, arrows show the shift from 15 to 28 days.

Table 3-4. Lime consumption using the Frattini test at the ages of 15 and 28 days

Materials	OH-15d mmol l^{-1}	CaO-15d mmol l^{-1}	Max theoretical CaO-15d	CaO Reduction (%)- 15d	OH-28d mmol l^{-1}	CaO-28d mmol l^{-1}	Max theoretical CaO-28d	CaO Reduction (%)- 28d
OPC	69.6	8.19	6.41	-27.90	68.8	7.62	6.51	-17.10
SF	39.3	9.46	14.43	34.50	37.0	8.77	15.91	44.90
FA	72.6	6.78	6.08	-11.50	71.2	4.21	6.23	32.40
PC	64.7	7.23	7.04	-2.80	63.2	4.40	7.27	39.40
BP	62.2	7.54	7.42	-1.70	62.7	5.70	7.33	22.20
LA	59.2	7.50	7.91	5.20	57.8	5.44	8.17	33.50
DS	61.1	9.19	7.60	-20.90	61.2	8.27	7.58	-9.10
GP	79.1	6.39	5.46	-17.00	78.6	4.48	5.50	18.60

3-5-3. TGA

The decomposition of portlandite (dehydroxylation) was observed at temperatures ranging from 400-500°C. The decomposition of calcite or calcium carbonate (decarbonation) was observed between 600-750°C for all tested samples except the sample containing DS. The calcite

decomposition for the sample with DS ranged from 600-800˚C. The amount of portlandite remaining in each sample was calculated using equation 3-3 [6].

$$M_{CH_r} = 4.11(CH) + 1.68(CC_3) \quad (3\text{-}3)$$

Where M_{CH_r} is the mass of remaining lime in mg, 4.11 and 1.68 are the molar mass ratios of $Ca(OH)_2/H_2O$ and $Ca(OH)_2/CO_2$, respectively. M_{CC_3} is the mass loss due to the decomposition of $CaCO_3$, and M_{CH} is the mass loss due to the decomposition of $Ca(OH)_2$.

The percentage of the lime consumption in the pozzolan-cement samples with 20% replacement of OPC was calculated following equation 3-4 [9].

$$lime\ consumption\ (\%) = \left[\frac{(M_{CHr,c} \times 0.8) - M_{CHr,p}}{(M_{CHr,c} \times 0.8)}\right] \times 100 \quad (3\text{-}4)$$

Where $M_{CHr,c}$ and $M_{CHr,p}$ are calcium hydroxide remaining in the control and pozzolan-cement samples, respectively. 0.8 is the fraction of OPC in cement-pozzolan samples (20% replacement of OPC with pozzolan) in this study. Table 3-5 shows mass loss due to portlandite and calcite decomposition and the percentage of the fixed lime in each sample after 28- and 90 days of curing. More portlandite was consumed by the tested pozzolans after 90 days compared to 28 days indicating continued pozzolanic reactivity at later ages. The order of the amount of fixed lime was as follows: SF> FA> PC> LA> BP> GP after 28- and 90 days. SF consumed the most (75.7%), and GP used the least amount of lime (7.3%) after 90 days. The calculated consumed lime was negative for the sample containing DS, indicating that it was not pozzolanic. There was a significant mass loss due to decarbonation since DS was mainly composed of dolomite ($CaMgCO_3$), and, therefore, Eq. 3-3 cannot properly estimate the remaining portlandite for DS.

Table 3-5. Mass loss and fixed lime of seven pozzolan-cement samples determined by TGA

Blended samples	28d			90d		
	Portlandite (%)	Calcite (%)	Fixed lime (%)	Portlandite (%)	Calcite (%)	Fixed lime (%)
SF	1.264	0.543	54.07	0.618	0.444	75.66
FA	2.470	0.398	27.07	2.338	0.457	35.88
PC	2.540	0.393	25.42	2.771	0.423	26.73
BP	2.404	0.990	13.71	2.388	1.129	19.33
LA	2.672	0.413	21.56	2.738	0.472	26.37
DS	3.059	3.294	-61.54	3.573	3.130	-53.77
GP	2.655	1.094	4.68	3.326	0.716	7.28

3-5-4. Electrical conductivity and pH

The $Ca(OH)_2$ remaining in the pozzolan-lime solution after 6 hours of reaction can be calculated to quantify the percentage of consumed $Ca(OH)_2$ (due to pozzolanic reaction) for each tested material using electrical conductivity and pH test results. A concentration-dependent relationship exists between electrical and molar conductivity based on Kohlrausch law (Eq. 3-5) [18].

$$\Lambda_m^s = 1000\frac{k}{[c]} \tag{3-5}$$

where Λ_m^s is the molar conductivity of a saturated salt solution (in Scm^2mol^{-1}), k is the electrical conductivity in Scm^{-1} at a specific temperature, and $[c]$ is the concentration of the solution in mol/l. Molar conductivity can also be calculated using Eq. 3-6.

$$\Lambda_m^s = \Lambda_m^\infty \alpha \tag{3-6}$$

where Λ_m^∞ is the molar conductivity at infinite dilution, and α is the degree of dissociation. Λ_m^∞ values for Ca^{2+} and OH^- are 118.88 and 198.6 Scm^2mol^{-1} at 25˚C, respectively [19]. The molar conductivity of calcium hydroxide (CH) at infinite dilution ($\Lambda_{m,CH}^\infty$) can be calculated using Eq. 3-7.

$$\Lambda^{\infty}_{m,CH} = [\Lambda^{\infty}_{m}\, Ca^{2+}] + 2[\Lambda^{\infty}_{m}\, OH^{-}] = (118.88) + (2\times198.6) = 516.08\ Scm^{2}mol^{-1} \quad (3\text{-}7)$$

In an ideal infinite dilution, $Ca(OH)_2$ is fully dissociated, so α=1 and $\Lambda^{s}_{m,CH} = \Lambda^{\infty}_{m,CH}$. Dissolution of solid $Ca(OH)_2$ and related dissociation reactions are as follows [20] :

$Ca(OH)_2$ (s) ⇄ Ca $(OH)^+$ + OH^-

$Ca(OH)^+$ ⇄ Ca^{2+} + OH^-

Since the value of $\Lambda^{\infty}_{m,CH}$ is at 25˚C. To convert the electrical conductivity at 40˚C to conductivity at 25˚C, the relationship between electrical conductivity and temperature is used, commonly defined as a linear equation (Eq. 3-8) [21].

$$k_{25°C} = \frac{k_T}{1 + \beta\,(T - 25)} \quad (3\text{-}8)$$

Where $k_{25°C}$ is the reference conductivity at 25˚C, k_T is the electrical conductivity at a specific temperature *T* (T= 40˚C in this study), and *β* is a compensation factor equal to 0.019 ˚C^{-1}.

The calcium hydroxide concentration of the saturated lime-water solution at 25˚C can be calculated using Eq. 9.

$$[CH]_0 = 1000\frac{k_{0,25°C}}{\Lambda^{s}_{m,CH}} \quad (3\text{-}9)$$

Where $[CH]_0$ is the initial concentration of calcium hydroxide, and $k_{0,25°C}$ is the electrical conductivity of the saturated lime-water solution (reference solution) before adding the pozzolan at 25˚C.

The calcium hydroxide concentration after a given time *t* (t=6h in this study) following the start of the chemical reaction of pozzolan with lime can be calculated using Eq. 3-10.

$$[CH]_t = 1000\frac{k_{t,25°C}}{\Lambda^{s}_{m,CH}} \quad (3\text{-}10)$$

where $[CH]_t$ is the concentration of calcium hydroxide and $k_{t,25°C}$ is the electrical conductivity of the saturated lime-water solution at a given time t following the start of the lime-pozzolan reaction at 25°C.

Calcium hydroxide concentration is half that of the hydroxyl ions [22]. Thus, calculating the consumed lime based on pH measurements can be performed using Eqs. 3-11 through 3-16.

$$pH + pOH = 14 \quad (3\text{-}11)$$

$$pOH = -\log[OH^-] \quad (3\text{-}12)$$

$$[OH^-]_0 = 10^{-pOH} \quad (3\text{-}13)$$

$$[OH^-]_t = 10^{-pOH} \quad (3\text{-}14)$$

$$[CH]_0 = \frac{[OH^-]_0}{2} \quad (3\text{-}15)$$

$$[CH]_t = \frac{[OH^-]_t}{2} \quad (3\text{-}16)$$

Where $[CH]_0$ and $[CH]_t$ are the calcium hydroxide concentration in the solutions at time 0 (reference solution) and at time *t* following the start of the chemical reaction between pozzolan and lime, respectively. pH is a measure of the hydrogen ion concentration $[H^+]$in a solution, and pOH is a measure of the hydroxide ion concentration $[OH^-]$ in a solution.

Finally, the consumption of calcium hydroxide by each pozzolan at time *t* (following the start of the reaction) and the percentage consumption of calcium hydroxide can be calculated using Eqs. 3-17 and 3-18.

$$\text{Consumed lime} = [CH]_0 - [CH]_t \quad (3\text{-}17)$$

$$\text{Consumed lime (\%)} = \frac{[CH]_0 - [CH]_t}{[CH]_0} \times 100 \quad (3\text{-}18)$$

The percentages of lime consumption by each pozzolan using both electrical conductivity and pH methods are shown in Table 3-6. These results indicate that SF and GP used the most and the least calcium hydroxide, respectively (Tables 3-6 and 3-7). The order of lime consumption using the electrical conductivity method is as follows: SF> FA> DS> LA> PC> BP> GP. DS showed more lime consumption compared to LA, PC, BP, and GP, likely due to the presence of dolomite and magnesium oxide in DS. From XRD analysis, dolomite is the most abundant component in DS. The oxide composition analysis of DS also revealed the presence of a noticeable amount of magnesium oxide (~17%) in the sample. In the presence of water, dolomite reacts with lime (dedolomitization reaction) and produces calcite and brucite ($Mg(OH)_2$) as follows[23]:

$Ca(OH)_2 + MgCa(CO_3)_2 \rightarrow 2CaCO_3 + Mg(OH)_2$

Calcite is an insoluble solid that precipitates out of the solution, while brucite is a weakly soluble compound [24] which remains in the solution and can have a significant effect on electrical conductivity.

The percentage of consumed lime from the pH method showed that SF, LA, FA, and BP used more lime than PC, DS, and GP. As a result, SF showed a very high amount of lime consumption (98.09 %), mainly due to the rapid reaction of SF fine particles with soluble lime in curing condition of 40°C.

Table 3-6. Consumption of lime by electrical conductivity method after 6h

Materials	CH_0	$CH_{t,6h}$	Consumed CH (%)
SF	10.797	1.357	87.44
FA	10.797	7.521	30.35
PC	10.797	8.923	17.36
BP	10.797	9.016	16.50
LA	10.797	8.392	22.28
DS	10.797	8.220	23.87
GP	10.797	10.110	6.36

Table 3-7. Consumption of lime by pH method after 6h

Materials	CH_0	$CH_{t,6h}$	Consumed CH (%)
SF	5.236	0.100	98.09
FA	5.236	1.377	73.70
PC	5.236	3.155	39.74
BP	5.236	2.624	49.88
LA	5.236	1.346	74.30
DS	5.236	4.064	22.38
GP	5.236	3.793	27.56

Table 3-8 illustrates the results of the pozzolanic reactivity tests for the seven materials with varying degrees of portlandite consumption. The Frattini method showed the highest lime consumption by SF, with a percentage of 34.50% and 44.90%, for 15- and 28-day tests, respectively. FA, PC, BP, GP, and DS showed no pozzolanic reactivity at 15 days, while they showed reactivity at 28d. In contrast, LA showed reactivity at both 15 and 28 days.

The TGA method, conducted at 28- and 90 days, showed higher lime consumption for SF, FA, and PC, with SF showing the highest percentage of consumed lime, 54.07% and 75.66%, respectively. The electrical conductivity method, conducted for six hours, showed the highest reactivity for SF, DS, and LA, with SF showing the highest percentage of consumed lime (87.44%). The pH method,

conducted for 6 hours, showed the highest consumption of lime for SF, LA, and FA, with SF showing the highest percentage of 98.09%.

Table 3-8. Percentage of consumed lime by tested pozzolans with different methods.

Materials	Frattini-15 d	Frattini-28 d	TGA-28d	TGA-90d	Conductivity-6h	pH-6h
SF	34.50	44.90	54.07	75.66	87.44	98.09
FA	-11.50	32.40	27.07	35.88	30.35	73.70
PC	-2.80	39.40	25.42	26.73	17.36	39.74
BP	-1.70	22.20	13.71	19.33	16.50	49.88
LA	5.20	33.50	21.56	26.37	22.28	74.30
DS	-20.90	-9.10	-61.54	-53.77	23.87	22.38
GP	-17.00	18.60	4.68	7.28	6.36	27.56

Figure 3-7 indicates relationships and linear correlations between various results using the four test methods. The strongest Pearson correlation was between Frattini-28d and TGA (both 28d and 90d), which indicates a strong relationship between these two tests (R= 0.9751, 0.9510 for Frattini at 28 days and TGA at 28 and 90 days, respectively). Other results showed various levels of Pearson correlation from low to high. However, as Figure 3-7 illustrates, there are clear outliers in various graphs that can substantially distort the Pearson correlation analyses. Therefore, it is important to either perform robust correlation analyses that automatically address the effect of outliers or identify and remove the outliers.

The outliers in the correlation analyses are mostly related to tests involving the dolostone material (which had high magnesium content compared to other samples). To systematically remove the effect of outliers, robust correlation analyses were employed using the “Taba Package” within the R software [25]. A robust correlation analysis is recommended when data may contain outliers. Additional correlation analyses were performed by removing the outlier (DS) and recalculating the Pearson correlation coefficients using the reduced dataset. In both robust and modified Pearson correlation analyses, the correlations increased substantially in

several analyses (Table 3-9). It was shown that the electrical conductivity method is well-correlated with the other direct methods after removing the outlier (e.g., R= 0.9856 for electrical conductivity and TGA 90 d). The pH and electrical conductivity results also show good correlation with each other. Finally, pH results correlate well with the Frattini results. It is clear, however, that dolostone materials with high magnesium oxide content would not be suitable for assessing pozzolanic reactivity using pH and electrical conductivity methods.

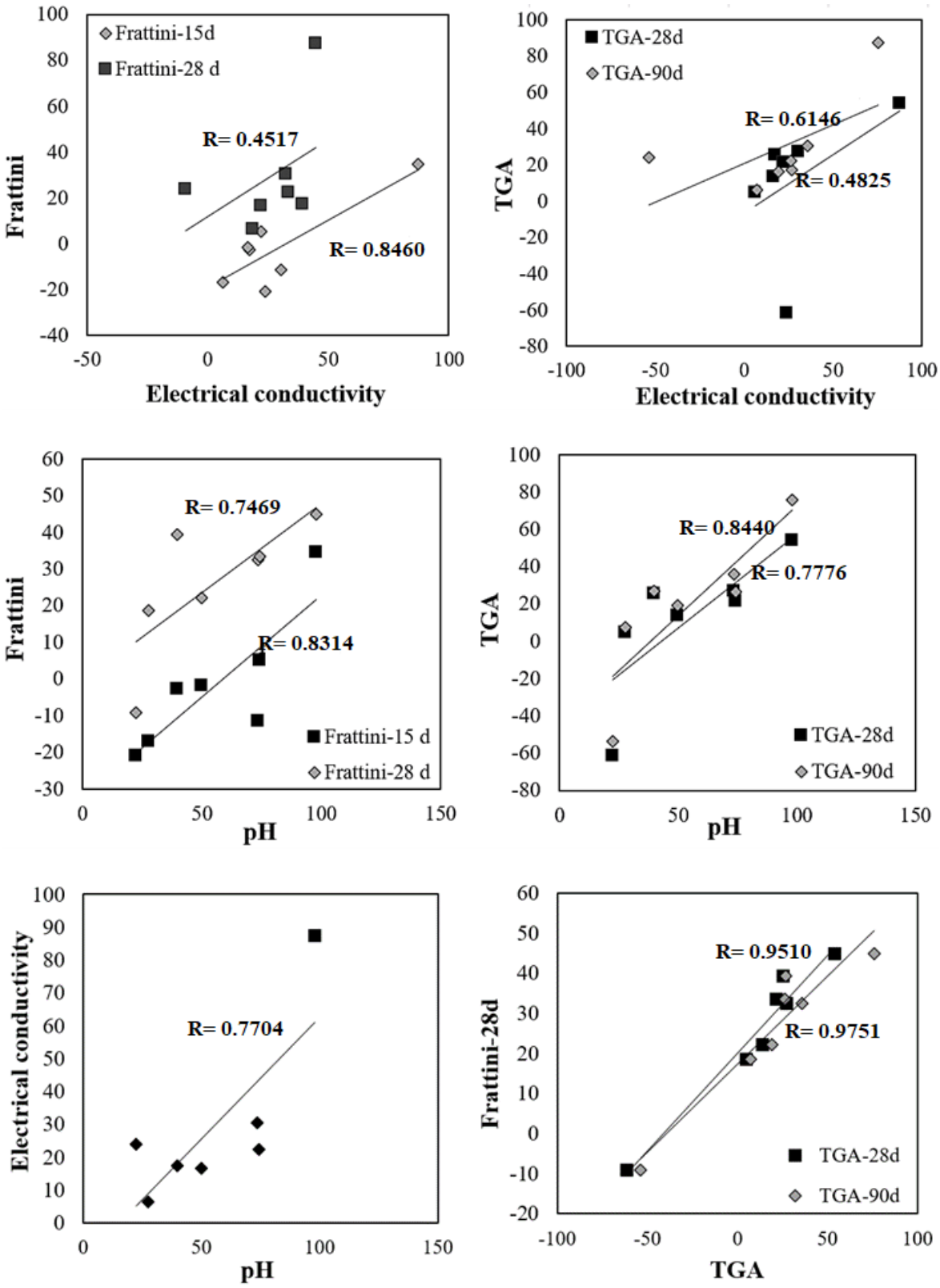


Figure 3-7. Correlations between four test methods.

Table 3-9. The relationship between different direct methods using Pearson and robust correlation.

Test methods relationship	Pearson correlation	Pearson correlation-outlier removed	Robust correlation (Taba R Package)
Conductivity & TGA 28 d	0.4825	0.9520	0.6012
Conductivity & TGA 90 d	0.6146	0.9856	0.7082
Conductivity & Frattini 15 d	0.8460	0.9065	0.4335
Conductivity & Frattini 28 d	0.4517	0.7443	0.5999
Frattini 15d & TGA 28 d	0.7398	0.8764	0.8602
Frattini 15d & TGA 90 d	0.8130	0.8890	0.8554
Frattini 28d & TGA 28 d	0.9751	0.9047	1.0000
Frattini 28d & TGA 90 d	0.9510	0.8299	1.0000
pH & Conductivity	0.7704	0.8510	0.7858
pH & TGA 28 d	0.7776	0.8487	0.8338
pH &TGA 90 d	0.8440	0.8730	0.8802
pH & Frattini 15 d	0.8314	0.7834	0.8679
pH & Frattini 28 d	0.7469	0.6924	0.7648

3-6. Conclusions

Direct methods (such as Frattini and TGA) are commonly employed to determine the pozzolanic reactivity of materials by quantifying the consumption of portlandite in a lime-pozzolan or cement-pozzolan blended sample. This study proposes the electrical conductivity and pH test methods as effective and rapid direct methods for assessing pozzolanic reactivity. Previously, these methods were considered by various researchers to be indirect methods. Analytical methods for determining the amount of consumed lime (due to pozzolanic reactivity) are presented.

This study compared the results of pH and electrical conductivity methods for seven different powdered materials with the commonly used Frattini and TGA tests. Overall, the results from the different test methods provide complementary information on the pozzolanic reactivity of the

materials. The Frattini and TGA methods provide information on the long-term reactivity of the pozzolans (e.g., 28 or 90 days). In contrast, it is possible to detect pozzolanic reactivity of the materials over a much shorter time of reaction using electrical conductivity and pH methods. Robust correlation analyses indicate that estimates of consumed lime using pH and electrical conductivity results are well correlated with the Frattini and TGA results at 15 and 90 days. Materials with high levels of magnesium oxide may produce misleading electrical conductivity and pH results. It is recommended that the electrical conductivity and pH methods be used only when the magnesium oxide content of the material is less than 6% pending further research. Results indicate that electrical conductivity and pH methods are viable and rapid tests to determine pozzolanic reactivity. The primary advantage of these methods is their relative simplicity and rapid results.

3-7. Acknowledgments

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3-8. References for chapter 3

[1] I. Diaz-Loya, M. Juenger, S. Seraj, R. Minkara, Extending supplementary cementitious material resources: Reclaimed and remediated fly ash and natural pozzolans, Cem Concr Compos. 101 (2019) 44–51. https://doi.org/10.1016/j.cemconcomp.2017.06.011.

[2] J.L. Provis, S.A. Bernal, Geopolymers and Related Alkali-Activated Materials, Annual Review of Materials Research . 44 (2014) 299–327. https://doi.org/10.1146/ANNUREV-MATSCI-070813-113515.

[3] S. Mohammed, Processing, effect and reactivity assessment of artificial pozzolans obtained from clays and clay wastes: A review, Constr Build Mater. 140 (2017) 10–19. https://doi.org/10.1016/J.CONBUILDMAT.2017.02.078.

[4] S. Donatello, M. Tyrer, C.R. Cheeseman, Comparison of test methods to assess pozzolanic activity, Cem Concr Compos. 32 (2010) 121–127. https://doi.org/10.1016/j.cemconcomp.2009.10.008.

[5] S. Kramar, V. Ducman, Evaluation of Ash Pozzolanic Activity by Means of the Strength Activity Index Test, Frattini Test and DTA/TG Analysis, Tehnicki Vjesnik - Technical Gazette. 25 (2018). https://doi.org/10.17559/TV-20171203193229.

[6] S.C.L. Lima, L.C.B. Costa, K.C.S. Defáveri, J.M.F. de Carvalho, R.A.F. Peixoto, G.J. Brigolini, Study on assessment of pozzolanic activity: Slate cutting waste, ACI Mater J. 117 (2020) 3–10.

[7] M.M. Tashima, L. Soriano, M. V Borrachero, J.L. Akasaki, J. Paya, New method to assess the pozzolanic reactivity of mineral admixtures by means of pH and electrical conductivity measurements in lime:pozzolan suspensions, Materiales de Construccion. 64 (2014) 30–32. https://doi.org/http://dx.doi.org/10.3989/mc.2014.00914.

[8] M.P. Luxán, F. Madruga, J. Saavedra, Rapid evaluation of pozzolanic activity of natural products by conductivity measurement, Cem Concr Res. 19 (1989) 63–68. https://doi.org/10.1016/0008-8846(89)90066-5.

[9] S. Velázquez, J. Monzó, M. Borrachero, J. Payá, Assessment of Pozzolanic Activity Using Methods Based on the Measurement of Electrical Conductivity of Suspensions of Portland Cement and Pozzolan, Materials. 7 (2014) 7533–7547. https://doi.org/10.3390/ma7117533.

[10] L.R.S. Carneiro, D.C.S. Garcia, M.C.F. Costa, M. Houmard, R.B. Figueiredo, Evaluation of the pozzolanicity of nanostructured sol-gel silica and silica fume by electrical conductivity measurement, Constr Build Mater. 160 (2018) 252–257. https://doi.org/10.1016/j.conbuildmat.2017.11.042.

[11] A.L. Borges, S.M. Soares, T.O.G. Freitas, A. de Oliveira Júnior, E.B. Ferreira, F.G. da S. Ferreira, Evaluation of the Pozzolanic Activity of Glass Powder in Three Maximum Grain Sizes, Materials Research. 24 (2021). https://doi.org/10.1590/1980-5373-mr-2020-0496.

[12] P. de Azevedo Basto, H. Savastano Junior, A.A. de Melo Neto, Characterization and pozzolanic properties of sewage sludge ashes (SSA) by electrical conductivity, Cem Concr Compos. 104 (2019) 103410. https://doi.org/10.1016/j.cemconcomp.2019.103410.

[13] S.C.L. Lima, L.C.B. Costa, K.C.S. Defáveri, J.M.F. de Carvalho, R.A.F. Peixoto, G.J. Brigolini, Study on Assessment of Pozzolanic Activity: Slate Cutting Waste, ACI Mater J. (2020). https://doi.org/10.14359/51724611.

[14] BS EN 196-5, BSI Standards Publication Methods of testing cement Part 5 : Pozzolanicity test for pozzolanic cement, (2011).

[15] Standard test methods for sampling and testing fly ash or natural pozzolans for use in Portland-cement concrete, ASTM C311-18, (2018).

[16] B. Uzal, L. Turanli, H. Yücel, M.C. Göncüoğlu, A. Çulfaz, Pozzolanic activity of clinoptilolite: A comparative study with silica fume, fly ash and a non-zeolitic natural pozzolan, Cem Concr Res. 40 (2010) 398–404. https://doi.org/10.1016/j.cemconres.2009.10.016.

[17] S.H. Shim, T.H. Lee, S.J. Yang, N.B.M. Noor, J.H.J. Kim, Calculation of cement composition using a new model compared to the bogue model, Materials. 14 (2021) 1–20. https://doi.org/10.3390/ma14164663.

[18] C.G. Zoski, Handbook of Electrochemistry, Handbook of Electrochemistry. (2006). https://doi.org/10.1016/B978-0-444-51958-0.X5000-9.

[19] D.R. Lide, CRC Handbook of Chemistry and Physics , 84th ed., National Institute of Standards and Technology, 2004. https://doi.org/10.1021/ja0336372.

[20] B. Liguori, P. Aprea, B. de Gennaro, F. Iucolano, A. Colella, D. Caputo, Pozzolanic Activity of Zeolites: The Role of Si/Al Ratio, Materials. 12 (2019) 4231. https://doi.org/10.3390/MA12244231.

[21] M. Hayashi, Temperature-Electrical Conductivity Relation of Water for Environmental Monitoring and Geophysical Data Inversion, Environ Monit Assess. 96 (2004) 119–128. https://doi.org/10.1023/B:EMAS.0000031719.83065.68.

[22] H. Justnes, C. Escudero-Oñate, Ø.A. Garmo, M. Mengede, Transformation Kinetics of Burnt Lime in Freshwater and Sea Water, Materials. 13 (2020) 1–24. https://doi.org/10.3390/MA13214926.

[23] S. Galí, C. Ayora, P. Alfonso, E. Tauler, M. Labrador, Kinetics of dolomite–portlandite reaction: Application to portland cement concrete, Cem Concr Res. 31 (2001) 933–939. https://doi.org/10.1016/S0008-8846(01)00499-9.

[24] J. Lanas, J.L. Pérez Bernal, M.A. Bello, J.I. Alvarez, Mechanical properties of masonry repair dolomitic lime-based mortars, Cem Concr Res. 36 (2006) 951–960. https://doi.org/10.1016/j.cemconres.2005.10.004.

[25] M. Tabatabai, S. Bailey, Z. Bursac, H. Tabatabai, D. Wilus, K.P. Singh, An introduction to new robust linear and monotonic correlation coefficients, BMC Bioinformatics. 22 (2021). https://doi.org/10.1186/S12859-021-04098-4.

Chapter 4: Comparative assessment of pozzolanic reactivity tests - an experimental study

4-1. Abstract

The use of pozzolanic materials as a sustainable partial replacement option for portland cement in concrete has been extensively studied over the last few decades. This study aimed to assess the pozzolanic reactivity of seven different powdered materials: pottery cull, brick powder, lightweight aggregate fines, class C fly ash, silica fume, glass powder, and dolostone. Pozzolanic reactivity was evaluated using seven different methods, including the Frattini test, strength activity index (SAI), ultrasound pulse velocity index (UPVI), thermogravimetric and differential thermal analyses (TG/DTA), calorimetry, electrical conductivity, and pH. The results obtained in this study provide important insights into the potential beneficial use of these pozzolanic materials. A comparative analysis was performed to find the relative effectiveness of various pozzolanic reactivity test methods for evaluating different materials through the application of robust correlation analyses and a ranking method. Results showed that Frattini and TGA, SAI and electrical conductivity, SAI and calorimetry, and UPVI and calorimetry were well correlated, suggesting that these methods may be suitable alternatives to each other. Electrical conductivity and calorimetry are recommended as rapid and efficient methods (in comparison to other longer-term reactivity test methods) for the assessment of different pozzolans.

4-2. Keywords

Pozzolanic reactivity, sustainable, Frattini, TGA/DTA, SAI, robust correlation

4-3. Introduction

The use of supplementary cementitious materials (SCMs) such as pozzolans to partially replace cement in concrete has gained popularity due to the growing concern over the impact of portland cement production on the environment, particularly its CO_2 emissions[1]. Pozzolans are siliceous and aluminous materials that react with excess calcium hydroxide in the presence of water to form cementitious hydration products such as calcium silicate hydrates and calcium silicate aluminate hydrates [2,3]. Several pozzolanic reactivity test methods are widely discussed in the literature. These tests are usually classified as direct or indirect methods [4]. It is understood that using only one method may produce misleading results [5,6].

The Frattini test is a common direct method that uses chemical titration to determine the amount of dissolved calcium and hydroxyl ions as well as the reduction in lime caused by pozzolanic reactions [7,8]. TG/DTA is another direct method that quantifies the consumption of portlandite or lime, $Ca(OH)_2$, which is commonly used for the characterization of pozzolanic reactivity [4,9–11]. In this method, the pozzolanic reaction can be assessed by comparing the weight loss of the sample to that of a control sample at particular temperature ranges [4].

SAI is the most widely used indirect method that evaluates pozzolanic reactivity by determining the ratio of the compressive strength of a pozzolan blended cement sample to that of a control sample (cement only). This method examines how pozzolanic reactions contribute to enhancing compressive strength through the densification of the cementitious matrix [12–14]. Calorimetry is an indirect method that has been used to assess pozzolanic reactivity by measuring the heat of hydration in samples with and without pozzolanic materials [15–18]. Measuring the heat of hydration over time helps determine the impact of various additives and admixtures (e.g.,

pozzolans) on the mixture's hydration kinetics [19]. Isothermal calorimetry is primarily used for the measurement of short-term heat evolution, but recent studies suggest monitoring longer-term heat evolution for SCMs [20–22]. Other pozzolanic reactivity assessment methods include electrical conductivity and pH, which are considered easy and rapid methods when compared with most other reactivity tests that are slow and time-demanding [23]. Through the reaction of silica and alumina from the pozzolan with dissolved Ca^{2+} and OH^- in a lime-pozzolan suspension, nonconductive products (e.g., C-S-H) are formed, which decrease the solution's conductivity over time [23–25]. The same pozzolanic reaction also decreases pH due to a decrease in OH^- ions [25]. Thus, pozzolanic reactivity in these tests is associated with changes in electrical conductivity and pH caused by the removal of calcium hydroxide. According to Luxán et al. [26], pozzolans can be classified based on change in electrical conductivity of lime-pozzolan solutions at a short period of time (e.g., 2 minutes). In accordance with their proposed classification system, a change in conductivity greater than 1.20 mS/cm indicates good pozzolanic reactivity, a change of less than 0.4 mS/cm indicates no pozzolanic reactivity, and a change between 0.4 and 1.20 mS/cm indicates variable pozzolanic reactivity.

Ultrasonic pulse velocity (UPV) is usually used to evaluate the uniformity and relative quality of concrete, detect cracks and voids, assess the effectiveness of crack repairs, and as an indirect indicator of the strength of concrete [27,28]. However, this test may also be used to investigate the interaction between pozzolanic materials and portlandite in cement composites [29]. Due to the pozzolanic reaction and formation of C-S-H gel, the pores are filled and refined, resulting in increased UPV [30–32]. The type of pozzolan, replacement level, curing temperature, and curing period significantly affect UPV results [33]. Pozzolanic reactivity can therefore be assessed

indirectly using the UPV test in a manner similar to the SAI. Considering that UPV alone does not provide a direct comparison between the results of samples prepared with and without pozzolans, it is beneficial to calculate a UPV index (UPVI), defined as the ratio of UPV of a sample with pozzolan to the UPV of the control sample without pozzolan. In this regard, UPVI was determined based on tests on 3-in cube specimens to evaluate pozzolanic reactivity.

In this experimental study, the pozzolanic reactivity of seven materials was assessed using the reactivity test methods discussed above (Frattini, SAI, UPVI, TGA, calorimetry, electrical conductivity, and pH). The results of these methods were analyzed using Pearson and robust correlation analyses to determine if there was a relationship between the outcomes of the different methods. The Pearson correlation coefficient is the most widely used measure of the relationship between two continuous variables. However, it is necessary to use robust correlation analyses when outliers are present since the Pearson correlation may not be reliable in the presence of outliers [34]. Based on the robust analysis, the test methods that were well correlated were determined. Additionally, a ranking approach was used to determine the most effective pozzolanic reactivity tests as well as the most reactive pozzolans. The results of this study provide valuable insights into the selection and testing of pozzolans, which can lead to improved quality and durability of concrete while reducing the environmental impact of cement production as the main binder of concrete.

4-4. Materials and methods

4-4-1. Materials

In this study, two types of calcined clay waste materials (pottery cull and fired clay brick) were utilized. Pottery cull (PC) is a by-product that is generated during the manufacturing of ceramic

sanitary wares (from products discarded due to manufacturing defects). The fired clay brick (BP) waste is commonly generated at construction demolition projects. The lightweight aggregate fines (LA) used in this study were by-products from the manufacturing of lightweight aggregates. This study also evaluated other materials, including silica fume (SF), waste glass powder (GP), class C fly ash (FA), and dolostone (DS) from a quarry in Wisconsin. The binder used in the study was Type I portland cement (CEM). All materials except SF and FA were air-dried at room temperature and ground using a ball mill. The resulting fine powder was sieved through a #200 (75µm) sieve.

A laser diffraction particle size analyzer (Malvern Mastersizer 3000) was used to determine the particle size distribution and specific surface area (SSA). Chemical analyses were performed by X-ray fluorescence (XRF) using a Bruker S4 Pioneer to determine the various oxides in each powder sample. The content of amorphous silica was determined using X- ray diffraction (XRD) using the DIFRRAC.EVA software and Origin software.

4-4-2. Pozzolanic reactivity test methods

4-4-2-1. SAI

The SAI test provides a comparative index (ratio) of compressive strengths of mortar specimens with and without a pozzolanic material. The comparative aspect allows an assessment of the influence of the pozzolan on compressive strength, an indirect measure of the pozzolanic reactivity. The specimens consisted of 2-in cubes made with either 100% cement binder (control) or with 20% cement replacement by the pozzolan. The strength ratio was determined in accordance with ASTM C311 [35] after 28 and 90 days of curing. The mixtures had graded standard sand and a water-to-cement ratio (w/c) of 0.484. Flow tests were performed on mortar

mixtures in accordance with ASTM C311 requirements. All cube mortars were cast, de-molded after 24 h, and placed in a sealed lime-water bath at 23˚C for 28 or 90 days of curing. At the time of compression testing, the samples were removed from the bath and surface dried before testing for compressive strength at 28 and 90 days (figure 4-1).

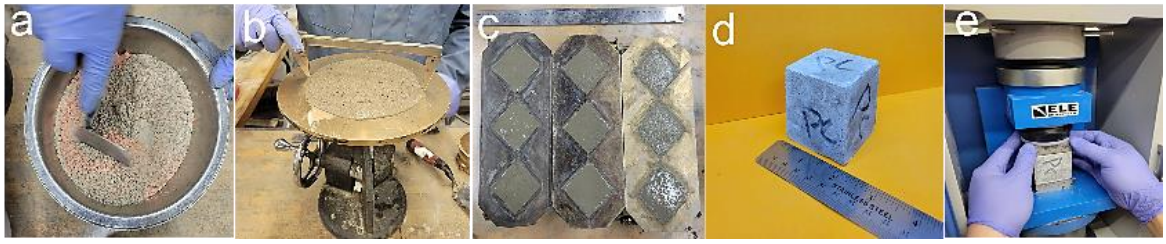

Figure 4-1. Preparation and testing of SAI specimens (a) blended cement mix (b) flow test (c) cube mold casting (d) a cube mortar after demolding (e) compressive strength test.

4-4-2-2. Frattini

The Frattini test was conducted following the EN 196-5 standard procedures [36]. Twenty grams of samples containing 80% OPC and 20% pozzolan were prepared and mixed with 100 ml of distilled water. The samples were then maintained at 40˚C for 15, 28, and 90 days. Subsequently, the samples were filtered using a vacuum filter and cooled at room temperature in sealed Buchner funnels. The resulting solutions were analyzed for hydroxyl ions [OH^-] and calcium ions [Ca^{2+}] by titration against 0.1 mol/L HCL and 0.03 mol/L EDTA, respectively. Before titration with EDTA, the pH of the solutions was adjusted to 12±0.5. Duplicate samples were prepared for each pozzolan, and three measurements were taken for each sample's reactivity assessment. After completion of the test, the consumed lime by each pozzolan was calculated.

4-4-2-3. TG/DTA

After each test period (28 d and 90 d), crushed mortar samples that were prepared for the SAI test were quickly employed for thermalgravimetric analysis. Mortars were finely ground by pestle and mortar and sieved through a #200 sieve. Small quantities of powder (20-23 mg) were

introduced into a TGA instrument (TA SDT 650). Thermal analysis was conducted under an argon atmosphere, with a constant heating rate of 10°C/min, in the temperature range of 23-1000°C. The TG/DTA test measures the weight loss of a sample as it is heated to 1000°C. Consumed lime was determined based on the weight loss at specific temperature ranges associated with portlandite and calcite.

4-4-2-4. Electrical conductivity and pH

Electrical conductivity and pH methods were conducted following the procedures described by Uzal et al. [37]. An aqueous suspension was prepared by dissolving 200 mg of lime powder in 250 ml of deionized water. An electrical conductivity meter (Accumet AB30) and a pH meter (AB15) were used for conductivity and pH measurements. At the beginning of the test, a beaker containing 250 ml of deionized water was placed in an electrical water bath equipped with a thermostatic magnetic stirrer to maintain the suspension's temperature at 40±1°C. Then, lime was added to the water, and the solution was allowed to attain a constant initial pH and electrical conductivity (pH_0 and EC_0) for approximately 15 minutes. Subsequently, 5 g of pozzolan was added to the solution, and electrical conductivity and pH were monitored for 6 hours. The loss in conductivity (LC) and the reduction in pH were measured after 6 h of pozzolanic reaction.

4-4-2-5. Calorimetry

Fresh pastes were prepared by mixing blended samples of 80% cement and 20% pozzolan with a w/c of 0.5. Approximately 25 g of each fresh paste was transferred into a high density polyethylene (HDPE) ampoule and placed inside the calorimeter, which was preconditioned at 23°C. The heat evolution was monitored using a TAM Air 8-channel Isothermal calorimeter for

short-term (48 h) and long-term (168 h) reactions. The heat evolution of the samples was recorded for 48 and 168 hours.

4-4-2-6. UPVI

Cube mortar specimens (3 in) were made according to ASTM C597 [8] with the same pozzolan-cement and cement (control) mixtures used for the SAI specimens. A portable commercial ultrasonic device (HC-6390 UPV) was used to measure ultrasonic pulse velocity with an accuracy of 0.1 μs. UPV was measured by placing the transmitting and receiving transducers at opposite faces of each mortar specimen. The UPV measurements were taken on the cube samples containing 20% pozzolans blended with 80% cement at 28 days and 90 days of curing. UPVI was calculated by dividing the UPV values for the pozzolan-cement cubes by the results from the control (cement only) cubes..

4-4-2-7. Comparative statistical assessment

Statistical analyses were performed on experimental results from all seven reactivity test methods to find correlations between results from different test methods. Data were analyzed using both Pearson and robust correlations. The robust correlations were determined using the RStudio software packages (Taba and WRS2 library) [34,38]. Robust correlation refers to determining a relationship's direction and strength by considering the influence of outliers. A strong correlation between the two sets of test results suggests that the results of these two methods are highly related, and the results can be predicted from one another.

4-5. Results and discussion

4-5-1. Characterization of materials

Table 4-1 shows the results of particle size analyses. D10, D50, and D90 are the 10, 50, and 90 percentile particle sizes in μm. Results indicate that SF had the smallest particles and GP had the largest particles.

Table 4-1. Particle size analysis by laser diffraction method

Materials	SSA(m^2/kg)	D10(μm)	D50(μm)	D90(μm)
OPC	249.5	3.97	14.8	34.0
SF	8569	0.16	0.34	3.55
FA	590.9	1.61	7.72	41.6
PC	435.0	2.19	15.0	52.8
BP	492.5	2.02	13.1	44.6
LA	739.9	2.17	11.4	41.1
DS	226.1	5.56	30.7	63.5
GP	112.7	9.03	39.2	68.3

Table 4-2 shows major and minor oxide compositions for all pozzolans as determined by X-ray fluorescence spectrometry (XRF). Content of amorphous silica was determined by XRD. It should be noted that DS had the highest content of magnesium oxide (~17%) and the lowest content of silica among the materials tested.

Table 4-2. Chemical composition (% by mass) of the raw materials

Chemical composition	Materials							
	BP	PC	LA	OPC	FA	GP	SF	DS
SiO_2	68.88	67.09	51.81	22.86	37.47	70.03	92.17	15.52
Al_2O_3	21.44	18.62	17.72	5.09	19.18	2.23	0.82	3.64
Fe_2O_3	5.28	1.27	7.24	2.61	5.95	0.35	0.72	1.47
CaO	0.22	3.04	6.39	68.04	25.22	8.95	0.53	24.92
MgO	0.87	1.18	2.03	3.47	5.33	1.79	1.67	16.62
Na_2O	0.25	2.1	0.32	0.09	1.72	13.4	0.16	0.04
K_2O	1.44	1.72	2.06	0.98	0.63	0.58	0.77	2.28
TiO_2	1.17	0.69	0.71	0.45	1.41	0.05	0.01	0.14
P_2O_5	0.12	0.07	0.35	0.07	1.33	0.05	0.09	0.04
LOI	0.18	3.04	6.72	0.314	0.53	2.5	2.71	48.01
Amorphous SiO_2	5.20	37.46	4.64	1.31	8.14	1.98	0.81	1.03

4-5-2. SAI

The contribution of various pozzolans to compressive strength compared to the strength of control mixture was evaluated using SAI at 28 and 90 days of curing. SAI was calculated as the relative compressive strength of the mortar containing pozzolan compared to the control mortar [35] (Eq. 4-1).

$$SAI = \frac{S_p}{S_c} \quad (4\text{-}1)$$

Where S_p is the average compressive strength of cement-pozzolan specimens, and S_c is the average compressive strength of the control cubes.

Figure 4-2 shows the SAI results from all tests. At 28 days, SF had the highest SAI of 1.29, while FA had the second highest SAI of 1.07. Other pozzolans (PC, BP, DS, and LA) with larger particle sizes had lower strength contributions compared to the control mixture. At 90 days, the SAI values of all samples were slightly higher than at 28 days, indicating the effect of age on the pozzolanic reaction.

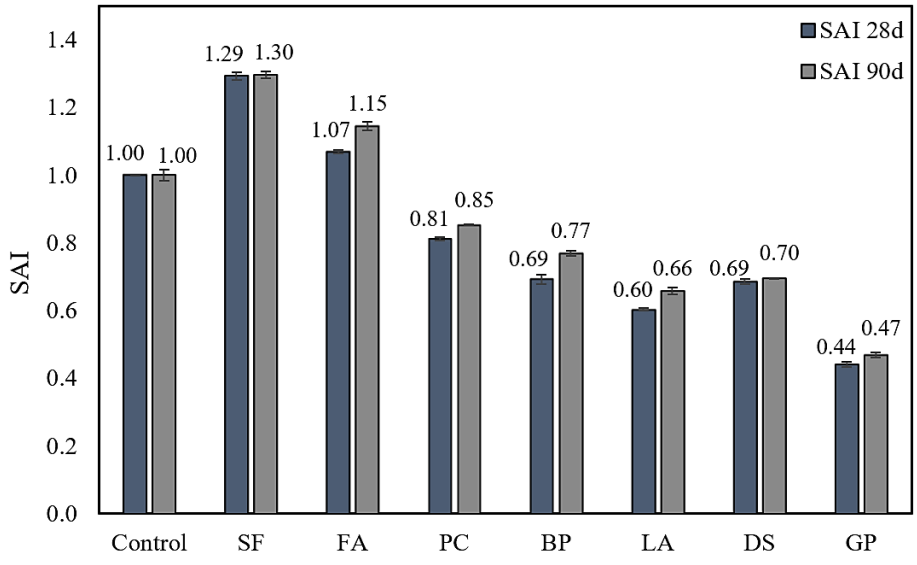

Figure 4-2: SAI results of control and blended cement-pozzolan samples.

4-5-3. Frattini

Figure 4-3 illustrates the Frattini diagram plotted according to EN 196-5 [36]. Results from tested materials that fall under the lime solubility curve show pozzolanic reactivity. The lime solubility curve and the maximum theoretical consumed lime (for estimation of the reactivity of pozzolans) were calculated according to equation 4-2 provided in EN 196-5 [36]. The percentage of consumed lime was calculated according to equation 4-3 [8].

$$Max\ [CaO] = \left[\frac{350}{[OH^-]-15}\right] \quad (4\text{-}2)$$

$$\text{Consumed } [CaO](\%) = \frac{\text{Max } [CaO] - [CaO]}{\text{Max } [CaO]} \times 100 \quad (4\text{-}3)$$

Where $Max\ [CaO]$ is the maximum theoretical consumed lime, $[CaO]$ and $[OH^-]$ are the lime and hydroxide ions consumed by each pozzolan. The results of Frattini tests are presented in Tables 4-3 through 4-5, showing that the consumed lime varied significantly among the different pozzolans and over time. The arrows show the progression of results at the ages of 15, 28, and 90 days. SF had the highest consumed lime at both 15 and 28 days, indicating that it had the highest pozzolanic reactivity in a shorter time compared to other pozzolans. However, at 90 days, SF did not noticeably consume any additional lime, indicating that SF used most of the free lime at earlier ages of hydration. At 15 days, LA exhibited low reactivity, whereas FA, PC, BP, GP, and DS were inactive. At 28 days, PC, BP, GP, and FA shifted below the saturation curve, indicating that these pozzolans show reactivity at later times. In general, SF and FA, due partly to their finer particle size, had a relatively high lime consumption at both 15 and 28 days, while LA, PC, and BP had higher lime consumption at 90 days. In comparison to all tested pozzolans, DS and GP had lower lime consumption at all ages.

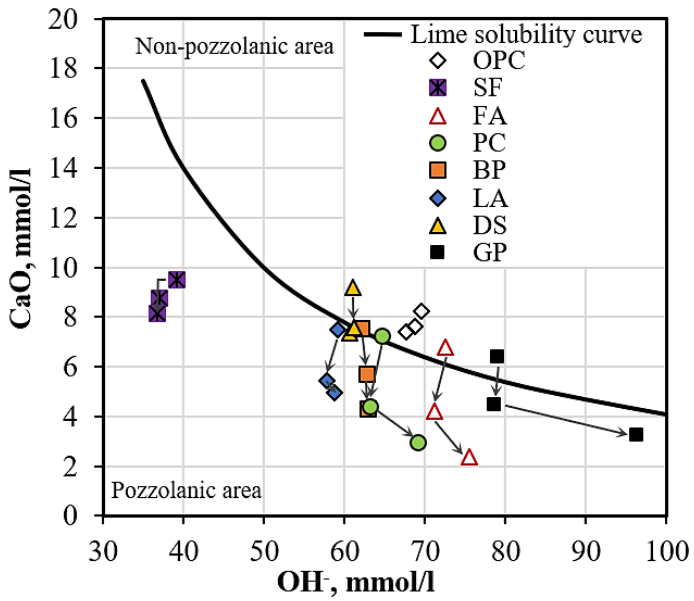

Figure 4-3. Results of Frattini at 15, 28, and 90 days, arrows show the shift from 15 to 90 days.

Table 4-3. Frattini results at 15 days.

Pozzolan-cement samples	OH-15d mmol l^{-1}	CaO-15d mmol l^{-1}	Max theoretical CaO-15d mmol l^{-1}	Consumed CaO (%)-15d
Control	69.6	8.19	6.41	-27.90
SF	39.3	9.46	14.43	34.50
FA	72.6	6.78	6.08	-11.50
PC	64.7	7.23	7.04	-2.80
BP	62.2	7.54	7.42	-1.70
LA	59.2	7.50	7.91	5.20
DS	61.1	9.19	7.60	-20.90
GP	79.1	6.39	5.46	-17.00

Table 4-4. Frattini results at 28 days.

Pozzolan-cement samples	OH-28d mmol l^{-1}	CaO-28d mmol l^{-1}	Max theoretical CaO-28d mmol l^{-1}	Consumed CaO (%)- 28d
Control	68.8	7.62	6.51	-17.10
SF	37.0	8.77	15.91	44.90
FA	71.2	4.21	6.23	32.40
PC	63.2	4.40	7.27	39.40
BP	62.7	5.70	7.33	22.20
LA	57.8	5.44	8.17	33.50
DS	61.2	8.27	7.58	-9.10
GP	78.6	4.48	5.50	18.60

Table 4-5. *Frattini results at 90 days.*

Pozzolan-cement samples	OH-90d mmol l^{-1}	CaO-90d mmol l^{-1}	Max theoretical CaO-90d mmol l^{-1}	Consumed CaO (%)- 90d
Control	60.60	7.35	7.67	4.20
SF	36.70	8.15	16.11	49.40
FA	75.60	2.37	5.78	58.90
PC	69.20	2.95	6.46	54.30
BP	62.00	4.29	7.44	42.40
LA	58.00	4.94	8.15	39.40
DS	60.60	7.35	7.67	4.20
GP	98.90	3.25	4.17	22.00

4-5-4. TG/DTA

In this test, the consumed lime is quantified by measuring the weight loss due to portlandite and calcite decomposition. Portlandite decomposed at temperatures between 400- 500˚C and calcite decomposed at 600- 800˚C (figure 4-4).

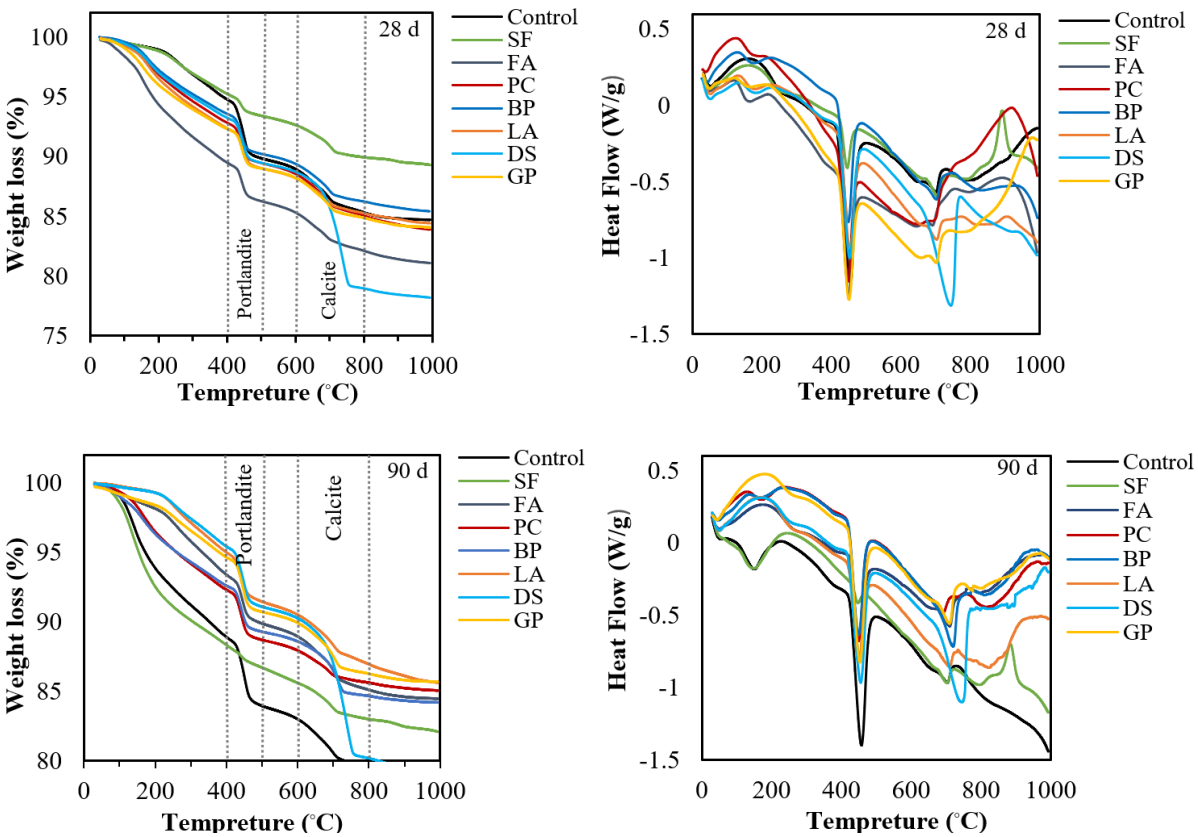

Figure 4-4. TG/DTA graphs for 28- and 90 days of curing.

Equation 4-4 was used to calculate the amount of remaining lime in each sample [9]. The percentage of consumed lime was calculated for the pozzolan-cement sample with 20% cement replacement versus the control sample following equation 4-5.

$$CH_r = 4.11(CH) + 1.68(CC_3) \quad (4\text{-}4)$$

$$CH_c(\%) = \left[\frac{(CH_{r,c} \times 0.8) - CH_{r,p}}{(CH_{r,c} \times 0.8)}\right] \times 100 \quad (4\text{-}5)$$

Where CH_r is the amount of remaining lime in the sample, CH is measured weight loss due to the decomposition of portlandite, and CC_3 is weight loss due to the decomposition of calcite. The molar mass ratios of the $Ca(OH)_2/H_2O$ and $Ca(OH)_2/CO_2$ are 4.11 and 1.68, respectively. $CH_c(\%)$ is the percentage of consumed lime for each sample. $CH_{r,c,}$ and $CH_{r,p}$ are the remaining lime for the control and pozzolan-cement samples, respectively. The portion of cement in the pozzolan-cement sample is 0.8, as 20% of cement was replaced with pozzolan.

Table 4-6 presents the percentage of consumed lime and weight loss due to the decomposition of portlandite and calcite in each sample after 28 and 90 days of curing. Results indicate an increase in pozzolanic reactivity with curing time, as the pozzolans consumed more portlandite at 90 days compared to 28 days. At 90 days, SF consumed the most lime (75.7%), followed by FA, PC, LA, BP, and GP (in that order). GP consumed the least lime (7.3%). The consumed lime for the DS sample is negative, which is related to a significant weight loss due to calcite's decarbonation.

Table 4-6. Mass loss and consumed lime for seven pozzolan-cement samples as determined by TGA

Pozzolan-cement samples	28 d			90 d		
	Portlandite (%)	Calcite (%)	Consumed lime (%)	Portlandite (%)	Calcite (%)	Consumed lime (%)
SF	1.26	0.54	54.07	0.61	0.44	75.66
FA	2.47	0.39	27.07	2.33	0.45	35.88
PC	2.54	0.39	25.42	2.77	0.42	26.73
BP	2.40	0.99	13.71	2.38	1.12	19.33
LA	2.67	0.41	21.56	2.73	0.47	26.37
DS	3.05	3.29	-61.54	3.57	3.13	-53.77
GP	2.65	1.09	4.68	3.32	0.71	7.28

4-5-5. Electrical conductivity and pH

Figure 4-5 shows the measured electrical conductivity of pozzolans tested with lime during 6 hours of reaction time. Loss of conductivity after 6 h of reaction was calculated using equations 4-6 and 4-7 [23].

$$\mathrm{LC}\ (\%) = \frac{C_0 - C_{6,c}}{C_0} \times\ 100 \tag{4-6}$$

$$C_{6,c}\ = C_6 - C_{6,pozz} \tag{4-7}$$

Where LC (%) represents the decrease (in percent) of electrical conductivity over time, C_0 is the electrical conductivity of the lime suspension before adding the pozzolanic material (t=0), C_6 is the measured electrical conductivity of the lime-pozzolan suspension at 6h, $C_{6,pozz}$, is the measured electrical conductivity of the pozzolan-deionized water suspension at 6h, and $C_{6,c}$ is the corrected electrical conductivity at 6h. This correction is needed to account for the effect of pozzolan alone in altering the conductivity.

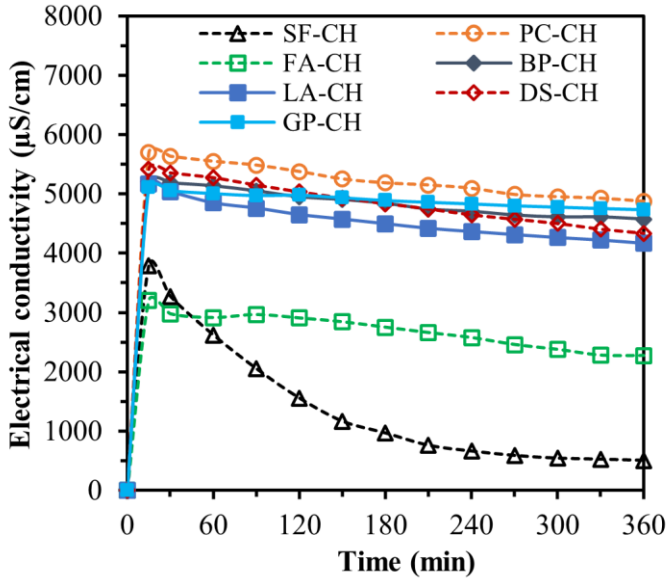

Figure 4-5: Variations of electrical conductivity of pozzolan suspensions.

The tested pozzolans exhibited varying loss of conductivity (figure 4-6). SF with its finer particle size distribution and higher content of amorphous silica showed the highest loss, followed by FA, DS, LA, PC, BP, and GP (in descending order). Notably, the loss of conductivity for PC, BP, and LA with generally similar oxide composition and particle size distribution was found to be similar. It is worth mentioning that the DS sample showed higher reactivity than LA, PC, and BP, while it showed lower reactivity in other test methods. The reason is the high amount of magnesium oxide (~17%) in the DS sample. A weakly soluble compound called brucite ($Mg(OH)_2$) forms during the reaction of dolostone with water and lime, which can significantly affect electrical conductivity [39].

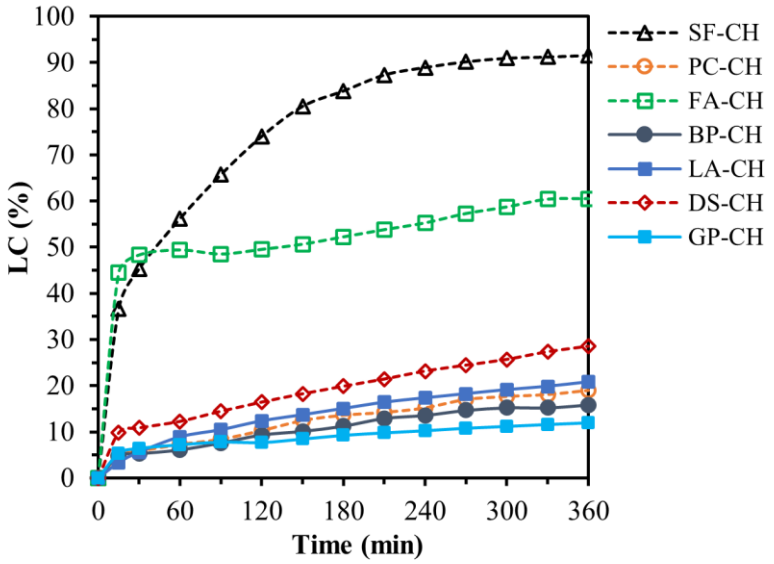

Figure 4-6. Loss of conductivity of lime-pozzolan suspensions.

Table 4-7 represents the classification of different tested pozzolans using the electrical conductivity method based on the ranges proposed by Luxan et al. [26]. It is clear that SF, FA, and DS showed good pozzolanic reactivity, while PC, BP, LA, and GP showed varying reactivity.

Table 4-7. Evaluation of pozzolanic activity based on change in electrical conductivity.

Materials	ΔC (mS/cm)	Variation in electrical conductivity (ΔC)	Classification of Pozzolans
SF	5.47	ΔC > 1.20	Good
FA	3.48	ΔC > 1.20	Good
PC	1.09	$0.4 \leq \Delta C < 1.20$	Varying
BP	0.91	$0.4 \leq \Delta C < 1.20$	Varying
LA	1.20	$0.4 \leq \Delta C < 1.20$	Varying
DS	1.64	ΔC > 1.20	Good
GP	0.69	$0.4 \leq \Delta C < 1.20$	Variable

Figure 4-7 shows the pH of the CH-pozzolan suspension after 6h of reaction, indicating that the degree of pH reduction varies among the tested materials. The pH of the SF-CH suspension decreased significantly from 12.30 to 10.30, mainly due to the rapid reaction of fine particles of SF with soluble CH at 40˚C, which resulted in more consumption of hydroxide ions.

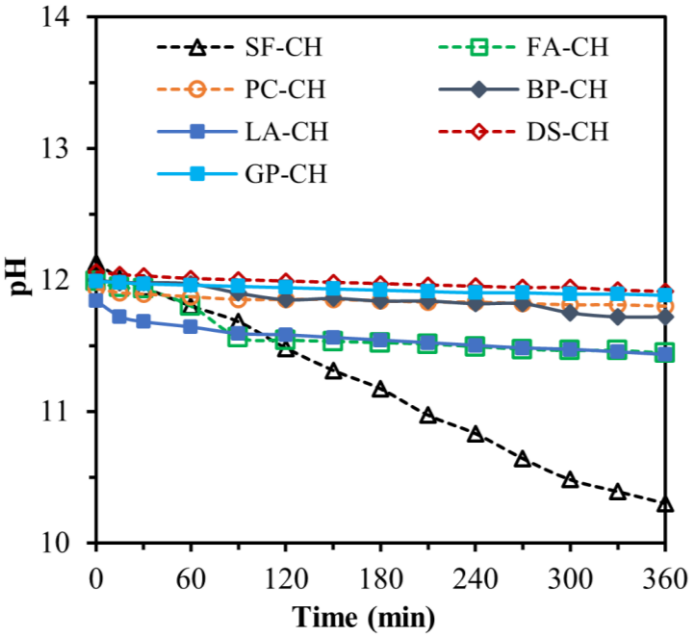

Figure 4-7. pH of CH-pozzolan suspensions.

The consumption of hydroxide ions was calculated using pH values following equations 4-8 through 4-11.

$$pH + pOH = 14 \quad (4\text{-}8)$$

$$pOH = -\log[OH^-] \quad (4\text{-}9)$$

$$[OH^-]_0 = 10^{-pOH} \quad (4\text{-}10)$$

$$[OH^-]_t = 10^{-pOH} \quad (4\text{-}11)$$

Where pH reflects the hydrogen ion concentration $[H^+]$ and pOH reflects hydroxide ion concentration $[OH^-]$ in a solution. $[OH^-]_t$ and $[OH^-]_0$ are the concentration of hydroxide ions at time 0 (only CH solution) and at time *t* (6h) following the start of the chemical reaction.

Figure 4-8 shows the relative hydroxyl ion consumption ($[OH_t^-]/[OH_0^-]$) or OH index for each pozzolan-lime suspension after 6h of reaction. SF had the greatest decrease in hydroxide ions, followed by FA and LA. In contrast, BP, PC, DS, and GP reduced fewer hydroxide ions. Table 4-8

demonstrates $[OH^-]$ index for the seven tested materials after 6 h of reaction. It can be mentioned that materials with OH index less than 0.8 showed pozzolanic reactivity.

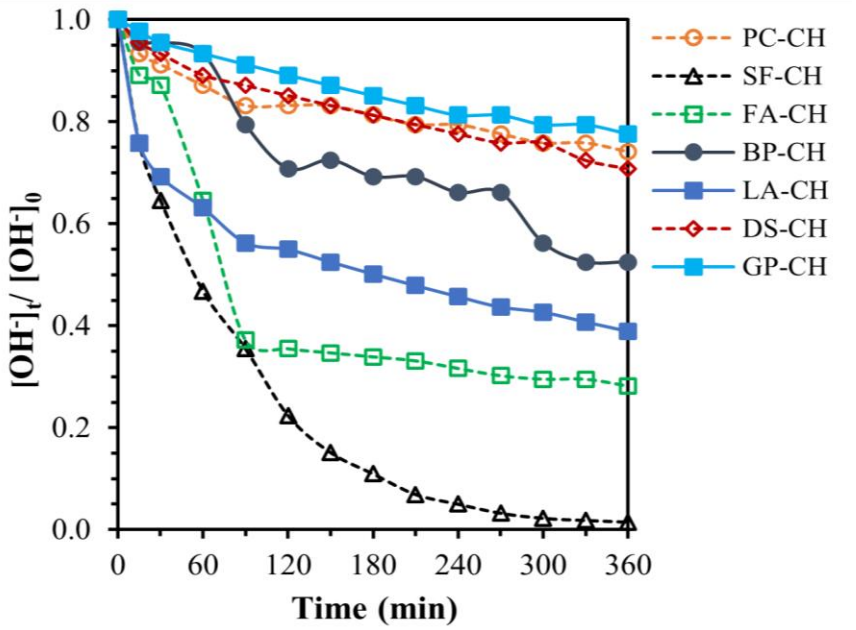

Figure 4-8. Relative hydroxyl ion consumption of CH-pozzolan suspensions

Table 4-8. $[OH^-]$ index for the CH-pozzolan suspensions at 6 h of reaction

Materials	$[OH_6^-]/[OH_0^-]$
SF	0.01
FA	0.28
PC	0.74
BP	0.52
LA	0.39
DS	0.70
GP	0.77

4-5-6. Calorimetry

The heat of hydration (HOH) of various pozzolans blended with cement was measured using calorimetry tests for 48 and 168 hours (figure 4-9). The results show that adding pozzolans to cement can significantly affect the HOH values. On the other hand, the control sample containing

only cement had the highest HOH values, indicating that the pozzolans significantly impact heat generation during early cement hydration.

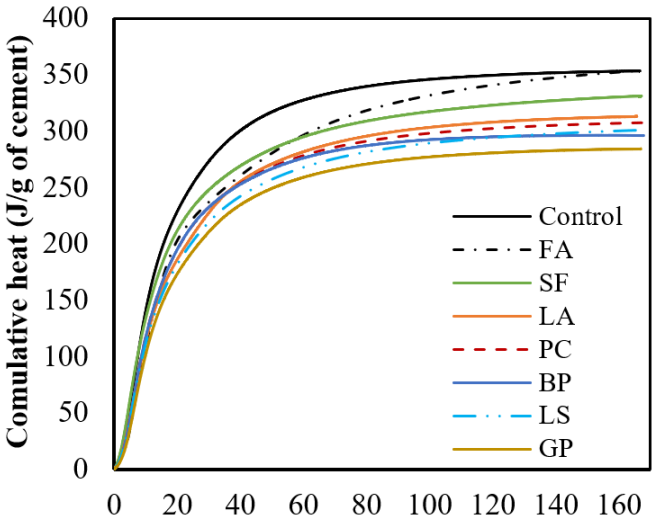

Figure 4-9. Calorimetry results for blended pozzolan-cement samples.

The control sample, which contained only cement, had the highest HOH at 313.10 and 353.53 J/g of cement at 48 and 168 hours, respectively. Among the pozzolans, the blended sample with SF had the highest HOH at 48 hours, while the blended sample with GP had the lowest HOH value hours at both 48 h and 168 h (table 4-9).

Table 4-9. Calorimetry results for the blended pozzolan-cement samples

Samples	HOH-48 hr	HOH-168 hr
Control	313.10	353.53
SF	280.64	330.84
FA	275.85	353.53
LA	267.28	312.70
PC	264.71	307.29
BP	263.38	296.06
DS	253.88	300.72
GP	245.89	283.98

4-5-7. UPVI

The UPV results for various pozzolan mixes were used to calculate the equation 4-12.

$$UPVI = \frac{U_p}{U_c} \tag{4-12}$$

Where U_p is the average UPV of pozzolan-cement samples and U_c is the average UPV of the control samples.

The results indicate that adding pozzolans to cement can significantly affect the UPVI values. Compared to other pozzolans, the blended cement sample with FA had the highest UPVI at 28 and 90 days, while GP had the lowest UPVI at both time intervals (Figure 4-10). The hydraulic properties of FA, in addition to its pozzolanic properties, contribute to its increased UPVI. In addition, pozzolans, such as SF and FA, have a finer particle size, leading to better particle packing and lower porosity, resulting in higher UPVI values. UPVI was improved at the later age (90 days of curing).

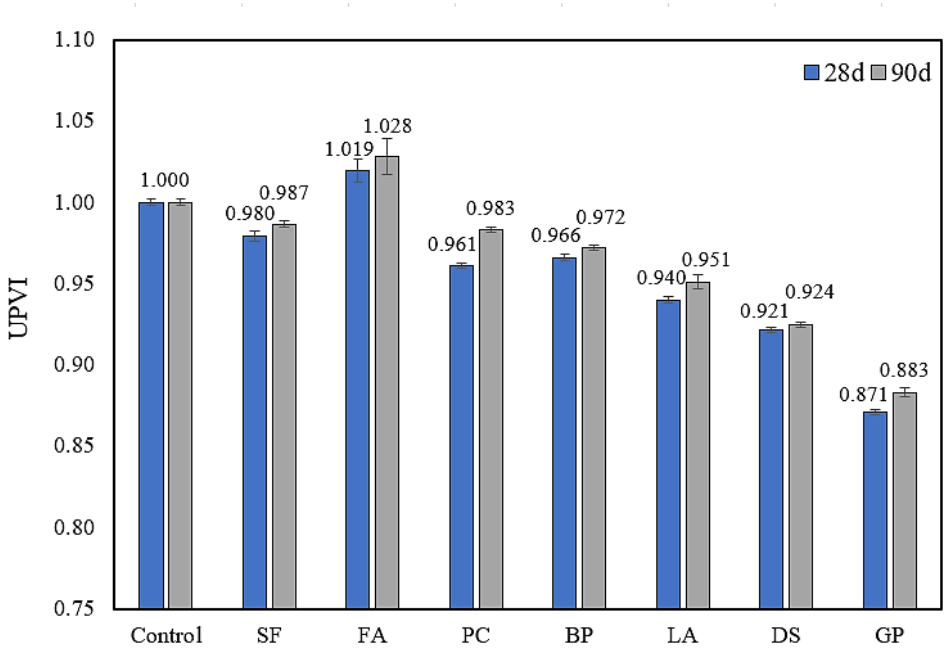

Figure 4-10. UPVI results of control and blended cement-pozzolan samples.

4-6. Comparative statistical analyses

4-6-1. Correlation analyses

Tables 4-9 and 4-10 present the Pearson correlation coefficients (R values) as well as robust correlation coefficients between the outcomes of different test results. Results show mostly moderate (R=0.79) to strong (R=0.99 or 1) correlations between various test methods in both Pearson and robust analyses. Based on the robust analyses, there is very strong positive correlation between pH and Frattini (28-d), calorimetry (48-h) and TGA (90-d), calorimetry (168 h) and SAI, TGA and Frattini (28 d), electrical conductivity and SAI . There is a very strong negative correlation between pH and calorimetry results. There is also a strong relationship between TGA and electrical conductivity, UPVI and Frattini (90 d), and UPVI and calorimetry (R > 0.95).

Furthermore, correlation results showed a strong relationship between TGA (28 d) and TGA (90 d), as did SAI (28 d) and SAI (90 d). Therefore, the shorter time (28 d) for these test methods can be a reliable indicator of the longer-term pozzolanic reactivity.

Some methods have higher robust correlation coefficients than Pearson, such as the correlation between electrical conductivity and TGA (90 d), which has a robust correlation coefficient of 0.98 compared to a Pearson correlation coefficient of 0.59. This suggests that there are outliers in the data affecting the Pearson correlation, while the robust correlation is less sensitive to outliers.

Table 4-10. R-value from Pearson correlation for different pozzolanic reactivity test methods, the shaded cells indicate R > 0.85

Test methods	Frattini 15 d	Frattini 28 d	Frattini 90 d	SAI2 8 d	SAI9 0 d	TGA 28 d	TGA 90 d	Electrical conductivity	pH (OH index)	Calorimetry 48 h	Calorimetry 168 h	UPVI 28 d	UPVI 90 d
Frattini 15 d	-	-	-	-	-	-	-	-	-	-	-	-	-
Frattini 28 d	0.72	-	-	-	-	-	-	-	-	-	-	-	-
Frattini 90 d	0.50	0.90	-	-	-	-	-	-	-	-	-	-	-
SAI 28 d	0.66	0.53	0.59	-	-	-	-	-	-	-	-	-	-
SAI 90 d	0.64	0.56	0.65	0.99	-	-	-	-	-	-	-	-	-
TGA 28 d	0.74	0.98	0.88	0.55	0.57	-	-	-	-	-	-	-	-
TGA 90 d	0.81	0.95	0.85	0.64	0.66	0.99	-	-	-	-	-	-	-
Electrical conductivity	0.66	0.42	0.40	0.94	0.92	0.46	0.59	-	-	-	-	-	-
pH (OH index)	0.74	0.96	0.88	0.53	0.57	-0.64	-0.74	-0.87	-	-	-	-	-
Calorimetry 48 h	0.72	0.71	0.79	0.91	0.94	0.70	0.76	0.78	-0.83	-	-	-	-
Calorimetry 168 h	0.31	0.45	0.69	0.87	0.91	0.46	0.52	0.76	-0.67	0.86	-	-	-
UPVI 28 d	0.40	0.52	0.76	0.79	0.85	0.46	0.50	0.61	0.50	0.91	0.92	-	-
UPVI 90 d	0.40	0.59	0.82	0.77	0.83	0.55	0.55	0.57	0.55	0.92	0.90	0.91	-

Table 4-11. R-value from robust correlation for different pozzolanic reactivity test methods, the shaded cells indicate R > 0.85

Test methods	Frattini 15 d	Frattini 28 d	Frattini 90 d	SAI 28 d	SAI 90 d	TGA 28d	TGA 90 d	Electrical conductivity	pH (OH index)	Calorimetry 48 h	Calorimetry 168 h	UPVI 28 d	UPVI 90 d
Frattini 15 d	-	-	-	-	-	-	-	-	-	-	-	-	-
Frattini 28 d	0.82	-	-	-	-	-	-	-	-	-	-	-	-
Frattini 90 d	0.54	0.88	-	-	-	-	-	-	-	-	-	-	-
SAI 28 d	0.50	0.60	0.88	-	-	-	-	-	-	-	-	-	-
SAI 90 d	0.70	0.79	0.90	0.99	-	-	-	-	-	-	-	-	-
TGA 28 d	0.86	1.00	0.94	0.92	0.89	-	-	-	-	-	-	-	-
TGA 90 d	0.86	1.00	0.91	0.86	0.95	1.00	-	-	-	-	-	-	-
Electrical conductivity	0.29	0.76	0.50	1.00	1.00	0.91	0.98	-	-	-	-	-	-
pH (OH index)	0.86	1.00	0.88	0.93	0.89	-0.88	-0.88	-0.80	-	-	-	-	-
Calorimetry 48 h	0.72	0.82	0.92	0.91	0.96	0.94	0.97	0.75	-1.00	-	-	-	-
Calorimetry 168 h	0.60	0.83	0.87	0.99	1.00	0.88	0.88	0.88	-0.70	0.94	-	-	-
UPVI 28 d	0.50	0.68	0.92	0.88	0.90	0.88	0.83	0.60	0.83	0.96	0.93	-	-
UPVI 90 d	0.59	0.73	0.97	0.92	0.94	0.91	0.92	0.62	0.91	0.97	0.96	0.96	-

4-6-2. Ranking analysis

A ranking approach was used to evaluate the different materials and pozzolanic reactivity tests. First, pozzolans were ranked from one to seven in each test, with one reflecting the pozzolan with the highest reactivity and seven reflecting the pozzolan with the lowest reactivity. For example, in most reactivity tests, SF displays the highest reactivity, so it is given a value of 1, and GP displays the lowest reactivity, which is given a 7. Table 4-11 represents the ranks for each pozzolan in various pozzolanic reactivity tests. As a result, the numerical average of ranks given to each pozzolan determines whether the order of each pozzolan (highly reactive will have the lowest average and the least reactive will have the highest average value). Based on the average values, the order of reactivity of tested materials (from high to low reactivity) is SF > FA > PC> LA> BP> DS> GP. SF with the lowest average of 1.14 is highly reactive and GP with the highest average of 6.71 has the lowest reactivity.

Table 4-11. Comparative analysis of seven tested pozzolans by a ranking method

Pozzolans	Frattini 28 d	SAI 28 d	TGA 28 d	Electrical conductivity	pH (OH index)	Calorimetry 48 h	UPVI 28 d	$\sum(x)$	Average ($\bar{x}$)
SF	1	1	1	1	1	1	2	8	1.14
FA	4	2	2	2	2	2	1	15	2.14
PC	2	3	3	5	6	4	4	27	3.86
BP	5	4	5	6	4	5	3	32	4.57
LA	3	6	4	4	3	3	5	28	4.00
DS	7	5	7	5	5	6	6	41	5.86
GP	6	7	6	7	7	7	7	47	6.71

Table 4-12 shows an evaluation of different reactivity tests using the least squares method. In this procedure, the numerical rank of each pozzolan (x) is subtracted from the average value $(\bar{x})$for that material. Consequently, the sum of the least squares values $(\sum[x-\bar{x}]^2)$ for each test method determines the level of effectiveness of the test method. The lowest value indicates the

most effective method, and the highest value indicates the least effective method. Therefore, the most effective methods are calorimetry, TGA, and electrical conductivity. In contrast, the less effective methods are pH, SAI, UPVI, and Frattini.

Table 4-12. Comparative analysis of seven different reactivity tests using the least squares method

Pozzolans	Frattini 28 d	SAI 28 d	TGA 28 d	Electrical conductivity	pH (OH index)	Calorimetry 48 h	UPVI 28 d
SF	0.02	0.02	0.02	0.02	0.02	0.02	0.74
FA	3.46	0.02	0.02	0.02	0.02	0.02	1.30
PC	3.46	0.74	0.74	1.30	4.58	0.02	0.02
BP	0.18	0.32	0.18	2.04	0.32	0.18	2.46
LA	1.00	4.00	0.00	0.00	1.00	1.00	1.00
DS	1.30	0.74	1.30	0.74	0.74	0.02	0.02
GP	0.50	0.08	0.50	0.08	0.08	0.08	0.08
$\sum[x-\bar{x}]^2$	9.93	5.93	2.77	4.21	6.77	1.35	5.63

Based on the results from the Frattini, TGA, calorimetry, and pH tests, DS (with its high content of magnesium oxide) exhibited low reactivity. In contrast, the electrical conductivity test indicated that DS had high reactivity. This indicated that the DS material produces anomalous results in the electrical conductivity test likely due to its relatively high magnesium oxide content. Therefore, the ranking calculations were repeated without the DS data (Table 4-13). As a result, the order of reactivity of the different materials (from the most reactive to the least reactive) are: SF> FA > PC> LA > BP> GP, where SF, FA, and PC are the most reactive pozzolans and BP and GP are the least reactive pozzolans.

Table 4-13. Comparative analysis of seven tested materials using various reactivity tests without DS

Pozzolans	Frattini 28 d	SAI 28 d	TGA 28 d	Electrical conductivity	pH (OH index)	Calorimetry 48 h	UPVI 28 d	$\sum(x)$	Average ($\bar{x}$)
SF	1	1	1	1	1	1	2	8	1.14
FA	4	2	2	2	2	2	1	15	2.14
PC	2	3	3	4	5	3	4	24	3.43
BP	5	4	5	5	4	4	3	30	4.29
LA	3	5	4	3	3	5	5	28	4.00
GP	6	6	6	6	6	6	6	42	6.00

Table 4-14 shows a numerical ranking of the effectiveness of various test methods after removing the DS data. As a result, TGA, calorimetry, electrical conductivity, SAI, and pH are determined to be more effective than Frattini and UPVI methods.

Table 4-14. Comparative analysis of seven different reactivity methods using the least squares method without DS

Pozzolans	Frattini 28 d	SAI 28 d	TGA 28 d	Electrical conductivity	pH (OH index)	Calorimetry 48 h	UPVI 28 d
SF	0.02	0.02	0.02	0.02	0.02	0.02	0.73
FA	3.45	0.02	0.02	0.02	0.02	0.02	1.31
PC	2.04	0.18	0.18	0.33	2.47	0.18	0.33
BP	0.51	0.08	0.51	0.51	0.08	0.08	1.65
LA	1.00	1.00	0.00	1.00	1.00	1.00	1.00
GP	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sum[x-\bar{x}]^2$	7.02	1.31	0.73	1.88	3.59	1.31	5.02

4-7. Conclusions

This paper presents a comprehensive study to evaluate and compare the pozzolanic reactivity of seven different pozzolans and to identify the most reliable and effective test methods for assessing pozzolanic reactivity using comparative analyses. The significant findings are as follows:

- Materials that exhibit a change in electrical conductivity greater than 0.4 mS/cm or an $[OH^-]$ index that is less than 0.8 can be considered pozzolanic.

- It is recommended that the electrical conductivity and pH methods be used only when the content of magnesium oxide in the material is less than 6%.
- A very strong correlation exists between several pozzolanic reactivity test methods used in this study. pH and Frattini, pH and TGA, electrical conductivity and TGA, Frattini and TGA, SAI and electrical conductivity, SAI and calorimetry, and TGA and calorimetry were highly correlated, suggesting that they may be good alternates for assessing pozzolanic reactivity.
- Some test methods, such as Frattini and electrical conductivity, showed weaker correlations, implying they may provide unique information not captured by the other methods.
- Correlation analyses indicate that pH and electrical conductivity are rapid and relatively easy tests that could be good alternatives for the long-duration test methods, such as SAI and Frattini, thus reducing cost and increasing efficiency.
- Calorimetry and electrical conductivity are effective test methods based on the comparative ranking analysis.

4-8. References for chapter 4

[1] B. Liguori, P. Aprea, B. de Gennaro, F. Iucolano, A. Colella, D. Caputo, Pozzolanic Activity of Zeolites: The Role of Si/Al Ratio, Materials. 12 (2019) 4231. https://doi.org/10.3390/MA12244231.

[2] R. Walker, S. Pavía, Physical properties and reactivity of pozzolans, and their influence on the properties of lime-pozzolan pastes, Materials and Structures/Materiaux et Constructions. 44 (2011) 1139–1150. https://doi.org/10.1617/S11527-010-9689-2/FIGURES/8.

[3] G. Bumanis, L. Vitola, L. Stipniece, J. Locs, A. Korjakins, D. Bajare, Evaluation of Industrial by-products as pozzolans: A road map for use in concrete production, Case Studies in Construction Materials. 13 (2020) e00424. https://doi.org/10.1016/J.CSCM.2020.E00424.

[4] S. Kramar, V. Ducman, Evaluation of Ash Pozzolanic Activity by Means of the Strength Activity Index Test, Frattini Test and DTA/TG Analysis, Technical Gazette. 25 (2018) 1746–1752. https://doi.org/10.17559/TV-20171203193229.

[5] Y. Wang, P. Suraneni, Experimental methods to determine the feasibility of steel slags as supplementary cementitious materials, Constr Build Mater. 204 (2019) 458–467. https://doi.org/10.1016/j.conbuildmat.2019.01.196.

[6] J. Hoppe Filho, C.A.O. Pires, O.D. Leite, M.R. Garcez, M.H.F. Medeiros, Characterization of Red Ceramic Waste for Application as Mineral Addition in Portland Cement, Journal of Materials in Civil Engineering. 33 (2021) 04021108. https://doi.org/10.1061/(ASCE)MT.1943-5533.0003719.

[7] K.K. Jurić, I. Carević, M. Serdar, N. Štirmer, Feasibility of using pozzolanicity tests to assess reactivity of wood biomass fly ashes, Gradjevinar. 72 (2021) 1145–1153. https://doi.org/10.14256/JCE.2950.2020.

[8] S. Donatello, M. Tyrer, C.R. Cheeseman, Comparison of test methods to assess pozzolanic activity, Cem Concr Compos. 32 (2010) 121–127. https://doi.org/10.1016/j.cemconcomp.2009.10.008.

[9] S.C.L. Lima, L.C.B. Costa, K.C.S. Defáveri, J.M.F. de Carvalho, R.A.F. Peixoto, G.J. Brigolini, Study on assessment of pozzolanic activity: Slate cutting waste, ACI Mater J. 117 (2020) 3–10.

[10] V.A. Baki, S. Nayır, Ş. Erdoğdu, İ. Ustabaş, Determination of the Pozzolanic Activities of Trachyte and Rhyolite and Comparison of the Test Methods Implemented, International Journal of Civil Engineering. 18 (2020) 1053–1066. https://doi.org/10.1007/s40999-020-00516-5.

[11] B. Uzal, L. Turanlı, H. Yücel, M.C. Göncüoğlu, A. Çulfaz, Pozzolanic activity of clinoptilolite: A comparative study with silica fume, fly ash and a non-zeolitic natural pozzolan, Cem Concr Res. 40 (2010) 398–404. https://doi.org/10.1016/j.cemconres.2009.10.016.

[12] H. Jang, Y.-T. Lim, J.-H. Kang, S. So, H. So, Influence of calcination and cooling conditions on pozzolanic reactivity of paper mill sludge, Constr Build Mater. 166 (2018) 257–270. https://doi.org/10.1016/j.conbuildmat.2018.01.119.

[13] L. Black, Low clinker cement as a sustainable construction material, in: Sustainability of Construction Materials, Elsevier, 2016: pp. 415–457. https://doi.org/10.1016/B978-0-08-100370-1.00017-2.

[14] R.T. Thorstensen, P. Fidjestol, Inconsistencies in the pozzolanic strength activity index (SAI) for silica fume according to EN and ASTM, Materials and Structures/Materiaux et Constructions. 48 (2015) 3979–3990. https://doi.org/10.1617/s11527-014-0457-6.

[15] P. Suraneni, T. Fu, V. Jafari Azad, O.B. Isgor, J. Weiss, Pozzolanicity of finely ground lightweight aggregates, Cem Concr Compos. 88 (2018) 115–120. https://doi.org/10.1016/j.cemconcomp.2018.01.005.

[16] S. Seraj, Evaluating natural pozzolans for use as alternative supplementary cementitious materials in concrete, (2014). https://repositories.lib.utexas.edu/handle/2152/28052 (accessed February 7, 2023).

[17] R. Snellings, H. Kazemi-Kamyab, P. Nielsen, L. van den Abeele, Classification and Milling Increase Fly Ash Pozzolanic Reactivity, Front Built Environ. 7 (2021). https://doi.org/10.3389/fbuil.2021.670996.

[18] X. Li, R. Snellings, M. Antoni, N.M. Alderete, M. ben Haha, S. Bishnoi, Ö. Cizer, M. Cyr, K. de Weerdt, Y. Dhandapani, J. Duchesne, J. Haufe, D. Hooton, M. Juenger, S. Kamali-Bernard, S. Kramar, M. Marroccoli, A.M. Joseph, A. Parashar, C. Patapy, J.L. Provis, S. Sabio, M. Santhanam, L. Steger, T. Sui, A. Telesca, A. Vollpracht, F. Vargas, B. Walkley, F. Winnefeld, G. Ye, M. Zajac, S. Zhang, K.L. Scrivener, Reactivity tests for supplementary cementitious materials: RILEM TC 267-TRM phase 1, Mater Struct. 51 (2018) 151. https://doi.org/10.1617/s11527-018-1269-x.

[19] M. Matysík, T. Vymazal, I. Plšková, Effect of Superplasticizers on the Cement Hydration Process, Adv Mat Res. 1100 (2015) 3–6. https://doi.org/10.4028/www.scientific.net/AMR.1100.3.

[20] V. Kocaba, E. Gallucci, K.L. Scrivener, Methods for determination of degree of reaction of slag in blended cement pastes, (2011). https://doi.org/10.1016/j.cemconres.2011.11.010.

[21] Y. Wang, P. Suraneni, Experimental methods to determine the feasibility of steel slags as supplementary cementitious materials, Constr Build Mater. 204 (2019) 458–467. https://doi.org/10.1016/j.conbuildmat.2019.01.196.

[22] P. Suraneni, J. Weiss, Examining the pozzolanicity of supplementary cementitious materials using isothermal calorimetry and thermogravimetric analysis, Cem Concr Compos. 83 (2017) 273–278. https://doi.org/10.1016/j.cemconcomp.2017.07.009.

[23] M.M. Tashima, L. Soriano, J. Monzó, M. v. Borrachero, J.L. Akasaki, J. Payá, New method to assess the pozzolanic reactivity of mineral admixtures by means of pH and electrical

conductivity measurements in lime:pozzolan suspensions, Materiales de Construcción. 64 (2014) e032. https://doi.org/10.3989/mc.2014.00914.

[24] L.R.S. Carneiro, D.C.S. Garcia, M.C.F. Costa, M. Houmard, R.B. Figueiredo, Evaluation of the pozzolanicity of nanostructured sol-gel silica and silica fume by electrical conductivity measurement, Constr Build Mater. 160 (2018) 252–257. https://doi.org/10.1016/j.conbuildmat.2017.11.042.

[25] S. Velázquez, J. Monzó, M. Borrachero, J. Payá, Assessment of Pozzolanic Activity Using Methods Based on the Measurement of Electrical Conductivity of Suspensions of Portland Cement and Pozzolan, Materials. 7 (2014) 7533–7547. https://doi.org/10.3390/ma7117533.

[26] M.P. Luxán, F. Madruga, J. Saavedra, Rapid evaluation of pozzolanic activity of natural products by conductivity measurement, Cem Concr Res. 19 (1989) 63–68. https://doi.org/10.1016/0008-8846(89)90066-5.

[27] 16 ASTM, 597-16 (2016) Standard test method for pulse velocity through concrete, Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA. (2016).

[28] M. Kamath, S. Prashant, M. Kumar, Micro-characterisation of alkali activated paste with fly ash-GGBS-metakaolin binder system with ambient setting characteristics, Constr Build Mater. 277 (2021) 122323. https://doi.org/10.1016/j.conbuildmat.2021.122323.

[29] I. Shooshpasha, A. Hasanzadeh, M. Kharun, Effect of silica fume on the ultrasonic pulse velocity of cemented sand, in: J Phys Conf Ser, IOP Publishing, 2020: p. 012017.

[30] M. Ashraf, A. Naeem Khan, Q. Ali, J. Mirza, A. Goyal, A.M. Anwar, Physico-chemical, morphological and thermal analysis for the combined pozzolanic activities of minerals additives, Constr Build Mater. 23 (2009) 2207–2213. https://doi.org/10.1016/j.conbuildmat.2008.12.008.

[31] F. Althoey, A.K.A. El-Aal, H. Shoukry, I. Hakeem, Performance of Cement Mortars Containing Clay Exposed to High Temperature, Arab J Sci Eng. 47 (2022) 591–599. https://doi.org/10.1007/s13369-021-05583-x.

[32] P.-T. Bui, T.-P. Huynh, Performance and Microstructural Evaluation of Rice Husk Ash–Ground Granulated Blast Furnace Slag–CFBC Fly Ash Mixtures Produced as an Eco-Cement, Journal of Materials in Civil Engineering. 34 (2022) 04021485.

[33] B. Demirel, O. Keleştemur, Effect of elevated temperature on the mechanical properties of concrete produced with finely ground pumice and silica fume, Fire Saf J. 45 (2010) 385–391. https://doi.org/10.1016/j.firesaf.2010.08.002.

[34] M. Tabatabai, S. Bailey, Z. Bursac, H. Tabatabai, D. Wilus, K.P. Singh, An introduction to new robust linear and monotonic correlation coefficients, BMC Bioinformatics. 22 (2021) 1–18. https://doi.org/10.1186/S12859-021-04098-4/FIGURES/9.

[35] Standard test methods for sampling and testing fly ash or natural pozzolans for use in Portland-cement concrete, ASTM C311-18, (2018).

[36] BS EN 196-5, BSI Standards Publication Methods of testing cement Part 5 : Pozzolanicity test for pozzolanic cement, (2011).

[37] B. Uzal, L. Turanli, H. Yücel, M.C. Göncüoğlu, A. Çulfaz, Pozzolanic activity of clinoptilolite: A comparative study with silica fume, fly ash and a non-zeolitic natural pozzolan, Cem Concr Res. 40 (2010) 398–404. https://doi.org/10.1016/j.cemconres.2009.10.016.

[38] P. Mair, R. Wilcox, Robust statistical methods in R using the WRS2 package, Behav Res Methods. 52 (2020) 464–488. https://doi.org/10.3758/S13428-019-01246-W.

[39] J. Lanas, J.L. Pérez Bernal, M.A. Bello, J.I. Alvarez, Mechanical properties of masonry repair dolomitic lime-based mortars, Cem Concr Res. 36 (2006) 951–960. https://doi.org/10.1016/j.cemconres.2005.10.004.

Chapter 5: Prediction of strength activity index using chemical and physical properties of pozzolans

5-1. Abstract

Reductions in cement use have essential benefits in reducing the embodied energy in concrete and CO_2 emissions. Hence, effective assessment of potential pozzolanic materials is highly desirable to facilitate usage as sustainable supplementary cementitious materials (SCMs). However, assessment of pozzolanic reactivity using conventional experimental tests is typically time demanding and expensive. Pozzolanic reactivity is mainly related to the chemical and physical characteristics of various pozzolans, such as amorphous silica and alumina contents and specific surface area. This study develops and presents an equation that can predict the strength activity index (SAI) of potential pozzolans using their chemical and physical properties, thus providing more efficient and timely assessments. At the first stage of this study, the strength activity index (SAI) of seven different materials with varying pozzolanic properties was measured at an age of 90 days. The powdered test materials included pottery cull, brick powder, lightweight aggregate fines, glass powder, silica fume, dolostone, and Class C fly ash. In the second stage, correlation analyses were performed to find parameters (based on chemical and physical properties) that were highly correlated with SAI. An equation was then developed as a function of the chemical and physical properties of raw pozzolanic materials using an optimization tool. Consequently, an equation predicting SAI was derived which had a high degree of correlation with measured SAI (correlation coefficient of 0.972).

5-2. Keywords

prediction equation, pozzolanic reactivity, SCMs, SAI, chemical composition

5-3. Introduction

Production of portland cement is contributing to growing concerns about greenhouse gas emissions [1]. Accordingly, the global construction industry strives to reduce the environmental impact of its activities, particularly the use of portland cement, by finding new and sustainable cement replacement materials with low carbon footprints and embodied energy [2]. In this respect, pozzolans, which are a type of SCMs, are sought to partially replace cement in concrete, enhance the strength and durability of cement matrices, and reduce the economic and environmental costs of portland cement manufacturing [3,4].

Prior to the introduction of portland cement, pozzolans had been used for making concrete and mortars. Greeks, Romans, and other ancient civilizations made concretes and mortars using various cementitious binders consisting of natural pozzolans such as volcanic ash, pulverized pumice, and diatomaceous earth [5]. A pozzolan is a siliceous and aluminous material that reacts with excess calcium hydroxide to form cementitious hydration products, such as calcium silicate hydrates (C-S-H) and calcium silicate aluminate hydrates (C-A-S-H), to improve concrete properties [6,7].

According to the ASTM C618 [8], the sum of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3) shall be more than 50% in fly ash and 70% in natural pozzolans for those materials to be considered pozzolanic. Several researchers have noted that the degree of amorphousness and the level of fineness of particles have a major effect on pozzolanic reactivity [6,9,10].

Amorphous silica and amorphous alumina contents as well as the specific surface area pf the pozzolan govern the pozzolanic reaction [6]. It is, therefore, necessary to consider the mineralogy and amorphousness of pozzolans in addition to their chemical composition. Studies have shown that, even among the same types of SCM, there is a considerable difference in reactivity, which is

likely due to differences in amorphous content, chemical composition, and fineness [11]. For example, good pozzolanic reactivity of bamboo leaf ash has been attributed to its fully amorphous silica content [12]. The high specific surface area of some pozzolans, such as silica fume and metakaolin, facilitates lime consumption, which leads to increased compressive strength [13].

The calcium oxide and amorphous silica contents are important chemical properties of pozzolans that affect the strength of concrete. It has been reported that the main contributor to the strength of portland cement-based concrete is related to the amorphous C-S-H phase with a lower average Ca/Si ratio [14]. The Ca/Si ratio of C-S-H is typically lower in the presence of SCMs [15,16].

The strength activity index is a common and indirect method for assessing pozzolanic reactivity through measurements of the compressive strength of pozzolan-cement blended mortars as a fraction of the strength of portland-cement mortars [17]. This method evaluates the effect of pozzolanic reactivity on the densification and packing of the cementitious matrix [18,19]. The SAI test reflects the impact of pozzolanic reactions on microstructure densification [20]. By partially replacing cement with pozzolanic materials, extra C-S-H is generated, which can increase strength at later ages [13].

In this paper, the SAI of seven blended cement-pozzolan mixtures was measured after 90 days of curing. Amorphous silica and amorphous alumina contents of pozzolans were determined based on the crystallinity index of each material. The objective of this study is to determine whether SAI can be predicted based solely on the specific surface area and amorphous composition of the raw materials without performing the compressive strength tests at various ages. Correlation analyses and an optimization tool were used to develop and verify a prediction equation based on available data from materials with varying degrees of pozzolanic reactivity.

5-4. Materials and methods

5-4-1. Materials

5-4-1-1. Physical and chemical characterization

Seven different materials, mostly waste and industrial by-product materials, were tested in this study. These materials include two types of fired clays, pottery cull (PC) and waste-fired brick (BP); lightweight aggregate fines (LA); silica fume (SF); class C fly ash (FA); glass powder (GP); and dolostone (DS). Ordinary (Type I) portland cement (OPC) was used as the main binder for the concrete mortars. Except for SF and FA, all materials were air-dried at room temperature and ground using a ball mill.

Particle size analysis was conducted using a Malvern Mastersizer 3000, which is a laser diffraction particle size analyzer, and chemical composition was determined using X-ray fluorescence spectrometry (XRF) (a Bruker S4 Pioneer).

It was shown that SF had the smallest particle size, with D90 of 3.5 μm (90% of particles being smaller than 3.5 μm), and GP had the largest particle size, with D90 of 68.3 μm (table 5-1). Consequently, SF had the highest specific surface area (SSA), and GP had the lowest SSA.

Table 5-2 shows the oxide compositions of all seven materials. The chemical composition tests indicated that SF and GP were primarily composed of silica. BP and PC, and LA were mainly composed of silica and alumina. In comparison, DS had a considerable amount of lime (~ 25%) and magnesia (~17%). FA had both hydraulic and pozzolanic properties because of a substantial content of lime and silica in its composition. These compositions are also plotted (on a ternary

phase diagram) based on the main oxides related to pozzolanic reactivity, CaO-SiO_2-Al_2O_3, (fig. 5-1).

Table 5-1. Particle size analysis by laser diffraction method

Materials	SF	FA	PC	BP	LA	DS	GP	OPC
SSA(m^2/kg)	8569	590.90	435.00	492.50	739.90	226.10	112.7	249.50
D10(µm)	0.16	1.61	2.19	2.02	2.17	5.56	9.03	3.97
D50(µm)	0.34	7.72	15.00	13.10	11.40	30.70	39.20	14.80
D90(µm)	3.55	41.60	52.80	44.60	41.10	63.50	68.30	34.00

Table 5-2. Chemical composition by XRF

	Chemical composition (%)									
Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	LOI
SF	92.17	0.82	0.72	0.53	1.67	0.16	0.77	0.01	0.09	2.71
FA	37.47	19.18	5.95	25.22	5.33	1.72	0.63	1.41	1.33	0.53
PC	67.09	18.62	1.27	3.04	1.18	2.10	1.72	0.69	0.07	3.04
BP	68.88	21.44	5.28	0.22	0.87	0.25	1.44	1.17	0.12	0.18
LA	51.81	17.72	7.24	6.39	2.03	0.32	2.06	0.71	0.35	6.72
DS	15.52	3.64	1.47	24.92	16.62	0.04	2.28	0.14	0.04	48.01
GP	70.03	2.23	0.35	8.95	1.79	13.4	0.58	0.05	0.05	2.50
OPC	22.86	5.09	2.61	68.04	3.47	0.09	0.98	0.45	0.07	0.314

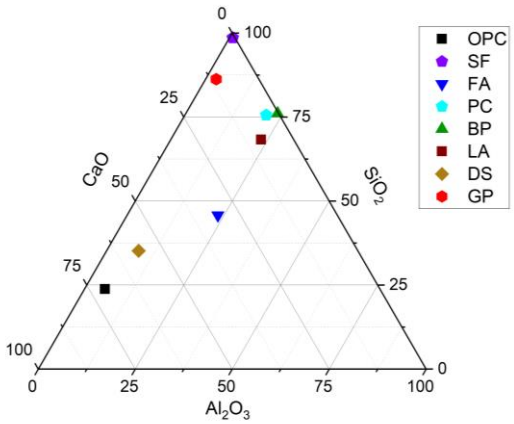

Figure 5-1. Position of each raw material in the CaO–SiO_2– Al_2O_3 ternary diagram.

Figure 5-2 shows the mineralogical phases of the materials, which were identified using an X-ray diffractometer (XRD). For PC and BP, quartz and mullite are the major peaks. GP exhibited an amorphous silica phase with distinct peaks related to quartz and calcite. LA had major peaks associated with quartz, gypsum, and olivine, while FA was dominated by quartz, C_3A, C_3S, gypsum, and lime (CaO). The major peaks in OPC included cement phases like C_3S, C_2S, C_3A, C_4AF, and gypsum. DS was mostly composed of dolomite, and SF displayed broad diffuse scattering associated with amorphous silica in its XRD pattern.

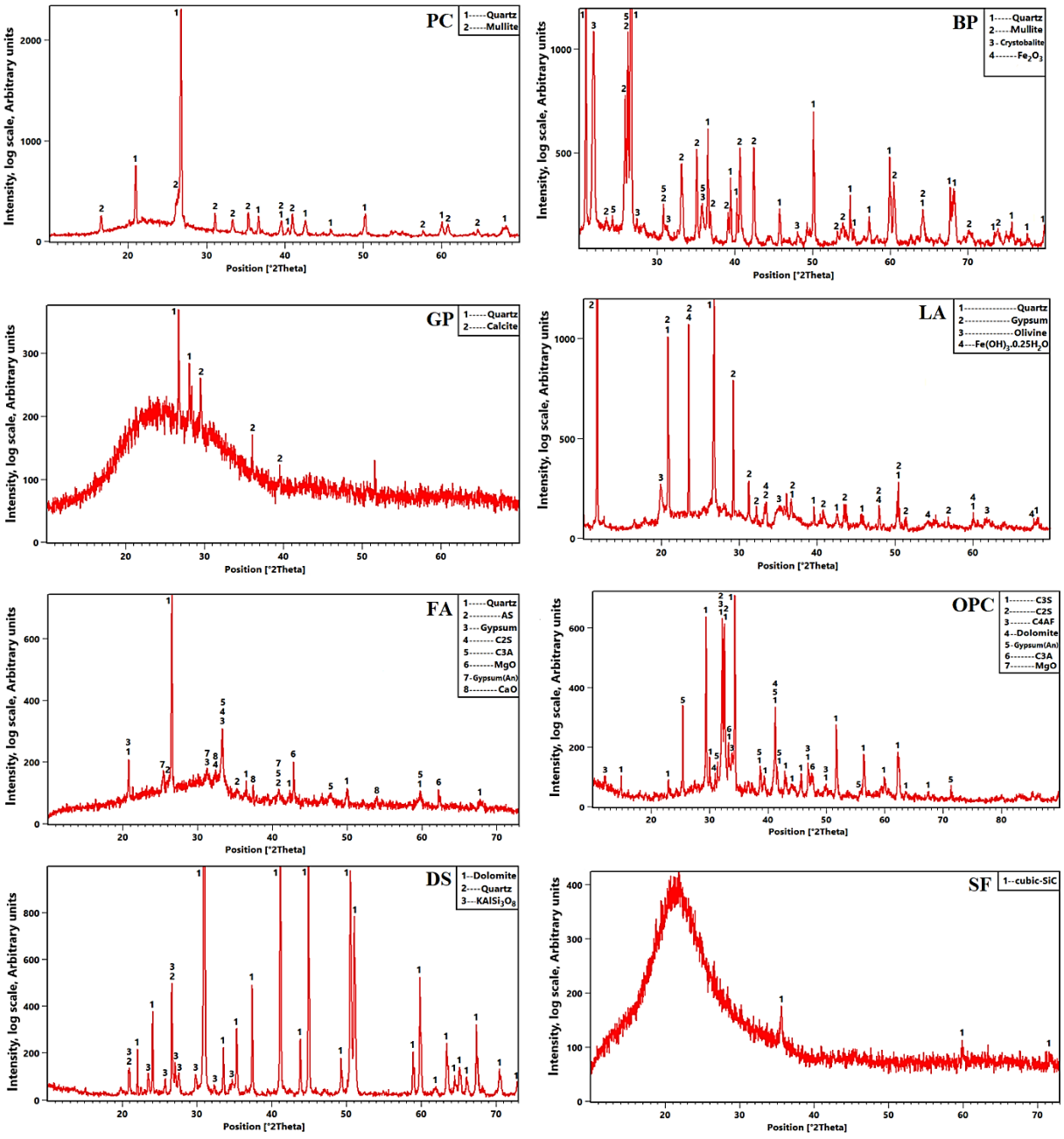

Figure 5-2. XRD patterns of PC, BP, GP, LA, FA, OPC, and DS.

The crystallinity index (CI) of all materials was determined by dividing the area of the crystalline phases and the total area (crystalline plus amorphous) as follows:

$$\mathrm{CI} = \frac{\text{Total area of crystalline peaks}}{\text{Total area of crystalline and amorphous peaks}}$$

Table 5-3 shows the amorphous silica (SiO_{2A}) and amorphous alumina (Al_2O_{3A}) contents that were calculated using the silica and alumina contents from XRF testing and CI values:

$$SiO_{2A}(\%) = (1 - CI) \times (SiO_2\%)$$

$$Al_2O_{3A}(\%) = (1 - CI) \times (Al_2O_3\%)$$

Table 5-3. Crystallinity index and content of amorphous silica and alumina (%)

Materials	SF	FA	PC	BP	LA	DS	GP	OPC
CI	0.0061	0.5757	0.4417	0.7575	0.7379	0.7182	0.1137	0.7436
SiO_{2A}	91.61	15.90	37.46	16.70	13.58	4.37	62.07	5.86
Al_2O_{3A}	0.81	8.14	10.40	5.20	4.64	1.03	1.98	1.31

5-4-2. Methods

5-4-2-1. SAI

The SAI of the 2-in cube mortar specimens was determined in accordance with ASTM C311 [21]. In this process, 20% of cement is replaced by a pozzolan with a water-to-cement ratio (w/c) of 0.484. The cube mortars were de-molded after 24 hours and placed in a sealed lime water bath for 90 days at 23°C. The samples were then removed from the bath, surface dried, and tested for their compressive strength after 90 days. Three specimens were tested for each cement-pozzolan mortar.

5-4-2-2. Development of prediction equation

Initially, the different combinations of chemical and physical parameters based on the lime, amorphous silica, and amorphous alumina contents, as well as SSA, were examined with respect to their correlation coefficients with SAI. Correlation analyses were conducted between individual parameters and the SAI results. Parameters that indicated higher correlations with SAI (i.e., CaO, amorphous silica, amorphous alumina, and SSA) were further evaluated. A parameter

(X) was therefore developed to obtain the best possible correlation with the measured SAI among all possible parameter sets.

$$X = \left[\alpha CaO^{a} + \beta {SiO_{2A}}^{b} + \gamma {Al_2O_{3A}}^{c}\right] \times \xi SSA^{d}$$

where α, β, γ, and ξ are coefficients and a, b, c, and d are defined as powers for the basic components of X. Amorphous silica and amorphous alumina are expressed as percentages, and SSA is expressed as m^2/kg. Then, the coefficients and powers in Equation --- were determined based on an optimization scheme using the Excel Solver by setting the objective as maximizing the correlation coefficient (R) between parameters X and Y (SAI values). The Excel Solver is an optimization tool that can find the optimal solution by adjusting coefficients a, b, g and ξ as well as powers a through d under a set of constraints. The parameter X with its optimized coefficients and powers, was then linearly related to SAI. Finally, a linear regression analysis was performed to find an equation to predict SAI between the predicted Y and the X parameter.

5-5. Results and discussion

Table 5-4 shows the SAI results for all test samples after 90 days of curing. It is shown that blended cement samples with SF and FAshowed higher strength than the control sample (OPC only). Blended cement samples with PC and BP displayed relatively high strength with measured SAI of 0.85 and 0.77, respectively. In comparison, specimens containing DS, LA, and GP showed lower strength than other specimens due to lower SSA and larger particle size. It is worth mentioning that SF contained mainly amorphous silica with high SSA, which positively affects its reactivity. Likewise, pozzolans with lower crystallinity and higher amorphousness, such as PC, showed higher SAI compared to other tested materials. It is clear that particle size (SSA) plays a significant

role in reactivity. Even though GP has a high content of amorphous silica (62.07%), it showed lower reactivity due to its larger particle size (D50 of 39.20 µm).

Table 5-5 presents the optimized coefficients and powers. Using these coefficients and powers, the correlation coefficient between X and Y was 0.969.

Table 5-4. SAI of cement-pozzolan blend and control samples at 90 days

Specimens	SF	FA	PC	BP	LA	DS	GP	Control
SAI	1.30	1.15	0.85	0.77	0.66	0.70	0.47	1.00

Table 5-5. Optimized powers and coefficients of equation x

α	β	γ	ξ	a	b	c	d
8.82	1.00	19.44	1.00	1.32	1.00	1.63	1.00

The parameter X was defined by means of the optimized values using equation 1.

$$X = \left[8.82CaO^{1.32} + SiO_{2A} + 19.44{Al_2O_{3A}}^{1.63}\right] \times SS \quad (1)$$

The prediction linear regression equation was then determined between X and Y (SAI) using equation 2.

$$Y = 8.2775 \times 10^{-7}X + 0.5252 \quad (2)$$

The correlation coefficient between the predicted SAI and the measured SAI is 0.969, indicating that the proposed equation can predict SAI with a high level of correlation (fig. 5-3). The relationship between the prediction equation and SAI was also determined by robust correlation using R Software using Taba robust correlation library [22].

A robust correlation is less sensitive to outliers implying a stronger relationship between the two variables. The robust correlation had a coeeficient of R=0.972, indicating a good fit for the data. The equation Y_{robust} was then derived based on the linear robust regression analysis by R software using equation 3.

$$Y_{robust} = 8.4374 \times 10^{-7} X + 0.5131 \quad (3)$$

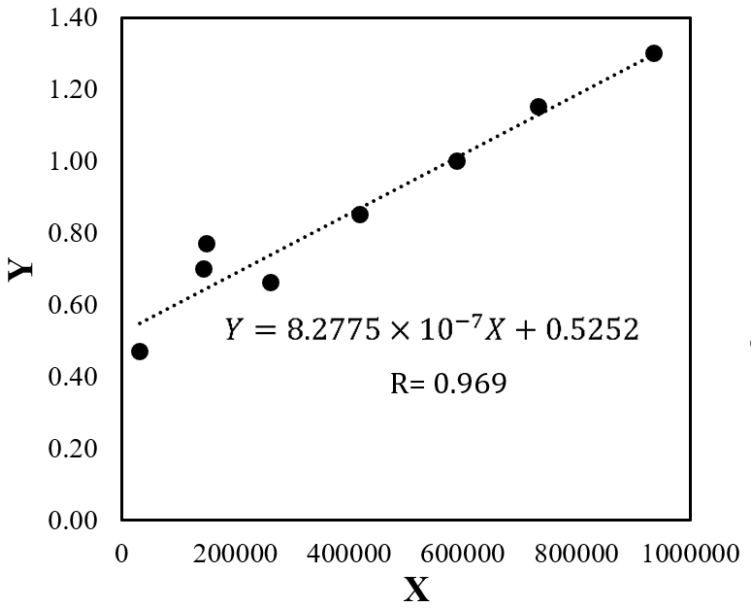

Figure 5-3. Relationship between X and predicted Y (SAI).

Table 5-6 shows the predicted and measured 90-day SAI values. The results showed a high degree of accuracy. The developed equations could predict SAI with an average accuracy of 7.3% when using linear regression and 7.1% when using robust regression analysis.

Table 5-6. Predicted SAI (SAI^P) by linear and robust model.

Specimens	SAI 90 d	SAI^P- linear	SAI^P-robust
SF	1.30	1.2999	1.3028
FA	1.15	1.1286	1.1282
PC	0.85	0.8708	0.8654
BP	0.77	0.6490	0.6393
LA	0.66	0.7413	0.7334
DS	0.70	0.6450	0.6352
GP	0.47	0.5514	0.5398
Control	1.00	1.0110	1.0083

5-6. Conclusions

Pozzolans can offer practical and sustainable solutions for addressing the environmental impact of portland cement usage in concrete. However, conventional assessments of the reactivity of potential pozzolanic materials, such as the strength activity index method, are time-consuming and inefficient. Since the chemical and physical properties of the raw materials play an important role in reactivity, it is important to develop reliable prediction equations to accelerate the process of finding suitable pozzolanic materials. In this study, a prediction equation is developed (equation 2) based on correlation and optimization analyses to predict SAI values with high accuracy using the chemical and physical properties of the raw materials.

The SAI results demonstrated that knowledge of SSA, the amorphous silica and alumina contents, and the lime content for each pozzolan can help predict the strength of blended cement-pozzolan samples. In other words, these factors have a significant impact on the reactivity of pozzolans. Therefore, the developed equation provides an accurate method of predicting SAI to assess the reactivity of pozzolans in a cost-effective and timely manner.

5-7. References for chapter 5

[1] I. Diaz-Loya, M. Juenger, S. Seraj, R. Minkara, Extending supplementary cementitious material resources: Reclaimed and remediated fly ash and natural pozzolans, Cem Concr Compos. 101 (2019) 44–51. https://doi.org/10.1016/j.cemconcomp.2017.06.011.

[2] J.L. Provis, S.A. Bernal, Geopolymers and Related Alkali-Activated Materials, Annual Review of Materials Research. 44 (2014) 299–327. https://doi.org/10.1146/ANNUREV-MATSCI-070813-113515.

[3] R.T. Thorstensen, P. Fidjestol, Inconsistencies in the pozzolanic strength activity index (SAI) for silica fume according to EN and ASTM, Materials and Structures/Materiaux et Constructions. 48 (2015) 3979–3990. https://doi.org/10.1617/s11527-014-0457-6.

[4] C.M. Martinez, I.S. del Bosque, M.F. G. Medina, M.S. de Rojas, Fillers and additions from industrial waste for recycled aggregate concrete, 2022. https://doi.org/10.1016/b978-0-12-824105-9.00012-3.

[5] ACI 232.1R, ACI 232.1R-12 Report on the Use of Raw or Processed Natural Pozzolans in Concrete, (2012). www.concrete.org (accessed September 2, 2021).

[6] R. Walker, S. Pavía, Physical properties and reactivity of pozzolans, and their influence on the properties of lime-pozzolan pastes, Materials and Structures/Materiaux et Constructions. 44 (2011) 1139–1150. https://doi.org/10.1617/S11527-010-9689-2/FIGURES/8.

[7] G. Bumanis, L. Vitola, L. Stipniece, J. Locs, A. Korjakins, D. Bajare, Evaluation of Industrial by-products as pozzolans: A road map for use in concrete production, Case Studies in Construction Materials. 13 (2020) e00424. https://doi.org/10.1016/J.CSCM.2020.E00424.

[8] ASTM C618-19, Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete, ASTM International: West Conshohocken, PA, USA. (2019).

[9] J. Henrique, A.A. Nepomuceno, N.P. Hasparyk, F.L. Vieira, Assessment of the Pozzolanic Reaction of Crystalline and Amorphous R Ice Husk-Ashes (Rha), (2004) 715–723.

[10] M.J. Mccarthy, G.M.S. Islam, L.J. Csetenyi, M.R. Jones, Evaluating Test Methods for Rapidly Assessing Fly Ash Reactivity for Use in Concrete, 2013 World of Coal Ash (WOCA) Conference. (2013) 2013. http://www.flyash.info/2013/095-McCarthy-Final-2013.pdf.

[11] P. Suraneni, A. Hajibabaee, S. Ramanathan, Y. Wang, J. Weiss, New insights from reactivity testing of supplementary cementitious materials, Cem Concr Compos. 103 (2019) 331–338. https://doi.org/10.1016/j.cemconcomp.2019.05.017.

[12] E. Villar-Cociña, E.V. Morales, S.F. Santos, H. Savastano, M. Frías, Pozzolanic behavior of bamboo leaf ash: Characterization and determination of the kinetic parameters, Cem Concr Compos. 33 (2011) 68–73. https://doi.org/10.1016/j.cemconcomp.2010.09.003.

[13] A. Mardani-Aghabaglou, G. İnan Sezer, K. Ramyar, Comparison of fly ash, silica fume and metakaolin from mechanical properties and durability performance of mortar mixtures viewpoint, Constr Build Mater. 70 (2014) 17–25. https://doi.org/10.1016/j.conbuildmat.2014.07.089.

[14] W. Kunther, S. Ferreiro, J. Skibsted, Influence of the Ca/Si ratio on the compressive strength of cementitious calcium-silicate-hydrate binders, (2017). https://doi.org/10.1039/c7ta06104h.

[15] A. Cuesta, I. Santacruz, A.G. De la Torre, M. Dapiaggi, J.D. Zea-Garcia, M.A.G. Aranda, Local structure and Ca/Si ratio in C-S-H gels from hydration of blends of tricalcium silicate and

silica fume, Cem Concr Res. 143 (2021) 106405. https://doi.org/10.1016/J.CEMCONRES.2021.106405.

[16] R. García-Giménez, M. Frias, R. Vigil de la Villa, S. Martínez-Ramírez, Ca/Si and Si/Al Ratios of Metakaolinite-Based Wastes: Their Influence on Mineralogy and Mechanical Strengths, (n.d.). https://doi.org/10.3390/app8040480.

[17] S. Donatello, M. Tyrer, C.R. Cheeseman, Comparison of test methods to assess pozzolanic activity, Cem Concr Compos. 32 (2010) 121–127. https://doi.org/10.1016/j.cemconcomp.2009.10.008.

[18] H. Jang, Y.-T. Lim, J.-H. Kang, S. So, H. So, Influence of calcination and cooling conditions on pozzolanic reactivity of paper mill sludge, Constr Build Mater. 166 (2018) 257–270. https://doi.org/10.1016/j.conbuildmat.2018.01.119.

[19] L. Black, Low clinker cement as a sustainable construction material, in: Sustainability of Construction Materials, Elsevier, 2016: pp. 415–457. https://doi.org/10.1016/B978-0-08-100370-1.00017-2.

[20] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Assessment of pozzolanic activity of different calcined clays, Cem Concr Compos. 37 (2013) 319–327. https://doi.org/10.1016/j.cemconcomp.2013.01.002.

[21] Standard test methods for sampling and testing fly ash or natural pozzolans for use in Portland-cement concrete, ASTM C311-18, (2018).

[22] M. Tabatabai, S. Bailey, Z. Bursac, H. Tabatabai, D. Wilus, K.P. Singh, An introduction to new robust linear and monotonic correlation coefficients, BMC Bioinformatics. 22 (2021) 1–18. https://doi.org/10.1186/S12859-021-04098-4/FIGURES/9.

Chapter 6: Summary and Conclusions

Pozzolans can offer practical and sustainable solutions for addressing the environmental impact of portland cement usage in concrete. A comprehensive study was performed to assess the pozzolanic reactivity of seven different powdered materials using seven different pozzolanic reactivity test methods. The test materials were pottery cull, brick powder, lightweight aggregate fines, class C fly ash, silica fume, glass powder, and dolostone. The pozzolanic reactivity tests were the Frattini test, strength activity index (SAI), ultrasound pulse velocity index, thermogravimetric analysis, calorimetry, electrical conductivity, and pH. The efficacy and efficiency of various test methods were evaluated using a ranking method. A comparative evaluation of the pozzolanic reactivity of the various test materials was performed. The primary findings of this study are provided as follows:

1. This study provides a comprehensive approach for evaluating and comparing the pozzolanic reactivity of different pozzolans and identifying the most reliable and effective test methods. Results indicated a strong correlation among several pozzolanic reactivity test methods used in this study. The results of the following test pairs were highly correlated: pH and Frattini, pH and TGA, electrical conductivity and TGA, Frattini and TGA, SAI and conductivity, SAI and calorimetry, and TGA and calorimetry. Therefore, these may be good alternatives for assessing pozzolanic reactivity. Moreover, some test methods, such as Frattini and electrical conductivity, show weaker correlations, implying they may provide unique information not captured by the other methods. Correlation analyses also indicate that pH and electrical conductivity are rapid and effective tests, which could be

good alternatives to long-standing methods such as SAI and Frattini. Also, calorimetry and electrical conductivity are efficient methods based on comparative ranking methods.

2. Direct methods such as Frattini and TGA are commonly employed to determine the pozzolanic reactivity of materials by quantifying the consumption of portlandite in a lime-pozzolan or cement-pozzolan blended sample. However, the Frattini and TGA methods require long periods of time to assess the reactivity of pozzolans (e.g., 28 or 90 days). In contrast, electrical conductivity and pH methods provide information on the reactivity of the materials over a much shorter time of six hours. This study proposes using electrical conductivity and pH test methods as effective, rapid, and direct methods for assessing pozzolanic reactivity. Previously, these methods were considered as indirect methods. Analytical methods for determining the amount of consumed lime due to pozzolanic reactivity are presented. The pH and electrical conductivity test results on seven different powdered materials were compared with the commonly performed Frattini and TGA tests. Robust correlation analyses indicated that estimates of consumed lime using pH and electrical conductivity results are well correlated with the Frattini and TGA results at 15 and 90 days. Therefore, electrical conductivity and pH methods are viable and rapid tests to determine pozzolanic reactivity. The primary advantage of these methods is their relative simplicity and rapid results.
3. A relatively simple equation for predicting the SAI test results using the chemical and physical properties of the raw materials has been developed, which could accelerate the process of finding suitable pozzolanic materials. An extensive correlation and optimization analysis set was used to develop the proposed equation. The conventional

assessments of pozzolanic reactivity, such as the strength activity index, are time-consuming and inefficient. The chemical and physical properties of the raw materials play an important role in their reactivity. Analyses of the SAI results demonstrate that knowledge of the specific surface area (SSA), amorphous silica and amorphous alumina contents, and the lime content for each pozzolan could help predict the strength of blended cement-pozzolan samples. In other words, these factors have a significant impact on the reactivity of pozzolans. The developed equation provides an accurate method of predicting SAI, which is an important and long-standing method for assessing the reactivity of pozzolans.

Recommendation for future research:

- Future studies should address whether the chemical and physical properties of pozzolans can be used to predict test outcomes other than SAI, compare those predictions with thermodynamic modeling, and determine whether this approach can complement thermodynamic modeling.
- Future studies should examine outcomes of pH and electrical conductivity as direct methods at different temperatures and test durations than those used in this study (6 h and 40°C)