

IMPERIAL

Circular Concrete through Acid Leaching and Carbonation of Cementitious Materials

By

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Abstract

Cementitious waste, especially the fine fraction (< 4.75 mm) of waste concrete, is either downcycled or landfilled. In this research, waste concrete fines and cement paste are treated by acetic acid leaching and carbonation for upcycling. The optimal leaching conditions are determined, which maximise the Ca^{2+} extraction and minimise acid use and dissolution of SiO_2 . The recycled sand extracted under the optimal leaching conditions are comparable to virgin sand. Total replacement of virgin sand with recycled sand produces cement mortars with improved compressive strength. The silica-rich residue (SR) from acid leaching has similar or higher pozzolanic reactivity than coal fly ash. After heat treatment under 900°C , the specific surface area of SR from cement paste is reduced by 99 %. The mortars with 20% cement replacement of this material have good workability and comparable compressive strength to mortars containing traditional supplementary cementitious materials. The Ca^{2+} -rich solution is carbonated, and 99.1% pure vaterite CaCO_3 is produced. Vaterite can be transformed to aragonite in a solution containing Mg^{2+} and Sr^{2+} under 60°C , forming a strong fibrous interlocked structure. The properties of aragonite binder can be controlled by the liquid/solid (L/S) ratio. Lower L/S ratios generate higher compressive strength. Higher L/S ratios lead to lower density, higher porosity and lower thermal conductivity. Aragonite binder can form novel lightweight load-bearing thermal insulating materials.

Currently, this process is costly and carbon positive. However, this can be improved by acid/alkali recovery, using ammonium salts and developing products with higher value. Based on laboratory results, this process can achieve a net CO_2 sequestration of 93.8 kg/tonne of waste concrete with the use of sustainable acetic acid and ammonia and zero-carbon energy. This research demonstrates the potential for the scaled-up application of indirect carbonation and the development of circular concrete.

Statement of originality

I declare that the work presented in this thesis is my own original research and all the contributions from others are appropriately referenced or acknowledged.

Tiejun Ding

26/02/2025

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List of notations

Abbreviations

CCUS	Carbon Capture, Utilisation and Storage
SCM	Supplementary cementitious material
WCCA	Waste concrete coarse aggregates
WCFA	Waste concrete fine aggregates
WCF	Waste concrete fines
WCP	Waste concrete fine powder
HCP	Ground hydrated cement powder
RH	Relative humidity
SR	Silica-alumina rich solid residue
GGBFS	Ground granulated blast furnace slag
FA	Coal fly ash
SF	Silica fume
C&D	Construction and demolition
ACC	Amorphous calcium carbonate
STPP	Sodium tripolyphosphate
GL	Ground limestone
QZ	Quartz sand
EDTA	Ethylenediaminetetraacetic acid
CMP	Calcein-methyl thymol blue-phenolphthalein
PAN	1-(2-pyridylazo)-2-naphthol
XRF	X-ray fluorescence
XRD	X-ray diffraction
SEM	Scanning electron microscopy
EDS	Energy dispersive analysis
SE	Secondary electrons
BSE	Backscattered electrons
TGA	Thermogravimetric analysis

DSC	Differential scanning calorimetry
BET	Brunauer-Emmett-Teller theory
ICP-OES	Inductively coupled plasma optical emission spectrometry
FTIR	Fourier transformation infrared spectrometry
ATR	Attenuated total reflection
MEA	Monoethanolamine
BMED	Bipolar membrane electrodialysis
AEM	Anion exchange membrane
CEM	Cation exchange membrane
BPM	Bipolar membrane
MSWIBA	Municipal solid waste incineration bottom ash
CdSR	Ca-depleted SR
TEAOH	Tetraethylammonium hydroxide

Roman letters

k_{sp}	Solubility product
J	Nucleation rate
S	Supersaturation ratio
ρ	Density
m	Mass
l	Length
w	Width

1 Introduction

1.1 Research background

Concrete is one of the most important materials in modern society. All the infrastructures where essential human activities take place contain concrete, making it the most consumed artificial material. Concrete is produced by mixing cement, sand, coarse aggregates and water, with other chemical additives depending on the use. It has a lower carbon footprint compared to other materials, due to the simple production method and CO₂ capture by carbonation that occurs through the service life. Cement is the ‘glue’ which binds the sand and coarse aggregates in concrete. The production of Portland cement is a major source of carbon emissions (Habert et al., 2020). Cement manufacturing accounts for about 8% of total anthropogenic carbon emissions (Jang et al., 2016). Producing 1 tonne of cement releases approximately 830 kg of CO₂ on a global average (The European Cement Association, 2023). This includes process-related and fuel-related emissions. Clinker is produced by heating a mixture of limestone and clay in a rotary kiln at 1450°C. This is then ground with ~5% gypsum (CaSO₄·2H₂O) to make Portland cement (Taylor, 1997). CO₂ is mainly emitted through the decomposition of CaCO₃ in limestone, and this contributes to 50 – 60% of the total carbon emissions. Other sources of CO₂ emissions are the combustion of fossil fuel to heat the kiln to 1450 °C and transport emissions. These account for 30 – 40% of the total CO₂ emissions (Guo et al., 2024). Global cement production reached 4.1 billion tonnes in 2022 (The European Cement Association, 2023). This is anticipated to increase in the future due to increasing urbanization and the need for concrete infrastructure. Therefore, there is an urgent need to develop CO₂ emission reduction technologies to meet the 2050 net zero carbon emission goals (The European Cement Association, 2023).

Efforts have been made to improve the energy efficiency of cement kilns and using alternative fuels sourced from waste, and this has successfully reduced the fuel-related emissions (Habert et al., 2020). However, process-related emission is inevitable. A simple and effective way to partly offset this is by replacing part of the clinker with supplementary cementitious materials (SCMs). SCMs are naturally or industrially sourced materials with lower CO₂ emissions than Portland cement. These can also contribute to cement hydration reactions. Commonly used SCMs are ground granulated blast furnace

slag (GGBFS), coal fly ash (FA), silica fume (SF), natural pozzolans and rice husk ash. Ground limestone is also used as a reactive filler material in concrete. Although reducing the cost and embedded CO₂ in the binder, the availability of many SCMs is limited compared to the amount of cement produced, and available stocks of SCM materials are rapidly being utilised. The annual availability of FA is about 30% of the annual production of cement. Due to the variation in quality, only a small proportion ($< 1/3$) form viable SCMs (Scrivener et al., 2018). The annual availability of GGBFS is 5 – 10% of the annual production of cement, and it is questionable that this proportion will increase because cement production is growing more rapidly than the production of iron, and more steel is being recycled (Scrivener et al., 2018). Also, their availability varies regionally, leading to increased scarcity in countries with fast growing demand for cement (Snellings, 2016; Scrivener et al., 2018). Thus, further CO₂ emission reduction in cement largely depends on the development of alternative viable SCMs.

Apart from the high CO₂ emissions associated with cement, the huge consumption of concrete also leads to the depletion of natural resources, especially aggregates. Based on data from 2012, 17.5 billion tonnes of sand and gravels were extracted to make concrete (Miller, Horvath & Monteiro, 2016). The need for sand and gravel is ~ 3 times greater than all the other materials and has been increasing over time. As such, materials are unlikely to be shipped internationally due to the cost, and the high demand can lead to over-exploitation of local aggregate deposits. This brings further environmental and social problems, such as land erosion and instability, ecosystem damage, illegal extraction and crime (Torres et al., 2017; Jiang et al., 2019; Habert et al., 2020; Shaji & Anilkumar, 2014). To alleviate these problems, technologies need to be developed that can extract useable sand and aggregate from alternative sources, and this has become an important research area.

Construction and demolition (C&D) waste is generated in huge amounts because of the continual renewal of buildings and infrastructure and most of it is waste concrete. In 2020, 6 Gt of waste concrete was produced globally, including end-of-life concrete and end-of-life mortar (Driver et al., 2024). Waste concrete is currently recycled by crushing and size sorting. The resulting particles above 5 mm are called waste concrete coarse aggregates (WCCA) and those below 5 mm are known as waste concrete fine aggregates (WCFA). WCCA and WCFA are porous and have low density, due to the microcracks formed by crushing, and the gel pores in the old cement paste that adheres to them (Poon et al., 2023). When replacing natural aggregates in concrete at high proportions, waste concrete aggregates introduce

multiple interfacial transition zones (ITZ) between the original aggregate, old paste and new paste, which are weak. Therefore, they are not generally suitable for reusing in new concrete. As a result, they are often used in low-grade applications such as road base or as pavement materials (Vázquez, 2016; Poon et al., 2023). The concrete crushing process generates fine waste concrete powder (WCP) which is less than 150 μm , and this accounts for 20 – 30% of the total mass of waste concrete. WCP is rich in hydrated cement paste, and this makes it more porous than WCCA and WCFA and it is less reactive than other SCMs. The direct use of WCP makes concrete less workable and it decreases the strength and surface resistivity. Therefore, WCP can only be used as an inert filler at low additions, typically less than 20 % (Likes et al., 2022; Poon et al., 2023). Also, a significant amount of waste concrete is not recycled. In 2018, about 20 % of the waste concrete was landfilled in the USA (United States Environmental Protection Agency, 2020). Novel approaches to upgrade the recycling of waste concrete are desired to make concrete more circular and sustainable.

Carbon capture, utilisation and storage (CCUS) includes a range of technologies that capture process-related CO_2 emissions from flue gases, and includes amine absorption, membrane processes, oxyfuel and mineral carbonation (Voldsund et al., 2019; Habert et al., 2020). The mineral carbonation process has gained much attention in recent years, because alkaline industrial wastes can be used as the feedstock to reduce material cost (Mun & Cho, 2013). Using waste concrete as a feedstock of mineral carbonation has benefits. End-of-life cement paste contains alkaline cement hydration products with high reactivity towards carbonation (Poon et al., 2023). It outweighs other wastes such as FA and GGBFS, which need to be activated to achieve sufficient carbonation efficiency (Ho et al., 2022; Hu et al., 2017). 1.39 Gt of the waste concrete generated annually is cement paste, which is nearly twice as the second most generated alkaline industrial waste, FA (0.68 Gt/y) (Driver et al., 2024). This improves the CO_2 sequestration potential. Moreover, mineral carbonation of waste concrete generates products suitable for construction and other value-added applications, which avoids landfill and turns a hugely produced waste into an urban mineral source (Poon et al., 2023). Considering its large availability, high carbonation reactivity, low cost and the environmental benefits by recycling, waste concrete is a preferred feedstock material for mineral carbonation.

Two mineral carbonation routes, direct carbonation and indirect carbonation, have been previously reported. Direct carbonation involves contacting CO_2 with a slurry containing water and waste concrete.

This process produces a solid mixture consisting of raw aggregates, CaCO_3 and pozzolanic reactive silica-alumina gel (Jiang, Shen & Poon, 2022; Shen et al., 2023b; Skocek, Zajac & Ben Haha, 2020). Indirect carbonation includes dissolving the old cement paste in waste concrete to extract the Ca^{2+} ions, leaving clean aggregates and silica-rich residue, and absorbing CO_2 using the Ca-rich solution (Mehdizadeh, Mo & Ling, 2023; Fang et al., 2021c, 2021b). Compared to direct carbonation, indirect carbonation has huge potential to separate clean aggregates from the hydrated cement paste and produce a highly reactive silica-rich SCM and pure precipitated calcium carbonate (CaCO_3).

Cement hydration products are mainly portlandite ($\text{Ca}(\text{OH})_2$), calcium silicate hydrate (C-S-H) phase, ettringite (AFt) and monosulfate (AFm), plus minor phases such as hydrogarnet and hydrotalcite (Taylor, 1997). All the cement hydration products are unstable under acidic conditions, and so old cement paste can be dissolved by acid. Due to the amphoteric properties of the silicates, aluminates and ferrites, cement paste can also be dissolved by alkali. Several acids (including acidic salts) and alkali have been used to remove the old hydrated cement paste, such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3), acetic acid (CH_3COOH), ammonium chloride (NH_4Cl) and sodium carbonate (Na_2CO_3) (Kim et al., 2017a; Santha Kumar & Minocha, 2018; Song & Ryou, 2014; Chen et al., 2017; Fang et al., 2021a, 2021c; Mun, Cho & Kwon, 2017; Mehdizadeh, Mo & Ling, 2023). Acetic acid is a weak acid and has buffering effect, so the pH during leaching can be controlled at moderate conditions to limit the dissolution of other elements (Al, Fe and Si). This can potentially improve the separation of Ca and other elements during reaction compared to strong acids. Its chelating effect can promote the extraction efficiency of Ca under moderate pH (Prabhu et al., 2024). Also, it has an abundant global supply of around 22 million tonnes per year (Statista, 2023). Although there has been no direct measurement of the effect of the materials obtained from acetic acid leaching of cement paste on concrete durability, acetate salt solution has been reported to improve the strength and reduce the porosity of concrete (Abed, Mojtahedi & Lotfollahi Yaghin, 2023). It is anticipated the residual acetate ions in the materials will not adversely affect the long-term durability of concrete. Therefore, acetic acid is used as the leaching agent of waste concrete in this thesis. Nevertheless, optimising this process and understanding the effect of reaction parameters on the extraction of calcium and other minor elements including aluminium, iron, silicon and sulphur is still limited.

The solid residue after acid leaching is rich in amorphous silica and alumina and potentially pozzolanic (Mehdizadeh, Mo & Ling, 2023). However, it has a high specific surface area compared to common SCMs, resulting in high water absorption and reduced workability as found in this thesis. To the author's knowledge, there has not been any reported research on improving the silica-rich SCM extracted from indirect carbonation of waste concrete to achieve better workability.

The carbonation of the Ca-rich solution produces CaCO_3 . There are four common polymorphs of CaCO_3 . These are calcite, aragonite, vaterite and amorphous calcium carbonate (Rodriguez-Blanco, Shaw & Benning, 2011). Calcite is the most thermally stable CaCO_3 polymorph under ambient conditions. It is mainly used as an inert filler in cementitious systems because of low reactivity. Recent research has investigated the self-cementing property of vaterite via polymorphic transformation into aragonite, making it a potentially carbon-negative construction material (Hargis et al., 2021). This provides new insights for producing value from the CaCO_3 extracted by indirect carbonation of waste concrete.

The technical feasibility of the indirect carbonation treatment of waste concrete and the viability of the recycled products in developing circular concrete and reducing the CO_2 emissions of cement remains to be investigated and this is the focus of the research reported in this thesis.

1.2 Aims and objectives

The overall aim of this research is to develop circular concrete using acetic acid leaching and carbonation. This aim will be achieved by addressing the following objectives:

- Optimising the acetic acid leaching process to extract clean reusable sand from waste concrete.
- Producing a viable SCM from the silica-rich residue after acetic acid leaching.
- Developing aragonite binder from the vaterite produced by the carbonation of the Ca^{2+} -rich leachate.
- Analysing the economic feasibility and carbon emissions of this technology.

1.3 Thesis structure

This thesis contains nine chapters. Chapter 1 introduces the research scope, defines the aim and objectives of the study, and outlines the structure of the thesis. Chapter 2 includes a literature review of the current research on extracting new material resources from waste concrete, highlighting key research gaps. Chapter 3 presents the methodology applied in this study, including raw material preparation, acetic acid leaching, carbonation, material characterisation technologies, pozzolanic reactivity test and fresh and mortar performance tests.

The main findings of this study are reported in Chapters 4 to 7. Real waste concrete fines < 4.75 mm (WCF) containing WCFA and WCP are collected from a recycling facility and used to extract recycled sand and silica-rich SCM. Laboratory-prepared ground hydrated cement paste (HCP) is used to simulate the real waste concrete powder in the silica-rich SCM extraction and CaCO_3 production. In Chapter 4, the acetic acid leaching conditions, including acid concentration, liquid/solid ratio, reaction time and temperature are optimised. The physical and chemical properties of the recycled sand are characterised. Finally, the effect of replacing standard sand by recycled sand on the strength of mortar is studied. In Chapter 5, the behaviour of Al, Fe and Si during acid leaching is understood. Also, the elemental composition, phase composition, thermal stability, chemical bonding, particle size, morphology and surface properties of the silica-rich residues extracted from the optimal acetic acid leaching of WCF and HCP, labelled as SR-wc and SR-cp respectively, are characterised. The pozzolanic reactivity of the silica-rich residues are tested and compared to each other, and the main commercially available SCMs. In Chapter 6, heat treatment of the silica-rich residue is investigated and optimised to improve the workability of mortars. The effect of temperature on the amorphous content, particle size, particle morphology, specific surface area and pozzolanic reactivity is studied. The effect of the silica-rich residue on the hydration of the binder and the microstructure of mortar is investigated. In Chapter 7, the vaterite produced by carbonating the Ca-rich solution is characterised. It is then activated and transformed to an aragonite binder by controlled curing. The effect of processing parameters on the chemical, physical, microstructural, mechanical and thermal properties of the binder are evaluated, and the potential engineering application of the aragonite binder is assessed.

Following the experimental results, Chapter 8 proposes a scale-up process, evaluates the economic feasibility and energy consumption, calculates the CO₂ emission saving potential and proposed methods of improving the economic benefit and reducing the CO₂ footprint of this treatment. This includes recovering the acid and alkali, producing high-value products, using sustainable acetic acid and ammonia and low-carbon energy supplies. Finally, Chapter 9 presents the key conclusions of this research, summarises the limitations and gives recommendations for future work.

2 Literature review

This chapter presents a literature review of the previous studies relevant to the scope of this research. To make concrete circular, all the components in waste concrete, including aggregates, sand and hydrated cement needs to be recycled and reused. The methods for transforming waste concrete to applicable recycled aggregates are reviewed and compared, and the influencing factors are discussed. Next, the mechanism for activating waste concrete powder to be used as a new SCM is described, and the corresponding methods are reviewed. Then, the carbonation methods are reported, the formation conditions of different CaCO_3 polymorphs and their potential value-added applications are reviewed. Finally, the research gaps are summarised.

2.1 Extracting viable recycled aggregates from waste concrete

As discussed in Chapter 1, the component in waste concrete that reduces the workability and strength of the new concrete is the old cement paste. Several treatment methods have been developed to improve the quality of recycled concrete aggregates, and these fall into two categories: (1) strengthening the old cement paste and (2) removing the old cement paste.

2.1.1 Strengthening the old cement paste

Strengthening involves filling the pores and cracks in the old cement paste to achieve higher density, lower porosity and lower water absorption, or coating the surface of the waste concrete aggregates with a layer of functional additives to reduce the water absorption and improve the bonding to new cement paste (Feng et al., 2022). Several chemical and bio-chemical processes have been investigated. The use of hydrophobic organic compounds, for example silane-based water repellents, can form a layer on the surface of waste concrete aggregates. This water-repelling coating can prevent the capillary water absorption and penetration of attacking ions. The water absorption of waste concrete coarse aggregates (WCCA) can be reduced by 61 – 96% (Zhu et al., 2013). Soluble silicate can react with the portlandite in the old cement mortar to form C-S-H phase that can fill the pores and cracks. Treating WCCA with 7 – 30% sodium silicate reduces the water absorption of WCCA by 23 – 40% (Spaeth & Djerbi Tegguer, 2013). A pozzolanic slurry containing silica fume, coal fly ash and nano- SiO_2 can form a less porous

layer surrounding the WCCA and suppress water penetration. Coated WCCA had 21 – 25% less water absorption and 0.2 – 0.9% higher apparent density than untreated WCCA (Shi et al., 2018). Direct carbonation of waste concrete aggregates forms CaCO_3 on the surface and in the open pores. This acts as a filler to facilitate the nucleation of cement hydration products and reacts with the aluminate to form monocarbonate AFm with strong pore-filling properties (Feng et al., 2022; Jiang, Shen & Poon, 2022). One route is wet carbonation, where the waste aggregates are exposed to CO_2 in an aqueous medium. The mechanism is illustrated in Figure 2.1. Portlandite in the old cement paste dissolves first, producing Ca^{2+} which can combine with the CO_3^{2-} in solution to deposit CaCO_3 on the surface of aggregates. After the portlandite is consumed, C-S-H dissolves, which further densifies the surface layer by forming more CaCO_3 . Ca-depleted silica gel and partially decalcified C-S-H phase are consequently generated and form a silica-rich middle layer. The core will be the inert aggregate and unreacted C-S-H phase (Jiang, Shen & Poon, 2022). This core-shell structure of carbonated waste concrete aggregates has reduced water absorption and enhanced binding strength (Jiang, Shen & Poon, 2022; Fang et al., 2021a).

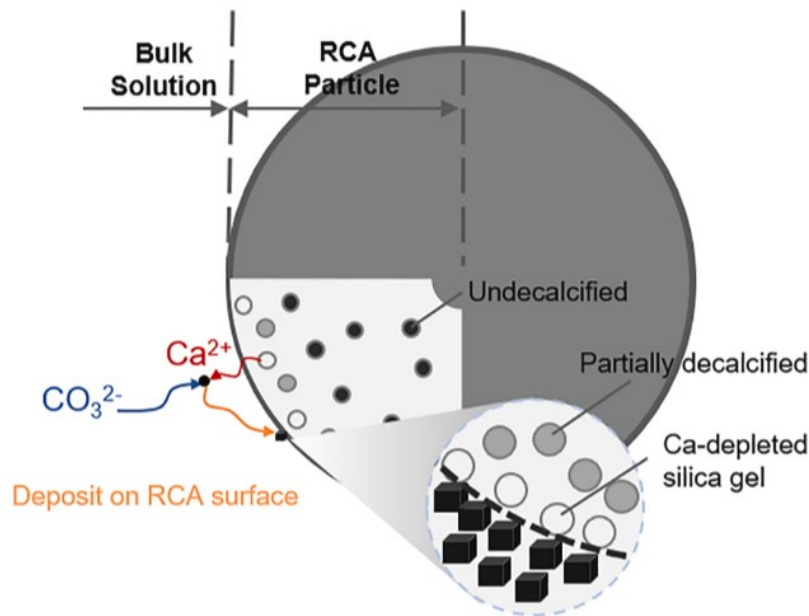


Figure 2.1 The mechanism of wet carbonation of waste concrete aggregates described by surface coverage model (Jiang, Shen & Poon, 2022).

The other route is bio-carbonation, which uses the metabolism of selected bacteria which generate carbonate ions. Grabiec et al. used bio-deposition of CaCO_3 by bacteria species *S. pasteurii* to reduce the water absorption of waste concrete aggregates. The bacteria were mixed with waste concrete

aggregates and then CaCl_2 and urea were added to provide a calcium and carbonate source. After 5-day treatment, the water absorption ratio was reduced by 14 – 22%, depending on the particle size and w/c ratio of the concrete (Grabiec et al., 2012).

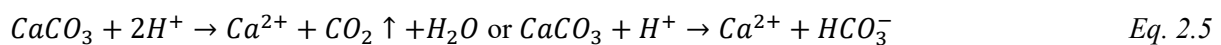
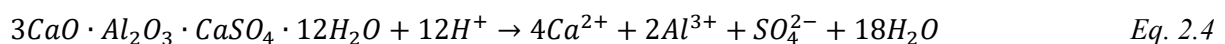
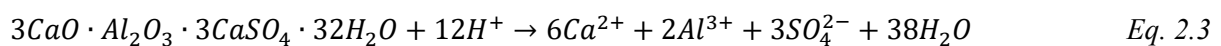
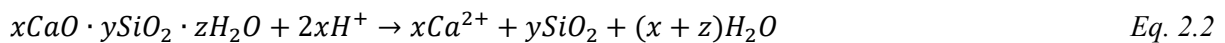
Strengthening old cement paste also impacts the strength and durability of concrete containing WCCA. Treatment with water repellents is reported to reduce the chloride penetration and carbonation depth but has a negative effect on the 28-day compressive strength. This is attributed to the retarding of hydration by the hydrophobic surface of treated recycled aggregates (Zhu et al., 2013). Combined treatments involving soaking in sodium silicate and coating in silica fume densifies the ITZ between old and new cement mortar by pozzolanic reaction. This results in an increase of 33 – 50% in the compressive strength of concrete compared to untreated WCCA. The chloride penetration resistance of concrete containing treated WCCA was also improved by 52 – 64% compared to the concrete containing natural aggregates (Bui, Satomi & Takahashi, 2018). A pozzolanic slurry can provide sites for fast hydration due to the smaller particle size of pozzolan compared to cement particles. An increase in 28-day compressive strength of 18 – 55% and a decrease in chloride penetration coefficient of 33– 84% compared to untreated WCCA is achieved by impregnating the WCCA in silica fume, coal fly ash and nano-silica slurries, with silica fume producing the best results (Shi et al., 2018). Fang et al. carbonated WCFA in aqueous solution using pure CO_2 gas under ambient pressure and temperature for 10 minutes. After carbonation, the water absorption of the WCFA was reduced by 2% and replacing virgin sand by 50% carbonated WCFA did not change the compressive strength of mortars (Fang et al., 2021a).

Most strengthening methods densify the old cement paste, and this improves the quality of waste concrete aggregates and increases the strength and durability of waste aggregate concrete. However, this method has some limitations. In most cases the recycled aggregates treated by strengthening methods retain a higher water absorption ratio than natural aggregates. Mortar containing recycled aggregates still had lower compressive strengths compared to mortar containing natural aggregates. Other issues associated with paste strengthening methods are long reaction time, temporary effect and difficulty in optimization (Feng et al., 2022; Grabiec et al., 2012; Bui, Satomi & Takahashi, 2018).

2.1.2 Removing the old cement paste

Removal of the adhered cement paste can be achieved through physical and chemical methods. Physical methods involve peeling off the cement paste from the aggregates, by applying mechanical or thermal forces. Vertical eccentric grinding, horizontal grinding, jaw crusher, impact crusher and hammer mills have been designed for this purpose (Feng et al., 2022). Particle shaping technologies, in which the recycled aggregate particles collide with each other under centrifugal force to remove the adhered paste and refine the particle shape, have also been reported, and this was found to be effective at reducing the water absorption by 55% and it improved the compressive strength by 9% (Pepe et al., 2014). Heating has also been applied for further quality improvement of recycled concrete aggregates. Decomposition of Ca(OH)_2 and dehydration of C-S-H phase occur at high temperature, weakening the bonding strength of the adhered paste, enabling improved paste removal (Feng et al., 2022). The physical methods can be simply operated. However, they are energy intensive, and they may damage the aggregates and equipment (Lippiatt & Bourgeois, 2012; Feng et al., 2022). The water absorption of the recycled concrete aggregates after treatment remains significantly higher than that of natural aggregates, and the compressive strength of recycled aggregate concrete remains lower than that of natural aggregate concrete (Pepe et al., 2014; Pedro, de Brito & Evangelista, 2015).

Alternative chemical removal methods can be applied to recycled concrete aggregate. As hydrated cement paste is mainly composed of portlandite (Ca(OH)_2), C-S-H phase ($x\text{CaO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O}$), ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$), AFm ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$) and small amount of limestone (CaCO_3) which are alkaline, it can be dissolved in acid solutions, as shown in the chemical reactions outlined in equations 2.1 – 2.5:



Acid dissolution efficiency is influenced by the type of acid, the concentration of the acid, the liquid to solid (L/S) ratio and the reaction time (Tam, Soomro & Evangelista, 2021). The effect of temperature has not been studied in acid leaching of waste concrete, but temperature was reported to have no significant impact on the acid treatment of other types of alkaline industrial waste, including cement kiln dust and blast furnace slag (Kim et al., 2017b; Kunzler et al., 2011; Chu et al., 2019). This is probably due to the low activation energy of the reaction between acid and alkaline industrial waste (Chu et al., 2019).

Recycled concrete aggregates have been leached using 0.1 mol/L HCl, H₂SO₄ and H₃PO₄ solutions for 24 hours, to determine the suitable leaching agent for paste removal (Tam, Tam & Le, 2007). It was found that HCl leaching resulted in a greater reduction in the water absorption of recycled aggregates, while H₂SO₄ leaching led to greater improvement in the 28-day compressive strength of mortar containing recycled aggregates.

In a similar experiment, recycled concrete fine aggregates have been reacted with 1:10 HCl and H₂SO₄ for 48 hours (Kim et al., 2017a). Contrary to the previous study, the 28-day compressive strength of mortar containing H₂SO₄ leached recycled aggregate was lower than that of mortar containing HCl leached recycled aggregate. This is because the reaction between H₂SO₄ and the calcium-bearing species in adhered cement paste generates gypsum (CaSO₄), which has a water solubility of 0.24g/100mL and precipitates in the recycled aggregates. In the early stages of cement hydration, the gypsum crystals can fill the pores and voids, increasing the density and strength. Excess gypsum will react with calcium aluminate to form ettringite, the undesirable expansion of which not only increases the porosity and decreases the strength but also causes swelling and cracks in concrete that adversely affects durability (Scrivener, 2003). Although HCl seems to be more effective for adhered cement paste removal, the chloride ions can accelerate the corrosion of steel reinforcements in concrete (Kim et al., 2017a). The pH of the recycled aggregates remained alkaline (8.55 – 9.35), indicating the leaching conditions need to be optimised (Tam, Tam & Le, 2007). Also, the use of strong acids can introduce safety and operation issues. Large amounts of wastewater can be generated from washing the recycled aggregate and this may cause additional environmental concerns.

Apart from strong acids, the viability of weak acids as a leaching agent has also been investigated. Ammonium salts, e.g. ammonium chloride (NH_4Cl), ammonium acetate ($\text{CH}_3\text{COONH}_4$) and ammonium nitrate (NH_4NO_3), are also gaining attention because of their weak acidity and potential to be recycled through a pH swing process (Mehdizadeh, Mo & Ling, 2023; Jo et al., 2014). Leaching efficiency is lower than when using acids. A study used 2 mol/L NH_4Cl solution at an L/S ratio of 10 mL/g and 85 °C to leach hydrated cement paste, which is a model system for waste concrete fines. After 1 hour of leaching, 65.7% of the calcium in the cement paste was extracted (Mehdizadeh, Mo & Ling, 2023). In a similar study comparing the Ca extraction efficiency of NH_4Cl , $\text{CH}_3\text{COONH}_4$ and NH_4NO_3 , the highest value was 70% for 1.0 mol/L NH_4NO_3 (Jo et al., 2014). In comparison, using acetic acid (CH_3COOH) gives a Ca extraction ratio of at least 80 %. CH_3COOH is also preferred because no adverse effects of acetate ions on the concrete strength and durability have been reported (Wang et al., 2017).

Recycled aggregates were soaked in 1, 3 and 5 % acetic acid solutions for 1, 3 and 5 days. 1-day of leaching using 1% acetic acid gave the best results. The water absorption of recycled aggregates was reduced by 17% and the compressive strength of mortar containing recycled aggregates was improved by 25% compared to mortar containing untreated recycled aggregate (Wang et al., 2017).

To further improve the efficiency of cement paste removal, hybrid methods have been used including chemical-mechanical, chemical-thermal and acid-carbonation treatments (Santha Kumar & Minocha, 2018; Kazmi et al., 2019; Santha Kumar et al., 2019). Among these methods, pre-heating the waste concrete aggregates at 600°C followed by acid leaching gives the most reduction in water absorption (up to 73 %). This is due to the cracks and increased brittleness caused by the dehydration of old cement paste (Santha Kumar & Minocha, 2018). Compared to single methods, hybrid methods are more effective at enhancing the physical and mechanical properties of recycled concrete aggregates. However, these are complicated methods, requiring long operation times which increases energy consumption and associated cost and CO_2 emissions.

Although most of the existing research has used long reaction time (normally 24 hours), and generated by-products including silica-rich residue (SR) and acidic wastewater, which can bring additional environmental issues, the acid leaching method is more efficient than strengthening and physical

removing processes because of its potential to produce clean reusable aggregates. There is also potential for the carbonation of the calcium-rich leachate to form value added products. There is therefore an urgent need to optimize the acid leaching parameters and valorise the by-products formed.

2.2 Extracting novel SCM from waste concrete

As discussed in section 1.1, apart from aggregates, recycling waste concrete also generates a fine powder, WCP. This contains more hydrated cement paste compared to WCCA and WCFA. Because hydrated cement is inert to re-hydration, WCP is mainly reused as a filler (Poon et al., 2023). Therefore, activating the old cement paste in WCP is key to the development of circular concrete.

Equation 2.2 shows that acid treatment of C-S-H phase extracts Ca^{2+} and produces silica. Most research on wet carbonation uses ^{29}Si and ^{27}Al NMR to study the evolution of the silica-containing phase. The coordination of silicate chain in the anhydrous clinker is Q^0 and that in C-S-H phase is mainly Q^1 and Q^2 , as illustrated in Figure 2.2. As calcium being removed, the silicate condenses to form amorphous silica gel with Q^3 and Q^4 configurations (Shen et al., 2022; Jiang, Shen & Poon, 2022). The aluminium phase in the old cement includes AFm and C-A-S-H gel, which are also reactive in carbonation, forming amorphous alumina and alumina-silica gels (Shen et al., 2022). As wet carbonation can be regarded as extracting Ca^{2+} by carbonic acid, these mechanisms are applicable to the Ca extraction processes using other acids.

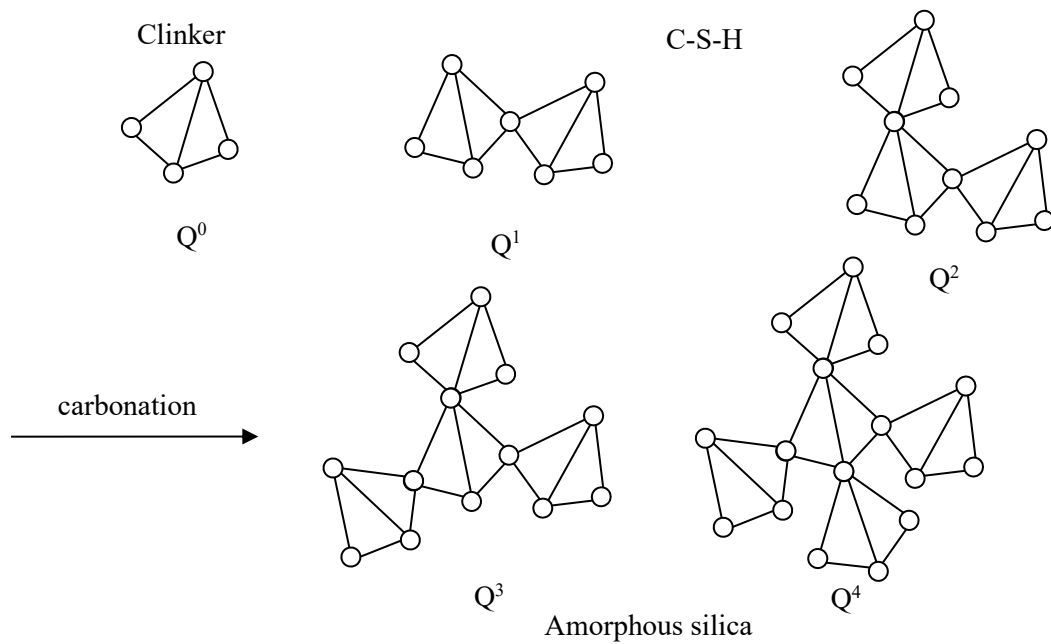


Figure 2.2 Change of the polymerisation degree of silica during the wet carbonation process.

The formation of silica-alumina gel is also governed by the pH of the solution. The relationship of the logarithm of silica gelation time (t) and the pH in the solution is an N-shaped curve shown in Figure 2.3. In strong acids such as HCl and H₂SO₄, dissolved silica is most stable at a pH of around 1.4. In weak acids such as CH₃COOH, it is most stable at a pH range of around 3.8 and most unstable at pH values around 8.5 (Tai, 1963). Al³⁺ also starts precipitating when the pH is above 5 (Cronan, Walker & Bloom, 1986). The endpoint pH of acid leaching of waste concrete reported so far were all higher than 3.2, which is favourable for silica gelation. Therefore, the acid dissolution of old cement paste generates an amorphous silica-alumina gel. Compared to crystalline silica and alumina, this amorphous gel is easier to be activated in alkaline environments, namely cementitious system. Therefore, it can be potentially used as an SCM. This provides insight into ways to improve the value of WCP.

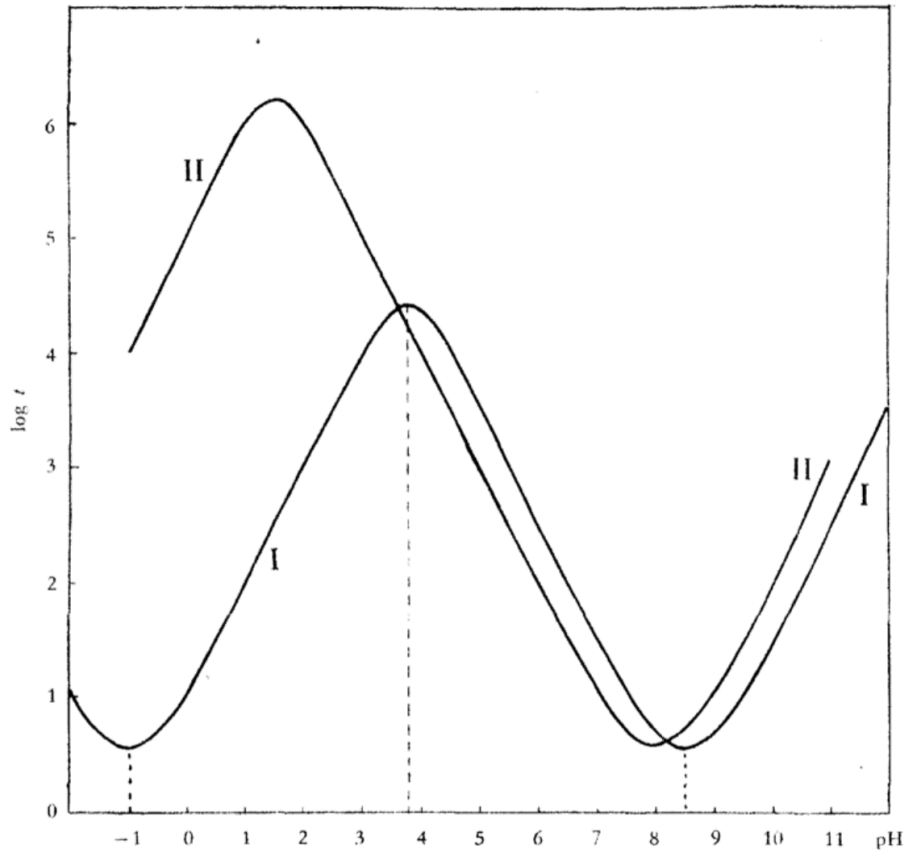


Figure 2.3 Curve of $\log(t)$ vs pH of silicic acid in (I) acetic acid and (II) HCl environment (Tai, 1963). x-axis: pH; y-axis: log of time of silica gelation ($\log t$).

The increase in temperature will also enhance the polymerization of silica gel, especially at low pH values (Alexander, 1954). In previous research using ammonium sulphate $[(\text{NH}_4)_2\text{SO}_4]$ to leach GGBFS at temperatures between 30 and 100°C, the gelation of silica started at 50°C and the gelation ratio increased to 98% at 100°C (Chu et al., 2019). Similar studies also observed the gelation of silica gel from the acetic acid leaching solutions of GGBFS at 60 to 70°C (Song et al., 2018; Teir et al., 2007).

The effect of directly wet carbonated WCP on the hydration kinetics, fresh properties and mechanical performance of composite cement has been extensively investigated. Isothermal conduction calorimetry shows that carbonated WCP promotes the dissolution of the clinker phases and accelerates sulphate depletion due to the high amount of alumina gel. However, it does not affect alite hydration (Zajac et al., 2020). Secondary C-S-H formed from the reaction of portlandite and the amorphous alumina-silica gel at earlier ages (less than 28 days) than coal fly ash (after 90 days), indicating its significant pozzolanic reactivity (Zajac et al., 2020). Carbonated WCP has a negative effect on workability.

Rheological data showed that at the same clinker replacement ratio, carbonated WCP leads to around 80% higher shear stress than untreated WCP (Ouyang et al., 2020). Unlike carbonated WCCA and WCFA covered by CaCO_3 , the surface of carbonated WCP is covered by silica-alumina gel. This is characterised by a similar zeta potential to C-S-H and quartz (Ouyang et al., 2020). Silica-alumina gel has a high surface area, thus the specific surface area of carbonated WCP ($20 - 40 \text{ m}^2/\text{g}$) is higher than commonly used SCMs such as GGBFS and FA (about $1 \text{ m}^2/\text{g}$). This leads to increased water absorption, which subsequently lowers the workability of concrete containing the composite cement (Poon et al., 2023). Due to the pozzolanic reaction induced by silica-alumina gel and the stabilisation of ettringite and monocarbonate, the porosity of the composite cement paste is reduced, and the compressive strength is improved (Lu et al., 2018). At 28 days, the compressive strength of paste containing 20% of carbonated WCP with a water/binder ratio of 0.4 was 12.1% higher than that containing 100% Portland cement and 36.4% higher than that with 20% untreated WCP (Lu et al., 2018).

Fewer studies have focused on the use of silica- and alumina-rich by-products from acid leaching of waste concrete as an SCM. HCP has been leached with NH_4Cl , acetic acid and HCl and the SR characterized. SR from NH_4Cl and HCl leaching contains crystalline $\text{Ca}(\text{Mg}, \text{Fe})$ -aluminosilicate and zeolite phases. This is due to the increased dissolution of Mg, Al, Fe and Si in the presence of Cl^- and their recrystallisation at elevated pH. In contrast, SR from acetic acid leaching is almost amorphous with small amounts of brownmillerite (C_4AF) present (Mehdizadeh, Mo & Ling, 2023). This may indicate acetic acid leaching can improve the pozzolanic reactivity of SR.

Silica-based SCM and silica-alumina composite have been produced from the acid leaching residue of serpentine $[(\text{Mg}, \text{Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4]$, lizardite $[\text{Mg}_3\text{SiO}_5(\text{OH})_4]$, olivine $[(\text{Mg}, \text{Fe})_2\text{SiO}_4]$ and GGBFS (Benhelal et al., 2018; Song et al., 2018; Sanna et al., 2012; Shanks et al., 2024). Thus, investigating the potential of acid leaching of waste concrete to deliver these valuable silica-based materials will be important to fill the research gap.

2.3 Extracting CaCO_3 from waste concrete

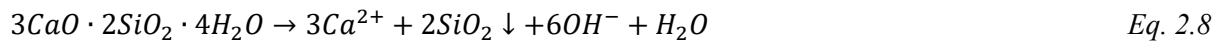
According to equations 2.1 – 2.4, the aqueous solution from acid leaching of waste concrete contains large amounts of Ca^{2+} , and this has huge potential as a CO_2 sink. Mineral carbonation of the Ca-rich

leachate causes CO₂ to be sequestered permanently in CaCO₃, a stable solid mineral. This not only reduces the carbon footprint in the lifecycle of concrete but also avoids the leakage risk and monitoring costs related to the geological CO₂ storage method (Chang et al., 2017a). By tuning the polymorphism of the CaCO₃ formed, value-added products can be obtained from this method.

2.3.1 Carbonation methods

There are two routes for the carbonation of waste concrete. These are direct carbonation and indirect carbonation. Direct carbonation involves mixing waste concrete with water or moisture and exposing the mixture to a CO₂ atmosphere or CO₂ bubbling. There are three stages that occur in this process, as shown in equations 2.6 – 2.10 (Ho et al., 2020).

(1) The dissolution of Ca²⁺ from waste concrete:



(2) The dissolution of CO₂ under highly alkaline environment:



(3) The precipitation of CaCO₃:



As discussed in section 2.1.1, the porous structure of WCCA and WCFA can be strengthened by the in-situ precipitation of CaCO₃ during direct carbonation. WCP has smaller particle size, usually less than 150 µm, and more hydrated cement paste, and therefore larger amount of CO₂ can be sequestered at a higher rate. The carbonated WCP contains pozzolanic aluminosilicate gel and CaCO₃. Therefore, direct carbonation is suitable for developing low-carbon construction materials from waste concrete.

Direct carbonation can be divided into three categories based on the amount of liquid phase. These are wet carbonation, semi-wet carbonation and semi-dry carbonation.

Wet carbonation uses a high water/solid (w/s) ratio, normally above 5 mL/g (Zajac et al., 2022). The setup is presented in Figure 2.4. W/s ratio, CO₂ concentration and temperature are the main influencing factors. Lowering the w/s ratio from 100 to 20 mL/g increases the pH from around 12 to 13, the concentration of Ca²⁺ from around 100 to 670 mg/L and the amount of dissolved CO₂ from 3.7 to 21.4 g, and this improves the carbonation efficiency from 0.19 to 0.22 gCO₂/gWCP (Ho et al., 2020). An increase in the CO₂ concentration from 5 to 30 % results in a substantial decrease in the maximum pH from 12.5 to 6.5. This leads to the re-dissolution of CaCO₃ to soluble Ca(HCO₃)₂ and reduces the carbonation efficiency (Ho et al., 2020). Increasing the temperature from 25 to 60°C results in higher diffusion coefficient of CO₂ and rate of reaction, therefore increasing the CaCO₃ content in WCFA from 24.5% to 28.8% (Jiang et al., 2023).

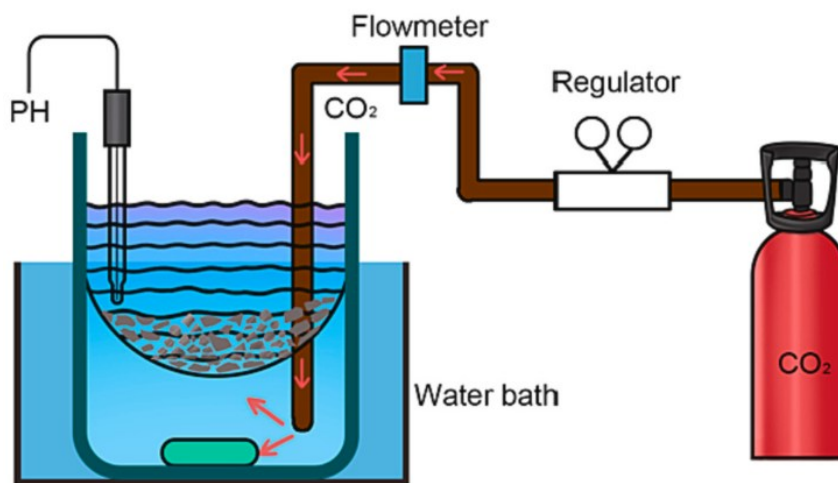


Figure 2.4 A typical experimental setup of wet carbonation (Jiang et al., 2023).

Semi-wet carbonation is mainly used to improve the carbonation rate of waste concrete aggregates. It involves the simultaneous reaction of waste concrete aggregates with micrometre-sized drops of water and CO₂, as shown in Figure 2.5. Compared to wet carbonation, this process generates ACC and poorly crystallised calcite with smaller particle size (0.2 – 1 µm). Adding NaHCO₃ into the water mist increases the pH and the CO₂ dissolution ratio, and this improves the rate and amount of CaCO₃ precipitation (Gao et al., 2024).

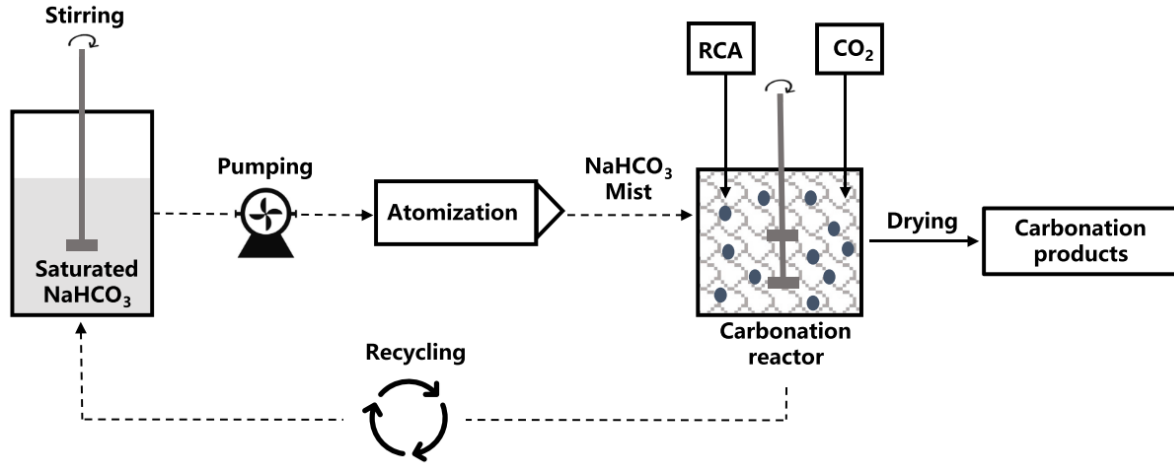


Figure 2.5 Schematic of the semi-wet direct carbonation process (Gao et al., 2024).

Semi-dry carbonation exposes waste concrete to CO_2 under a relative humidity (RH) of 50 – 100% (Zajac et al., 2022). A typical experimental setup is shown in Figure 2.6. This process is predominantly controlled by RH. The carbonation degree remains low and steady across the RH range from 50 to 80%. More amorphous calcium carbonate (ACC) and aragonite start to form when the RH is lower than 90 %. When the RH rises to 100%, the carbonation rate is higher, and the carbonation degree increases by 3 times compared to 80% RH. This is because under 100% RH all the pores in WCP are completely saturated with water, while only pores smaller than 0.1 μm are water-saturated under lower RH (Zajac et al., 2022). CO_2 concentration and the particle size of the raw material slightly affect the semi-dry process. Decreasing the CO_2 concentration from 25 to 5% reduces the carbonation rate but does not affect the carbonation degree. Using coarser materials also decreases the early-age carbonation rate (Zajac et al., 2022). Although being faster and reducing the amount of wastewater, the amount of CO_2 absorbed in this process is only 44 – 78% of that using the wet carbonation process due to decreased CO_2 diffusion. As a result, the carbonation potential of cementitious materials is not fully exploited.

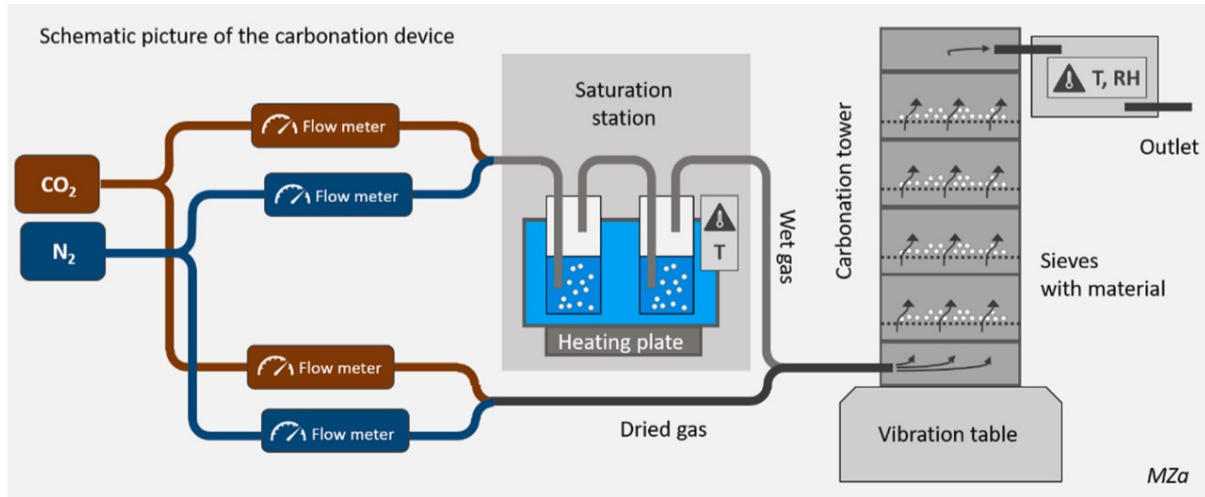


Figure 2.6 Experimental setup of semi-dry direct carbonation of WCP (Zajac et al., 2022).

Indirect carbonation includes a pH-swing process, where Ca is initially dissolved under acidic conditions, and then precipitated as CaCO_3 under alkaline conditions (Chen et al., 2017; Jo et al., 2014; Vanderzee & Zeman, 2018). To completely extract the available Ca in waste concrete, acidic extractant is added stoichiometrically or in excess. Therefore, the pH in the Ca^{2+} -rich solution after leaching is acidic or neutral, where formation of CO_3^{2-} is unfavourable. Waste concrete contains other metal elements such as Mg, Al and Fe which also dissolve in acidic solution (Vanderzee & Zeman, 2018). Thus, an alkali, including $\text{Ca}(\text{OH})_2$, NaOH, KOH and $\text{NH}_3\cdot\text{H}_2\text{O}$ is added to raise the pH to > 9 to stabilize the CO_3^{2-} and precipitate the Mg-, Al- and Fe-hydroxides to maximise the yield and purity of CaCO_3 (Shuto et al., 2015; Mehdizadeh, Mo & Ling, 2023; Vanderzee & Zeman, 2018). When a strong acid such as HCl is used in the leaching step, significant amounts of silica is also extracted into the solution due to the low pH. Dissolved silica is likely to precipitate with Ca^{2+} forming amorphous calcium silicates under $\text{pH} > 9$, and this is removed with the metal hydroxides, hence reducing carbonation efficiency (Vanderzee & Zeman, 2018). Therefore, controlling the dissolved Si is important to maintain a high carbonation efficiency.

After pH adjustment, the Ca^{2+} -rich solution is suitable for CO_2 sequestration. This is carried out in a simple gas-liquid reactor. The carbonation reaction is usually completed in around 30 min, which is faster than the direct carbonation (normally above 1 hour), because of the higher amount of free Ca^{2+} in solution (Shuto, Nagasawa & Yamasaki, 2014; Mehdizadeh, Mo & Ling, 2023; Vanderzee & Zeman, 2018). Because carbonation is exothermic and the solubility of CO_2 decreases with increased

temperature, higher temperature inhibits the CaCO_3 precipitation (Kim & Jung, 2020). An increase in temperature from 25 to 70°C causes about a 20% reduction in carbonation efficiency (Mehdizadeh, Mo & Ling, 2023). An increased CO_2 pressure from atmospheric pressure (0.025 MPa) to 1 MPa also does not increase the carbonation efficiency, because the adsorption-desorption of CO_2 in aqueous solution is already equilibrated at atmospheric pressure (Mehdizadeh, Mo & Ling, 2023). These indicate that indirect carbonation can be readily operated under room temperature and atmospheric pressure.

Despite that direct carbonation processes are less complicated and uses less chemicals, the product is a mixture of CaCO_3 , aluminosilicate gel and inert phases (e.g. C4AF and quartz). Therefore, the application of the directly carbonated waste concrete is limited to cement and natural aggregate replacements, which have relatively low economic value. Alternatively, indirect carbonation has the advantage of separating pure CaCO_3 from the aluminosilicate gel and inert phases. By tuning the polymorph types of CaCO_3 , value-added carbon negative products can be extracted from waste concrete.

2.3.2 Controlling CaCO_3 polymorphs

CaCO_3 has four common types of polymorphs: amorphous calcium carbonate (ACC), spherical vaterite, needle-like aragonite and rhombohedral calcite, as shown in Figure 2.7. It also has hydrated forms including monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$), ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) and hemihydrate ($\text{CaCO}_3 \cdot 1/2\text{H}_2\text{O}$) which are unstable under ambient conditions (Zou et al., 2019). The solubility product (k_{sp}) values of ACC, vaterite, aragonite and calcite at 25 °C and 1 atm are 9.10×10^{-7} , 1.22×10^{-8} , 4.61×10^{-9} and 3.31×10^{-9} , respectively (Rodriguez-Navarro et al., 2015; Chen et al., 2024). Therefore, the order of thermodynamic stability of CaCO_3 polymorphs at 25 °C is calcite > aragonite > vaterite > ACC. In aqueous solutions under normal conditions, the reaction of Ca^{2+} and CO_3^{2-} forms unstable ACC first. Then the ACC loses the structural water and re-organises to form metastable vaterite. Finally, the vaterite transforms into calcite via dissolution-reprecipitation following Ostwald ripening (Rodriguez-Blanco, Shaw & Benning, 2011; Chen et al., 2024).

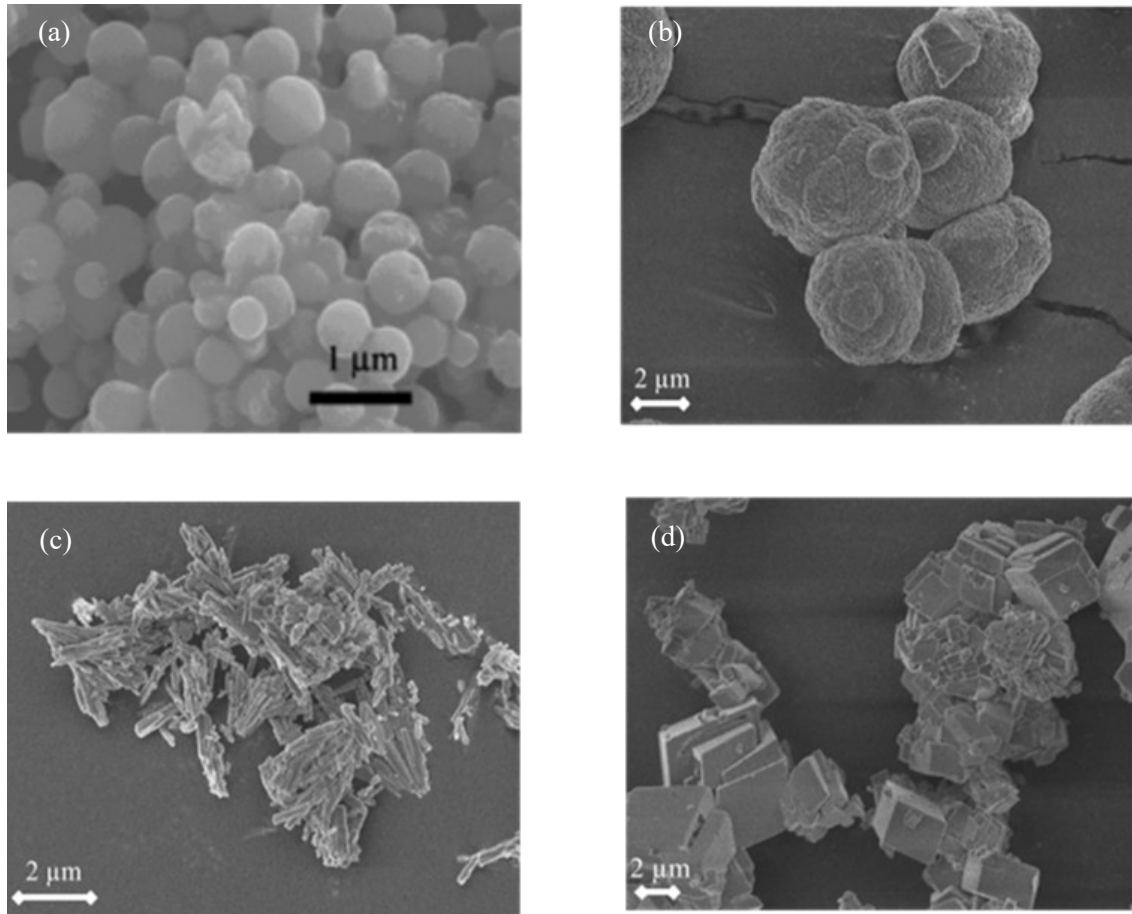


Figure 2.7 SEM images of (a) ACC (Shen et al., 2006), (b) vaterite, (c) aragonite and (d) calcite (Zhao et al., 2023b).

In most of the reported indirect carbonation processes on waste concrete, without purposely controlling the reaction parameters, a mixture of vaterite and calcite is formed (Jo et al., 2014; Chen et al., 2017; Vanderzee & Zeman, 2018). To selectively produce pure CaCO_3 polymorph, several controlling factors have been studied. Temperature affects the polymorph of CaCO_3 thermodynamically. Jiang et al. investigated this effect using a double-jet method to precipitate CaCO_3 from CaCl_2 and Na_2CO_3 solutions. The preferred polymorph at various temperature without aging was vaterite and calcite (0°C), pure vaterite (25°C), vaterite and aragonite (38°C) and pure aragonite (50°C) (Jiang et al., 2009). As the surface energy of aragonite is 1.25 times that of vaterite, and twice that of calcite, aragonite is stabilised by elevated temperature (De Leeuw & Parker, 1998).

pH controls the kinetics of CaCO_3 polymorph precipitation. CO_2 dissolves rapidly at higher pH, creating a high supersaturation, where the nucleation of CaCO_3 is improved (Sheng Han et al., 2006). The nucleation rate, J , is described by the Gibbs-Thomson formula (equation 2.11):

$$J = A \exp[-B(\ln S)^{-2}]$$

Eq. 2.11

where A is a constant, S is the supersaturation ratio, and B is related to the interfacial energy of CaCO_3 polymorphs. J is determined by B and S of a polymorph. When S is high, the effect of B is more dominant. Therefore vaterite, with a higher interfacial energy, will precipitate more rapidly than calcite at higher pH (Kitamura, 2002; Sheng Han et al., 2006; Li et al., 2018). pH and time interactively affect the purity of CaCO_3 polymorph. Lower pH creates lower supersaturation and hence a lower nucleation rate, so the formation of a stable polymorph is slowed down (Trushina et al., 2014). Sheng Han et al. precipitated vaterite by bubbling CO_2 into CaCl_2 solution for 10 minutes while continuously adding ammonia to keep a constant pH. The calcite content increases with increasing pH, because vaterite nucleates faster, hence leaving more time for the polymorphic transformation to take place (Sheng Han et al., 2006). Similar results were obtained by other research reacting CO_2 with the Ca-rich solution from NH_4Cl leaching of HCP. Vaterite was the dominant phase formed at $\text{pH} < 9$, and calcite was formed at pH between 9 and 11 after 30 minutes of carbonation (Mehdizadeh, Mo & Ling, 2023).

Chemical additives can stabilise certain type of CaCO_3 polymorph by inducing kinetic constraints and altering the thermodynamic stability (Chang et al., 2017b). This facilitates the selective precipitation of CaCO_3 for value-added applications. Sodium tripolyphosphate (STPP) is reported to delay the polymorph transformation of ACC from several hours to more than 3 days through interaction with Ca^{2+} (Cheng et al., 2024). Mg^{2+} can stabilize ACC by forming a MgCO_3^0 complex with dissolved CO_3^{2-} , hence retarding the re-precipitation of crystalline CaCO_3 . This effect becomes more significant with the increase of Mg^{2+} concentration. Improved ACC stability from 30 seconds to 11.5 hours was observed when MgCl_2 concentration increased from 0 to 1.1 mol/L (Konrad et al., 2018). Mg^{2+} can substitute part of the Ca^{2+} in the crystal lattice of calcite. Mg^{2+} is readily hydrated because it has a smaller ionic radius than Ca^{2+} , which decreases the stability of calcite. If Mg/Ca molar ratio is less than 3, aragonite is thermodynamically more stable than calcite. At higher Mg/Ca ratios, monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$) is favoured (Zhang et al., 2012). Sr^{2+} can promote aragonite formation. It has a larger size than Ca^{2+} and can coordinate with nine CO_3^{2-} ions, rather than six for Ca^{2+} . This modifies the surface energy and makes aragonite more stable than calcite (Sunagawa, Takahashi & Imai, 2007). Organic additives, such as amino acids, proteins, polymers and alcohols, are reported to stabilise vaterite. The electron intensive $-\text{C}=\text{O}$ or $-\text{OH}$ groups will temporarily attract or coordinate with Ca^{2+} , generating a local area with

increased supersaturation. As discussed above, nucleation of vaterite is preferred at high supersaturation. Furthermore, these compounds can be absorbed onto the surface of vaterite through hydrogen bonding, and the dissolution-reprecipitation of vaterite to calcite is inhibited (Li et al., 2002; Trushina et al., 2014).

By controlling the reaction conditions, metastable CaCO_3 polymorphs can be selectively precipitated. Given the different shape, surface conditions and reactivity of CaCO_3 polymorphs, each of them has unique applications which will be summarised in the next section.

2.3.3 Applications of CaCO_3 polymorphs

Calcite is the most thermodynamically stable polymorph and is widely used as a filler or coating material in the plastics, sealants, paint and paper industries (Kirboga & Oner, 2013; Chang et al., 2017a). Aragonite whiskers are used as a filler in the production of lightweight plastics (Ramakrishna et al., 2016). Vaterite, due to its porous surface, hydrophilicity and biocompatibility, has potential in regenerative medicine and drug delivery (Trushina et al., 2022, 2014).

Most importantly, CaCO_3 is mainly used in the construction industry. Calcite is the predominant phase in limestone, which is not only the feedstock material for cement production, but also a widely used SCM. It provides growth sites for cement hydration products as a filler and stabilises AFm by reacting with C3A forming hemi- or monocarbonate. It is also a major component in calcined clay limestone cement (LC^3), which contains 50% clinker, 30% calcined kaolinite clay, 15% limestone and 5% gypsum. This binder can achieve comparable strength to Portland cement while achieving a lower embedded CO_2 emission (Scrivener et al., 2018).

Aragonite, due to its needle-like shape, can serve as a micro fibre to improve the flexural strength of cement paste by bridging cracks. A 10 % substitution of CEM I by aragonite in the paste can increase the flexural strength by 20.9% at 7 days and 9.3% at 28 days, compared to pure CEM I paste (Li, Cao & Yin, 2019). When deposited on the surface of recycled concrete aggregates, aragonite can form an interconnected 3D structure with the new cement hydration products and react with the aluminate phases to form mono- and hemi-carbonate AFm. These improve the frictional bonding strength between carbonated recycled concrete aggregates and new mortar, which is 28 – 34% higher when using

untreated aggregates (Shen et al., 2023a). In addition, aragonite can be used to adjust the rheology of cement paste. The needle-shaped aragonite has an interlocking effect to bind the cement particles and hydration products. In addition, aragonite tends to form clusters, which interrupt the flow of the surrounding solvent more strongly than calcite and vaterite, as illustrated in Figure 2.8. During mixing, the aragonite needles can adapt their orientation to the direction of shear. This results in a high static yield stress and low dynamic yield stress. Cement paste containing 20% aragonite has a static yield stress around 7 times as that of pure CEM I paste. This helps to lower the pressure by self-consolidation and has implications for the 3D printing of concrete (Zhao et al., 2023b).

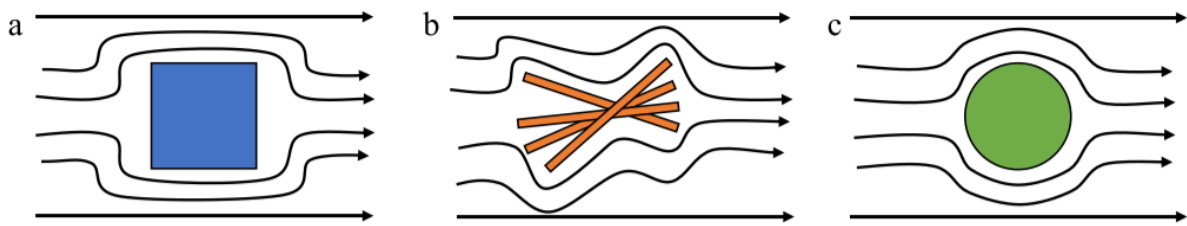


Figure 2.8 Illustration showing the effect of shapes of (a) calcite (b) aragonite and (c) vaterite on the flow lines of the surrounding fluid (Zhao et al., 2023b).

Vaterite has a spherical shape and porous surface, and this impacts on the flow properties of blended cements. It reduces the flow compared to pure CEM I paste because of higher surface area ($65.7 \text{ m}^2/\text{g}$) compared to cement ($1.3 \text{ m}^2/\text{g}$). However, it improves the flowability of LC^3 cements, due to its spherical shape. The flow of LC^3 paste containing 15 % vaterite is 50 mm higher than that containing the same amount of calcite (Li et al., 2024). In contrast, vaterite is reported to have negligible effect on the rheology of cement paste (Zhao et al., 2023b). It should be noticed that the specific surface area of vaterite was $65.7 \text{ m}^2/\text{g}$ in Li et al.'s research and $2.09 \text{ m}^2/\text{g}$ in Zhao et al.'s research. The D_{50} of the latter vaterite is $8.8 \text{ }\mu\text{m}$, which is slightly higher than the former ($5.92 \text{ }\mu\text{m}$) and this is unlikely to cause such a large difference (Zhao et al., 2023b; Li et al., 2024). This suggests that synthesis conditions affect the properties and the applications of vaterite. Due to the higher solubility of vaterite compared to aragonite and calcite, its phase transformation in aqueous media occurs more readily. This feature makes it possible to turn vaterite into targeted polymorphs, forming designated microstructure. Vaterite has been compressed and activated using a solution containing 0.1 mol/L magnesium chloride (MgCl_2) and strontium chloride (SrCl_2) at a liquid/solid ratio of 0.35 and cured in the same solution at 40 to 80°C (Hargis et al., 2021). Under these conditions, spherical vaterite gradually transforms into needle-like

aragonite through a dissolution-precipitation process, which develops an interlocked ‘honeycomb’ microstructure with high strength (Figure 2.9). The fastest compressive strength development was 40 MPa at 3 days under 80°C curing. Lower temperatures slow down the process, but a compressive strength of 40 MPa can still be achieved within 14 days which is faster than normal concrete (Hargis et al., 2021). This self-cementing property indicates that vaterite has massive potential value as a sustainable carbon-negative binder. Therefore, extracting vaterite from waste concrete is a focus of the research reported in this thesis.

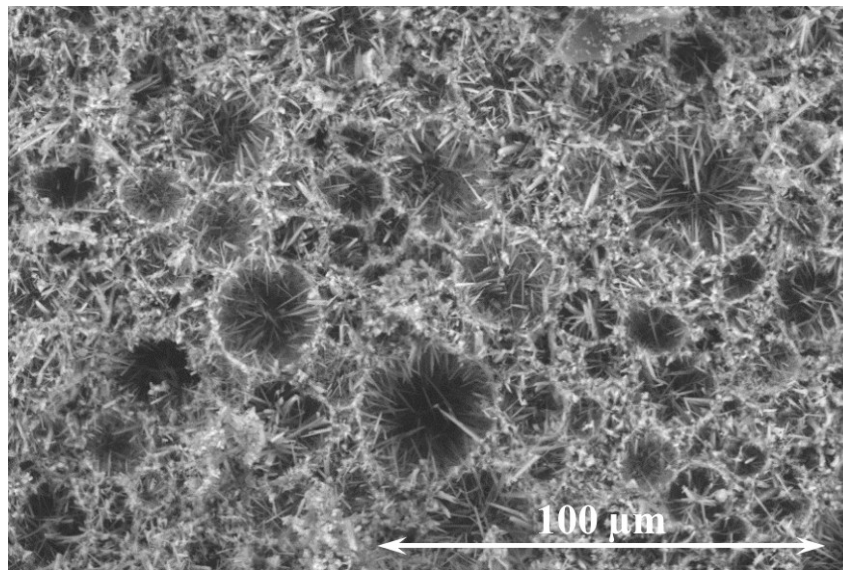


Figure 2.9 SEM image showing the microstructure of hardened vaterite cement (Hargis et al., 2021).

ACC is unstable and is subject to polymorphic transformation in the presence of moisture within days, which limits its long-term storage and use (Konrad et al., 2016). Therefore, it is mainly reported as a precursor for producing different crystalline CaCO_3 . However, a recent study found that by retarding the polymorph transformation of ACC using STPP, more nano-sized poorly crystalline CaCO_3 can be formed in the matrix, and this has the binding effect through structure rearrangement to form strong cross-linking structures. A compressive strength of 70 MPa can be achieved by 3-day carbonation of wollastonite with 0.1% STPP (Cheng et al., 2024).

2.4 Summary of research gaps

Among all the approaches for waste concrete recycling, indirect carbonation has the advantage of effectively producing clean sand and aggregate, activating the hydrated cement paste and producing pure CaCO_3 phase with tuneable properties. However, the optimisation of the reaction parameters, including acid concentration, liquid/solid ratio, temperature and reaction time has not been extensively studied. The behaviour of other major elements in waste concrete, namely Si, Al and Fe is still unclear. Furthermore, actual waste concrete is often contaminated by other wastes, such as crushed brick, ceramic and waste plasterboard, which influences the physical properties and chemical composition. Some research used actual waste concrete (Chen et al., 2017; Mun, Cho & Kwon, 2017; Kim et al., 2017a), but others used hydrated cement paste to simulate the waste concrete (Mehdizadeh, Mo & Ling, 2023; Shen et al., 2021). The effect of the difference between actual and simulated waste concrete on the reaction parameters and quality of recycled products, especially silica-rich SCM, needs to be investigated.

The investigations on utilisation of the SR from indirect carbonation of waste concrete as an SCM is also limited. A detailed assessment of pozzolanic reactivity and the effect on hydration is needed. Because acid dissolution of cement paste extracts pure silica-alumina gel, the specific surface area of SR is expected to be higher than for directly carbonated waste concrete. Therefore, engineering this product to reduce its specific surface area and improve the workability of SR-containing concrete is also key to the viability of this technology.

The technical feasibility of extracting vaterite from cementitious material by indirect carbonation has been shown. The controlled polymorphic transformation of vaterite to aragonite gives unique interlocked fibrous structure with connected porosity. Previous research has attempted to reduce the porosity and increase the strength of aragonite binder by compaction, but this added complexity to the process. High porosity provides the possibility of developing new low-carbon lightweight functional materials with acceptable strength, but good heat adsorption and thermal insulation properties. The effect of process parameters such as liquid-to-solid ratio and curing time on the mechanical performance, physical properties, phase composition, microstructure and thermal properties of the CaCO_3 binder needs to be investigated to optimise the production and application of this new material.

3 Methodology

This chapter describes the main materials, experimental and characterisation methods adopted in this research that uses an indirect carbonation process. In the first step, waste concrete is leached by an acetic acid solution. This results in a slurry. Recycled sand, an aluminosilicate gel-rich residue and a Ca^{2+} -rich solution are obtained by liquid/solid separation. Ammonia solution is added to the Ca^{2+} -rich solution to increase the pH so that CO_2 exists as carbonate ions. Then, CO_2 is bubbled through the solution to precipitate vaterite. The process diagram is presented as Figure 3.1.

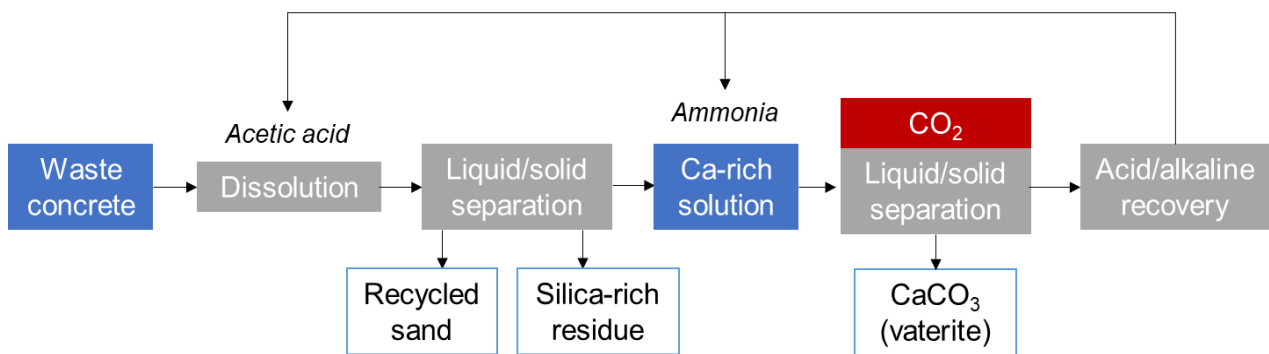


Figure 3.1 Process flow diagram showing the indirect carbonation of waste concrete.

3.1 Materials

Representative samples of waste concrete fines (WCF) were collected from a waste concrete recycling facility in Shanghai, China. The age and strength of the original concrete cannot be determined because several sources of waste concrete had been processed at the same recycling facility. The as-received particles were dried in an oven at 80°C until the mass remained constant and the material passing a 4.75 mm sieve was used in subsequent experiments. This material contains WCFA and WCP.

CEM I 52.5N (Breedon, UK) was used to prepare ground hydrated cement paste (HCP). It has a D_{10} , D_{50} and D_{90} values of 2.8, 14.2 and 45.6 μm and a specific gravity of 3.10, respectively. Siliceous sand from Thames Valley with a particle size less than 5 mm was used as the fine aggregate in mortars. It has a water content of 0.2 %.

Hydrated cement paste (HCP) was prepared at a water/cement ratio of 0.4, using CEM I 52.5 N and tap water. The paste was thoroughly mixed and cast into a polyethylene bag, which was sealed to prevent water evaporation, and rotated for the first 24 hours of hydration at 20 rpm on a tube rotator, to prevent bleeding. After 90-day curing at 20°C, the cement paste was removed from the polyethylene bag and dried at 40°C to constant mass, to remove any moisture. It was then crushed and ground using a mortar and pestle, and the material passing through a 300 µm sieve was used in subsequent experiments.

Commercially available SCMs used in this research were Class-F coal fly ash (FA, Heidelberg Materials), silica fume (SF, Elkem) and ground granulated blast furnace slag (GGBFS, Heidelberg Materials). Ground limestone (GL, Heidelberg Cement) and Thames Valley quartz sand ground to less than 150 µm (QZ) were used as inert references.

The chemical compositions of WCF (determined by titration), CEM I 52.5N, HCP, FA, GGBFS, SF, GL and QZ are summarised in Table 3.1.

Table 3.1 Chemical compositions of the raw materials used in this thesis.

Material	Weight percentage (%)									
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	LOI
CEM I 52.5N	63.6	18.5	5.5	2.8	3.7	1.0	0.7	0.2	-	3.2
WCF*	12.5	63.4	8.2	3.3	0.5	-	-	-	-	9.7
HCP	48.0	13.5	4.1	2.2	2.8	0.8	0.3	0.1	0.1	27.4
FA	4.9	52.5	26.4	6.6	0.4	1.6	1.4	0.5	0.9	2.3
SF	0.3	93.3	0.4	0.2	0.4	0.5	1.6	0.3	0.2	2.3
GL	54.4	0.9	0.2	0.3	-	0.9	-	-	-	43.1
QZ	5.5	82.4	1.4	1.1	0.1	0.3	0.5	0.2	0.1	4.1

* The contents of MgO, K₂O, Na₂O and P₂O₅ are either non-detectable or very complicated using titration method, and they have little effect on the reaction process, so these components in WCF are not measured.

3.2 Acetic acid leaching

99.7 % glacial acetic acid (VWR, UK) was diluted with de-ionized water to form acetic acid solutions with different concentrations, and these were used to leach the WCF and HCP. The experimental setup is shown in Figure 3.2. For every batch experiment, waste concrete and acetic acid solutions were mixed in a glass beaker by magnetic stirring at 300 rpm on a heating plate. For experiments at high temperature, the beaker was immersed in a water bath. The pH and temperature of the mixture were monitored using a pH meter (Hanna HI-8424) and a glass thermometer. After acetic acid leaching, the slurry containing Ca^{2+} -rich solution and SR was extracted by simple pouring, leaving the recycled sand with higher density in the bottom of the beaker. The Ca^{2+} -rich solution and SR were further separated by using a centrifuge at 3000 rpm for 5 minutes (Eppendorf 5910 Ri) and vacuum filtration through hardened ashless filter paper (Whatman 541). The detailed experimental conditions are presented in chapters 4 and 5.

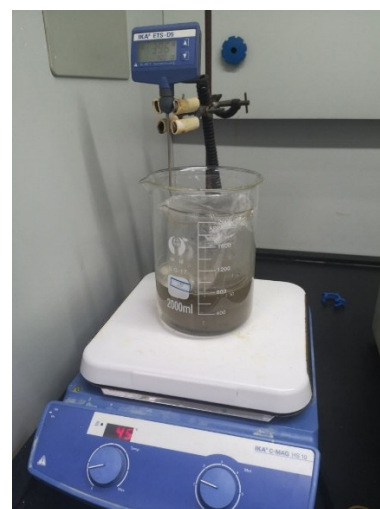
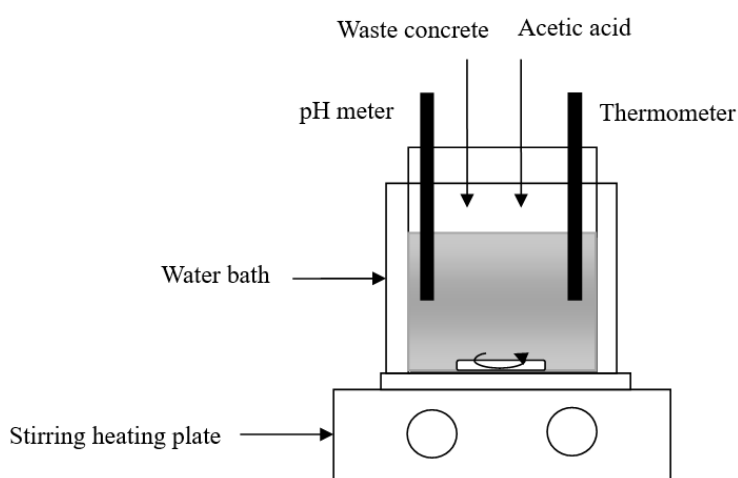


Figure 3.2 (Left) schematic and (right) real photograph showing the experimental setup of acetic acid leaching of waste concrete.

3.3 Carbonation

Before carbonation, the pH of the Ca^{2+} -rich solution needs to be raised to remove the impurity ions such as Al, Fe and Mg and stabilise CO_2 as CO_3^{2-} . $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ precipitate at pH values of 4, 8 and 10.5, respectively (Park et al., 2021). Therefore, 25% ammonia solution (VWR, UK) was added to the Ca^{2+} -rich solution until the pH reached 10.5. The hydroxides formed in this step and are removed by centrifugation at 4000rpm for 5 minutes (Eppendorf 5910 Ri) and vacuum filtration through glass fibre filter paper (Whatman GF/A).

The carbonation of Ca^{2+} -rich solution follows a gas-liquid route, as shown in Figure 3.3. 100% pure CO_2 gas from a cylinder containing compressed CO_2 was bubbled through the Ca^{2+} -rich solution through a pumice stone, which diffuses the gas into small-sized bubbles. This increases the contact area between the CO_2 gas and the solution and enhances the dissolution of CO_2 . A floating element flow meter was used to control the gas flow rate. The mixture was stirred magnetically. A pH meter (Hanna HI-8424) was used to monitor the change of pH during the reaction. Detailed reaction conditions are given in chapter 7.

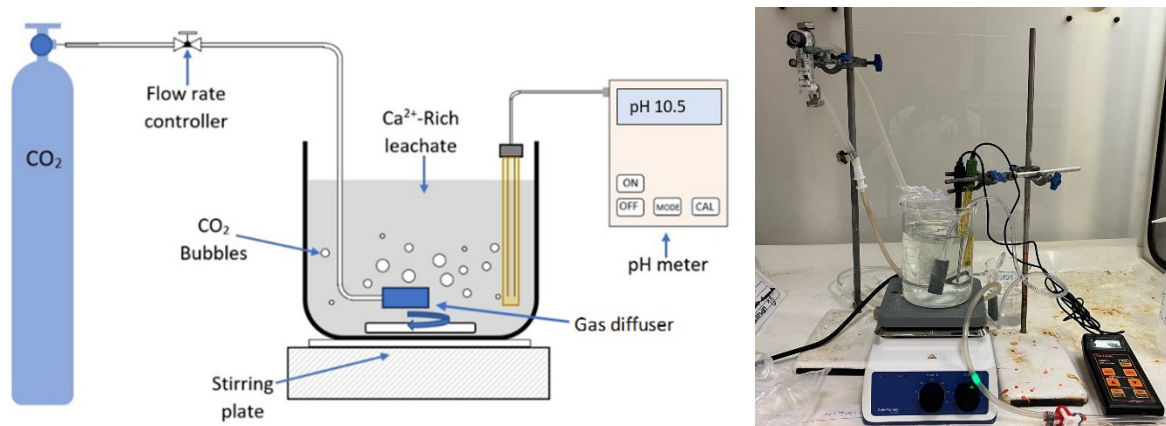


Figure 3.3 (Left) schematic and (right) real photograph of the carbonation experimental setup.

3.4 Assessment of pozzolanic reactivity

3.4.1 Frattini test

The Frattini test is a well-established and widely adopted pozzolanic reactivity assessment method, which directly determines the concentration of Ca^{2+} and OH^- dissolved from a mixture of CEM I and the test pozzolan (Donatello, Tyrer & Cheeseman, 2010). It is carried out following the method specified in BS EN 196-5. 6 g of test pozzolan and 14 g of CEM I 52.5N are mixed with 100 mL of deionised water in a plastic container and incubated at 40°C for 8 days. The supernatant was collected by vacuum filtration through glass fibre filter paper (Whatman GF/A) and stored in a sealed conical flask to avoid carbonation. After the supernatant is cooled to room temperature, the concentrations of OH^- is measured by titration with 0.1 mol/L HCl solution using methyl orange indicator, and the concentration of Ca^{2+} measured by titration with 0.025 mol/L EDTA solution using Patton and Reeder's indicator. The results reported are average values of duplicate tests and are plotted against the solubility curve of $\text{Ca}(\text{OH})_2$ at 40°C plotted from equation 3.1.

$$[\text{CaO}](\text{mmol/L}) = \frac{350}{[\text{OH}^-] - 15} \quad \text{Eq. 3.1}$$

Where $[\text{CaO}]$ is the concentration of Ca^{2+} expressed as dissolved CaO, and $[\text{OH}^-]$ is the concentration of OH^- ranging from 0 to 90 mmol/L. Data points below the curve indicate that the test material is pozzolanic.

3.4.2 Rapid, relevant and reliable (R^3) test

The R^3 test is a recently developed method for assessing the pozzolanic reactivity of materials. Compared to traditional methods, it uses a simpler system to extract the reaction of the test pozzolan, avoiding the influence of clinker. The results show good correlations between hydration heat, chemically bound water and compressive strength of mortars containing test pozzolans (Avet et al., 2016).

The R^3 method based on isothermal conduction calorimetry as specified in ASTM 1897-20 is used to determine the pozzolanic reactivity of the SRs and commercially available SCMs. A potassium solution is prepared by dissolving 4 g of potassium hydroxide (KOH) and 20 g of potassium sulphate (K_2SO_4) in 1 L of deionized water. This is to simulate the pH and chemical environment of real concrete pore solution. 10 g of test pozzolan, 30 g of $Ca(OH)_2$, 5 g of $CaCO_3$ and 54 g of potassium solution are thoroughly mixed by manually stirring for 5 minutes, forming a homogeneous paste. For every sample, 15 g of the paste was added to a glass ampoule and tested in the isothermal conduction calorimeter (TAM Air) at 40°C for 7 days. 9.4 g of deionized water is used as reference. The 7-day cumulative heat of the test samples is normalised against the mass of test pozzolan, and the resulting curves are recorded.

3.5 Fresh and hardened properties of mortar

3.5.1 Mixing, casting and curing of mortar

The mortar samples were prepared according to the BS EN 196 regime. CEM I or composite cements containing SCMs were mixed with water using a paddle mixer (CONTROLS, USA) at low speed for 30 seconds. Sand was steadily added during the following 30 seconds. Then the mixing was stopped for 90 seconds, and the mortar adhered to the wall was removed with a spatula and placed in the middle of the mixing bowl. Finally, the mortar was mixed at high speed for 60 seconds.

After mixing, the fresh mortar was poured into 50 mm or 20 mm cubic steel moulds and compacted on a vibration table for 2 minutes. For mortars containing untreated SR and SF, extended vibration for 4 minutes was applied to compensate for the low workability. Excess mortar on the perimeter of the mould was wiped off. Then the moulds were covered with a layer of plastic sheet and placed in the high humidity curing room ($T = 20^\circ\text{C}$, $RH = 95\%$). After 24 hours, the mortars were demoulded and cured by submerging in a tank containing saturated lime water at 20°C until the required test age. The detailed mixing proportions and curing ages are specified in chapters 5 and 6.

3.5.2 Workability – flow table test

The workability of fresh mortars was measured using the flow table test following BS EN 1015-3. In this test a truncated conical mould is placed at the centre of the flow table. Around 400 g of the fresh mortar is introduced into the mould in two layers. Each layer is compacted 10 times with a steel tamper to achieve good compaction. Any excess mortar is removed by a spatula. Then, the mould is slowly removed in the vertical direction and the mortar is spread on the flow table by jolting for 15 times. The diameter of the mortar is measured by a calliper in two perpendicular directions. The flow of the mortar is expressed as the average of two measurements.

3.5.3 Compressive strength test

The compressive strength of mortar specimens was tested following BS EN 196-1. In this, the mortar specimens are extracted from curing at the required ages and the excess water on the surfaces is removed using a paper tissue. The exact length and width of the surface to be loaded is measured by a calliper. The compressive strength of 50 mm cubic specimens is tested on a compression machine (CONTROLS Automax) with a loading rate of 0.3 MPa/s. The compressive strength of 20 mm cubic specimens is measured on a universal testing machine (Instron 5980) with a loading rate of 0.5 mm/min. The results are calculated by dividing the failure load by the area of loaded surface and are presented as an average of six replicates.

3.6 Characterisation methods

3.6.1 Chemical composition – X-ray fluorescence (XRF)

Chemical compositions of powder samples were determined by XRF. Before measuring the chemical composition, the solid samples were ground using a mortar and pestle and sieved using a 300 µm mesh. After all the material passes through the sieve, the collected materials were dried in an oven at 60°C until reaching constant mass.

The loss on ignition (LOI) of solid samples was determined by calculating the mass change of samples after drying under 60°C and heating to 1050°C for 1 hour, using equation 3.2:

$$LOI(\%) = \frac{m_{60} - m_{1050}}{m_{60}} \times 100 \quad \text{Eq. 3.2}$$

Where m_{60} is the mass of sampled dried under 60°C and m_{1050} is the mass of sample heated under 1050°C.

XRF measurements are carried out on samples prepared by the fused bead method. In this, around 0.9 g of sample is mixed with 9 g of lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) flux and 10 drops of 25 g/L lithium iodide (LiI) releasing agent solution. The mixture is fused at a temperature of 1050°C for 30 minutes in a furnace (Claisse LeNeo Fluxer), generating glass beads. The chemical composition of the sample beads is measured on an XRF bulk analyser (Malvern PANalytical Zetium) equipped with wavelength dispersive detection system, using the Omnia programme. The results are expressed in oxides contents.

3.6.2 Phase composition – X-ray diffraction (XRD)

The phase composition of solid materials was determined by X-ray diffraction (Malvern PANalytical Empyrean) with Bragg-Brentano geometry configuration. The powder samples are back loaded into a 16 mm diameter sample holder to minimise the preferred orientation. For qualitative XRD analysis, the samples are measured using Cu $K\alpha$ radiation at 40 mA and 45 kV and scanned from 5° to 70° 2 θ at a scanning speed of 0.044°/min. Internal standard method is used for the quantitative analysis of phases. The powder samples are mixed with 100% pure corundum (Al_2O_3) at a mass ratio of 4:1 by grinding in an agate mortar. In some cases, pure zincite (ZnO) is used instead of corundum to minimise the overlapping of peaks. The measuring conditions are the same as used in the qualitative analysis. The diffraction patterns are analysed using Highscore Plus 4.0 software with ICDD PDF-4 database. Rietveld refinement is used to quantify the amount of crystalline and amorphous phases in the samples. The amorphous content is calculated from equation 3.3:

$$W_{am}(\%) = \frac{5}{4} \left(100 - 20 \times \frac{100}{W_s} \right) \quad \text{Eq. 3.3}$$

where $W_{am}\%$ is the amorphous content of the sample and W_s is the content of internal standard determined by Rietveld refinement.

3.6.3 Particle size distribution – laser diffraction

The particle size distribution of powder samples was measured using laser diffraction (Malvern PANalytical Mastersizer 3000). Generally, the samples are added into the dispersant to achieve an obscuration range of 10 – 15% and sonicated for 60 seconds before starting the measurement. Isopropanol is used as the dispersant for measuring anhydrous clinker, and water is used for other materials. The measurements were carried out at a stirring speed of 2400 rpm and repeated 5 times. Different from other materials, SF is sonicated with the dispersant in a sonication bath for 6 hours before measurement to de-agglomerate the particles. The results are presented as distributive and cumulative particle size distribution curves with the D_{10} , D_{50} and D_{90} values specified.

3.6.4 Morphology and phase distribution – scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is used to observe the morphology of powder samples and fracture surfaces, and to assess the phase and elemental distribution of the polished surfaces. A tabletop microscope (Hitachi TM4000 Plus) is used to take low resolution pictures, and a field emission microscope (Zeiss Sigma 500VP FESEM) is used for high resolution pictures and energy dispersive spectrometry (EDS) analysis.

The powder and fracture surface samples are loaded onto the sample holders covered by a layer of conductive tape. They are then coated with a 10-20 nm thin layer of carbon in a sputter coater (Emitech K550X). The images are taken in secondary electrons (SE) mode using an accelerating voltage of 5 kV. The mortar samples are cut using a precision saw (Buehler IsoMet 1000) and dried at 35°C until the mass is stable. After drying, the samples are impregnated in the mixture of epoxy resin and hardener (22:3 weight ratio) in a plastic mould. The entrained gas is removed by vacuum and the impregnated samples are let stand for 24 hours for the resin to harden. The samples are then ground on 220, 500 and 1200 mesh abrasive papers and polished using 3, 1 and $\frac{1}{4}$ μm polishing diamonds. They are loaded onto the sample holders and carbon coated using the same method mentioned above. The polished surface is

observed in backscattered electrons (BSE) mode with EDS mapping to determine the phase and elemental distributions using an accelerating voltage of 15 kV.

3.6.5 Thermal stability – thermogravimetric analysis (TGA)

The thermal stability and phase assemblage of samples was determined using a thermogravimetric analyser (NETZSCH STA 449 F5). The heat flow is measured using differential scanning calorimetry (DSC). For every measurement, around 25 mg of powder sample is added to an alumina crucible and heated from 30 to 1000°C at a heating rate of 10°C/min and an N₂ flow rate of 50 mL/min.

3.6.6 Elemental extraction ratio - inductively coupled plasma optical emission spectrometry (ICP-OES)

The extraction ratios of Ca, Al, Fe and Si during acetic acid leaching of waste concrete were determined by ICP-OES test. Multi-element standard solution containing 1000 mg/L Ca, Al and Fe in 4% nitric acid and Si standard solution containing 1000 mg/L Si in 2% NaOH (VWR, UK) are used to prepare the standard calibration solutions. The calibration set contains 0, 10, 20, 30, 40 and 50 ppm solutions for Ca, Al and Fe, and 0, 1, 2, 5, 10 and 20 ppm solutions for Si in 1 mol/L HNO₃ matrix.

1 mL samples of acetic acid leachate are filtered through a 0.45 µm syringe filter to remove any solid residues. Because the working range of the ICP optical emission spectrometer (PerkinElmer Avio 500) is 0.05 – 100 ppm, the samples are diluted using 1 mol/L HNO₃ solution. For the measurements of Al, Fe and Si, the samples are diluted by 100 times. For the measurement of Ca, the samples are diluted by 1000 times. The standard calibration solutions are measured to establish an accurate relationship between the elemental concentration and the intensity of signal. Finally, the diluted samples are measured on the spectrometer, and the results are presented as the average of three replicated measurements.

3.6.7 Chemical bonding – Fourier transformation infrared spectrometry (FTIR)

The chemical bonding in the powder samples is tested by FTIR using the attenuated total reflection (ATR) mode (Thermofisher Nicolet iS50). In this method, the infrared light travels through a diamond crystal and is reflected by the sample pressed on the crystal. The reflected light is collected by the detector and the absorbance is quantified. The resulting spectra are measured in a frequency range of 400 – 4000 cm⁻¹ and presented as an average pattern of 16 scans.

3.6.8 Specific surface area – N₂ adsorption and desorption (BET)

The specific surface area of samples is measured by N₂ adsorption and desorption using Brunauer-Emmett-Teller (BET) theory. Before measurements, the samples are vacuumed under 40°C for 24 hours to remove the absorbed moisture and gas. The BET surface area of degassed samples is measured on a surface area and porosity analyser (Micromeritics 3Flex 3500) using N₂ gas as the adsorbate and liquid nitrogen as the cryogen.

3.7 Summary

The raw materials, methods and experimental setups of acetic acid leaching and carbonation, the methods for testing pozzolanic reactivity, the methods for testing the properties of mortar and the material characterisation methods including the instruments have been summarised. The reaction conditions, mixing design and sample preparation are different according to the objectives of this research, and will be described in the corresponding results chapters. Due to the influence of covid-19, the work in chapter 4 was conducted at the Changshu Research Institute of East China University of Science and Technology. Therefore, the mixing, casting, curing and testing of mortar specimens and the material characterisation methods in chapter 4 are different from those used in other chapters. To avoid confusion, they are not included in this section and will be individually presented in chapter 4 instead.

4 Clean reusable sand from acetic acid leaching of waste concrete fines

In this chapter, the acetic acid leaching method was used to extract clean recycled sand from waste concrete fines (WCF). The evolution of pH and dissolution of Ca^{2+} under the reaction conditions are studied. The reaction conditions are optimised to maximize the extraction of Ca^{2+} and produce clean reusable recycled sand with comparable properties to virgin sand. This work has been published as ‘Developing circular concrete: Acid treatment of waste concrete fines’ in Journal of Cleaner Production (<https://doi.org/10.1016/j.jclepro.2022.132615>).

4.1 Introduction

Urbanization and infrastructure development have resulted in increasing demand for construction materials, particularly sand and aggregate. Over-extraction of river sand can have extreme environmental consequences that are associated with the depletion of natural resources, changes in channel form, landscape instability and land degradation (Iizuka et al., 2010; Jiang et al., 2019). Therefore, developing technologies that can extract sand from waste concrete so it can be reused is an important research priority.

WCF has previously been used to replace sand in concrete. However, this has high porosity and low density, and it produces weak interfacial transition zones in concrete, causing low strength and poor durability and limiting reuse (Geng & Sun, 2013; Evangelista et al., 2015; Xiao et al., 2013; Khatib, 2005; Zhu et al., 2013).

Different approaches have been used to improve the performance of WCF. One method is to fill the pores in cement mortar adhered to sand particles by carbonation, or by coating particle surfaces with a pozzolanic slurry, water repellent chemicals or bio-deposited calcium carbonate (Shi et al., 2018; Zhu et al., 2013; Zhang et al., 2015; Grabiec et al., 2012; Wang et al., 2020). An alternative approach removes the adhered cement paste by physical and chemical processing, or by using combined

treatments including crushing, freeze-thaw cycling and soaking in acid (Santha Kumar & Minocha, 2018; Santha Kumar et al., 2019; Huang et al., 2020; Kim et al., 2019, 2017a).

WCF consists of sand, cement hydration products including portlandite ($\text{Ca}(\text{OH})_2$), calcium silicate hydrate (C-S-H) gel, ettringite and AFm phases and CaCO_3 due to the CO_2 uptake during the service life, demolition and recycling of concrete. According to equations 2.1 – 2.5, acid treatment produces a Ca^{2+} -rich leachate from these materials. The Ca^{2+} -rich leachate solution is suitable for sequestering CO_2 by forming precipitated calcium carbonate (Sanna et al., 2014).

Hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) have been used to treat WCF (Kim et al., 2017a; Santha Kumar & Minocha, 2018; Song & Ryou, 2014). However, these introduce Cl^- or SO_4^{2-} ions into recycled aggregates that impact on concrete durability. The use of strong acids also introduces various safety and operational issues, with large volumes of water needed to remove Cl^- and SO_4^{2-} ions, generating wastewater, the disposal of which creates additional environmental issues.

The use of WCF as a sand replacement after immersion in acetic acid solutions at ambient temperature for 24 hours has been reported (Santha Kumar et al., 2019). This reduced water absorption of the fines by up to 34 %. The compressive strength of mortar samples containing acid treated concrete fines decreased when the acid concentration exceeded 1 mol/L. An additional thermal treatment at 400 °C for 40 minutes was applied following acid leaching, and this increased the 28-day compressive and flexural strength of mortar samples containing treated fines. Although acetic acid has been applied to treat waste concrete fines, a long reaction time was used and the optimum reaction conditions, including the concentration of acetic acid, liquid/solid (L/S) ratio, time and temperature has not been reported.

In this chapter, WCF is leached with acetic acid at different acid concentration, L/S ratio, temperature and time. The optimal conditions for acetic acid leaching of waste concrete fines to produce clean extracted sand are identified. The properties of recycled sand and mechanical performance of cement mortars containing the recycled sand are evaluated. The potential of the Ca^{2+} rich solution to sequester CO_2 and form CaCO_3 is calculated and the potential for this type of processing to deliver circular concrete discussed.

4.2 Experimental

4.2.1 Raw materials

WCF as described in section 3.1 is used as the raw material. Before characterisation, a representative sample of WCF is ground using a planetary ball mill (Nanda Instrument, China) and sieved using a 150 μm mesh. After all the material passes through the sieve, the collected WCF powder are dried in the oven under 80°C until reaching constant mass. Portland cement P.O 42.5 N (Yangchun Cement, China) and standard quartz sand (Xiamen ISO, China) are used as the fine aggregate and binder for mortar preparation.

The chemical compositions and LOI of solid materials are analysed by titration according to the Chinese standard GB/T 176 (Appendix A), and the data is shown in Table 4.1. The crystalline phases present in WCF are analysed by X-ray diffraction (XRD, Bruker AXS D8 Advance) and thermal stability determined by TG-DSC (Netzsch STA 449), as presented in Figure 4.1 and 4.2.

Table 4.1 Chemical composition of materials used in this chapter, determined by titration.

Material	Percentage (%)					
	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	SO ₃	LOI
WCF	12.5	63.4	3.3	8.2	0.5	9.7
P.O 42.5 N	49.6	28.6	3.4	8.3	2.2	3.3
Recycled sand	2.3	85.9	3.1	5.3	-	1.5

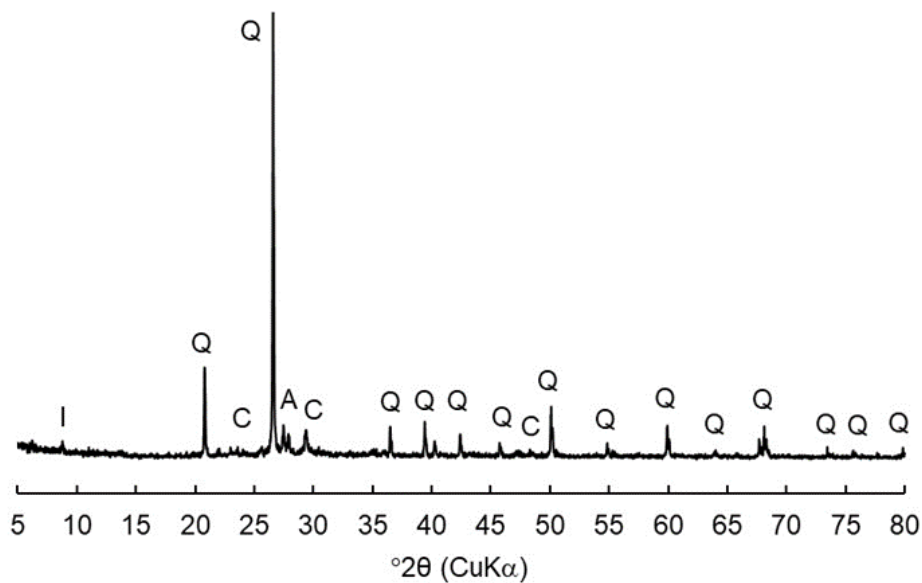


Figure 4.1 XRD data of WCF. Q: Quartz; C: Calcite; A: Albite and I: Illite.

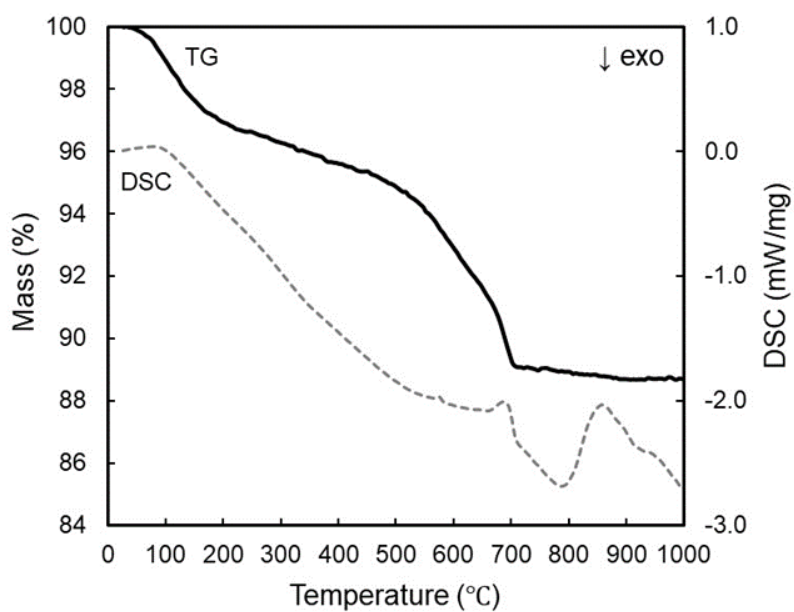


Figure 4.2 TG-DSC curves of WCF.

4.2.2 Acetic acid leaching of WCF

Glacial acetic acid (Shanghai Macklin) is diluted with de-ionized water to form acidic solutions with different concentrations, and these are used to leach the WCF. The acetic acid leaching experiments use the method described in section 3.2.

The effect of acid concentration is investigated by leaching 50 g of samples with 0.4, 0.5, 0.6 and 1 mol/L acetic acid solutions using a liquid/solid (L/S) ratio of 9 ml/g, with the leaching tests run at 20 °C. The effect of L/S ratio is investigated by leaching 50 g of WCF in 250, 350 and 450 mL of acetic acid giving an L/S ratio of 5, 7 and 9 ml/g. The acid concentration (0.6 mol/L) and the temperature (20 °C) are kept constant.

The effect of temperature is investigated by completing tests at 20 °C (control), 40, 60 and 80 °C using a water bath to control the temperature of the reaction vessel. Other conditions are kept constant at 0.6 mol/L acetic acid and an L/S ratio of 7 ml/g.

Duplicate 1 mL samples of leachate are extracted after 10, 30, 60, 120, 180, 240, 300, 360, 420 and 480 minutes using a 2 ml syringe. The leachate samples are filtered through a 0.45 µm filter prior to analysis and the concentration of Ca²⁺ ions in solution determined by titration with EDTA and calcein-methyl thymol blue-phenolphthalein (CMP) indicator according to the Chinese standard GB/T 176 (Appendix A). The Ca²⁺ extraction is calculated using equation 4.1,

$$Ca^{2+} \text{ extraction (\%)} = 100\% \times \frac{m_{Ca}}{M_{Ca}} \quad \text{Eq. 4.1}$$

where m_{Ca} is the mass of calcium element in the leachate, and M_{Ca} is the mass of calcium element in the WCF.

4.2.3 Physical and mechanical properties of recycled sand

After acid leaching the slurry formed was poured into a centrifuge bottle, leaving the higher density sand in the beaker. The collected sand was rinsed with de-ionized water for 5 times to remove any residual leachate and dried at 105 °C to constant mass. The particle size distribution, apparent density, bulk density, void ratio, and water absorption of the extracted sand were determined according to the Chinese standard GB/T 14684, and the results compared to those for new river sand (i.e. standard sand) and the original waste concrete fines.

A flow table test following Chinese Standard GB/T 2419 was used to determine differences in mortar rheology associated with the sand types. Control mortars containing 1350 g of standard sand, 450 g of P.O 42.5 N and 225 g of water at a water/cement ratio 0.5 had a flow of 180 ± 5 mm and this was also achieved using the same water content for test samples containing acetic acid extracted sand. However, an additional 150 g of water, to give a total of 375 g and water/cement ratio of 0.83, was needed to achieve the same flow when preparing test mortars using untreated WCF.

The test mortar mixes containing the three different sands (untreated WCF, standard sand, and recycled sand) were made using the water/cement ratios mentioned above and cast into $40 \times 40 \times 160$ mm moulds. Samples were demoulded after 24 hours and cured in saturated lime solution at 20 ± 2 °C for 7 and 28 days. The compressive strength of these mortars samples was determined according to the Chinese standard GB/T 17671, using six replicates tested in a universal strength testing machine (Wuxi Jianyi Model TYE 300).

4.3 Results

4.3.1 Properties of WCF

According to Table 4.1, WCF contains 12.5 % CaO by weight and therefore the mass of Ca (M_{Ca}) in 50 g of WCF is calculated by equation 4.2:

$$M_{Ca} = 50 \times \frac{12.5}{100} \times \frac{40.08}{56.08} = 4.47 \text{ g} \quad \text{Eq. 4.2}$$

where 40.08 and 56.08 are the molar mass of Ca and CaO (g/mol), respectively.

1 mole of CaO reacts with 2 moles of acetic acid, assuming the CaO exists predominantly as C-S-H and CaCO_3 in the waste concrete fines. As the amount of CaO present in 50 g of waste concrete fines is $4.47/40.08 = 0.11$ moles, the theoretical amount of acetic acid required to react with the CaO in the sample is 0.22 moles. This corresponds to an acetic acid solution of 0.5 mol/L at L/S ratio of 8.8 ml/g for complete reaction. Therefore, a range of acetic acid concentrations, 0.4, 0.5, 0.6 and 1 mol/L, and L/S ratios, 5 – 9 ml/g, were used to optimize the leaching conditions. WCF also has high Al_2O_3 and

Fe₂O₃ contents, which is probably due to the contamination of ceramics, bricks and soil as shown in Figure 4.6(a).

XRD data in Figure 4.1 shows that the most abundant crystalline phase in the waste concrete fines is quartz (SiO₂), due to the strong diffraction intensities of siliceous sand compared to cement hydration products. There are additional small peaks associated with calcite (CaCO₃), albite [(Na, Ca)Al(Si, Al)₃O₈] and illite [(K, H₃O)Al₂Si₃AlO₁₀(OH)₂], which form due to carbonation during the concrete service life and end-of-life recycling (crushing and sieving), and from the residual coarse aggregates, respectively. Although calcite releases CO₂ upon acid leaching, this can be reacted with the Ca²⁺-rich solution and re-sequestered to produce pure CaCO₃. Therefore, this process is applicable to carbonated Ca feedstocks.

The TG-DSC curve in Figure 4.2 shows two major mass losses. The first one is below 200 °C and this is due to dehydration of part of C-S-H, AFm and ettringite. The other, between 500 and 700 °C, is associated with decomposition of calcite and small amounts of dehydrated hydration products and these account for 4.2 % of the total mass. Very little mass loss occurs between 400 and 500 °C, which suggests that the calcium hydroxide originally present in the waste concrete has carbonated during service life or end-of-life recycling (crushing and sieving). The endothermic peak between 800 and 900 °C is related to decomposition of C-S-H to form wollastonite (CaSiO₃).

4.3.2 Ca²⁺ leaching vs acid concentration, L/S ratio, temperature, and time

Figure 4.3 illustrates the variation of pH and calcium extraction with different acetic acid concentrations at a constant L/S ratio of 9 ml/g and a temperature of 20 °C. In all experiments, approximately 92 % of the total Ca²⁺ extraction occurs within the first 3 hours. Increasing acid concentration does not significantly increase the rate of extraction. After 6 hours, the Ca extraction at 0.4, 0.5, 0.6 and 1 mol/L acetic acid are 73.8, 80.6, 84.2 and 84.3 %, respectively. 100 % Ca leaching is not achieved because there is residual Ca in the recycled sand (Table 4.1) and the silica-rich residue (Table 5.1). Leaching beyond 6 hours also only produces a marginal increase of around 1.0 % in leached Ca²⁺.

The endpoint pH decreases with increasing acid concentration. Acid concentrations of 0.4, 0.5, 0.6 and 1 mol/L result in an endpoint pH of 5.4, 4.9, 4.7 and 4.1, respectively. Increasing the acid concentration from 0.6 to 1 mol/L results in almost the same Ca^{2+} extraction ratio but reduces the endpoint pH. The results show that 0.6 mol/L acetic acid is effective at extracting Ca^{2+} from the cement mortar in crushed concrete fines.

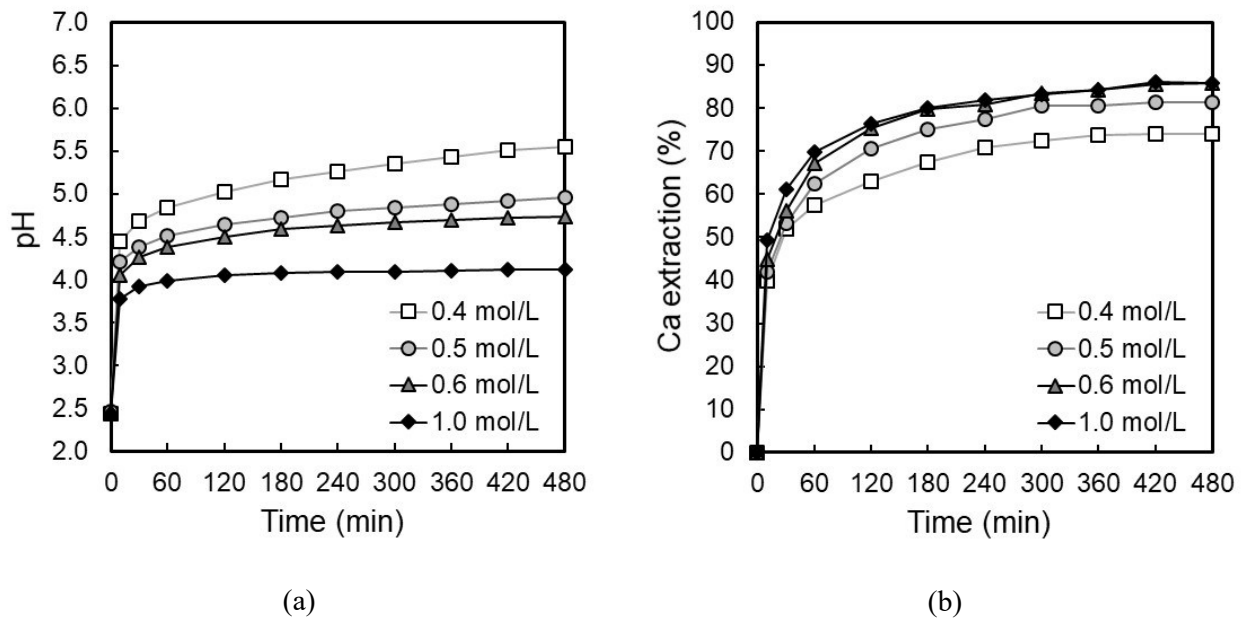


Figure 4.3 Variation of (a) pH and (b) calcium extraction with time at different acetic acid concentrations and constant L/S ratio of 9 ml/g and temperature of 20°C.

Figure 4.4 shows the variation in pH and Ca^{2+} extraction at different L/S ratios with constant 0.6 mol/L acetic acid concentration at a temperature of 20 °C. Approximately 91 % of the Ca^{2+} dissolution occurs within 3 hours and the dissolution plateaus after 6 hours. At 6 hours, the calcium extraction at 5, 7 and 9 ml/g L/S ratio are 71.9, 82.0 and 84.2 %, respectively. The endpoint pH decreases with increasing L/S ratio. L/S ratios of 5, 7 and 9 ml/g result in endpoint pH values of 6.2, 5.0 and 4.7, respectively. The Ca extraction is only slightly increased when the L/S ratio increases from 7 to 9 ml/g. An L/S ratio of 7 ml/g is therefore effective at leaching Ca^{2+} from waste concrete fines. This also reduces the amount of chemicals needed to increase the pH of the leachate prior to carbonation and minimizes the volume of waste solution.

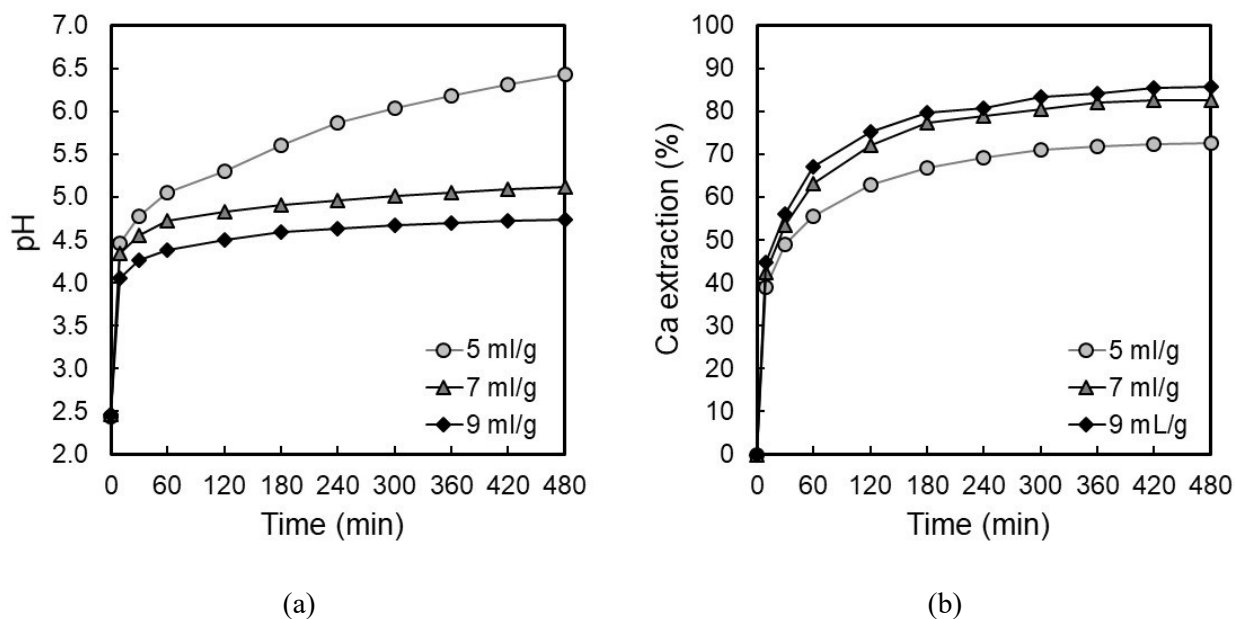


Figure 4.4 Variation of (a) pH and (b) calcium extraction with time at different L/S ratios, and constant acetic acid concentration of 0.6 mol/L and temperature of 20°C.

Figure 4.5 shows the variation of pH and Ca^{2+} extraction at various temperatures using 0.6 mol/L acetic acid and an L/S ratio of 7 ml/g. As the temperature increases, the rate of Ca^{2+} extraction marginally increases, while the extraction potential and pH do not change as the amount of acetic acid was constant. Temperature therefore has a minimal effect on Ca^{2+} leaching.

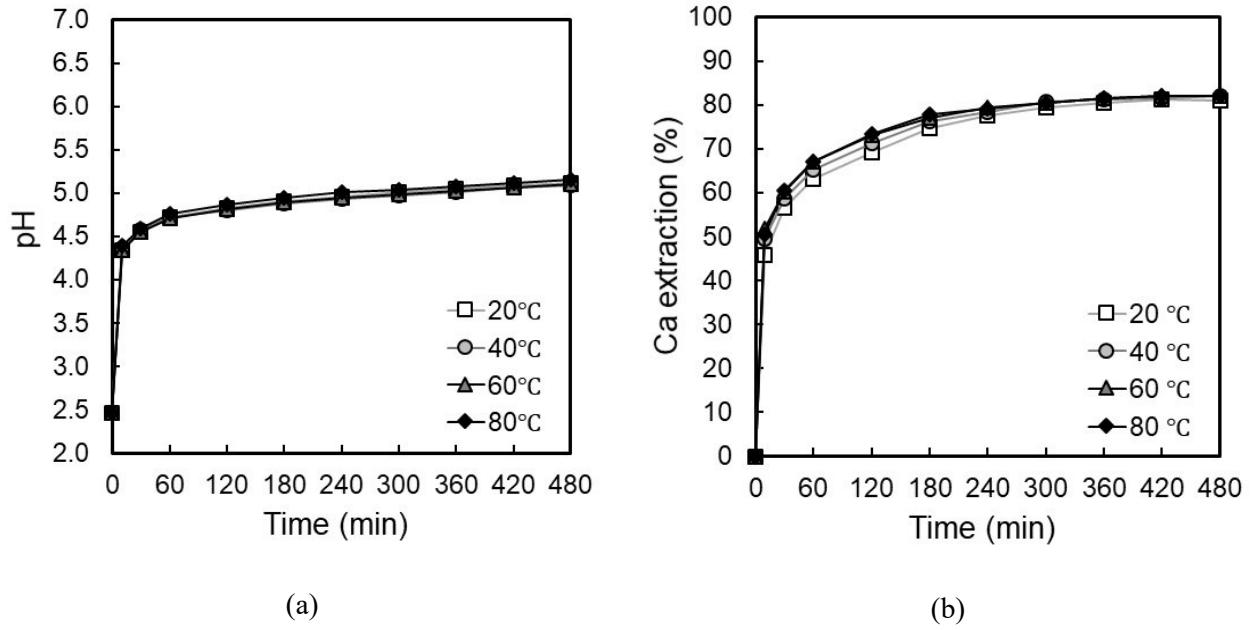


Figure 4.5 Variation of (a) pH and (b) calcium extraction with time at different temperatures, and constant acetic acid concentration of 0.6 mol/L and L/S ratio of 7 ml/g.

4.3.3 Properties and performance of recycled sand

WCF from crushed concrete are shown in Figure 4.6(a). After leaching using 0.6 mol/L acetic acid solution, an L/S ratio of 7 ml/g, and a leaching time of 6 hours at 20 °C with 300 rpm stirring the clean dry sand extracted from the fines is shown in Figure 4.6(b). The chemical composition of the extracted sand is given in Table 4.1. An 82% decrease in CaO content and a 36 % decrease in Al_2O_3 content indicate efficient removal of cement paste and production of clean recycled sand from WCF.

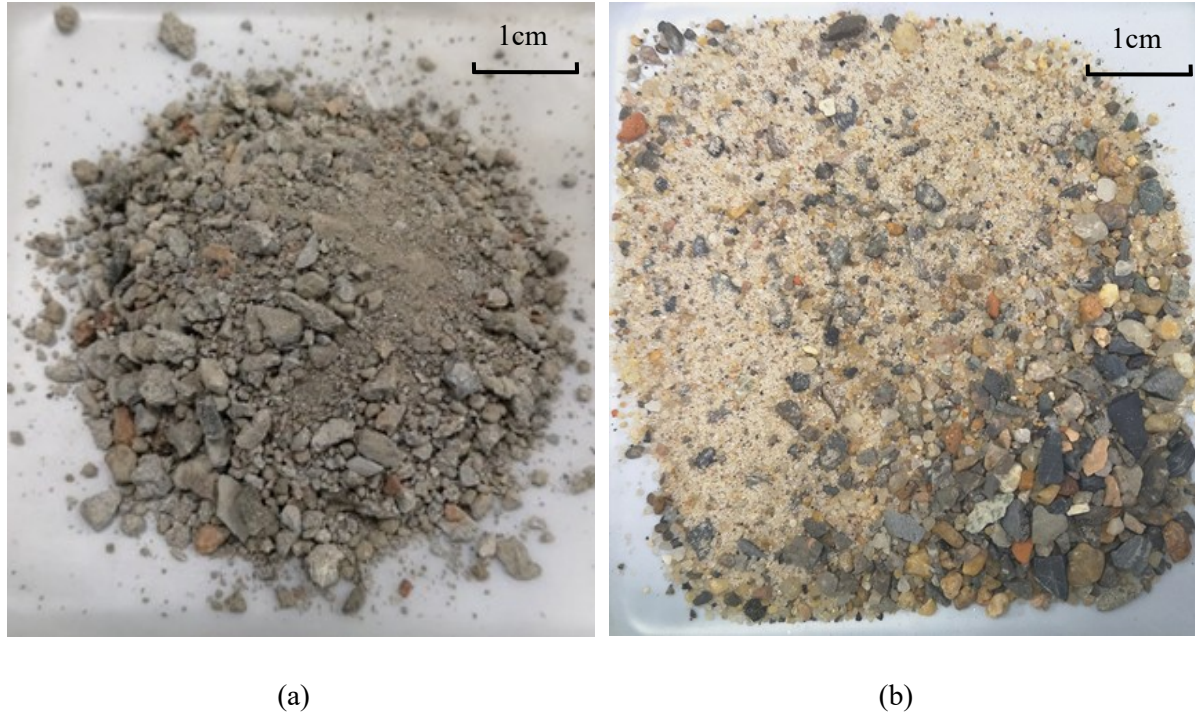


Figure 4.6 (a) WCF and (b) clean recycled sand extracted using the acid leaching process.

The physical properties of standard (river) sand, recycled sand and untreated WCF are compared in Table 4.2. The apparent density, bulk density, void ratio and water absorption of recycled sand are 2660 kg/m³, 1890 kg/m³, 28 % and 1.0 %, respectively. These values are comparable to those of standard sand. In contrast, untreated WCF has much lower apparent and bulk densities (2110 and 1290 kg/m³) and higher void ratio and water absorption (39 % and 13.4 %) due to the porous adhered cement paste. Figure 4.7 presents the particle size distribution data of the three sands. The particle size of waste concrete fines was reduced by removing the attached cement paste via acid leaching.

Table 4.2 Comparison of physical properties of WCF, standard sand and recycled sand obtained using the methods described in Chinese standard GB/T 14684.

Sample	Apparent density (kg/m ³)	Bulk density (kg/m ³)	Void ratio (%)	Water absorption (%)
WCF	2110	1290	39	13.4
Standard sand	2640	1890	28	0.4
Recycled sand	2660	1890	28	1.0

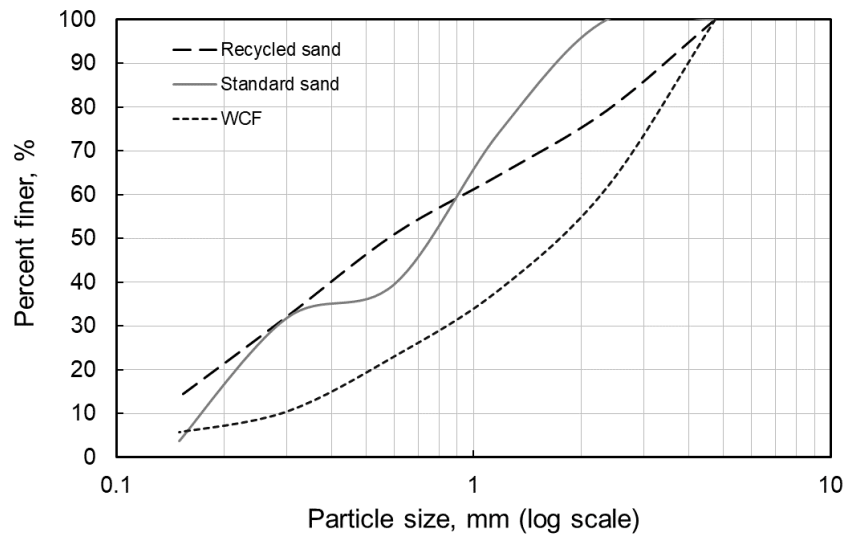


Figure 4.7 Particle size distribution of standard sand, recycled sand and WCF.

Figure 4.8 presents the 7 and 28-day compressive strength data of mortars containing standard quartz sand (control), recycled sand and WCF. At 7 days, the average compressive strengths of mortars containing WCF, standard sand and recycled sand are 17.3, 34.2 and 35.6 MPa, respectively. These increase to 32.9, 50.6 and 55.1 MPa at 28 days. The mortars containing untreated WCF have low compressive strength compared to the control mortars due to (i) the low density of cement paste and the weak bond between the old cement paste and new matrix and (ii) the increased porosity resulting from the excess water demand of waste concrete fines (Wang et al., 2017; Sideris & Konsta-Gdoutos, 1996).

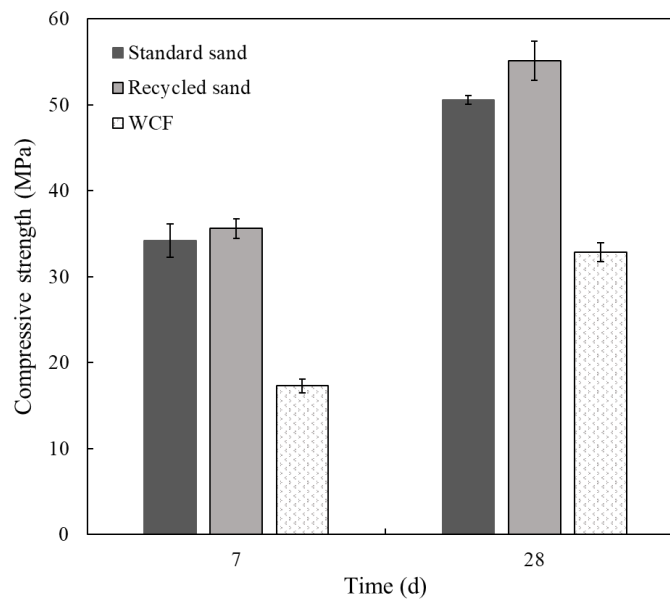


Figure 4.8 Comparison of compressive strength of mortars containing standard river sand, recycled sand (from acid leaching) and WCF.

4.4 Discussion

4.4.1 Optimal acid leaching conditions

Acetic acid leaching of WCF using different conditions shows that acid concentration, L/S ratio and leaching time have a significant influence on Ca^{2+} extraction. Higher acid concentration and a greater volume of solvent promotes the dissolution of Ca in cement hydration products (Kim et al., 2017b; Ho et al., 2020). Increasing the temperature did not significantly influence the Ca^{2+} extraction. This is consistent with the results reported on the acid leaching of cement kiln dust and steel slag (Kunzler et al., 2011; Kim et al., 2017b). This probably indicates that the activation energy of the reaction between acetic acid and cement hydration products is low (Chu et al., 2019). However, a low temperature may reduce the polymerization rate of silica and affect the reactive silica content in the SR. However, this can also be achieved by properly elongating the reaction time. Due to the large particle size of WCF, the complete dissolution of adhered paste is finished in 6 hours, and this can offset the temperature effect. The effect of temperature on the dissolution of Si will be investigated in chapter 5.

Only marginal variation in the Ca^{2+} extraction (1 – 3 %) was observed for acid concentrations ranging from 0.6 to 1 mol/L, an L/S ratio between 7 and 9 ml/g and a reaction time between 6 and 8 hours. Effective leaching can therefore be achieved using 0.6 mol/L acetic acid, an L/S ratio of 7 ml/g, and a reaction time of 6 hours at ambient temperature. This corresponds to 0.25 g of glacial acetic acid reacting with 1 g of concrete fines. Using the optimal leaching conditions, 25 g of recycled sand and 14.8 g of silica-rich residue are produced from 50 g of WCF in this process.

4.4.2 Feasibility of 100 % replacement of virgin sand by recycled sand

Compared to untreated WCF, the apparent density and bulk density of recycled sand increases by 26.1 % and 46.5 %, and the void ratio and water absorption of recycled sand decreases by 28.2 % and 92.5 %. 100 % replacement of virgin sand with the recycled sand from acetic acid leaching results in higher 7-day and 28-day compressive strengths. The average compressive strengths of mortars with recycled sand were 4.1 % and 8.9 % greater than the control mortars. This is probably because (i) the recycled sand has more finer fractions (< 0.9 mm) than standard sand (Figure 4.7) which improves the

compaction and (ii) the recycled sand contains crushed coarse aggregates which is more angular than standard sand and generates stronger interfacial friction bonding with cement paste (Wu et al., 2019).

Previous research has used a 1 mol/L acetic acid solution and a leaching time of 24 hours to extract sand from mortar. Because the recycled sand is not washed, a 400°C-heat treatment stage was necessary to decompose the calcium acetate to calcium carbonate fillers which improve the quality of the recycled sand (Santha Kumar et al., 2019). In comparison, the process reported in this research achieved extraction of clean sand using less concentrated acid, within a shorter time without requiring thermal treatment. The waste solution can be used to prepare the acetic acid solution or combined with the leachate to be used in carbonation. This saves on chemicals, reduces energy consumption, and eliminated the potential CO₂ emissions associated with heating.

4.5 Conclusions

Clean usable sand and Ca²⁺-rich CO₂ absorbent can be recovered by acetic acid leaching of waste concrete fines. The optimal acid leaching conditions of WCF use an acid concentration of 0.6 mol/L, an L/S ratio of 7 ml/g, and a reaction time of 6 hours at ambient temperature. The chemical and physical and properties of recycled sand are comparable to new sand. 100 % replacement of virgin sand by standard sand increases both the 7-day and 28-day mortar compressive strength.

5 A novel aluminosilicate SCM from acetic acid leaching of waste concrete

In this chapter, the valorisation of the silica-rich solid residue (SR) extracted from the acetic acid leaching of waste concrete is reported. Hydrated cement paste (HCP) is used as a model system of waste concrete. The evolution of pH and dissolution of Ca, Al, Fe and Si under the reaction conditions are studied. The chemical composition, phase composition, physical properties and pozzolanic reactivity of SR extracted from HCP and WCF are compared. The mechanical performance of cement mortars containing SR is assessed. The reaction conditions are optimised to produce an aluminosilicate gel based novel SCM with high reactivity from waste concrete. This work has been published as ‘Production of amorphous aluminosilicate and vaterite from acid leaching of hydrated cement paste’ in Journal of Sustainable Cement-based Materials (<https://doi.org/10.1080/21650373.2024.2397484>).

5.1 Introduction

Using SCMs to partially replace cement clinker is an effective and simple way to reduce the carbon emissions related to cement. SCMs contribute to the strength of cement paste because of pozzolanic reactivity and filler effects (Shah & Scott, 2022). The most widely used SCMs are coal fly ash (FA), ground granulated blast furnace slag (GGBFS) and silica fume (SF). These are produced from energy-intensive processes that are likely to become less viable in the future as industry become more sustainable (Zhou et al., 2017). To meet the high demand for cement, developing new low-carbon SCMs with high availability and quality is an important research area.

Chapter 4 has investigated the acetic acid leaching to extract Ca^{2+} from WCF and produce clean reuseable sand. However, the long leaching time (6 hours) is a potential barrier for this process to meet the large demand of construction sand. This is because the large particle size of WCF (< 4.75 mm) reduces the reaction rate. WCP is also suitable to be treated by this process due to its rich cement paste content and fine particle size. Real WCP is contaminated by crushed aggregates and have variable chemical composition, and therefore it is interesting to use HCP as a model system to simulate the actual WCP. Previous work has reported the production of Ca^{2+} -rich solution and silica/alumina-rich residue

by acid dissolution of cementitious materials. 90-day HCP is leached with 2 mol/L ammonium chloride (NH_4Cl) solution at an L/S ratio of 10 mL/g and a temperature of 85°C. This extracted 65.7% of the Ca from HCP and produced a mostly amorphous solid residue containing 37.8 % SiO_2 and 7.2 % Al_2O_3 (Mehdizadeh, Mo & Ling, 2023). Although there have been some investigations on Ca^{2+} leaching from cementitious wastes under acidic conditions, few studies have reported on the dissolution of other major elements such as Al, Fe and Si (Chen et al., 2017; Mun, Cho & Kwon, 2017; Mehdizadeh, Mo & Ling, 2023). These have an impact on the pozzolanic reactivity, and studying their dissolution and precipitation in this process can help control the reactivity of the silica-rich residue. The pozzolanic reactivity of the silica-rich residue extracted from real and simulated waste concrete needs to be assessed for the potential application as a novel SCM.

Therefore, in this chapter, the effect of key process variables on acetic acid leaching of HCP to optimise dissolution of Ca, Al, Fe and Si is understood. The physical properties, chemical properties and pozzolanic reactivity of the silica-rich residue extracted from WCF and HCP are assessed and compared with conventional SCMs. Carbonation of the Ca^{2+} -rich leachate solution to form vaterite will be reported later in chapter 7. To the author's knowledge, this is the first study considering the reuse of the acid leaching residue from cementitious materials as a novel SCM.

5.2 Experimental

5.2.1 Characterisation of materials

The HCP, commercially available SCMs and inert reference materials used in this chapter are described in section 3.1. The chemical compositions of the HCP and test SCMs are determined by XRF (Malvern PANalytical Zetium) as presented in Table 5.1. The loss on ignition (LOI) is calculated from the mass difference between 30°C and 1000°C by TGA (Netzsch STA 449 F5). HCP has a lower CaO content (48.0 %) than hydrated cement pastes with the same w/c ratio reported in other studies (64 – 71 %) because the LOI is considered (Fang et al., 2021b; Mehdizadeh, Mo & Ling, 2023). The large LOI (27.4 %) is due to chemically bound water and CO_2 .

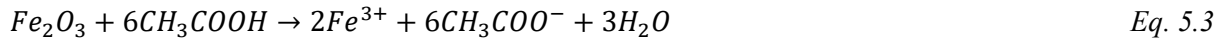
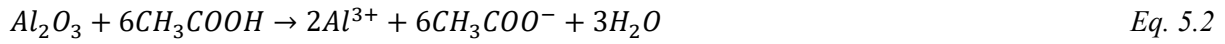
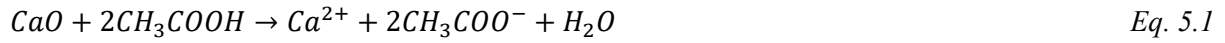
The phase composition of materials is determined by XRD (Malvern PANalytical Empyrean). The amount of amorphous phase is measured using QXRD with the Rietveld method, using corundum (Al_2O_3) as the internal standard. The BET specific surface area of materials is measured using N_2 adsorption and desorption (Micromeritics 3Flex). The particle size of the test SCMs is determined using laser diffraction (Malvern Mastersizer 3000). The thermal stability of materials is measured by TGA (Netzsch STA 449 F5) in the temperature of 30 – 1000°C at a heating rate of 10 °C/min. The particle morphology was observed using scanning electron microscopy (SEM, ZEISS Gemini).

Table 5.1 XRF oxide composition data and LOI of the hydrated cement paste (HCP), silica-rich solid residue from cement paste (SR-cp) and waste concrete fines (SR-wc), test pozzolans (FA and SF) and inert references (GL-ground limestone and QZ-quartz sand).

Material	Percentage (%)									
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	LOI
HCP	48.0	13.5	4.1	2.2	2.8	0.8	0.3	0.1	0.1	27.4
SR-cp	5.1	54.7	11.9	4.1	0.3	0.1	0.2	N/A	0.1	24.3
SR-wc	2.9	59.7	16.4	5.0	0.2	1.8	0.9	2.4	0.2	9.2
FA	4.9	52.5	26.4	6.6	0.4	1.6	1.4	0.5	0.9	2.3
SF	0.3	93.3	0.4	0.2	0.4	0.5	1.6	0.3	0.2	2.3
GL	54.4	0.9	0.2	0.3	N/A	0.9	N/A	N/A	N/A	43.1
QZ	5.5	82.4	1.4	1.1	0.1	0.3	0.5	0.2	0.1	4.1

5.2.2 Acetic acid leaching of HCP

Acetic acid leaching experiments on HCP are carried out according to the method specified in section 3.2. The effect of acetic acid concentration, L/S ratio, temperature, and time on the dissolution of Ca, Al, Fe and Si from HCP and the leachate pH are investigated. The theoretical amount of acetic acid required to react with all the Ca, Al and Fe in 20 g of cement paste is 0.4 moles, based on the CaO content and the acid dissolution reactions (equation 5.1 – 5.3).



Nevertheless, the actual required acetic acid will be slightly lower because Al^{3+} and Fe^{3+} hydrolyse and release H^+ when the pH is higher than 4 and 2, respectively (Martin, 1991). The dissolution of Si is a reversible process induced by hydrolysis of Si-O-Si network and influenced by pH (Sjöberg, 1996). It needs to be minimised to extract silica-rich SCM from cement paste. Therefore, the required amount of acetic acid on Si leaching is not considered. 20 g of HCP is reacted with 220 mL acetic acid solutions with various concentrations (1.2, 1.6 and 2 mol/L). In another set of experiments, 20 g of HCP is added to different volumes of 1.6 mol/L acetic acid solutions, to give various L/S ratios (9, 11 and 13 mL/g). These values are used to avoid either overconcentrated or overdiluted acid solution. Finally, 20 g of hydrated cement paste is mixed with 220 mL (L/S ratio of 11 mg/L) of 1.6 mol/L acetic acid solution at 20, 40 and 60°C. All the experiments are conducted according to section 3.2. At 5, 10, 30, 60, 120 and 240 minutes, the pH of the solution is recorded (Hanna HI-8424), and 1 mL samples of leachate are extracted. The concentration of Ca, Al, Fe and Si in the samples is determined by ICP-OES (PerkinElmer AVIO 500), and the results are reported as an average extraction (%) from three replicate measurements calculated according to equation 5.4:

$$Extraction \% = \frac{m_x}{M_x} \times 100\% \quad Eq. 5.4$$

where m_x and M_x are the mass of the test element (Ca, Al, Fe, Si) dissolved in the solution and in the HCP, respectively.

5.2.3 SR production and pozzolanic reactivity test

SR produced from acid leaching of HCP is extracted following the method in section 3.2. The silica-rich residue from the acetic acid leaching of cement paste (SR-cp) is produced under the optimal leaching conditions reported in section 5.3.1. SR produced from waste concrete fines (SR-wc) is obtained from the optimal acetic acid leaching of WCF determined in section 4.4. The SRs are washed

with deionised water and dried at 60°C to constant mass. They are then ground using a mortar and pestle into a fine powder passing a 300 µm sieve.

The pozzolanic reactivity test uses Frattini test and R^3 method as described in section 3.4. The results of SR-wc and SR-cp are compared to those of FA, SF, GL and QZ to assess the technical viability of reusing the SR as a novel SCM.

5.2.4 Fresh and mechanical properties of mortar containing SRs

The mixing protocol of mortars follows the method in section 3.5.1. Seven mortars are prepared using water: binder: sand ratio of 0.5: 1: 3 by mass. The reference mortar uses 100 % CEM I as the binder, while other test mortars use composite binders containing 80 % CEM I and 20 % test SCM. The mixing proportions are shown in Table 5.2. Mortar flow is determined using a flow table according to the method specified in section 3.5.2. A polycarboxylic ether (PCE) based super-plasticizer (Master Builders MasterGlenium 315C) with a solids content of 35 % is used to adjust the flow of mortar mixes to give similar flow to the reference mortar. The water contained in the super-plasticizer is subtracted from the mixing water to ensure a constant w/b ratio.

Mortar samples are cast into 50×50×50 mm cubic moulds (ASTM C109, 2016), compacted on a vibration table, demoulded after 24 hours, and cured in saturated lime water at 20 °C for 3, 7 and 28 days. After each curing age, the compressive strength is measured using a compressive strength testing machine (CONTROLS) and data is reported as the average from three replicates.

Table 5.2 Mix composition and flow of mortars. SR: silica-rich residue; FA: coal fly ash, SF: silica fume, GL: ground limestone, QZ: quartz sand, and SP: superplasticiser.

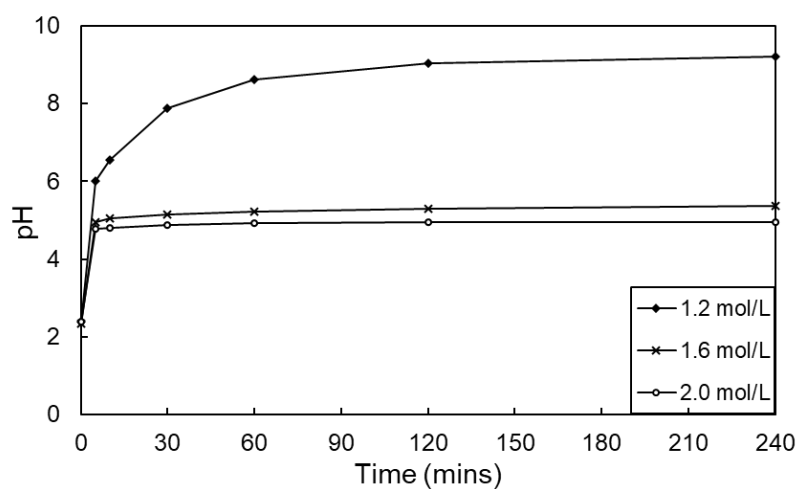
Mixture	Mass (g)										Flow (mm)
	CEM I	SR-cp	SR-wc	FA	SF	GL	QZ	Sand	SP	Water	
M-Ref	600	0	0	0	0	0	0	1800	0	300.0	125.8
M-SR-cp	480	120	0	0	0	0	0	1800	30.0	280.5	123.5
M-SR-wc	480	0	120	0	0	0	0	1800	6.6	295.7	121.1
M-FA	480	0	0	120	0	0	0	1800	0	300.0	124.3
M-SF	480	0	0	0	120	0	0	1800	4.2	297.3	118.7
M-GL	480	0	0	0	0	120	0	1800	0	300.0	126.3
M-QZ	480	0	0	0	0	0	120	1800	0	300.0	125.0

5.3 Results

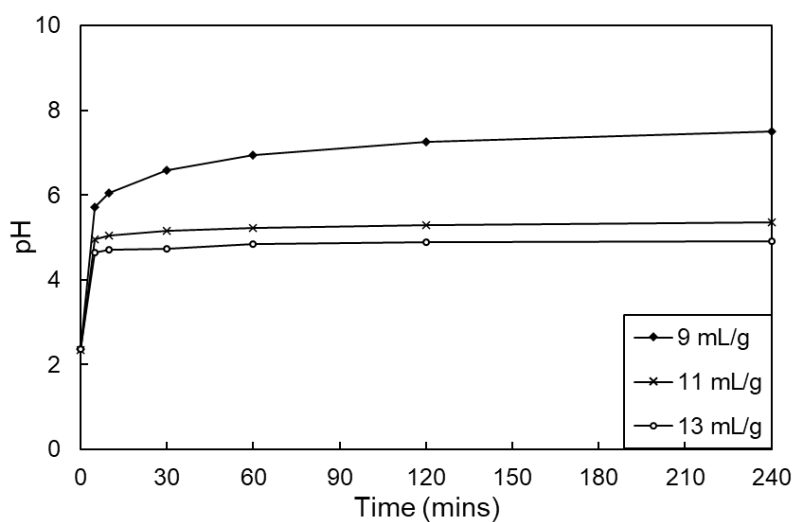
5.3.1 Effects of acid concentration, L/S ratio, temperature, and time on leaching

Figure 5.1 shows the change in pH against time under different leaching conditions. Varying acid concentration and L/S ratio gives different starting amount of acetic acid, resulting in different pH evolution. When the amount of acetic acid is less than the theoretical value of 0.34 moles required for complete reaction (1.2 mol/L in Figure 5.1(a) and 9 mL/g in Figure 5.1(b)), the pH gradually increases to greater than 7 as the reaction proceeds. When the amount of acid is equal to or higher than 0.34 moles, the pH stabilises rapidly within a few minutes to about 5 and remains relatively constant up to 240 minutes. Temperature influences the rate of pH change, but the effect is marginal. At 60 °C the pH increases slightly faster than at 20 and 40 °C, as shown in Figure 5.1(c).

(a) L/S = 11 mL/g, 20°C



(b) concentration = 1.6 mol/L, 20°C



(c) concentration = 1.6 mol/L, L/S = 11 mL/g

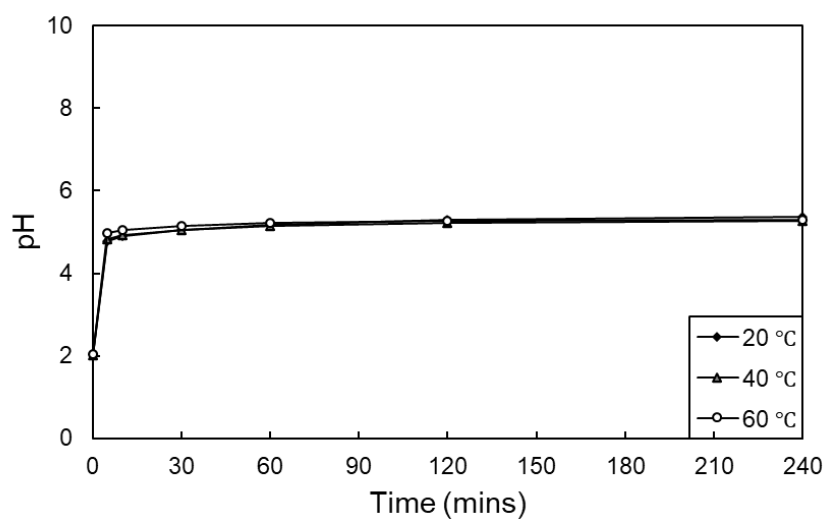
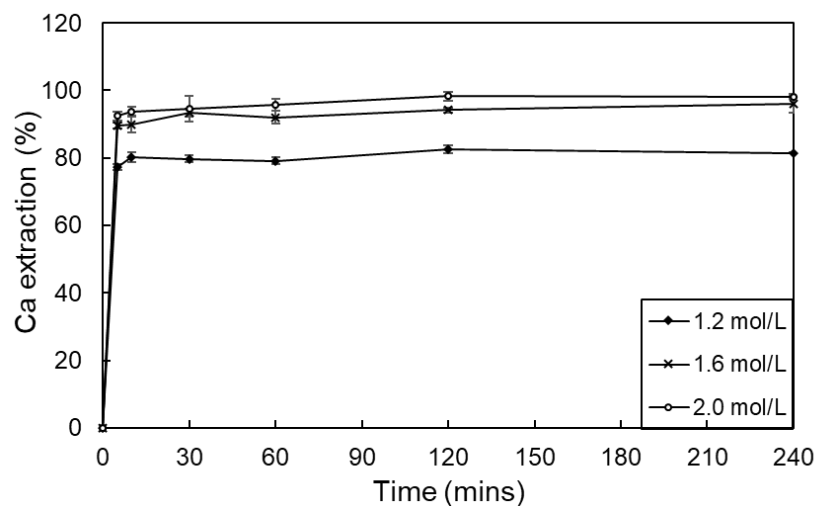


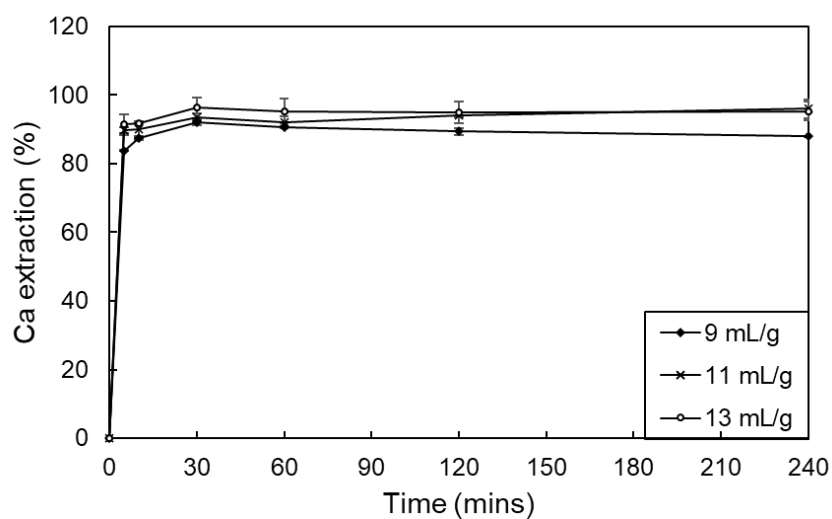
Figure 5.1 Effect of (a) acetic acid concentration, (b) L/S ratio and (c) temperature on the change in pH of the mixture containing 20 g HCP.

Figure 5.2 shows the effect of leaching conditions on Ca^{2+} extraction from HCP. At all tested conditions 90 – 95 % of the reaction is completed within 5 minutes. Figure 5.2(a) shows increasing the acid concentration can promote the extraction of Ca. At 240 minutes, the Ca extraction is 80.9 % at 1.2 mol/L acid, 96.0 % at 1.6 mol/L acid and 98.1 % at 2.0 mol/L acid. Figure 5.2(b) shows increasing L/S ratio from 9 to 11 mL/g will extract 8 % more Ca, but a further increase to 13 mL/g has marginal effect. Similarly, increasing the reaction temperature has negligible effect on the leaching of Ca^{2+} as shown in Figure 5.2(c). This implies that the reaction has a low activation energy. It seems that once the amount of acid is sufficient (0.34 moles), L/S ratio and temperature do not have a significant effect on the extraction ratio.

(a) $L/S = 11 \text{ mL/g}$, 20°C



(b) concentration = 1.6 mol/L , 20°C



(c) concentration = 1.6 mol/L , $L/S = 11 \text{ mL/g}$

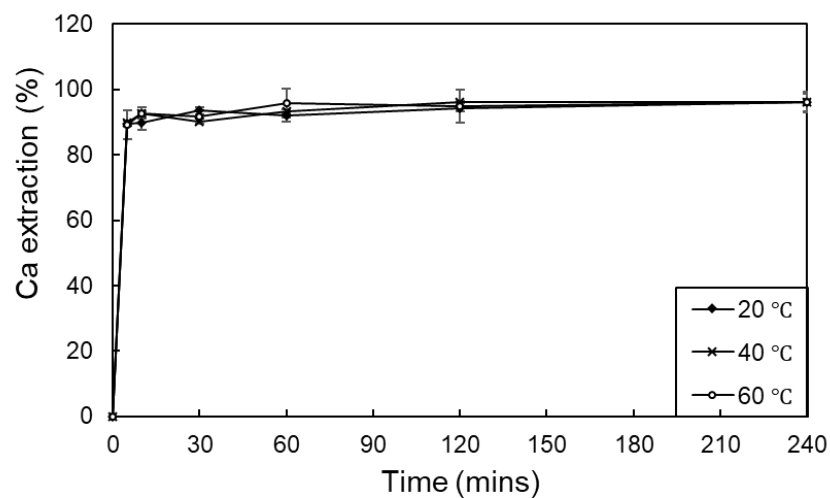
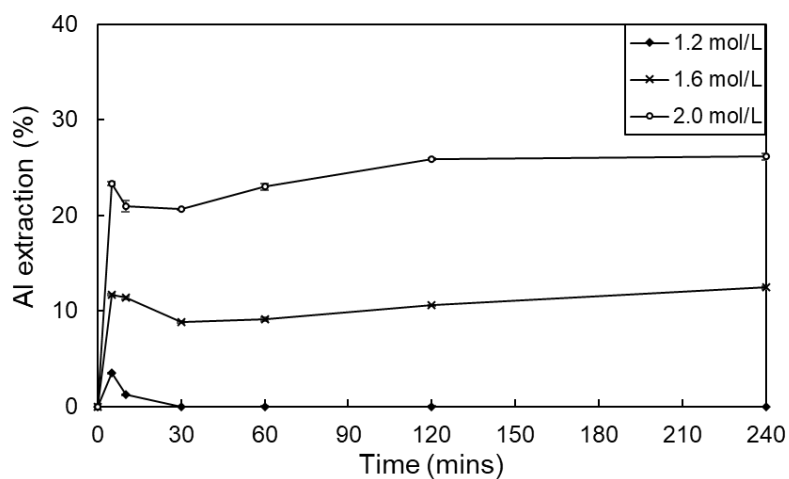


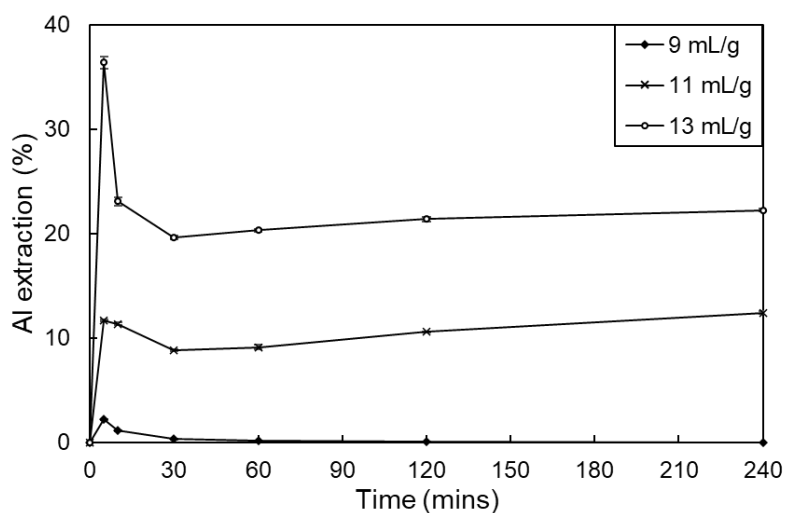
Figure 5.2 Effect of (a) acetic acid concentration, (b) L/S ratio and (c) temperature on percentage Ca extraction with time.

Figure 5.3 shows data for Al leaching. In Figure 5.3(a), Al extraction increases rapidly to 3.5%, 11.7% and 23.3% at 5 minutes and decreases to 0%, 8.8% and 20.7% at 30 minutes under 1.2, 1.6 and 2.0 mol/L acid, respectively. Similar trend is found in Figure 5.3(b). At L/S ratios of 9, 11 and 13 mL/g, Al extractions are 2.2%, 11.7% and 36.4% at 5 minutes and 0.4%, 8.8% and 19.6% at 30 minutes. This effect is due to the change in pH. Al is soluble at low pH (2 – 5) and precipitates as $\text{Al}(\text{OH})_3$ when the pH is above 5 (Cronan, Walker & Bloom, 1986). The pH of initial $\text{Al}(\text{OH})_3$ precipitation was slightly different from expected because of the high ion activity in the cement paste solution, which affects the solubility product of $\text{Al}(\text{OH})_3$. After 30 minutes, if the pH continues to increase above 7, in the case of 1.2 mol/L and 9 mL/g, $\text{Al}(\text{OH})_3$ will keep precipitating until Al extraction reached zero at 60 minutes. If the pH stays below 7, Al extraction gradually increases due to the formation of Al-acetate complex which dissolves part of the precipitated $\text{Al}(\text{OH})_3$ (Marklund, Öhman & Sjöberg, 1989). Increasing the acid concentration and L/S ratio significantly improves dissolution of Al by increasing the acidity and the amount of chelate available. Temperature also has a strong influence on Al leaching. Figure 5.3(c) indicates at 240 minutes Al extraction decreased from 12.4% at 20°C to 0.9% at 60°C, indicating a reduction in the solubility of Al ions and stability of the Al-acetate complex.

(a) L/S = 11 mL/g, 20°C



(b) concentration = 1.6 mol/L, 20°C



(c) concentration = 1.6 mol/L, L/S = 11 mL/g

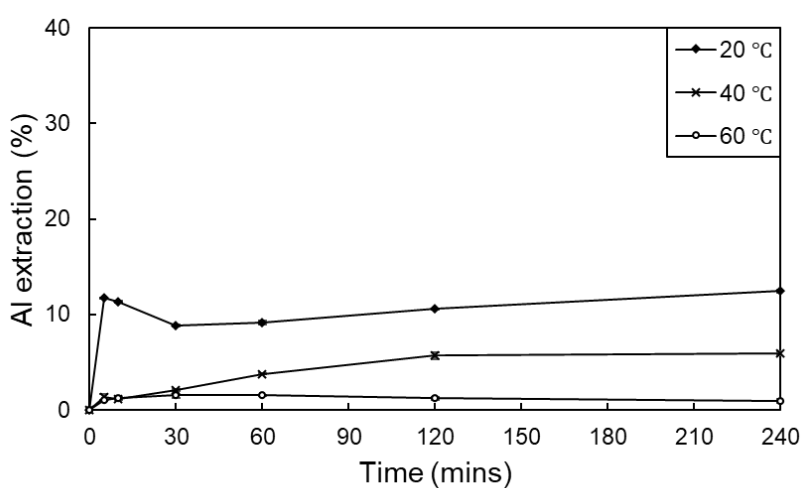
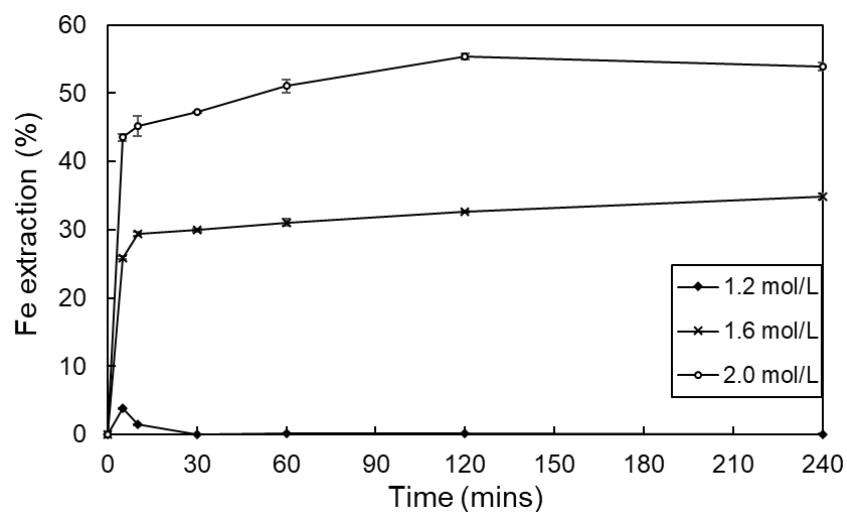


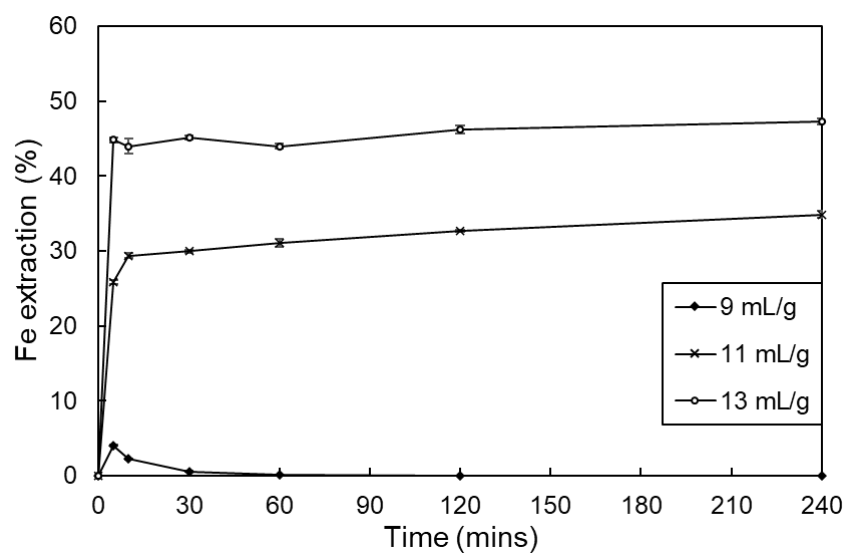
Figure 5.3 Effect of (a) acetic acid concentration, (b) L/S ratio and (c) temperature on the percentage Al extraction with time.

Similar trends are observed in the dissolution of Fe, as shown in Figure 5.4. Acetic acid can also form complexes with Fe^{3+} , making it more stable under higher pH conditions (Taylor, Nasr-El-Din & Al-Alawi, 1999). When the pH is below 7, Fe does not precipitate in the early stages of the acid leaching (between 5 and 30 minutes). This is because of the higher stability of Fe-acetate complexes (stability constant = 2.8 – 3.23) than Al-acetate (stability constant = 1.47) at pH ~5 (Starke, 1960). At 240 minutes, Fe extraction increases from 0% to 53.0% when acid concentration rises from 1.2 to 2.0 mol/L, and from 0% to 48.8% when L/S ratio increases from 9 to 13 mL/g, respectively. This is due to the increased amount of Fe-acetate chelates formed. Fe extraction also decreases by 74.4 % at 240 minutes with temperature increased from 20 to 60°C.

(a) L/S = 11 mL/g, 20°C



(b) concentration = 1.6 mol/L, 20°C



(c) concentration = 1.6 mol/L, L/S = 11 mL/g

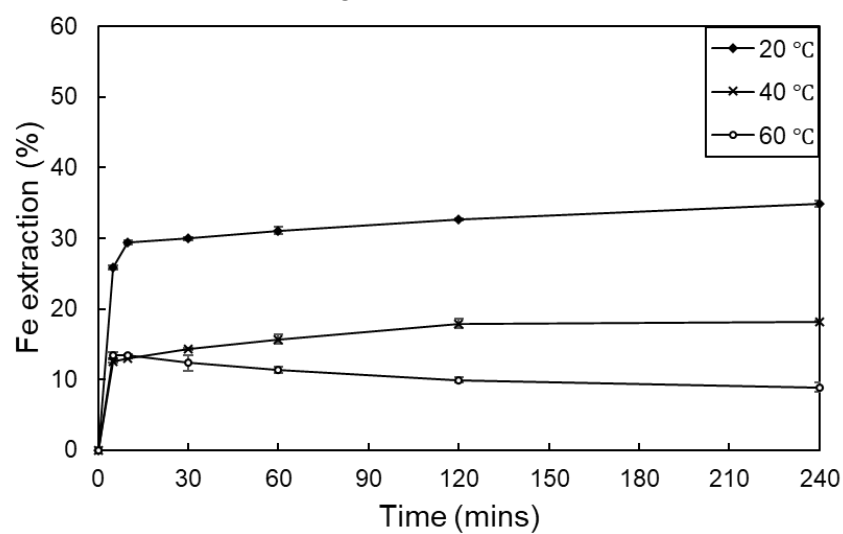
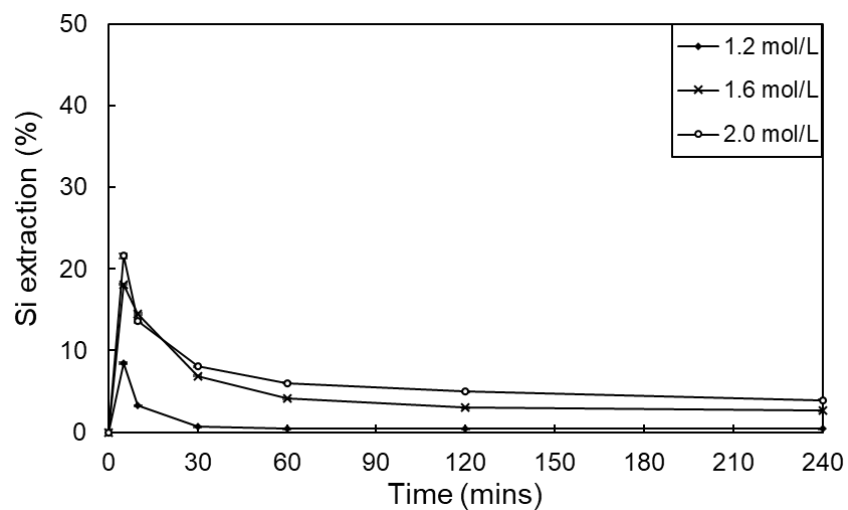


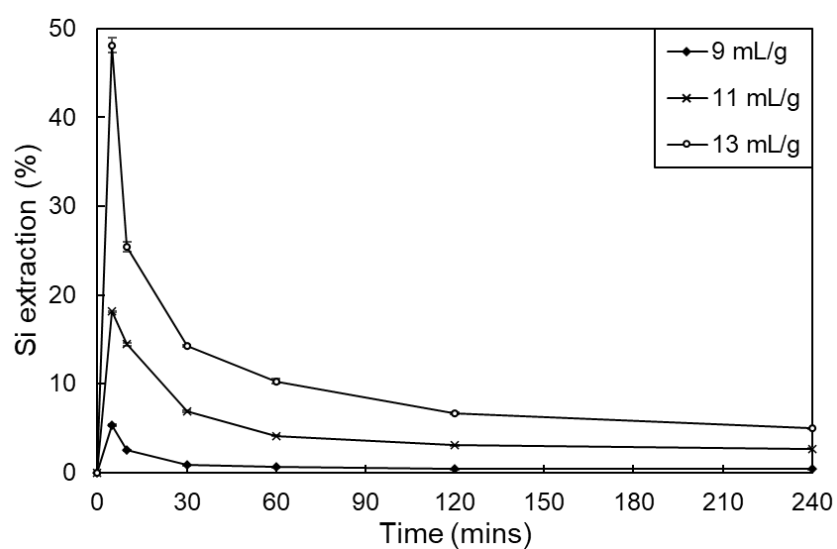
Figure 5.4 Effect of (a) acetic acid concentration, (b) L/S ratio and (c) temperature on percentage of Fe extracted with time.

Figure 5.5 presents the variation of dissolved Si. In an acidic environment, Si dissolves in the form of silicic acid (H_4SiO_4) with stability controlled by pH and temperature (Tai, 1963; Alexander, 1954). A high acid concentration and L/S ratio results in a lower pH after the same reaction duration. This prevents the polymerisation of silicic acid and increases the dissolution of Si from cement paste, as shown in Figure 5.5(a) and 5.5(b). The Si extraction ratio rapidly increases to its maximum at 5 minutes and then decreases. 48.1% of the Si can be extracted at an L/S ratio of 13 mL/g, while 21.6% is dissolved in 2.0 mol/L acid, indicating a higher L/S ratio increases the undersaturation of silicic acid. The dissolved silica is most stable at a pH of 3 (Tai, 1963). After 5 minutes the pH in all tests is above 3, where the silica gel polymerisation accelerates, and the Si extraction ratio is reduced. Increasing the temperature also accelerates the polymerisation of silicic acid, and all the Si is precipitated after 30 minutes at 60 °C.

(a) L/S = 11 mL/g, 20°C



(b) concentration = 1.6 mol/L, 20°C



(c) concentration = 1.6 mol/L, L/S = 11 mL/g

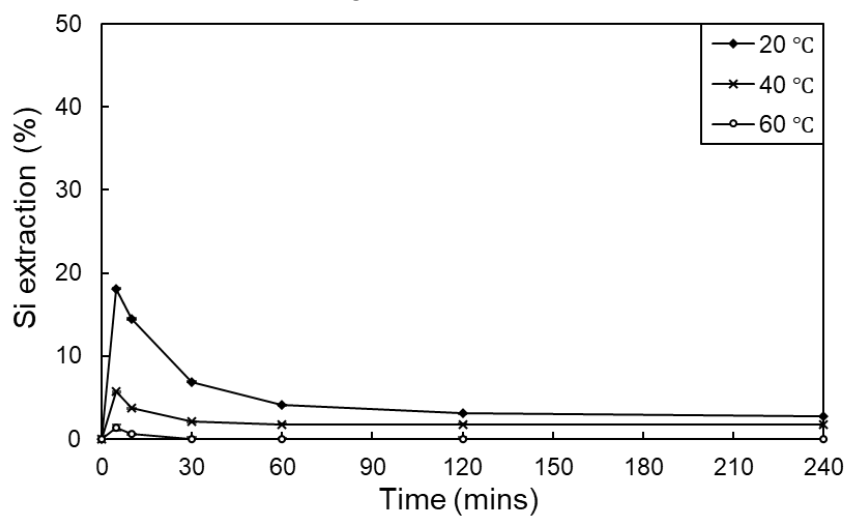


Figure 5.5 Effect of (a) acetic acid concentration, (b) L/S ratio and (c) temperature on percentage of Si extraction with time.

Higher acid concentrations and L/S ratio promote the leaching of Ca, Al, Fe and Si. However, this increases the excess acetic acid in the slurry which subsequently increases the amount of reagent, such as ammonia, required in the carbonation stage. Elevated temperature reduces the dissolved Al, Fe and Si, but not Ca. To maximise the amount of aluminosilicate gel formed in the solid residue and Ca extracted for carbonation at reduced reagent consumption, the optimal leaching condition were 1.6 mol/L acetic acid, an L/S ratio of 11 mL/g, at 60 °C using a reaction time of 1 hour. This yields a Ca extraction of 96%, reduced the Fe extraction to 11.4% and minimises the dissolution of Al and Si to 1.5% and 0% respectively, with an endpoint pH of 5.3. The SR-cp produced under these conditions has been used in subsequent experiments.

5.3.2 Properties of silica-rich residue

The appearance of WCF, HCP, SR-wc and SR-cp is shown in Figure 5.6. The colour changed from grey to dark yellow after acetic acid leaching is due to the removal of Ca and the accumulation of Fe_2O_3 in the solid residue as indicated by their chemical compositions in Table 5.1 (Wang et al., 2023). SR-wc has a darker grey colour due to its higher Fe content than SR-cp. SR-cp has a lower $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio compared to SR-wc. This is due to differences in the cement used in WCF and HCP, and contamination (e.g. crushed aggregates and Al-containing ceramics) in WCF as shown in Figure 4.6(a). SR-cp has a higher LOI value (24.3 %) than SR-wc (9.2 %) because it contains more aluminosilicate gel, which loses water through condensation of silanol groups during heating (Farias & Airolidi, 1998).

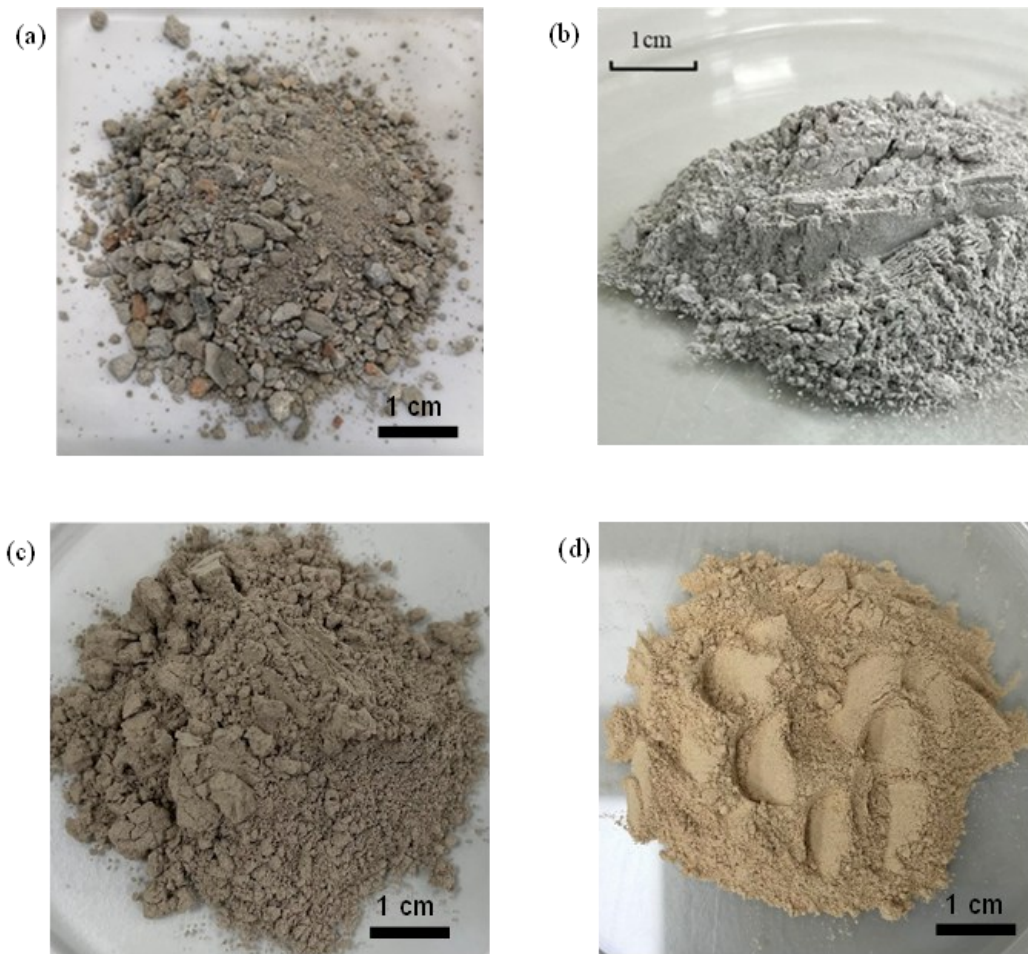


Figure 5.6 Visual appearance of (a) WCF, (b) HCP, (c) silica-rich residue extracted from waste concrete fines (SR-wc) and (d) silica-rich residue from hydrated cement paste (SR-cp).

This is also evident from the thermogravimetric data presented in Figure 5.7, where SR-cp shows greater weight loss than SR-wc between 80 and 200 °C due to the removal of physically absorbed water from the surface of the aluminosilicate gel. This difference also resulted in a higher residual Ca content in SR-cp, as Ca^{2+} can be adsorbed by the aluminosilicate gel (Chu et al., 2019).

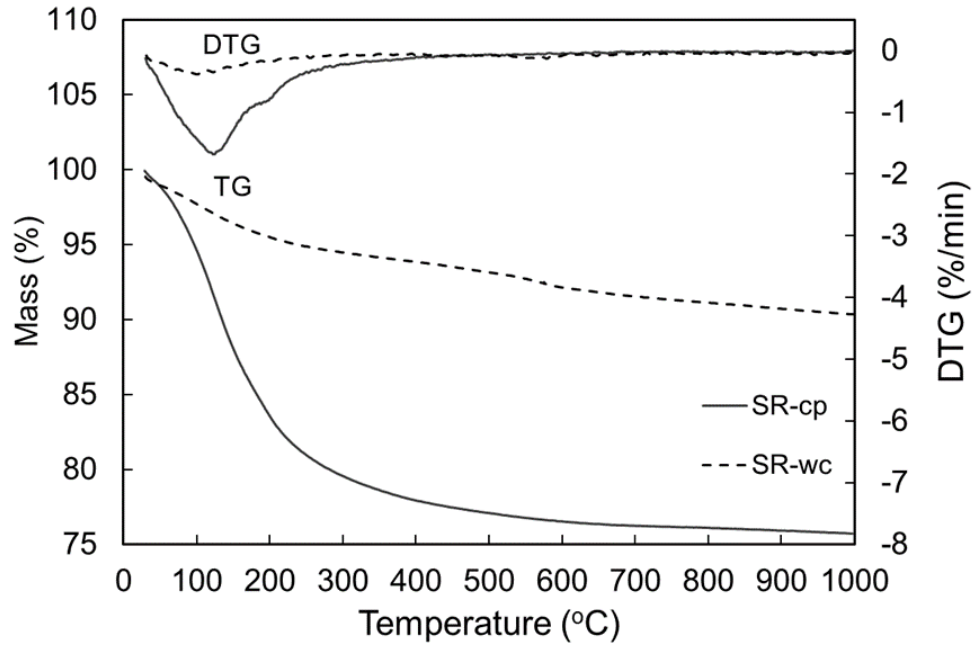


Figure 5.7 Thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of the silica-rich solid residue from cement paste (SR-cp) and waste concrete fines (SR-wc).

The XRD data for SR-cp, SR-wc and the corresponding raw materials are compared in Figure 5.8. In HCP, high intensity peaks of portlandite are observed. Sharp peaks associated with calcite CaCO_3 are also evident. This is from the limestone filler in CEM I and from carbonation of the cement paste during drying and size reduction. The peaks associated with ettringite and monocarbonate AFm can also be seen. This indicates the reaction of calcium carbonate and monosulphate AFm, generating monocarbonate and stabilizing ettringite (Lothenbach et al., 2008). Peaks associated with quartz and anhydrous larnite ($\beta\text{-C}_2\text{S}$) were also observed. In WCF, the predominant crystalline phase is quartz, with small amounts of calcite, albite $[(\text{Na}, \text{K})\text{AlSi}_3\text{O}_8]$ and illite $[(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O}]$.

After leaching, almost all the crystalline phases in HCP are dissolved. SR-cp is predominantly amorphous as indicated by the large hump between 15° and $35^\circ 2\theta$ and the absence of peaks in the diffractogram. QXRD shows that SR-cp is 98.4 % amorphous. However, SR-wc contains the same crystalline phases in the WCF, which are inert to acid leaching. The calcite phase dissolves after leaching. This results in its lower amorphous content of 55.1 %.

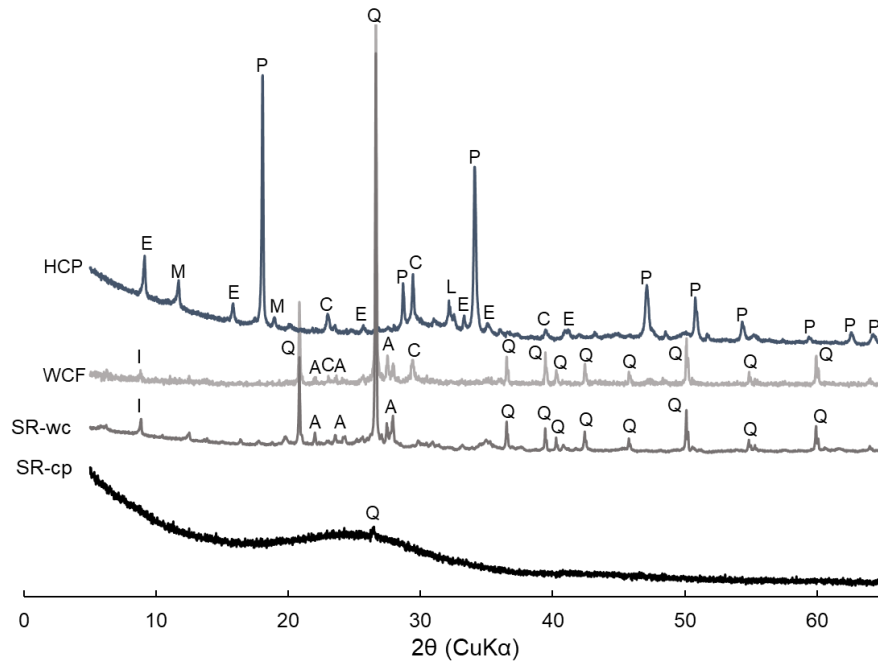


Figure 5.8 XRD of the 90-day hydrated cement paste (HCP), the silica-rich solid residue from hydrated cement paste (SR-cp) and waste concrete fines (SR-wc) and precipitated calcium carbonate. E: ettringite, M: monocarbonate, P: portlandite, C: calcite, Q: quartz, L: larnite, A: albite and I: illite.

Figure 5.9 shows the particle size distribution of the silica-rich residues compared to conventional SCMs and ground quartz. SR-cp has the largest particles. FA, GL and QZ are similar in size distribution and coarser than SR-wc and SF. SF has the finest particles with a d_{50} of 0.1 μm and a d_{90} of 0.3 μm . The particle size distribution of SR-wc is bimodal, which is probably due to the presence of crystalline impurities from the crushed aggregates.

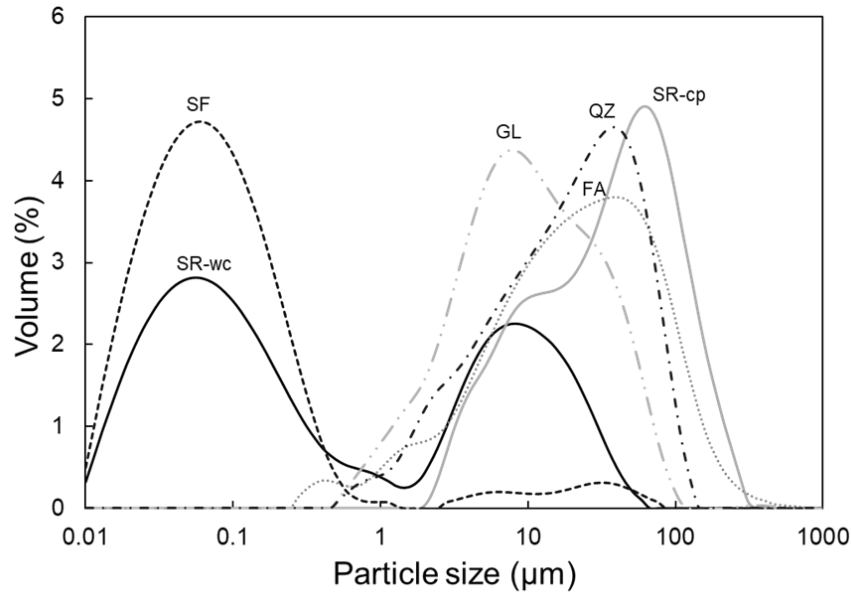


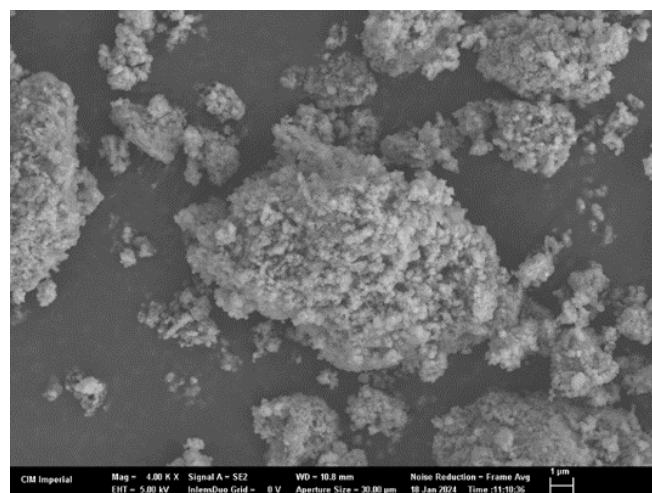
Figure 5.9 Particle size distribution curves of the silica-rich solid residues, conventional SCMs (FA, SF, GL) and ground quartz (QZ).

Table 5.3 BET specific surface area (SSA) and D_{50} values of SR-cp, compared to SR-wc and commonly used SCMs and ground quartz.

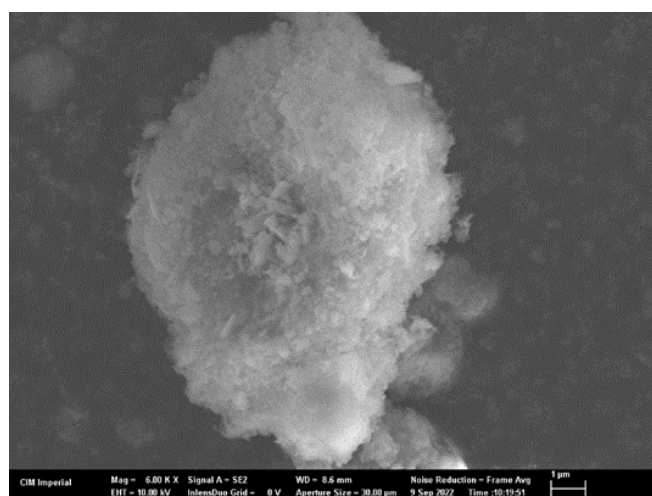
Material	SR-cp	SR-wc	FA	SF	GL	QZ
SSA (m^2/g)	155.0	30.4	1.3	22.8	1.2	1.0
D_{50} (μm)	40.6	0.2	23.4	0.1	10.2	21.0

Table 5.3 compares the BET surface area and D_{50} of test SCMs. Silica-rich residues have larger BET specific surface area than other SCMs. Acetic acid leaching induces decalcification of C-S-H phase, which exposes more surface area to N_2 adsorption (Thomas et al., 2004). The higher C-S-H content in cement paste compared to waste concrete fines results in a higher surface area of SR-cp. In addition, some of the extracted Si precipitates as nano-sized polymerised silicic acid forming agglomerates (Fang et al., 2021c). This produces higher specific surface area of the SRs than other SCMs. The surface area of SR-cp ($155.0 \text{ m}^2/\text{g}$) is ~ 5 times of SR-wc ($30.4 \text{ m}^2/\text{g}$) despite coarser particle size distribution. The d_{50} of SR-cp ($40.6 \mu\text{m}$) is around 200 times than that of SR-wc ($0.2 \mu\text{m}$). This indicates that the increase in specific surface area is not because of particle size but surface morphology. SEM images (Figure 5.10(a)-(c)) show that SR-cp particles are agglomerates of nanosized silica resulting in a rough and porous surface structure, while SR-wc comprises of both porous amorphous and smooth crystalline particles with less surface area than SR-cp.

(a)



(b)



(c)

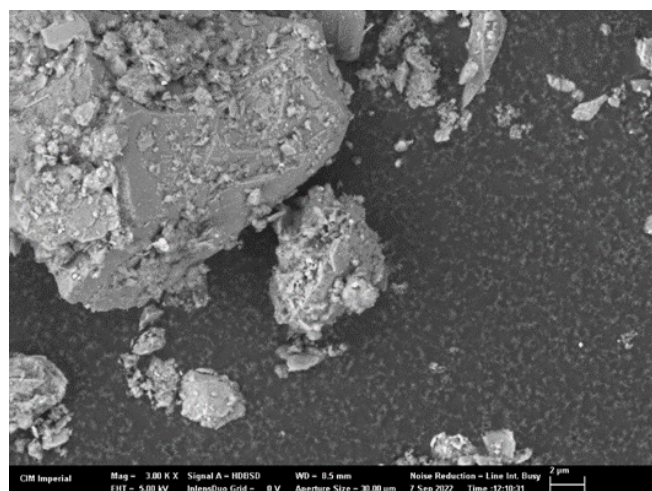


Figure 5.10 SEM images showing (a) SR-cp, (b) amorphous component of SR-wc, and (c) crystalline component of SR-wc.

5.3.3 Pozzolanic reactivity of silica-rich residue

Figure 5.11 shows the results of the Frattini test. SR-cp, SR-wc, SF and FA gave results below the saturated solubility curve of Ca(OH)_2 at 40 °C indicating their pozzolanic reactivity. SR-cp has increased pozzolanic reactivity compared to SR-wc due to the higher content of amorphous aluminosilicate gel. The results of QZ and ground GL are either slightly above or on the saturated solubility curve of Ca(OH)_2 because they act as fillers and are not pozzolanic.

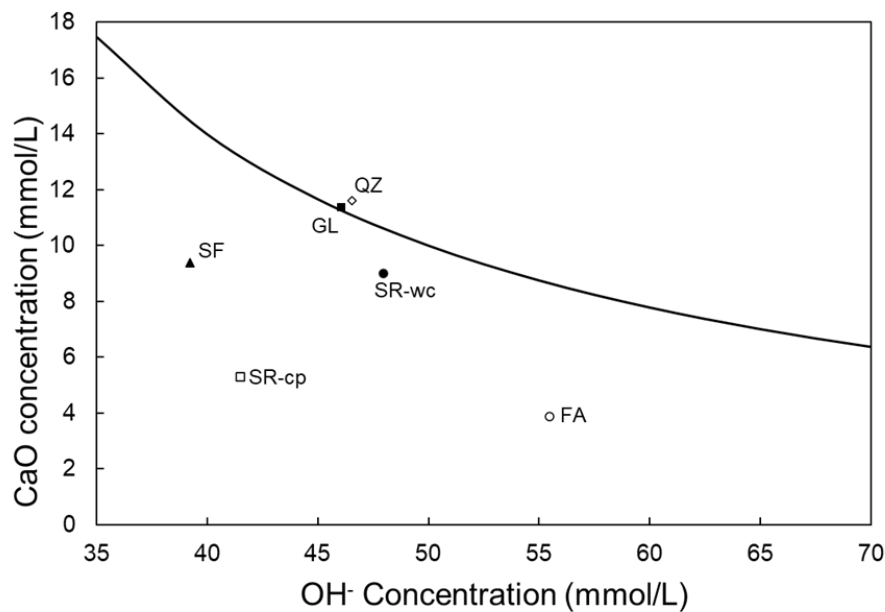


Figure 5.11 Assessment of pozzolanic activity of the test pozzolans by Frattini test.

R^3 isothermal calorimetry results are presented in Figure 5.12. After 7 days, SF is the most reactive, releasing 363.1 J/g of heat, followed by SR-cp (265.1 J/g). The reactivity of SR-wc (165.4 J/g) and FA (162.5 J/g) are similar. FA shows a slow reaction rate that continues to later stages. Similar trends have previously been reported, and this is explained by the large particle size of FA (Snellings et al., 2019). The heat release of quartz sand and ground limestone are close to zero, indicating that these are inert materials that do not react. The heat release rate for SR-cp and SR-wc are higher than other test pozzolans during the first 24 hours, due to high amorphous content combined with high specific surface area.

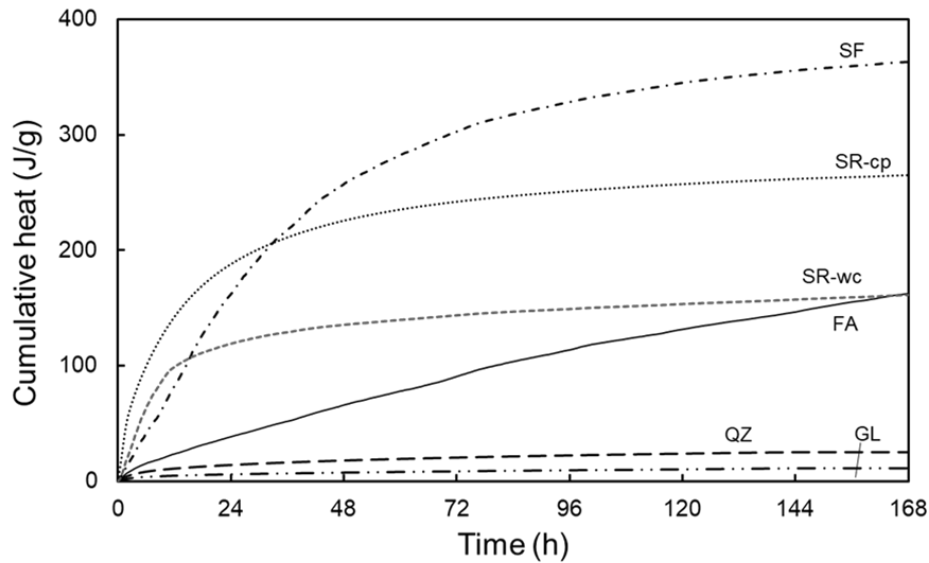


Figure 5.12 Cumulative heat flow from R^3 test on silica-rich solid residues, conventional SCMs (FA, SF, GL) and ground quartz (QZ) at 40°C for 7 days.

5.3.4 Workability and compressive strength of mortars

The superplasticiser dosage required for each blended mortar to achieve a similar flow as the reference mix is given in Table 5.2. Mortars containing FA, GL and QZ have sufficient flow without superplasticiser. The mortar containing SR-cp needs the largest amount of superplasticiser (5.0 %) followed by SR-wc (1.1 %) and SF (0.7 %) and this is consistent with the specific surface area data of the three materials (Table 5.3).

Compressive strength of the mortars is summarised in Figure 5.13. The 3, 7, and 28-day strength of the reference mortar containing 100 % CEM I are 34.5 MPa, 42.6 MPa and 51.2 MPa, respectively. The compressive strength of M-SR-cp is relatively low at 3 days (26.7 MPa) but then increases rapidly. It reaches 41.5 MPa at 7 days which is similar to M-Ref, and further increases to 63.6 MPa at 28 days which is higher than M-Ref. The delayed pozzolanic reactivity of SR-cp probably results from the retarding effect of the superplasticiser, which forms a hydrophobic layer surrounding the cement particles and complexes with dissolved Ca^{2+} (Puertas et al., 2005). M-SR-wc shows higher compressive strength than M-SR-cp at 3 days (28.6 MPa). The 7-day (32.9 MPa) and 28-day strength (42.3 MPa) are lower than M-SR-cp and M-SF (49.5 MPa at 28 days), but comparable to M-FA and higher than M-GL and M-QZ.

The higher later strength of M-SR-cp compared to M-SF is mainly because of the PCE-based superplasticiser. It has been reported that PCE addition improves the compaction and reduce the porosity of mortar (Fernández et al., 2013). Besides, it was observed that the high dosage of superplasticizer in M-SR-cp caused bleeding after casting and vibration. This reduces the actual water/binder ratio and increases the compressive strength.

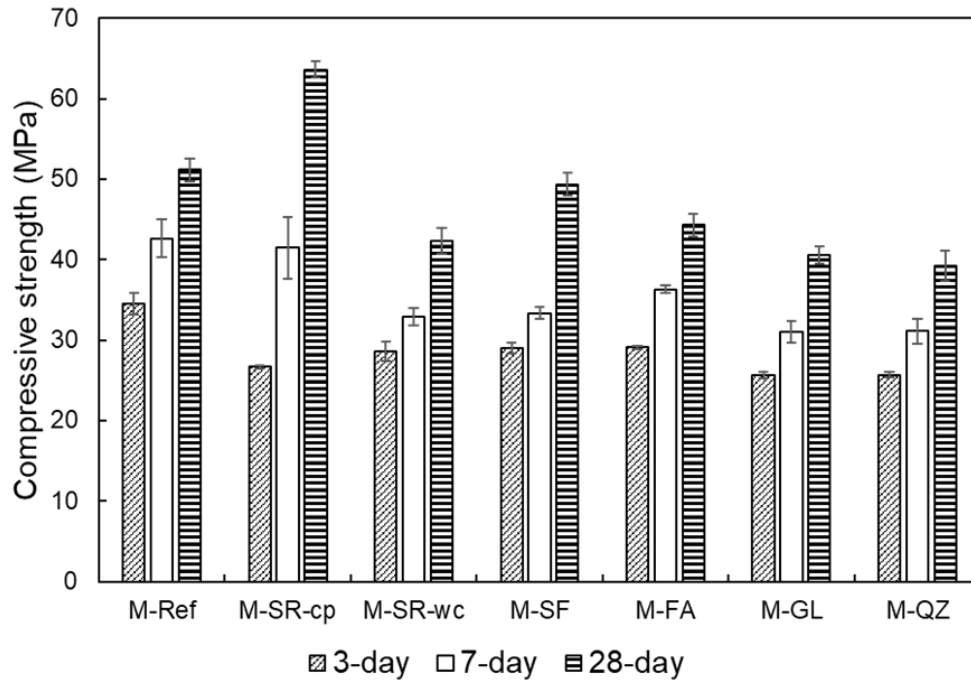


Figure 5.13 Compressive strength of 0.5 w/b ratio mortars containing 20% of the test pozzolans after 3, 7 and 28 days. M-Ref is the reference mortar with 100 % CEM I.

5.4 Discussion

5.4.1 Acetic acid leaching conditions of HCP and WCF

The optimal leaching conditions for HCP obtained in this study are 1.6 mol/L, 11 mL/g, 60 °C and 1 hour, respectively. This is different from that found in previous research on WCF, which are 0.6 mol/L acetic acid, an L/S ratio of 7 ml/g, and a reaction time of 6 hours at ambient temperature. Optimal leaching of HCP required 1.06 g/g of acetic acid/HCP, higher than 0.25g/g for WCF. This is because HCP has a higher calcium content than WCF, so more acid is needed. The finer particle size of HCP (< 300 μm) compared to WCF (< 4.75 mm) promote the rate of dissolution, hence requires shorter time for the reaction to complete. The optimal temperature is 60 °C, which is lower compared to a similar

study using NH_4Cl to leach cement paste (85 °C), because of the stronger acidity of acetic acid (Mehdizadeh, Mo & Ling, 2023). Optimal conditions for WCF uses lower temperature which leads to concerns of reduced content of the amorphous aluminosilicate gel. However, as the precipitation of aluminosilicate gel is a kinetic process, it is also achieved by properly elongating the reaction time. As HCP has small particle size, the acid leaching reaction finishes within 1 hour. Thus, increasing the temperature significantly increases the production of aluminosilicate gel. Due to the large particle size of waste concrete aggregates, complete reaction of adhered paste happens after 6 hours, and this can offset the temperature effect.

The resulting Ca^{2+} -rich leachate from the acetic acid treatment is carbonated and the data are reported in chapter 7. The contaminants in WCF are removed by centrifugation and filtration after acid leaching so will not affect the quality of CaCO_3 . The leached Mg, Al and Fe elements will be removed by adding ammonia solution before carbonation, so the purity of CaCO_3 will not be influenced.

Although the process described has been used to leach HCP in this work, it can be used to treat WCF which have a lower Ca content. This can further reduce the cost of chemicals. The acetic acid can also be recovered from the waste solution after carbonation which will be discussed in section 8.4.1.

5.4.2 Applicability of SRs extracted from cementitious materials as SCM

SR-cp has 40% higher R^3 heat release and higher 7-day and 28-day mortar strength than FA. SR-wc has lower R^3 heat release and mortar strength than SR-cp but is comparable to FA. This indicates that the aluminosilicate residue from acid leaching of cementitious materials has sufficient pozzolanic reactivity can be used as a novel SCM.

The difference in amorphous content results in different pozzolanic reactivity and mortar strength of SR-cp and SR-wc. SR-wc released 62.4 % of the heat produced by SR-cp in the R^3 test. The 28-day strength of M-SR-wc is 66.5 % of that of M-SR-cp. These are consistent with the ratio of amorphous content in the SR-wc and SR-cp (56.0 %). This indicates that the presence of crystalline impurities in waste concrete, mainly quartz sand, reduces reactivity. Better separation of sand and silica gel can be achieved using surfactants such as Triton X-100 followed by centrifugation (Lazaro et al., 2019). Alkali

treatment and carbonation can be applied to recover highly reactive silica gel from the impure silica-rich residue due to the relatively low reactivity of quartz sand (Shen et al., 2021). Most importantly, crushing waste concrete to a finer particle size and good separation of hydrated cement paste from aggregates and other impurities prior to acid treatment can improve the pozzolanic reactivity of the silica-rich residue and reduce the process complexity.

SR-cp has a higher specific surface area than SR-wc. This can provide more sites for the growth of cement hydration products, promoting the early-stage rate of pozzolanic reaction. However, this is also a possible barrier to the use of waste concrete derived aluminosilicate SCM, as demonstrated by the higher water absorption and superplasticiser demand compared to other SCMs to achieve similar workability. This is caused by the removal of Ca^{2+} from the C-S-H sheets, leaving a porous structure. If the flow is solely adjusted by superplasticiser, 5 wt% of binder is needed to reach a similar value to 100 % CEM I (Table 5.2). This is higher than the normally recommended dosage (less than 1 %) and has cost and setting time implications (Puertas et al., 2005). Further research is needed to engineer this material to give improved flow properties to reduce the superplasticiser usage.

5.5 Conclusions

Increasing the acetic acid concentration increases leaching of Ca, Al, Fe and Si. L/S ratio and temperature have a marginal effect on Ca but a more significant impact on Al, Fe and Si. The optimal leaching condition for the cement paste used is an acid concentration, L/S ratio, temperature, and time of 1.6 mol/L, 11 mL/g, 60 °C and 1 hour, respectively. This maximises the amount of amorphous aluminosilicate gel formed in the solid residue (98.4 %) and the Ca extracted (96 %) for carbonation. The silica-rich residue derived from cement paste has high amorphous content, larger particle size and higher specific surface area than that derived from waste concrete fines. The pozzolanic reactivity of the silica-rich SCM derived from cement paste is 40% higher than FA. 0.5 w/b mortars containing 20 % CEM I replacement of the silica-rich residue from cement paste have a 28-day compressive strength of 63.6 MPa.

6 Engineering aluminosilicates extracted from waste concrete to form a viable supplementary cementitious material

In this chapter, the aluminosilicate SCM extracted from waste concrete is heat-treated. The mechanism of specific surface area reduction is investigated. The effect of temperature on the physical properties and pozzolanic reactivity of the engineered aluminosilicate SCM, and the workability and mechanical performance of mortars containing the engineered aluminosilicate SCM is reported. This work has been published as ‘Engineering aluminosilicates with high surface area extracted from waste concrete to form a viable supplementary cementitious material’ in Construction and Building Materials (<https://doi.org/10.1016/j.conbuildmat.2025.139981>).

6.1 Introduction

Given the enormous amounts of waste concrete available, extracting viable aluminosilicate SCMs with carbonation to form CaCO_3 to make low-carbon construction materials, is an interesting option. The high specific surface area of the aluminosilicate gel has been found to improve the early stage pozzolanic reactivity (Zajac et al., 2023a; Peng et al., 2023). However, high specific surface area induces high water absorption, reducing the workability of concrete and making use as a viable SCM problematic. Waste concrete powder carbonated by a wet carbonation process under 25 °C using pure CO_2 has a specific surface area of 56.54 m^2/g . 20 % replacement of CEM I by the carbonated waste concrete powder causes around 50 % decrease in the paste flow without vibration (Peng et al., 2023). The specific surface area of carbonated cementitious materials can be reduced using a modified direct carbonation process. A semi-dry direct carbonation process for WCP has been developed (Zajac et al., 2023b). In this, pure CO_2 in saturated water vapour at elevated temperatures (45 – 55 °C) is used. Compared to WCP carbonated in solution, the BET surface area of semi-dry carbonated WCP was reduced by 36 %. However, the resulting surface area remains high ($\sim 34 \text{ m}^2/\text{g}$). In another study, monoethanolamine (MEA) is added during the direct carbonation of WCP to increase the repulsion of carbonated WCP particles and unlock the trapped water. Cement paste containing 30 % of WCP

carbonated in 45 % MEA solution results in the same flowability as the reference consisting of 100 % CEM I (Mao et al., 2024). However, this method results in low early-age strength and increased cost. To our knowledge, there have not been any reported research focusing on engineering the aluminosilicate material to improve the flow properties of the concrete containing this SCM.

In chapters 4 and 5, acetic acid has been used to leach cementitious materials including WCF and HCP, generating clean sand, a pozzolanic aluminosilicate-rich SR, and a Ca^{2+} -rich solution that can be converted into CaCO_3 via reaction with CO_2 . The SR mainly consists of amorphous aluminosilicate gel with crystalline impurities, such as quartz. The Frattini and R^3 test results showed that the SR had comparable pozzolanic reactivity to coal fly ash (FA), indicating the potential to be used as an SCM. However, the SR significantly reduced the workability of cement mortar. A superplasticiser dosage of 1.1 – 5% was needed to achieve good workability, with additional costs. Therefore, there is a need to process the SR to improve workability.

Sintering converts compacted ceramic powder samples into dense structures, typically using temperatures above 1000 °C. It has been used to densify silica and alumina-rich industrial wastes, such as FA to produce glass ceramics and lightweight aggregates. During sintering, particles fuse and bond together, and the specific surface area of the sintered material is reduced (Song et al., 2023; Ilic et al., 2003; Biernacki, Vazrala & Wayne Leimer, 2008). Inspired by this theory, this research has used heat treatment to reduce the specific surface area of SR and improve the workability of SR-blended cement mortars. The effect of heat treatment temperature on particle size distribution, specific surface area and pozzolanic reactivity of SR is reported. Data on heat of hydration, mortar workability and compressive strength is also reported. The temperature-induced microstructural changes are characterised, and the potential use of heat-treated SR extracted from waste concrete is discussed.

6.2 Experimental

6.2.1 Materials

Untreated SR is produced from the optimal acetic acid leaching of HCP described in chapter 4, using 1.6 mol/L CH_3COOH , L/S ratio of 11 mL/g, temperature of 60 °C and reaction time of 1 hour. Thames

River siliceous sand (< 4 mm), CEM I 52.5N (Breedon, UK), commercially available SF (Elkem Norway), GGBFS (Heidelberg Materials, Germany) and class-F FA (Heidelberg Materials, Germany) as described in section 3.1 are used to prepare the mortar samples.

6.2.2 Heat treatment of SR

10 g samples of SR are heated in a porcelain crucible to 840, 870, 900, 950 and 1000°C and kept for 1 hour in a furnace (Carbolite Gero HTF 17/5). These temperatures are selected based on the TGA-DSC results and will be discussed later in section 6.3. The heat-treated SR samples are cooled to room temperature in the furnace and are labelled SR840, SR870, SR900, SR950 and SR1000, respectively. After heating, SR840, SR870 and SR900 remained as powder, while SR950 and SR1000 form hard bulk solids, and they are ground to less than 300 µm using a mortar and pestle before subsequent experiments.

Apart from the abovementioned samples, SR samples heated at 250, 400, 600, 700 and 800°C are also prepared for specific surface area and R^3 cumulative heat measurements to study the effect of temperature on the surface area and pozzolanic reactivity of the SR.

6.2.3 Characterisation methods

Thermal analysis (TGA-DSC, Netzsch STA 449 F5) to determine the sintering temperature range and loss-on-ignition (LOI) is completed using ~20 mg of sample heated from 30 to 1050°C, at a heating rate of 10 °C/min. The chemical composition of test materials is determined using XRF (Malvern PANalytical Zetium). The crystalline phases present are determined using XRD (Malvern PANalytical Empyrean). To determine the phase compositions, quantitative XRD with Rietveld refinement is performed, using 20 wt.% corundum (Al_2O_3) as an internal standard. The amorphous content is calculated from equation 3.3. FTIR-ATR (Thermofisher Nicolet iS50) is used to analyse the chemical bonding in SR. The BET specific surface area of untreated and heat-treated SR is determined as an average of three measurements using N_2 adsorption-desorption (Micromeritics 3Flex 3500). Particle size distribution of the untreated and heat-treated SR is obtained using laser diffraction (Malvern Mastersizer 3000), with tap water as dispersant. The D_{10} , D_{50} and D_{90} values are calculated using an

average of five measurements. The particle morphology of SR is observed using SEM (Zeiss Sigma 500VP FESEM) on carbon-coated samples. The phase distribution in the microstructure of 28-day cured mortars is studied by SEM using BSE mode.

6.2.4 Pozzolanic reactivity (R^3 test) and heat of hydration

R^3 test following the method described in section 3.4.2 within the ASTM C1897 regime is used to assess the pozzolanic reactivity of the SR samples. The 7-day cumulative heat of the test samples was normalised against the mass of SR and plotted against the heat treatment temperature.

Seven cement pastes consisting of a 100% CEM I reference mix and six blended mixes with 20% CEM I replaced by untreated SR, SR840, SR870, SR900, SR950 and SR1000 were prepared with a constant water-to-binder (w/b) mass ratio of 0.4. Superplasticizer (MasterGlenium 315C) was added at 5% wt. binder to the mix containing untreated SR to achieve a workable paste. The heat of hydration of the pastes was determined at 20°C for 7 days using isothermal conduction calorimetry (TAM Air) in accordance with British standard BS EN 196-11. The heat flow and cumulative heat were normalised using the mass of Portland cement in the paste.

6.2.5 Mortar production, flow properties and strength testing

Mortar samples are prepared using 100% CEM I (reference) and binders containing 80 % CEM I and 20 % untreated and heat-treated SR. These are compared to mortars containing the same CEM I replacement using FA, SF or GGBFS. CEM I replacement of 20% is feasible, as shown by the results of chapter 5. Siliceous sand (< 4 mm) is used as the fine aggregate and the sand-to-binder mass ratio is 3.0. The water-to-binder ratio is set to 0.56 to achieve a workable reference without requiring superplasticizer. The workability of fresh mortar is assessed using a flow table. Cube samples are cast into 20×20×20 mm steel moulds and vibrated for 2 minutes. For mortars containing SF or untreated SR, extended vibration for 4 minutes is applied to compensate for the low workability. Test cubes are demoulded after 24 h and cured in saturated lime water at 20 ± 1 °C for 3, 7, 28 and 60 days. The compressive strength of mortar cubes is determined using six replicates at each curing age on a universal testing machine (Instron 5980 Universal Testing System).

6.3 Results

6.3.1 Physical properties, chemical compositions and pozzolanic reactivity of heat-treated SR

TGA-DSC data of the untreated SR is shown in Figure 6.1. The major mass loss occurs before 200°C. The DSC data shows that an endothermic peak exists at 130°C, which is attributed to the heat absorption due to removal of physically adsorbed water. This agrees with previous research on amorphous silica gel which showed that multi-layer adsorbed water is eliminated to form a monolayer that is then completely removed when the temperature reaches ~200°C. Above 200°C, silanol condensation occurs when the vicinal silanol, geminal silanol and isolated silanol are condensed and evaporated with increasing temperature (Zhuravlev, 2000). These are not directly observed from the DSC data because it is masked by other exothermic processes such as the combustion of the adsorbed acetate and densification of the SR, as shown in the exothermic hump and continuous mass loss between 200 and 800°C (Brinker & Mukherjee, 1981; Pramanik et al., 2013). A broad exothermic peak is observed in the DSC curve at 870°C, indicating sintering. This is attributed to the release of surface energy due to reduction in surface area (Hirono et al., 2020). Therefore, heat treatment temperatures are selected to span this exothermic peak (800 - 1000°C) as described in Section 6.2.2.

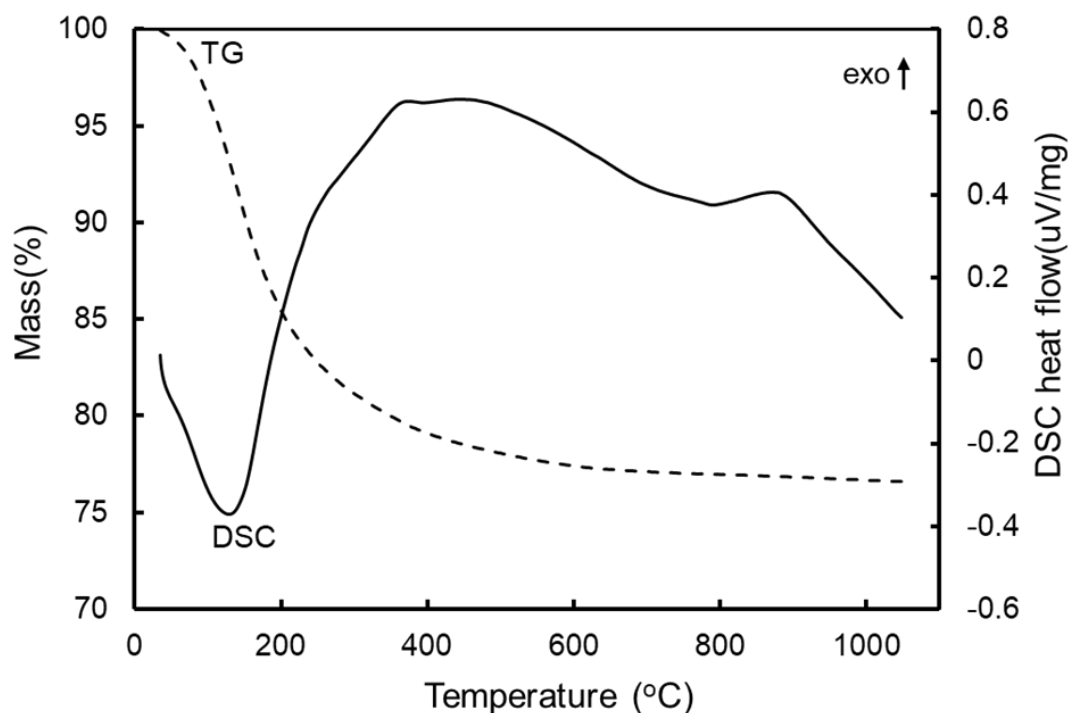


Figure 6.1 TGA and DSC curves of the untreated SR.

Table 6.1 compares the chemical composition of untreated and heat-treated SR to commercially available SCMs and hydrated cement paste (HCP). Acetic acid treatment of HCP leaches CaO, producing a solid residue that contains mainly silica and alumina. Untreated and heat-treated SR have similar chemical composition to FA, although with generally higher SiO₂/Al₂O₃ ratio. Heating does not affect the composition of the aluminosilicate residue but reduces the loss-on-ignition (LOI) due to removal of physically absorbed water by evaporation, and chemically bound water by silanol condensation.

Table 6.1 Chemical composition expressed as oxide % and LOI of CEM I and the test materials.

Sample	Percentage (%)								
	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	TiO ₂	K ₂ O	SO ₃	LOI
SR untreated	51.5	13.6	5.2	3.7	0.5	0.7	0.5	0.2	23.4
SR840	65.3	17.3	7.0	5.1	0.7	0.8	0.7	0.5	0.3
SR870	66.2	17.4	6.9	5.3	0.6	0.8	0.8	0.4	0.3
SR900	67.1	17.6	6.9	5.1	0.7	0.8	0.7	0.4	0.2
SR950	67.7	17.8	6.5	4.6	0.7	0.8	0.6	0.3	0.2
SR1000	67.8	17.9	6.5	4.7	0.7	0.9	0.6	0.3	0.1
SF	93.3	0.4	0.3	0.2	0.5	-	1.6	0.4	2.3
GGBFS	33.7	11.4	40.6	0.6	5.9	1.3	0.7	1.7	3.1
FA	51.3	25.7	4.8	6.5	1.5	1.5	1.4	0.4	2.3

The XRD data for untreated and heat-treated SR are shown in Figure 6.2. Untreated SR is predominantly amorphous with some quartz, which is present in the cement paste and is resistant to acid dissolution. Similar XRD data was obtained for heat-treated SR at temperatures up to 900°C. At higher temperatures transition from amorphous to crystalline phases occurs. At 950°C the diffraction peaks of cristobalite (SiO₂) and anorthite (Ca(Al₂Si₂O₈)) appeared. At 1000°C the intensity of these peaks increased, and hematite (Fe₂O₃) is detected. QXRD shows that untreated SR, SR840, SR870, SR900, SR950 and SR1000 have amorphous contents of 98.6, 98.8, 98.7, 98.1, 80.7 and 47.6 %, respectively. This indicates that the crystallisation of amorphous aluminosilicate gel in SR commences above 900°C and the extent increases with increasing temperature. In comparison, the amorphous contents of SF, GGBFS and FA are 99.1 %, 94.3 % and 65.2 % respectively. All the SR treated below 950°C have similar amorphous content to SF and GGBFS and are more amorphous than FA.

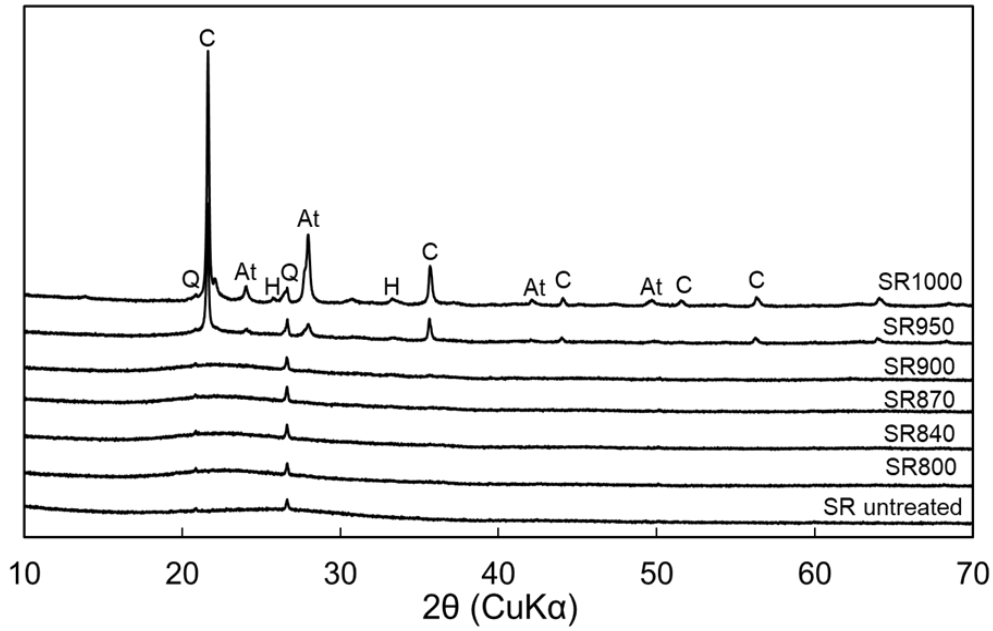


Figure 6.2 XRD data of raw and heat-treated silica-rich residue. Q: Quartz; C: Cristobalite; At: Anorthite; H: Hematite.

Figure 6.3 shows FTIR results of untreated and heat-treated SR. The absorbance peak at around 800 cm^{-1} is associated with the symmetric stretching of Si-O-Si (Imoisili & Jen, 2023). The intense peak around 1000 cm^{-1} denotes the asymmetric stretching vibration of Si-O-Si, and this slightly shifts to the right as the temperature increases because of changes in the silica structure. The Si-OH silanol bond is characterised by a peak at 1640 cm^{-1} (Mohammadi et al., 2021; Imoisili, Ukoba & Jen, 2020). The wide hump at $\sim 3400\text{ cm}^{-1}$ is formed from hydrogen bonded silanol structures (Si-O-H) (Paukshtis et al., 2019). As the heat treatment temperature increases, the peaks associated with absorbed water and silanol at 3400 and 1640 cm^{-1} disappear, corresponding to the evaporation and the condensation of silanol structures. A peak at 470 cm^{-1} emerges at 950°C and becomes distinct at 1000°C , which is characteristic of cristobalite (Zhang, Tie & Zhang, 2018). At 1000°C , a new peak appears at 916 cm^{-1} which is characteristic for anorthite (Yilmaz, 2012), and this is consistent with the XRD results.

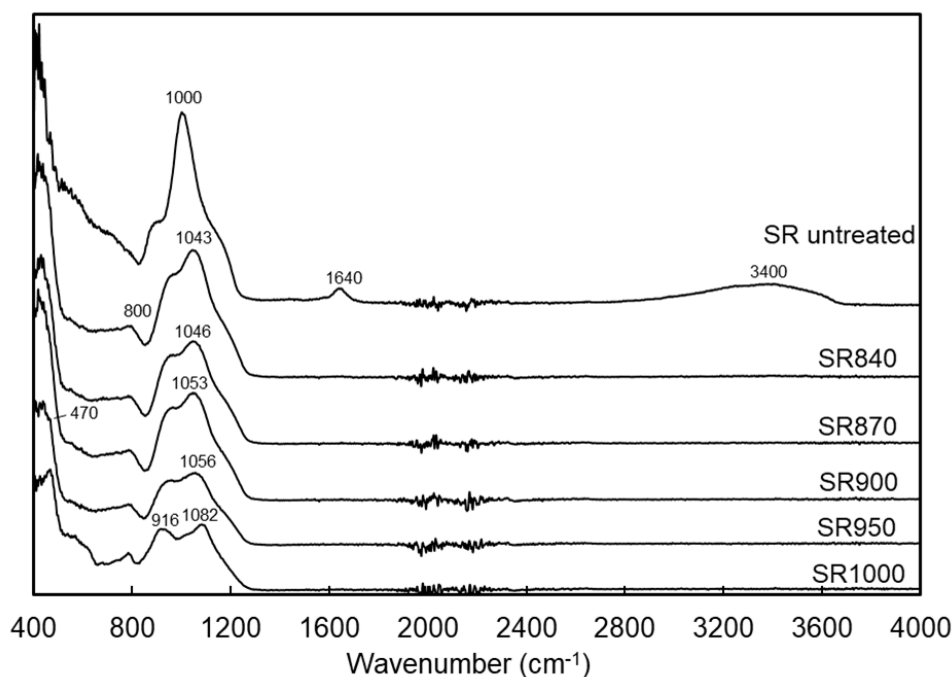


Figure 6.3 FTIR-ATR spectra of raw and heat-treated silica-rich residue.

SEM images showing representative morphological changes of heat-treated SR are presented in Figure 6.4(a) – (f). Figure 6.4(a) shows that untreated SR particles consist of agglomerates of nano-sized primary particles, resulting in a porous and rough surface structure. When heated at 840°C (Fig. 4b), the rough surface texture remains but the primary particles appear larger compared to untreated SR, with dense surfaces starting to form. The sintering is further promoted at 870°C (Fig. 4c), where more voids between primary particles are closed and smoother surfaces formed. At 900°C (Fig. 4d), sintered bodies with smoother surfaces have replaced the porous particles. At 950°C (Fig. 4e), small-sized 0.1 – 0.3 μm crystals are seen on particle surfaces, indicating the sintering process is complete and crystallisation occurs. At 1000°C (Fig. 4f), the crystals become larger due to increased crystallisation of cristobalite, anorthite and hematite.

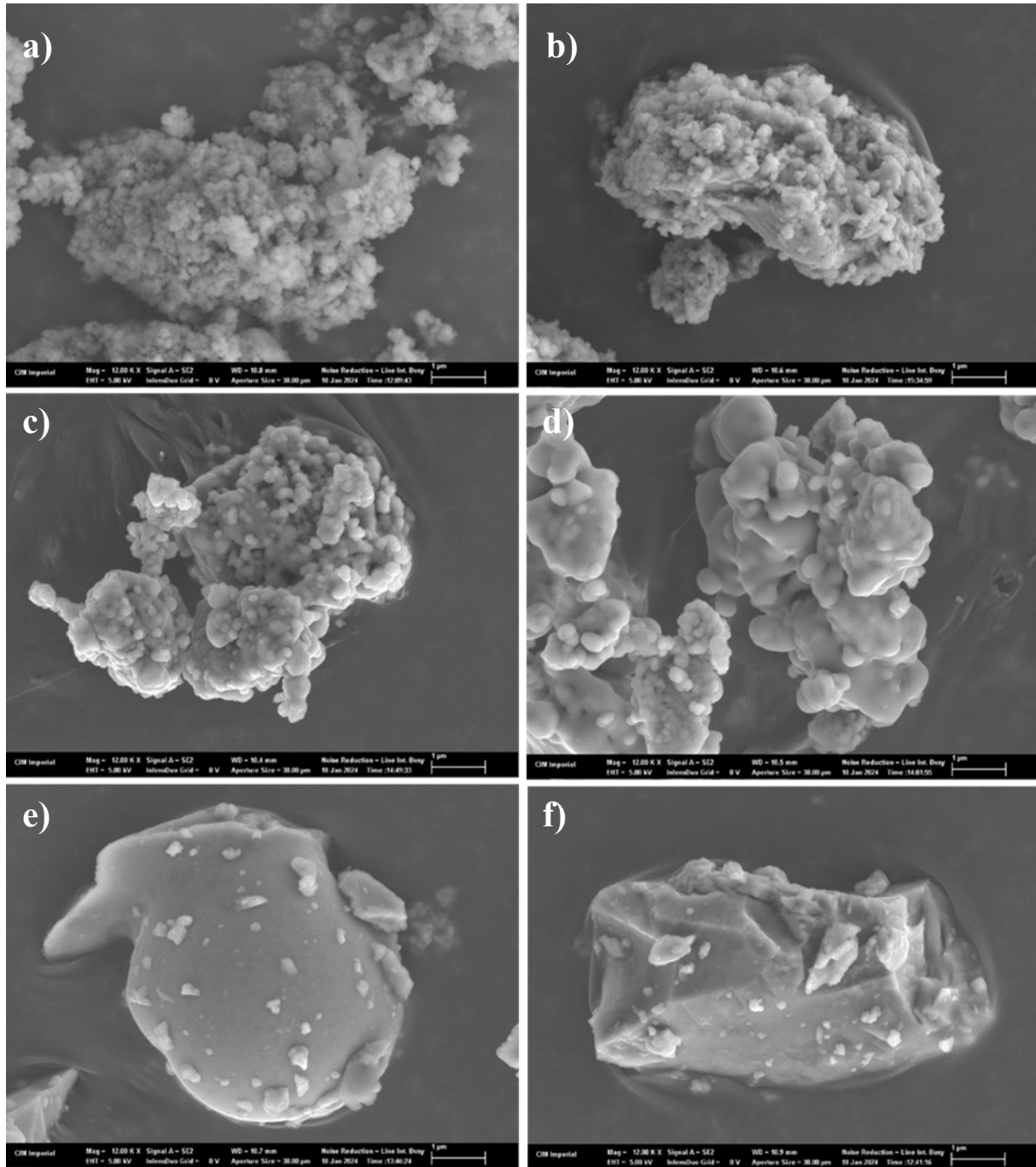


Figure 6.4 SEM images of raw and heat-treated silica-rich residue samples magnified at 12000 times. a) SR untreated, b) SR840, c) SR870, d) SR900, e) SR950, f) SR1000.

The effect of heat treatment temperature on the particle size distribution of SR samples is shown in Table 6.2. This indicates that the D_{10} and D_{50} of SR increase with temperature because small particles melt and form larger agglomerates during sintering. The D_{90} of SR slightly decreases from 840 to 900°C, indicating there is some breakdown of larger particles during sintering. The particle size and specific surface area of SR samples are compared to those of FA, GGBFS and SF in Table 2. All SR samples

tested have particle sizes greater than FA, GGBFS and SF. However, the specific surface area of untreated SR (154.95 m²/g) is around 120 times as that of FA (1.26 m²/g) and GGBFS (1.42 m²/g) and about 7 times as that of SF (22.80 m²/g). This indicates that untreated SR is highly porous. The specific surface area of SR substantially reduces by 89.0 – 99.8 % after heat treatment at or above 840 °C.

Table 6.2 Particle size (D₁₀, D₅₀ and D₉₀) values and specific surface area of raw and heat-treated silica-rich residue and commercial SCMs.

Sample	Particle size (μm)			Specific surface area (m ² /g)
	D ₁₀	D ₅₀	D ₉₀	
SR untreated	6.7 ± 0.0	40.6 ± 0.3	130.6 ± 2.2	154.95 ± 11.24
SR840	7.5 ± 0.0	61.6 ± 0.4	180.4 ± 1.6	17.06 ± 1.68
SR870	8.9 ± 0.1	64.7 ± 1.4	180.0 ± 3.1	6.49 ± 0.94
SR900	10.1 ± 0.2	65.6 ± 2.0	172.0 ± 3.0	2.09 ± 0.29
SR950	14.5 ± 0.4	93.9 ± 1.5	230.6 ± 3.4	0.85 ± 0.67
SR1000	21.7 ± 0.1	124.8 ± 0.8	297.2 ± 1.6	0.44 ± 0.53
FA	3.2 ± 0.1	23.4 ± 0.2	99.0 ± 2.6	1.26 ± 0.54
GGBFS	1.7 ± 0.0	10.1 ± 0.2	27.2 ± 0.6	1.42 ± 0.36
SF	0.03 ± 0.0	0.14 ± 0.0	64.0 ± 0.3	22.80 ± 0.63

The effect of temperature on the pozzolanic reactivity (R³) and specific surface area of SR is shown in Figure 6.5. Untreated SR releases 250 J/g of heat during 7 days of pozzolanic reaction. Under heat treatment up to 700°C, the amount of heat released at 7 days increased by a factor of 2. This is due to the removal of physically adsorbed and chemically bound water which increases the concentration of the reactive silica and alumina as shown in Table 6.1. Besides, the specific surface area of SR is reduced by around 50 % at 700°C. This indicates that physically adsorbed water removal and silanol condensation processes, shown in the TGA-DSC data (Figure 6.1), result in the drop of surface area.

With increasing temperature from 700°C to 900°C, the pozzolanic reactivity of SR decreases from 467 to 307 J/g, and the specific surface area also falls from 81.58 to 2.09 m²/g. This is because sintering occurs in this temperature range, which closes voids and produces larger particles with lower surface energy and surface area. This reduces the dissolution rate and provides fewer nucleation sites for the growth of cement hydration products, resulting in reduced pozzolanic reactivity.

Above 900°C, the reduction in surface area is much slower and almost plateaus, while the pozzolanic reactivity of SR is drastically reduced. This suggests that the sintering of aluminosilicate gel in the SR

completes at around 900°C, and a further reduction in pozzolanic reactivity is caused by the crystallisation forming stable crystallites on the surface and shielding the amorphous silica (de Azevedo Basto, Estolano de Lima & de Melo Neto, 2023). As classified by Kalina et al., a material is highly pozzolanic, moderately pozzolanic and inert with a 7-day R^3 cumulative heat release of > 200 , $100 - 200$ and < 100 J/g, respectively (Kalina et al., 2019). SR870 and SR900 have a surface area of 6.5 and 2.1 m^2/g , and 7-day heat release of 403 and 307 J/g, respectively. This indicates that a heat treatment temperature between 870 and 900°C generates highly pozzolanic materials, with specific surface area lower than directly carbonated waste concrete powder and comparable to commonly used SCMs.

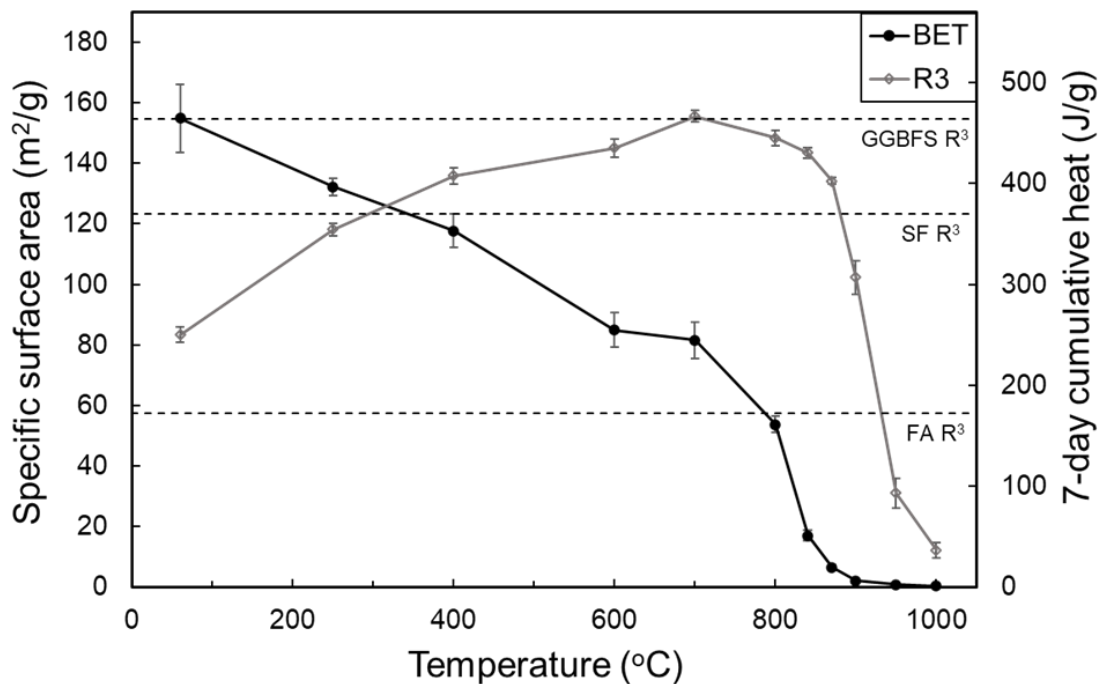
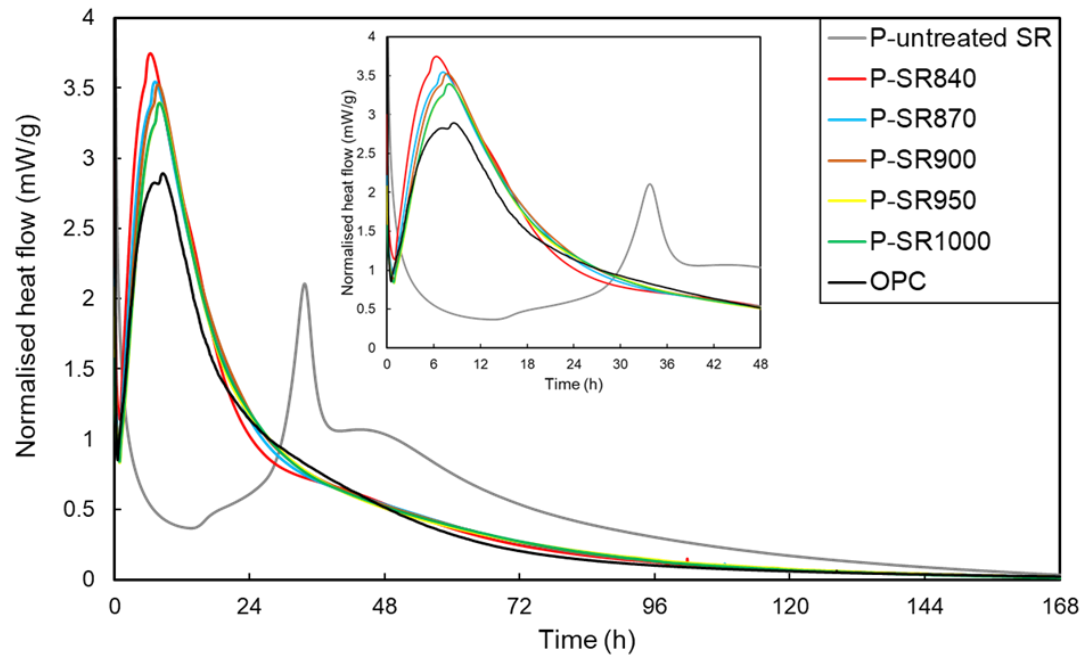


Figure 6.5 Variation in BET specific surface area and 7-day cumulative heat from R^3 test of the silica-rich residue against temperature. For comparison, the BET specific surface area of SF, FA and GGBFS are 22.80 ± 0.74 , 1.26 ± 0.54 and 1.42 ± 0.30 m^2/g , respectively. The 7-day R^3 heat of SF, FA and GGBFS are marked as dashed lines. Error bars show the standard deviation of the results.

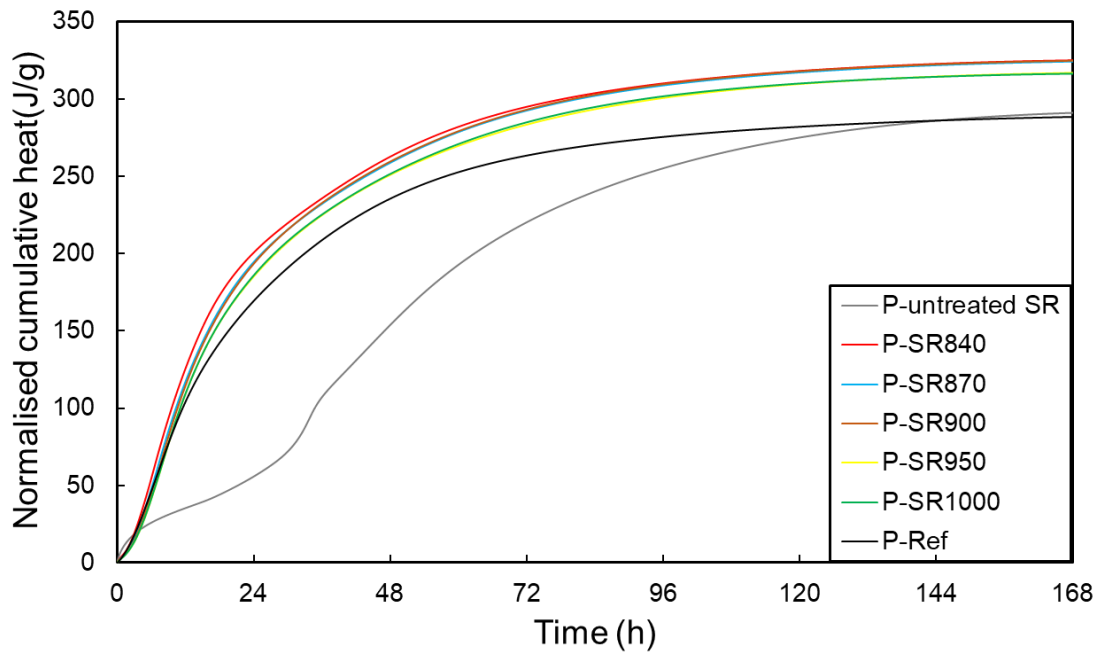
6.3.2 Hydration heat of paste

Figure 6.6 presents the heat flow and cumulative heat of hydration from isothermal conduction calorimetry of cement paste for 7 days. The main peak at ~ 8 h in Figure 6.6(a) indicates C3S hydration, with a shoulder that relates to sulphate depletion and C3A reaction. However, the main peak for the paste containing untreated SR is delayed by around 24 hours due to the retarding effect of the

significantly large amount of superplasticiser (Puertas et al., 2005). All blended pastes with heat-treated SR show a higher C3S hydration peak and cumulative heat (Figure 6.6(b)) than the 100% CEM I reference paste, indicating the pozzolanic reactivity and filler effect of SR. Compared to P-Ref, the shoulder corresponding to sulphate depletion occurs earlier for all blended pastes with heat-treated SR, because of the higher Al_2O_3 content. P-SR840, P-SR870 and P-SR900 show higher cumulative heat of hydration (Figure 6.6(b)) than P-SR950 and P-SR1000, which can be attributed to the differences in pozzolanic reactivity of the heat-treated SR (Figure 6.5). It has been reported the hydration heat at 72 h of cement paste containing 20 % of directly carbonated waste concrete powder is 322 J/g CEM I (Peng et al., 2023). In comparison, the 72-h hydration heat of P-SR840, P-SR870 and P-SR900 are around 295 J/g CEM I. Given the lower water/cement content used in this research (0.4 versus 0.5 in the reported work), the pozzolanic reactivity of optimally heat-treated SR is comparable to that of carbonated waste concrete powder.



(a)



(b)

Figure 6.6 Isothermal conduction calorimetry curves showing (a) heat flow and (b) cumulative heat of hydration of cement pastes containing 20 % replacement of SRs.

6.3.3 Flow and compressive strength of mortar

The flow table test results are presented in Figure 6.7. It is observed that the mortar containing untreated SR has the lowest workability of all the test mortars. This results in poorly compacted samples showing substantial surface voids even after extended vibration. In comparison, the flow of mortars containing heat-treated SR increased by 11.5%, 16.2%, 26.3%, 37.0% and 38.4% for samples heated to 840, 870, 900, 950 and 1000°C compared to the untreated SR. Furthermore, mortars containing heat-treated SR show improved flow properties compared to SF. The improved workability helps to achieve good compaction without requiring superplasticizer.

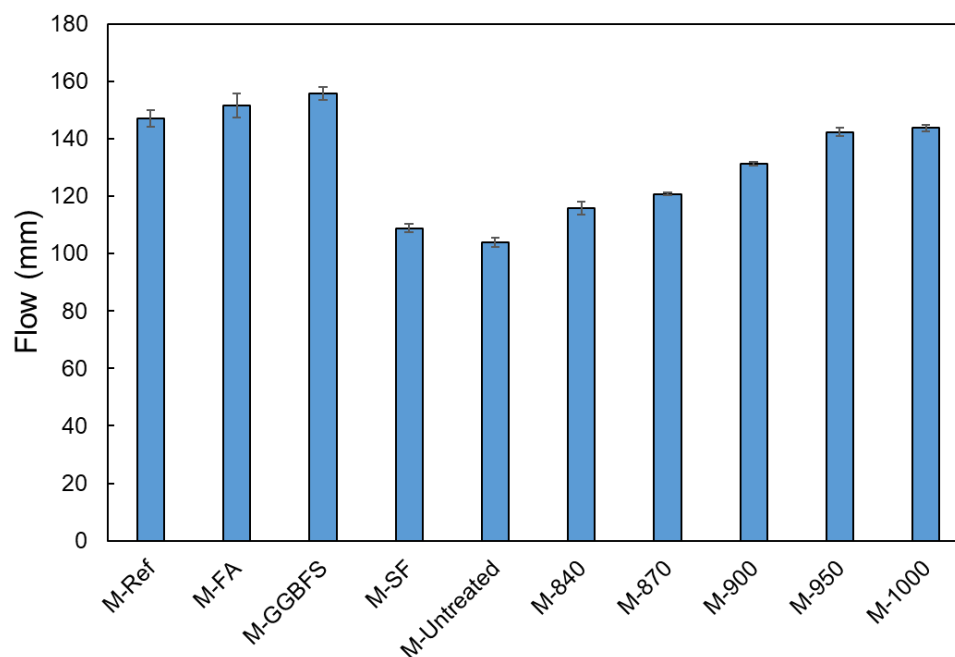


Figure 6.7 Flow values of the test mortars at 0.56 w/b ratio. M-ref contains 100% CEM I 52.5 N. Other mortar samples contain 20 % CEM I replaced with SR or conventional SCM. Error bars show the standard deviation of the results.

Figure 6.8 presents the compressive strength of mortars containing untreated and heat-treated SR, compared to those containing 100% CEM I (M-Ref) and 20% CEM I replaced with FA, GGBFS or SF. The strength of mortars containing untreated SR is less than 10 MPa and increases marginally after 7 days due to poor workability and inadequate compaction. Mortars with heat-treated SR up to 900°C show an increase in compressive strength at all ages with increasing temperature, due to improvements in workability and pozzolanic reactivity. Mortars with heat-treated SR (up to 900°C) have higher strengths than M-FA, and comparable strengths to M-Ref, M-GGBFS and M-SF. The later age strength

gain is related to the continuous consumption of $\text{Ca}(\text{OH})_2$ by the unreacted aluminosilicate gel and the C-(A)-S-H phase with a low Ca/Si ratio that forms due to the pozzolanic reaction (Zajac et al., 2023b). Increasing heat treatment temperature above 900°C causes a reduction in pozzolanic reactivity and this outweighs the benefits of improved workability, shown in the reduced 28-day and 60-day strength of M-950 and M-1000. This is due to the increased inert cristobalite, anorthite and hematite phases, as shown in the XRD data (Figure 6.2). It should be noted that M-950 has a large compressive strength gain (21.4 %) between 28 and 60 days, probably because of its later stage pozzolanic reactivity as SR950 is 80.7 % amorphous.

In general, SR900 gives good workability, higher early-age strength and similar long-term strength compared to SR treated at other temperatures. Therefore, 900°C is considered the optimal temperature for improving the performance of aluminosilicate residue extracted from waste concrete powder.

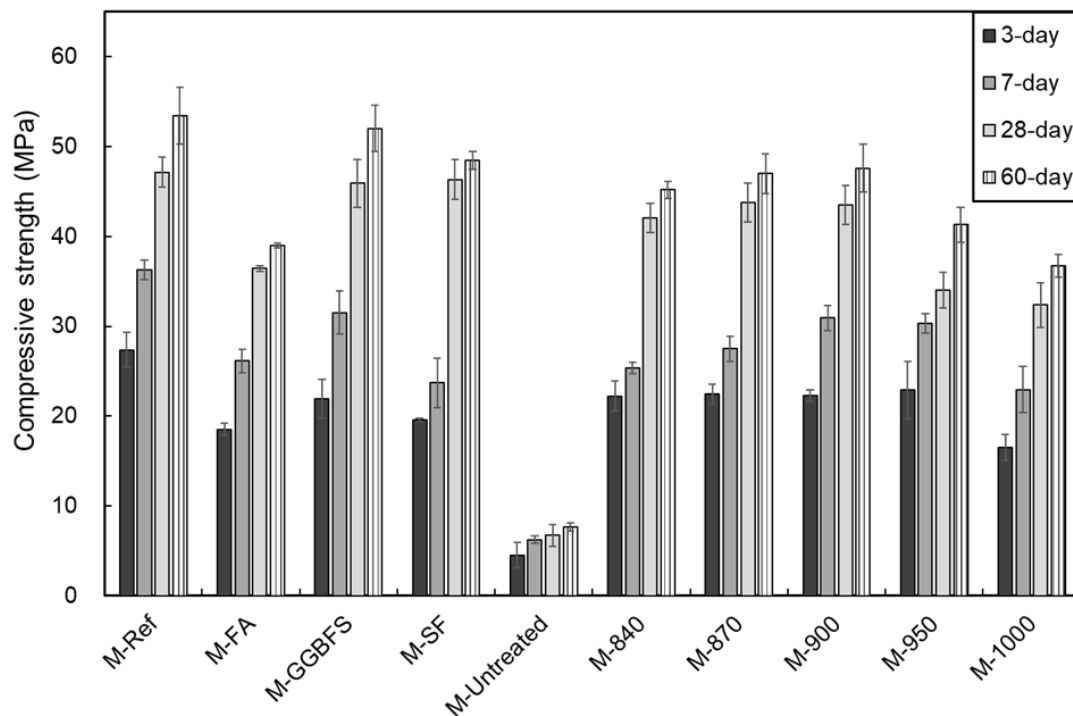


Figure 6.8 Compressive strength of test mortars at 3, 7, 28 and 60 days. Error bars show the standard deviation of the results.

6.3.4 Solid phase distribution in mortars containing SR

Figure 6.9 shows the SEM-BSE images of M-Ref, M-FA, M-SF, M-GGBFS, M-900 and M-1000. The microstructure of mortars consists of anhydrous clinker, hydration products, SCM particles and pores which are clearly identified in the images. C-S-H phase and portlandite nucleates on the surface of the partially hydrated clinker particles and the SCMs. In M-FA and M-SR900, needle-shaped AFm crystals can be observed on the rim of the SCM grains. SR900 generates more needle-shaped crystals than FA. This is due to its stronger pozzolanic reactivity generated from the amorphous aluminosilicate gel. In contrast, no AFm is observed in M-1000, indicating the crystalline aluminosilicates are less reactive.

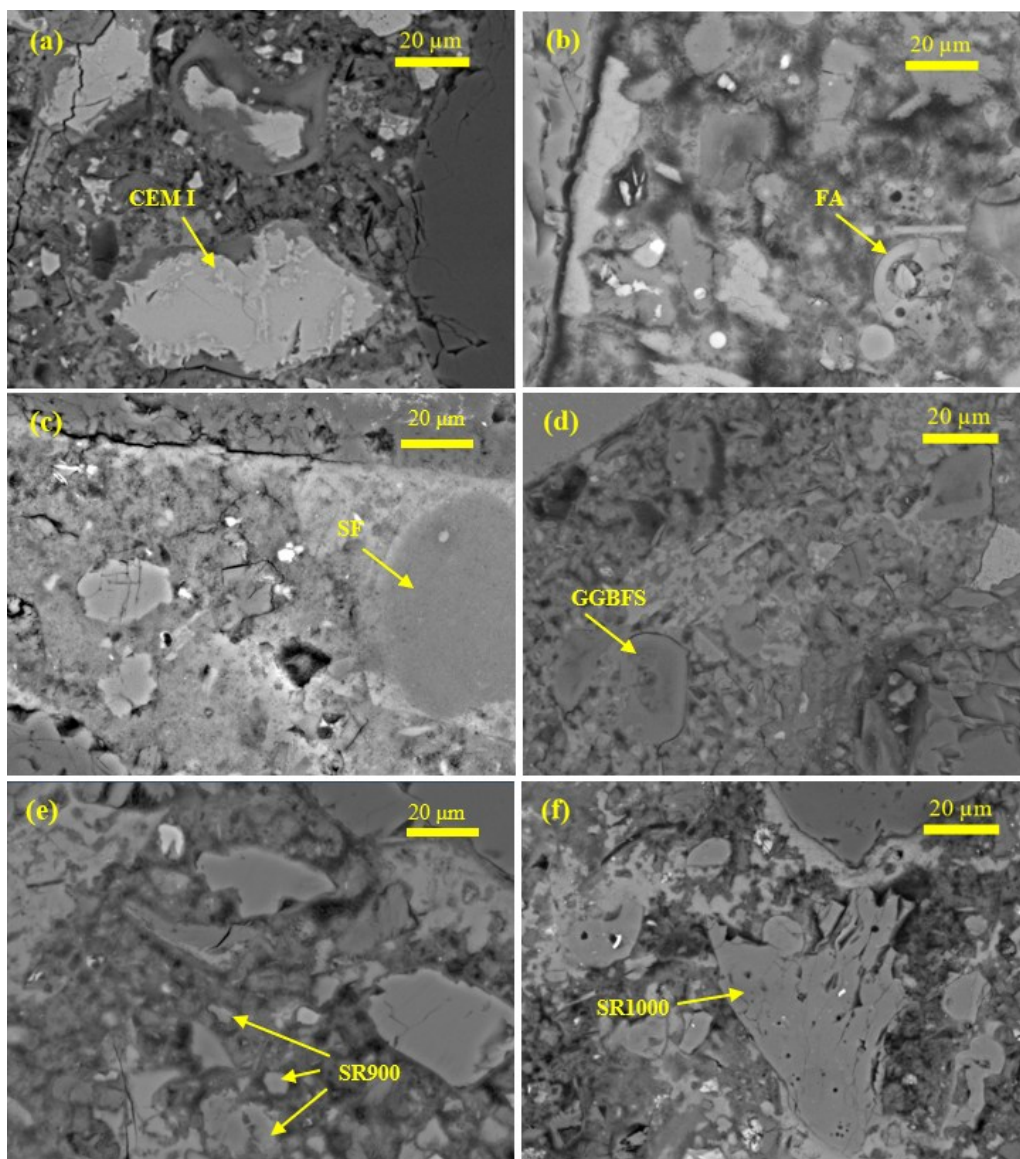


Figure 6.9 SEM-BSE images of 28-day mortars at 2000 times magnification. (a) M-Ref; (b) M-FA; (c) M-SF; (d) M-GGBFS; (e) M-900; (f) M-1000.

The composition of C-S-H phase of M-900 is compared to M-Ref, M-1000 which represents the mortar with inert filler and M-GGBFS which represents the mortar with a highly reactive SCM (Figure 6.10). The Si/Ca ratio of C-S-H phase increases from 0.49 ± 0.07 in M-GGBFS, 0.53 ± 0.06 in M-1000 and 0.54 ± 0.06 in M-Ref to 0.58 ± 0.07 in M-900. The Al/Ca ratio increased from 0.06 ± 0.02 in M-Ref to 0.09 ± 0.03 in M-1000 and M-GGBFS and further to 0.10 ± 0.03 in M-900, respectively. This is due to the pozzolanic reaction of the amorphous aluminosilicate gel in the composite cement which gives higher Si/Ca and Al/Ca ratios compared to neat CEM I and composite cements with inert filler and slag (Lothenbach, Scrivener & Hooton, 2011).

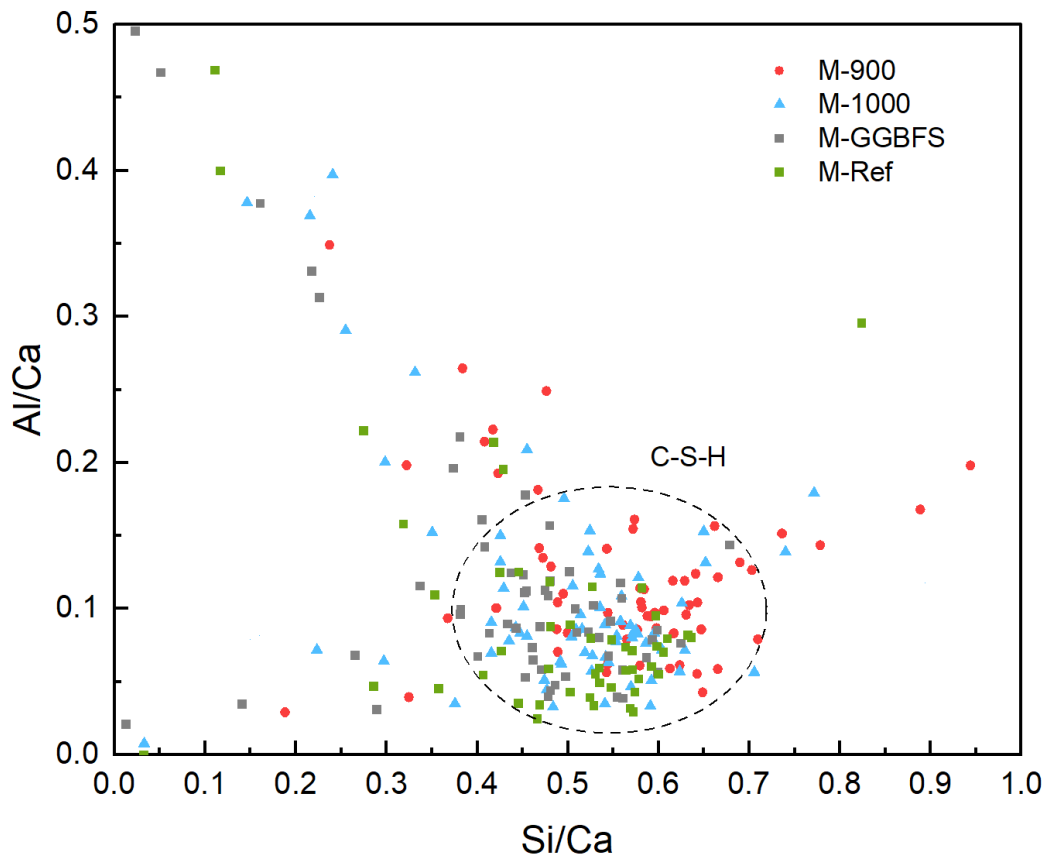


Figure 6.10 The 2D scatter plot of the EDS analysis of C-S-H composition on 28-day mortar samples. The points related to C-S-H is marked with a dashed ellipse.

6.4 Discussion

6.4.1 Comparison of heat-treated SR and other SCMs

Heat treatment can reduce the porosity and surface area of the aluminosilicate residue from waste concrete. At the optimal temperature of 900 °C, the specific surface area of SR was reduced by 99% compared to untreated SR and the specific surface area was 2.09 m²/g, which is just slightly higher than that for GGBFS and FA. Furthermore, the cumulative heat release of SR900 after 7 days in the R³ test was increased by 22.8 % compared to the untreated SR, while the loss in pozzolanic reactivity compared to SR700 (34.3%) is acceptable. In comparison to the directly carbonated waste concrete powder, SR900 has 96.3 % lower surface area and improves the workability by 40 % at 20 % clinker replacement ratio (Peng et al., 2023). Direct comparison of the mechanical performance of heat-treated SR and directly carbonated waste concrete powder is difficult because of the different particle size of fine aggregate and mixing ratio used in preparing mortar samples. Alternatively, comparisons can be made by examining the compressive strength gain versus the inert reference. The 20-mm cube mortars using 20% of CEM I replaced by directly carbonated waste concrete powder and sand less than 0.4 µm mixed at a sand : binder : water ratio of 1:1:0.55 have a ~16 % higher 28-day compressive strength (50 MPa) than reference with limestone filler (43 MPa) (Zajac et al., 2023b). The 28-day compressive strength of M-SR900 (43.5 MPa) is 34 % higher than that of M-SR1000 (32.4 MPa) with is regarded as an inert reference. The results show that heat treatment of SR extracted from waste concrete can improve the workability and strength of mortars, making it a viable candidate as an alternative SCM. Also, indirect carbonation process can produce purer CaCO₃ for other value-added applications, further adding to the merit.

Crystallization of SR occurs above 900°C as it transforms into cristobalite, anorthite and hematite. The crystallization process redistributes network modifier ions (Al³⁺, Fe³⁺ and Ca²⁺), and this reduces pozzolanic reactivity. Non-reactive crystalline phases reduce the surface area (de Azevedo Basto, Estolano de Lima & de Melo Neto, 2023). Additionally, the degree of polymerization of the remaining reactive amorphous aluminosilicate is increased due to the loss of network modifier ions, resulting in a reduction of the pozzolanic reactivity (Skibsted & Snellings, 2019). It is therefore important to keep the heat treatment temperature below 950°C to avoid these effects.

6.4.2 Yield and feasibility of heat-treatment process

Construction and demolition waste and particularly end-of-life concrete needs to be properly valorised. Crushed concrete fines are a problematic waste but this work shows that this should be regarded as a valuable resource. Extracting SR using indirect carbonation of crushed concrete fines can form new SCMs and this is an essential step towards achieving circular concrete. Based on this research, it was found that 1 kg of hydrated cement powder produces around 0.26 kg of untreated SR and 0.2 kg of heat-treated SR. Waste concrete powder constitutes ~30% of the total waste concrete (Poon et al., 2023). Based on the current global production of waste concrete of ~2 billion tonnes per annum, 120 million tonnes of heat-treated SR could be produced, and this is expected to increase as ageing concrete infrastructure reaches end-of-life and is demolished. Therefore, aluminosilicates from waste concrete can be an important supplement to existing SCMs and contribute to higher clinker replacement levels.

Optimum heat treatment at 900°C preserves the glassy aluminosilicate structure and maintains high pozzolanic reactivity. This is a lower temperature than used in traditional sintering processes, which are typically above 1000°C. This is because the aluminosilicate residue contains small amounts of CaO and MgO which act as a flux to lower the sintering temperature (Huang et al., 2024). This temperature is also much lower than the temperature required to make cement clinker and can be achieved using biomass or other green, low carbon energy. From the DSC curve of SR (Figure 6.1), the release of heat due to sintering starts from around 800 °C, so the heat treatment under lower temperatures between 800 and 870 °C could also work. The trade-off between reactivity, surface area and energy consumption can be influenced by temperature and heating time. According to Arrhenius' equation, reaction rate is slower at lower temperature, so longer time could be needed to achieve same reduction in surface area, and this is recommended for future research.

6.5 Conclusions

The specific surface area of the aluminosilicate residue produced by acid leaching of cement paste can be reduced by thermal treatment. The optimum heat treatment temperature is ~900°C. At this temperature, the heat-treated aluminosilicate residue has a comparable specific surface area and pozzolanic reactivity to commercially available SCMs. Higher temperatures result in crystallisation of

cristobalite, anorthite and hematite and reduced pozzolanic reactivity, while lower temperatures result in insufficient reduction in surface area. Mortars with 20% cement replacement of optimally heat-treated aluminosilicate residue achieve 90 % flow of reference mortars with 100 % CEM I. Their 3-, 7-, 28- and 60-day compressive strengths are comparable to mortars containing same addition level of SF and GGBFS and are 18.3 – 22.2 % higher than those containing same addition of FA, respectively.

7 Aragonite binder from indirect carbonation of waste concrete fines

In this chapter, the Ca^{2+} -rich solution from acetic acid leaching of hydrated cement paste is carbonated to produce pure vaterite. The vaterite formed has spherical particles, but it can be converted, when mixed and cured with a solution containing 0.1 mol/L MgCl_2 and 0.1 mol/L SrCl_2 under 60°C , into an interlocked fibrous structure consisting of needle-like aragonite CaCO_3 . The properties of the aragonite binder are engineered by controlling the processing parameters. A liquid/solid ratio of 1.0 and 3-day curing produces CaCO_3 binder with low density (750 kg/m^3), high level of connected porosity (around 90%) and thermal conductivity (0.177 W/mK) and compressive strength (4 MPa) comparable to foam concrete. This verifies the viability of extracting a viable aragonite binder with engineering potential from waste concrete.

7.1 Introduction

Vaterite CaCO_3 is gaining increasing attention because of its metastability, porous surface and higher solubility compared to aragonite and calcite. This offers the possibility of vaterite to be a precursor for carbonate-based materials. Vaterite is rarely available in nature because it quickly transforms into calcite on contact with water (Song et al., 2021). Instead, it often forms as an intermediate phase during the carbonation of concrete (von Greve-Dierfeld et al., 2020). In laboratory, it is mainly synthesised by mixing Ca- and CO_3 -containing salt solutions or bubbling CO_2 through a Ca-containing solution (Zhao et al., 2023a; Hargis et al., 2021; Li et al., 2024).

Vaterite with 99% purity has been extracted from indirect carbonation of carbide lime sludge and used as a binder (Hargis et al., 2021). It was mixed with a solution containing 0.1 mol/L MgCl_2 and 0.1 mol/L SrCl_2 at a liquid/solid ratio of 0.35 and pressed in the mould to form a paste. Then paste was cured in the same mixing solution at 40, 60 and 80°C for up to 14 days, during which the vaterite transforms into acicular aragonite and forms a strong interlocking structure like a bird's nest. A compressive strength of 40 MPa was achieved at all curing temperatures within 14 days, and this was accelerated at higher temperature (Hargis et al., 2021). Because vaterite is hydrophilic and has high specific surface

area, it absorbs large amounts of water during mixing and result in poor workability of the paste. Besides, the interlocking structure of the aragonite paste contains high level of porosity, making it not as strong as the cement paste with the same water/binder ratio. To solve this issue, the researchers applied pressing to form a paste, reduce the porosity and achieve high compressive strengths (Hargis et al., 2021).

In chapter 5, a Ca^{2+} -rich solution is produced from acetic acid leaching of HCP. Producing vaterite with high purity as a binder from this solution enables recovering new carbonate-based construction material from waste concrete. Therefore, this chapter aims to produce vaterite using the carbonation of the Ca^{2+} -rich solution and transform it to an aragonite binder. This is the first study to develop an aragonite binder from cementitious waste.

Although pressing the fresh paste improves its flowability and compressive strength, it adds complexity to the manufacturing process. Alternatively, this chapter uses various liquid/solid (L/S) ratio to improve the flowability. This results in various levels of open porosity. A high level of porosity leads to weaker structure but reduces the conduction and convection of heat hence is a key indicator for thermal insulating properties (Abu-Jdayil et al., 2019). Thus, there is a potential to develop a load-bearing insulation material from the aragonite binder. The phase composition, physical properties, microstructure development, mechanical performances under different L/S ratio and curing time are investigated. The thermal conductivity of aragonite binder with various L/S ratio are measured and compared to standard load-bearing insulation materials.

7.2 Experimental

7.2.1 Production of vaterite

HCP was produced as described in section 3.1. The indirect carbonation process is initialized by reacting the HCP with 1.6 mol/L acetic acid at an L/S ratio of 11 mL/g under constant 300 rpm stirring for 1 hour at 60°C, which is the optimal conditions reported in section 5.4.1. The Ca^{2+} -rich leachate is collected by vacuum filtration. Concentrated ammonia solution (25 %) was added to form 10 vol.% of the leachate, and this increased the pH from around 5.3 to 10.5. This causes Mg^{2+} , Al^{3+} and Fe^{3+} ions in the solution to precipitate as hydroxides and there were removed by centrifugation and vacuum filtration

as reported in section 3.3. 100% pure CO₂ gas was then passed through a pumice stone at a flow rate of 1 L/min, so that it bubbled through the solution. The initially clear solution was stirred at 300 rpm until the pH dropped to 8.5. The high CO₂ flow rate improved the degree of carbonation, and this ensured that the reaction finished before vaterite starts to transform into calcite. Under these controlled conditions the carbonation duration was approximately 30 minutes. The precipitated vaterite was collected by vacuum filtration. It was then washed with deionized water and isopropanol and dried at 60°C overnight before subsequent experiments.

The chemical composition, loss on ignition, phase composition, particle size distribution, morphology and specific surface area of vaterite were determined by XRF (Malvern PANalytical Zetium), TG (Netzsch STA 449 F5), XRD (Malvern PANalytical Empyrean), laser diffraction (Malvern PANalytical Mastersizer 3000), SEM (Zeiss Sigma 500VP FESEM) and BET (Micromeritics 3Flex 3500), following the corresponding methods described in section 3.6. The BET surface area of analytical grade calcite powder (Sigma Aldrich, USA) was also determined for comparison.

7.2.2 Production of aragonite paste

The production of aragonite paste followed the method used in previous work (Hargis et al., 2021), as illustrated in Figure 7.1. The activating solution was prepared by dissolving 0.1 mole of MgCl₂ and 0.1 mole of SrCl₂·6H₂O in 1 L of deionized water. Vaterite was then mixed with the activating solution at L/S ratios of 0.5, 0.6, 0.7 and 1.0. The L/S ratio was increased from that used in the work by Hargis et al. to create a highly homogeneous mix without pressing. Samples are denoted as P-0.5, P-0.6, P-0.7 and P-1.0, respectively. The pastes formed were transferred into 20 × 20 × 20 mm cubic steel moulds and vibrated for 2 minutes on a vibration table to eliminate entrapped air voids. The moulds were then covered with cling film to prevent rapid water loss and stored in a 60°C oven for 5 hours before demoulding. After demoulding, the cubes were further cured in a sealed plastic container containing the activating solution at 60°C for 1, 3, 7 and 28 days. On completion of the curing period, the samples were removed from the solution and dried in a 105°C oven for 4 hours.

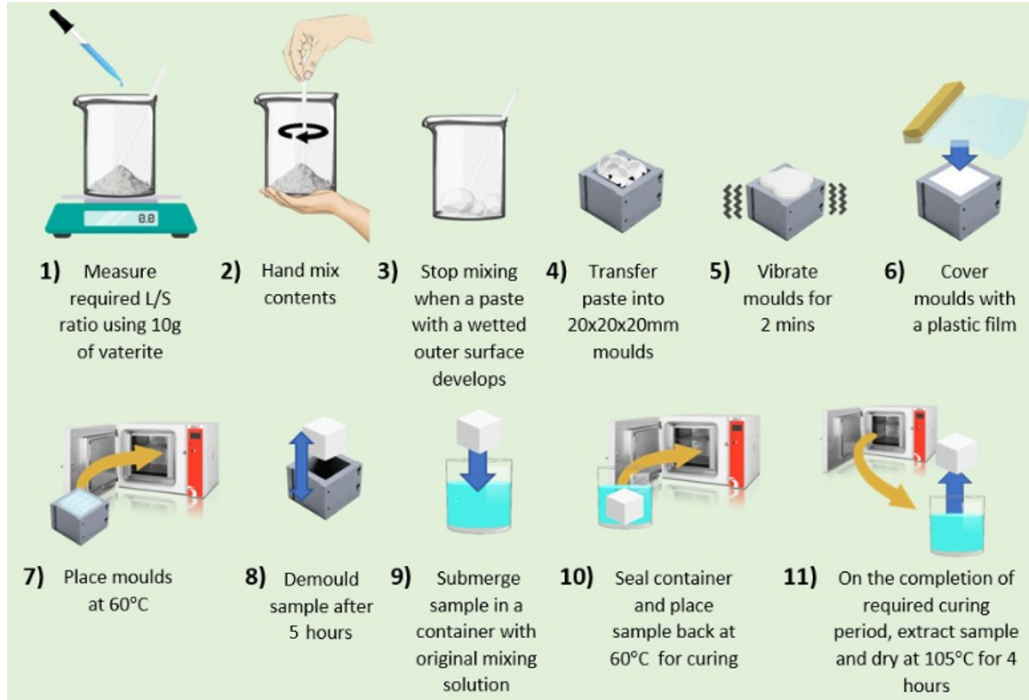


Figure 7.1 Schematic of the preparation of aragonite paste samples.

7.2.3 Phase composition, physical properties, microstructure and performance of aragonite binder

The phase composition of the hardened aragonite pastes with different L/S ratios and curing period was characterised by using XRD. The dried samples were crushed and ground using a mortar and pestle into powders with particles less than 150 μm and stored in a vacuum desiccator prior to testing. The XRD data was analysed using HighScore software to identify the crystalline phases presented in the samples. QXRD is performed on powdered samples containing 80% aragonite binder and 20% crystalline zincite (ZnO) and Rietveld refinement is applied to analyse the results, according to section 3.6.2.

The bulk density of the aragonite binder was determined from an average of three replicates, using the following equation:

$$\rho_{bulk} = \frac{m}{l \times w \times h} \quad \text{Eq. 7.1}$$

where m is the mass of the sample, l , w and h are the length, width and height of sample measured with a caliper, with the bulk density expressed in kg/m^3 .

After 105 °C drying, the dry mass of aragonite binder measured. Then the binder was soaked in tap water at room temperature for 24 hours, after which the total mass of the saturated surface dried samples was recorded. The mass of absorbed water was obtained by subtracting the dry mass from the total mass. The open porosity was then calculated using Equation 7.2:

$$P (\%) = 100 \times \frac{m_w}{m_{total}} \quad \text{Eq. 7.2}$$

Where P is percentage open porosity, m_w is the mass of absorbed water and m_{total} is the mass of saturated surface dried samples. The theoretical open porosity for aragonite binder with different L/S ratio was calculated using m_w based on the mass of activating solution added.

The compressive strength of the aragonite binder was determined on dried cube samples using a universal test machine (Instron 5980) with a loading rate of 0.1 mm/min to minimize the failure caused by excess deformations. An eccentricity correction ring was applied to avoid errors due to eccentric load. The compressive strength is averaged from three replicates calculated from Equation 7.3:

$$f_s = \frac{F_{max}}{l \times w} \quad \text{Eq. 7.3}$$

where f_s is the compressive strength of the samples in MPa, F_{max} is the maximum load the samples sustained before failure in N and l and w are the length and width of the load-bearing surface in mm measured by a caliper.

The microstructure and morphology of the aragonite binder was characterized by observing the fractured surfaces of cubes after compressive strength testing using SEM (Hitachi TM4000 Plus).

The thermal conductivity of aragonite binder was determined on $50 \times 50 \times 20$ mm board samples of P-0.6, P-0.7 and P-1.0 cured for 3 days using a thermal conductivity meter equipped with a Kapton-insulated sensor (Hot Disk M1). The results are reported as the average of five measurements.

7.3 Results

7.3.1 Characterisation of vaterite

The chemical composition of vaterite produced from indirect carbonation of HCP is 52.8% CaO, 0.4% MgO and 46.7% LOI. This shows the product is predominantly CaCO_3 . Minor trace of MgO in the vaterite comes from the residual Mg^{2+} after the ammonia purification process. The XRD pattern of the product is given in Figure 7.2, showing no diffraction peaks of other crystalline phases. These findings reveal a vaterite content of 99.1 % in the product, indicating that the controlled indirect carbonation process yields high purity vaterite.

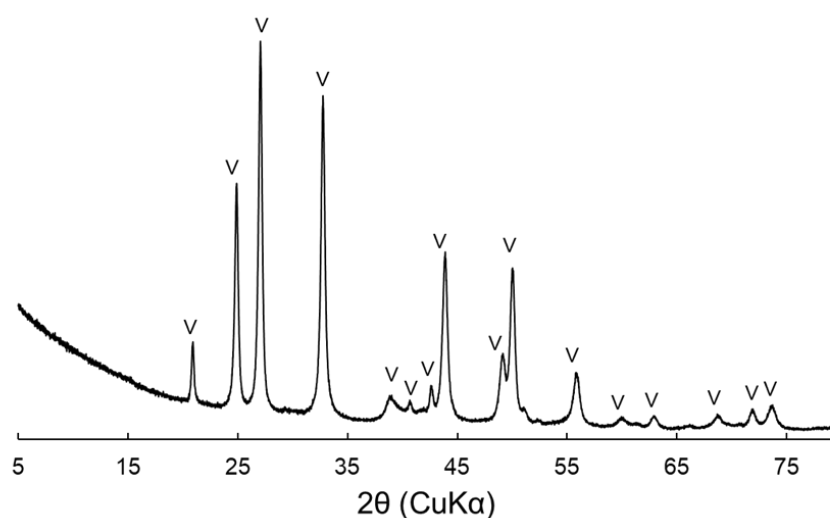


Figure 7.2 XRD pattern of the carbonation product. V – vaterite.

Figure 7.3 shows the morphology of vaterite particles observed in SEM. The particles are approximately spherical, and this is characteristic of vaterite. The spherical vaterite particles consist of agglomerated nanosized grains, and the small spheres grow by fusion to form larger spheres. This unique surface structure gives vaterite a porous surface. This is also seen in the BET surface area data. Vaterite has a specific surface area of $3.73 \pm 0.04 \text{ m}^2/\text{g}$, which is around 3.6 times as that of calcite ($1.04 \pm 0.03 \text{ m}^2/\text{g}$).

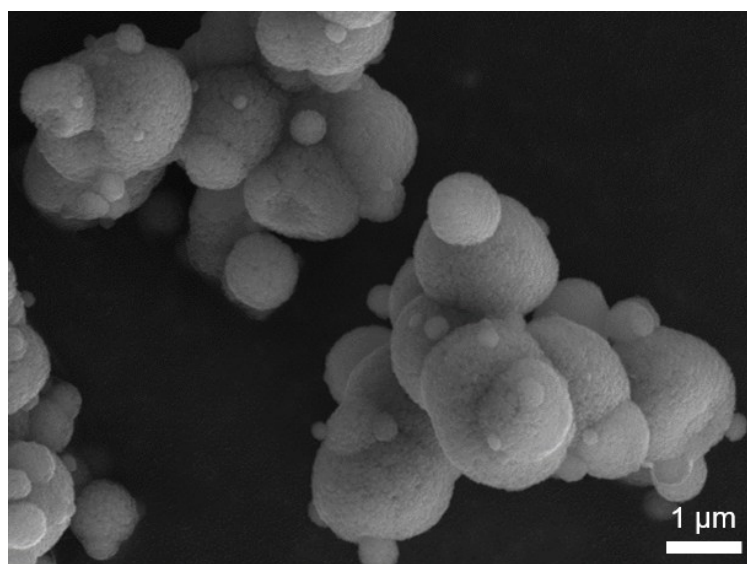


Figure 7.3 SEM image of the precipitates formed from the carbonation of the Ca^{2+} -rich leachate showing spherical particles characteristic of vaterite.

Figure 7.4 presents the TG-DSC curves of the vaterite. The constant weight loss between 100 to 400 °C is due to the removal of water adsorbed by the porous surface structure. The small exothermic peak in the DSC curve at ~500°C indicates the phase transition from vaterite to calcite. This is consistent with previously reported results (Chakoumakos et al., 2016; Bahrom et al., 2019). The weight loss at around 800 °C is due to decomposition of CaCO_3 to CaO and CO_2 .

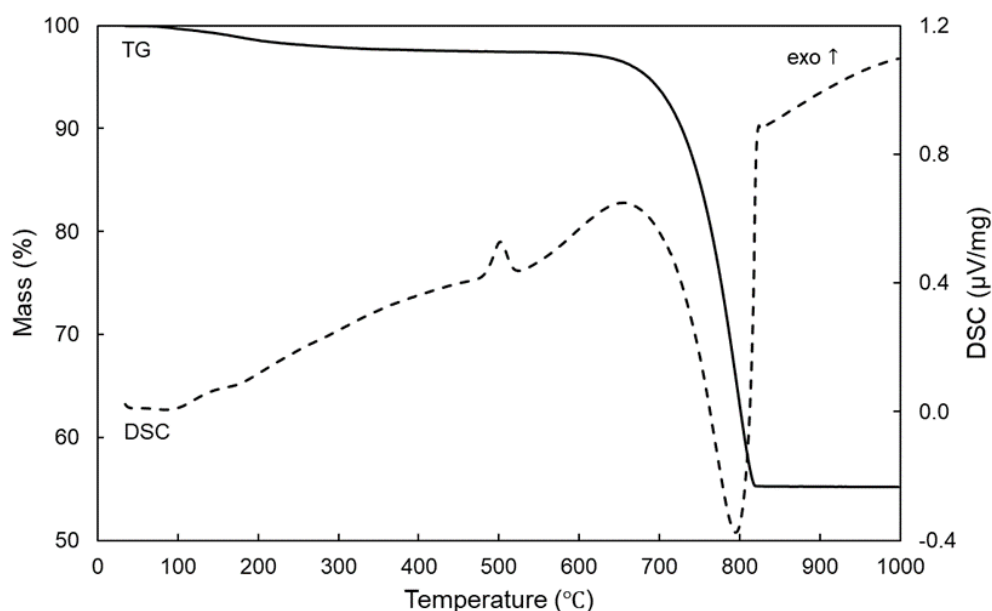


Figure 7.4 TG and DSC curves of vaterite.

The particle size distribution of vaterite is shown in Figure 7.5. The D_{10} , D_{50} and D_{90} values are 0.8, 4.7 and 14.5 μm , respectively. There is a broad shoulder in the particle size distribution data (Figure 7.5(a)) corresponding to the single vaterite crystals and agglomerated vaterite finer than 1 μm , which accounts for around 10 % of the particles. The majority of the vaterite is present in larger agglomerates that range from 1 to 30 μm .

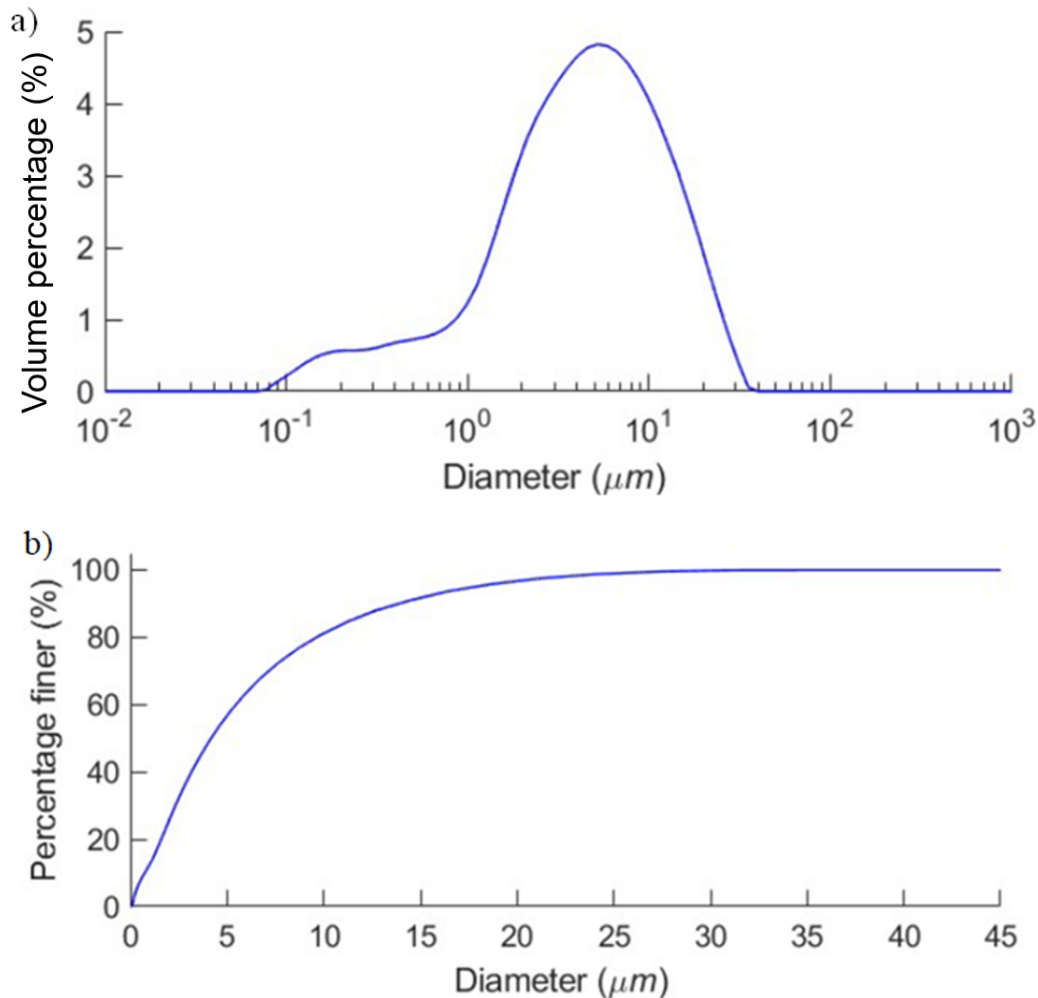


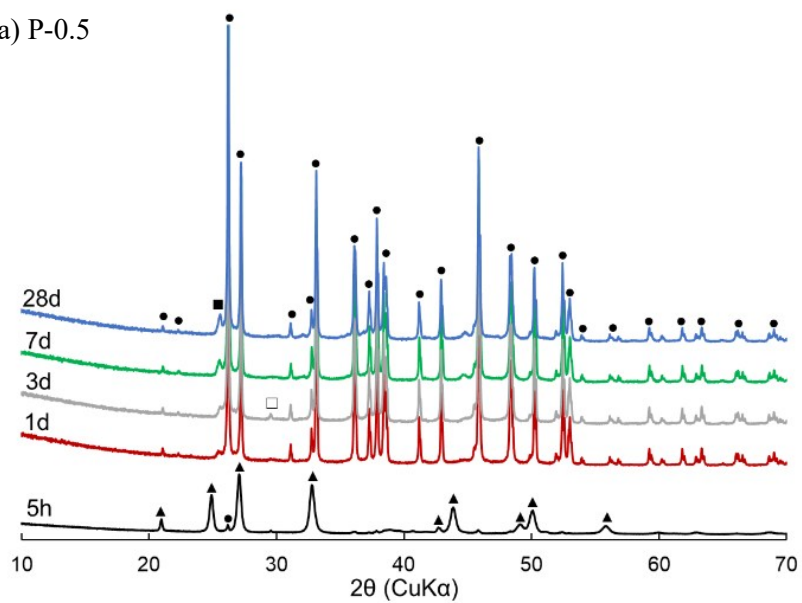
Figure 7.5 Distributed (a) and cumulative (b) particle size of vaterite.

7.3.2 Phase assemblage of aragonite binder

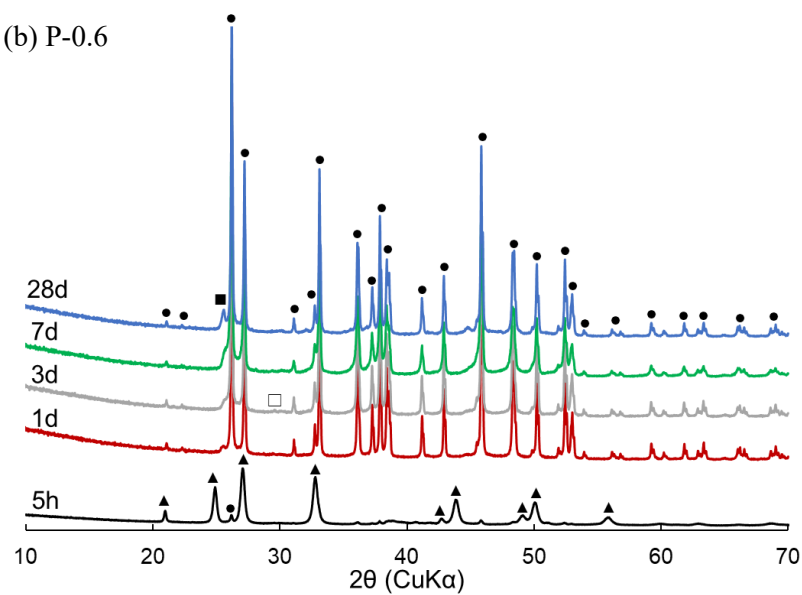
The XRD data showing the development of phases in the aragonite binder with different L/S ratios and curing periods are given in Figure 7.6. Polymorphic transformation from vaterite to aragonite starts within 5 hours and the rate increases with the L/S ratio. After 5 hours, the predominant crystalline phase is vaterite in the samples with L/S ratios of 0.5, 0.6, and 0.7, while aragonite dominated in the sample with an L/S ratio of 1.0. A higher L/S ratio creates a solution that is less saturated with vaterite, and this

promotes the dissolution of vaterite and improves the rate of polymorphic transformation to aragonite. This is also confirmed by the QXRD results shown in Figure 7.7. The aragonite content increases from 9.2% in P-0.5-5h to 96.9% in P-1.0-5h. Some poorly crystalline CaCO_3 is also detected. The amount rises when the L/S ratio increases from 0.5 to 0.6 and then decreases with L/S ratio up to 1.0. This indicated that the polymorph transformation from vaterite to aragonite includes an intermediate poorly crystalline CaCO_3 phase. After curing for more than 1 day, no vaterite was present in any of the samples, indicating complete polymorphic transformation. Small amounts of magnesian calcite $[(\text{Mg,Ca})\text{CO}_3]$ is observed in samples cured for less than 7 days with an L/S ratio of 0.5 and 0.6, and the amount decreases with increasing L/S ratio. The characteristic peak of Ca-bearing strontianite $[(\text{Sr,Ca})\text{CO}_3]$ at $2\theta = 25^\circ$ occurs in all aragonite pastes, indicating the polymorph transformation from vaterite to aragonite is via dissolution-reprecipitation process and minor amounts of dissolved Ca^{2+} and CO_3^{2-} precipitates with Sr^{2+} . Because the amount of Ca^{2+} released by the dissolution of vaterite is relatively small, the $\text{Sr}^{2+}/(\text{Ca}^{2+}+\text{Sr}^{2+})$ ratio of the curing solution is near 1. Precipitation of strontianite is favoured when $\text{Sr}^{2+}/(\text{Ca}^{2+}+\text{Sr}^{2+})$ ratio is above 0.25, and it has an aragonite-like structure (Tovani et al., 2018). Therefore, strontianite can provide interlocking binding same as aragonite.

(a) P-0.5



(b) P-0.6



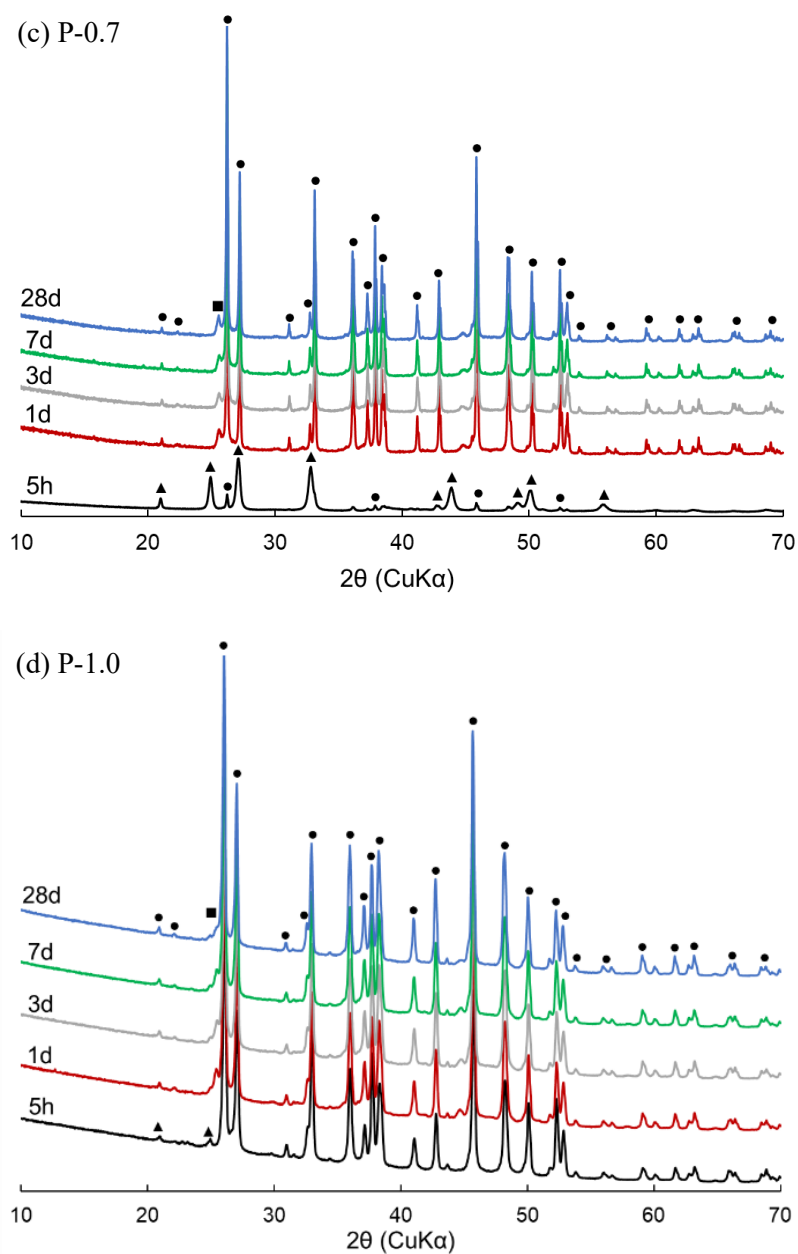


Figure 7.6 XRD patterns for aragonite binder prepared by a liquid/solid ratio of (a) 0.5, (b) 0.6, (c) 0.7 and (d) 1.0 cured for 5 hours, 1 day, 3 days, 7 days and 28 days at 60°C (▲ – vaterite, ● – aragonite, ■ – strontianite, □ – magnesian calcite).

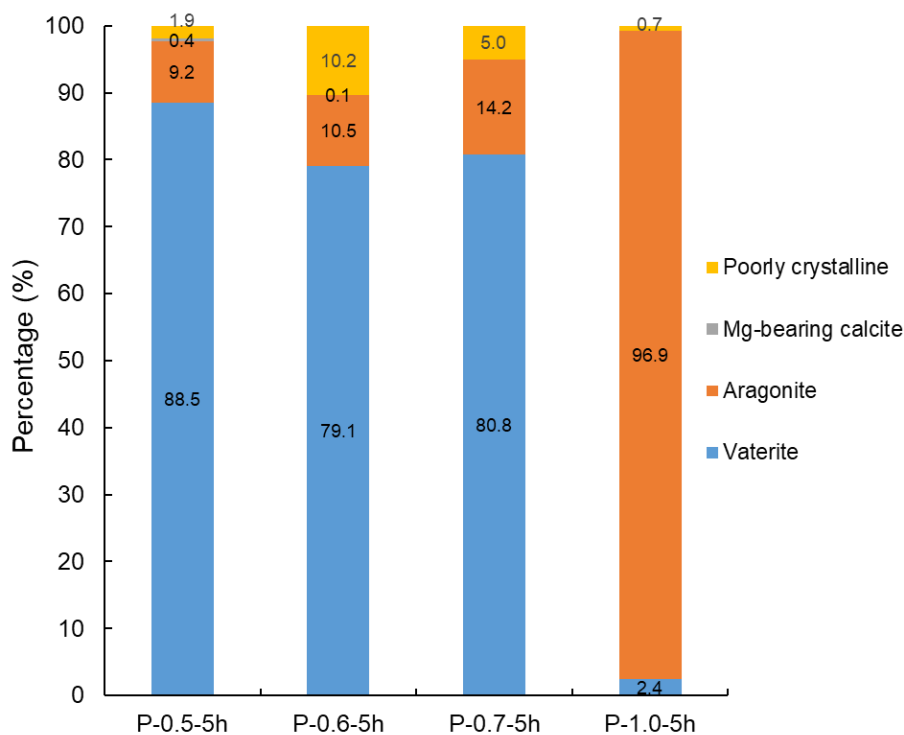


Figure 7.7 Phase composition of CaCO_3 binder with various L/S ratios (0.5, 0.6, 0.7 and 1.0) cured for 5 hours to compare the polymorph transformation rate. The numbers marked on the columns are the percentage of each phase.

7.3.3 Physical properties of aragonite binder

Figure 7.8 shows the variation in the density of aragonite binder prepared with different L/S ratios and curing periods. The early-stage density increase from 5 hours to 1 day is due to the polymorphic transformation from low-density vaterite (2.65 g/cm^3) to high-density aragonite (2.95 g/cm^3) (Bolze et al., 2002). After 1 day, the density remains approximately constant, with minor fluctuations up to 28 days. The higher the L/S ratio, the lower the density of the aragonite binder. P-0.5 achieved the highest density of $\sim 1180 \text{ kg/m}^3$ and this reduced to around 750 kg/m^3 for P-1.0 which is less than the density of water. The results indicate that the aragonite binder form a lightweight material, and this reduces the weight of material-carrying vehicles and leads to less CO_2 emissions during transportation (Liu, Li & Miao, 2024).

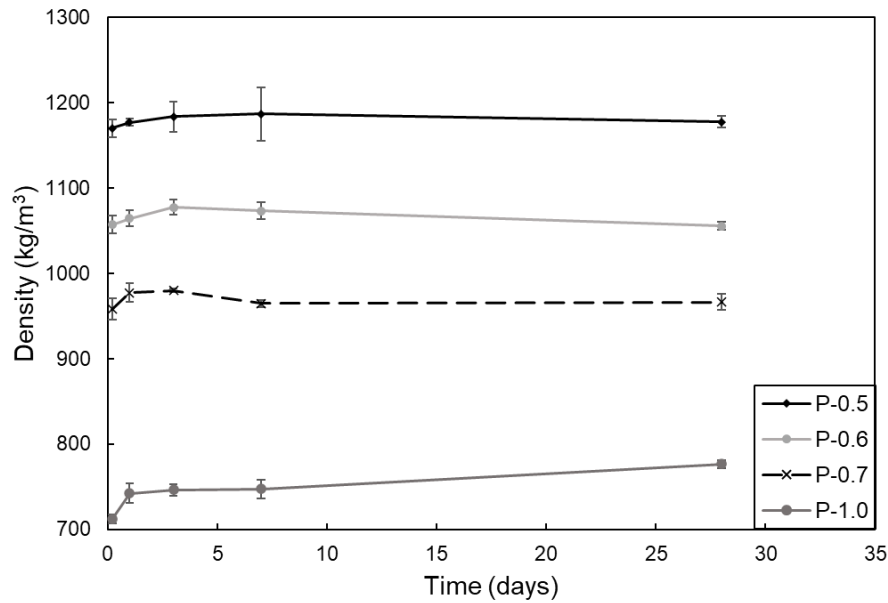


Figure 7.8 Variation in the density of aragonite binder with L/S ratios of 0.5, 0.6, 0.7 and 1.0 and cured for 5 hours and 1, 3, 7 and 28 days.

Figure 7.9 shows the change in open porosity of the aragonite binder with different L/S ratio and curing times. For samples at all L/S ratios, the open porosity increases from 5 hours to 1 day, indicating the polymorphic transformation from vaterite to aragonite increases the porosity. After 1 day, the porosity stays relatively constant or even reduces slightly. The open porosity level of the aragonite binder is proportional to the water content. Water does not participate in the polymorphic transformation, but it is the medium for the dissolution of vaterite and it is removed after drying, leaving porosity (Hargis et al., 2021). The porosity of aragonite binder at all L/S ratios and curing ages are slightly lower than theoretical values, which is probably due to the drying shrinkage of aragonite pastes. Surface treatment, such as adding surfactant can be used to reduce the drying shrinkage and maintain the porosity of aragonite binder (Tran et al., 2021).

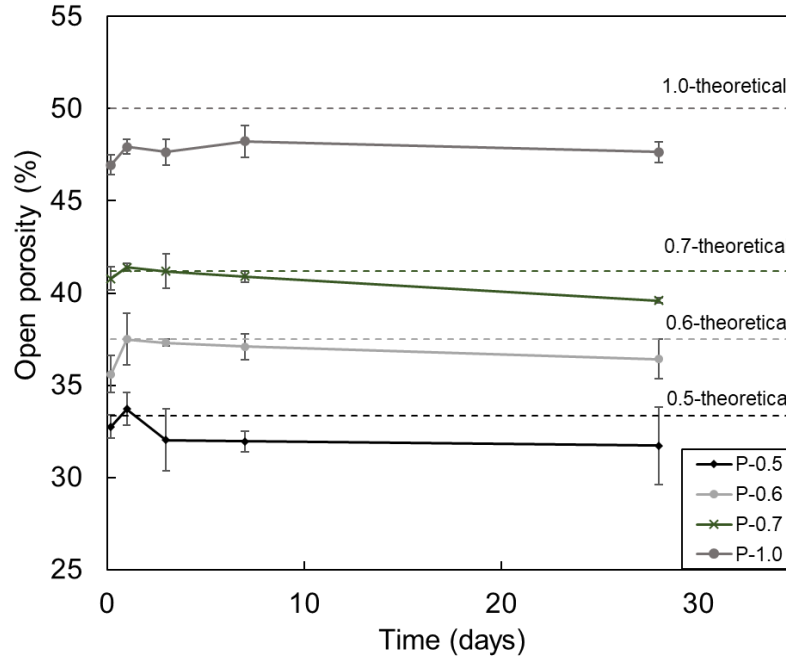


Figure 7.9 The variation in the open porosity of aragonite binder with different L/S ratio and curing time measured by water absorption method. The dashed lines show the theoretical open porosity of aragonite pastes with each L/S ratio.

7.3.4 Microstructure evolution of aragonite binder

The surface morphology of the aragonite binder with different L/S ratios and cured at different times are presented in Figures 7.10 – 7.13. For P-0.5, and P-0.6, the microstructure consists of spherical vaterite particles bridged by needle-like aragonite crystals that were about 3 μm long and 0.1 μm wide at 5 hours. The amount of aragonite increases with increasing L/S ratio (Figure 7.10(a) and 7.11(a)). The vaterite particles completely dissolve by 1 day, forming spherical voids. At the same time the aragonite crystals grow towards the interparticle space between vaterite particles, with an increased length and width of around 5 μm and 0.3 μm , generating a fibrous interlocked microstructure (Figures 7.10(b) and 7.11(b)). With increasing curing to 28 days, the aragonite whiskers gradually grow inwards the spherical voids. For P-0.7, similar microstructure development is found before 7 days. After 7 days, an increase of the width of aragonite is observed, generating $\sim 0.5 \mu\text{m}$ wide prisms. P-1.0 showed a faster polymorphic transformation rate, with almost all the vaterite transformed into aragonite after 5 hours. Small-sized aragonite crystals of around 2.5 μm long and 0.3 μm wide grow from the surface of vaterite forming a sea-urchin like structure unit (Figure 7.13(a)). A residual vaterite particle observed

under higher magnification shows that the nanosized grains are dissolving and nano-sized aragonite grows on the surface of the vaterite. As the curing time increases from 5 hours to 28 days, the needle-like aragonite crystals gradually increase in length and width and finally form interlocked hexagonal prisms of around 10 μm long and 1 μm wide (Figure 7.13(b)-(e)). The length and width of aragonite whiskers affects the interlocking, which is reflected in the compressive strength of the binder and will be discussed in section 7.3.5.

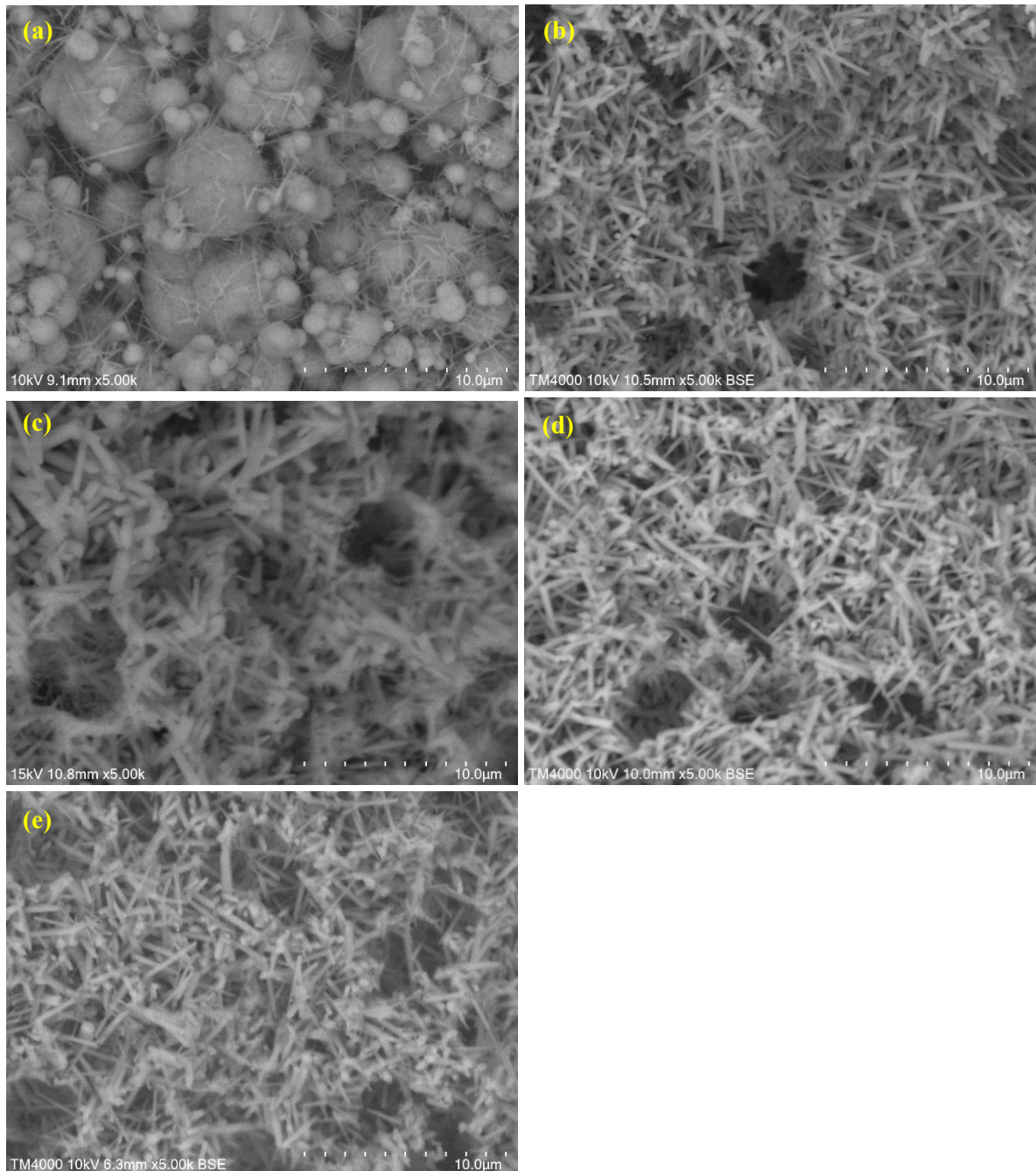


Figure 7.10 SEM images at 5000 times magnification of the morphology of the fracture surfaces of P-0.5 cured at (a) 5 hours, (b) 1 day, (c) 3 days, (d) 7 days and (e) 28 days.

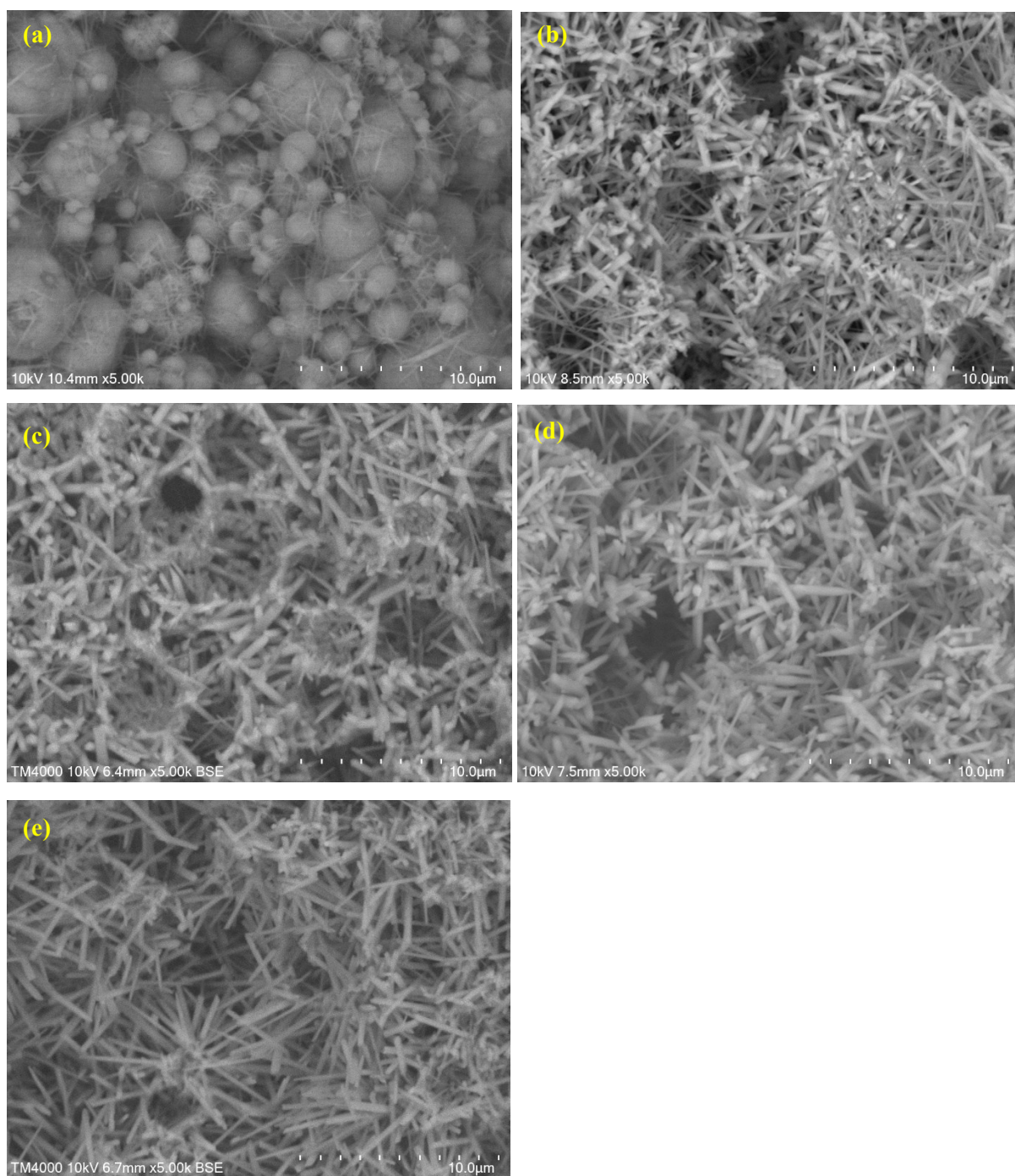


Figure 7.11 SEM images at 5000 times magnification of the morphology of the fracture surfaces of P-0.6 cured at (a) 5 hours, (b) 1 day, (c) 3 days, (d) 7 days and (e) 28 days.

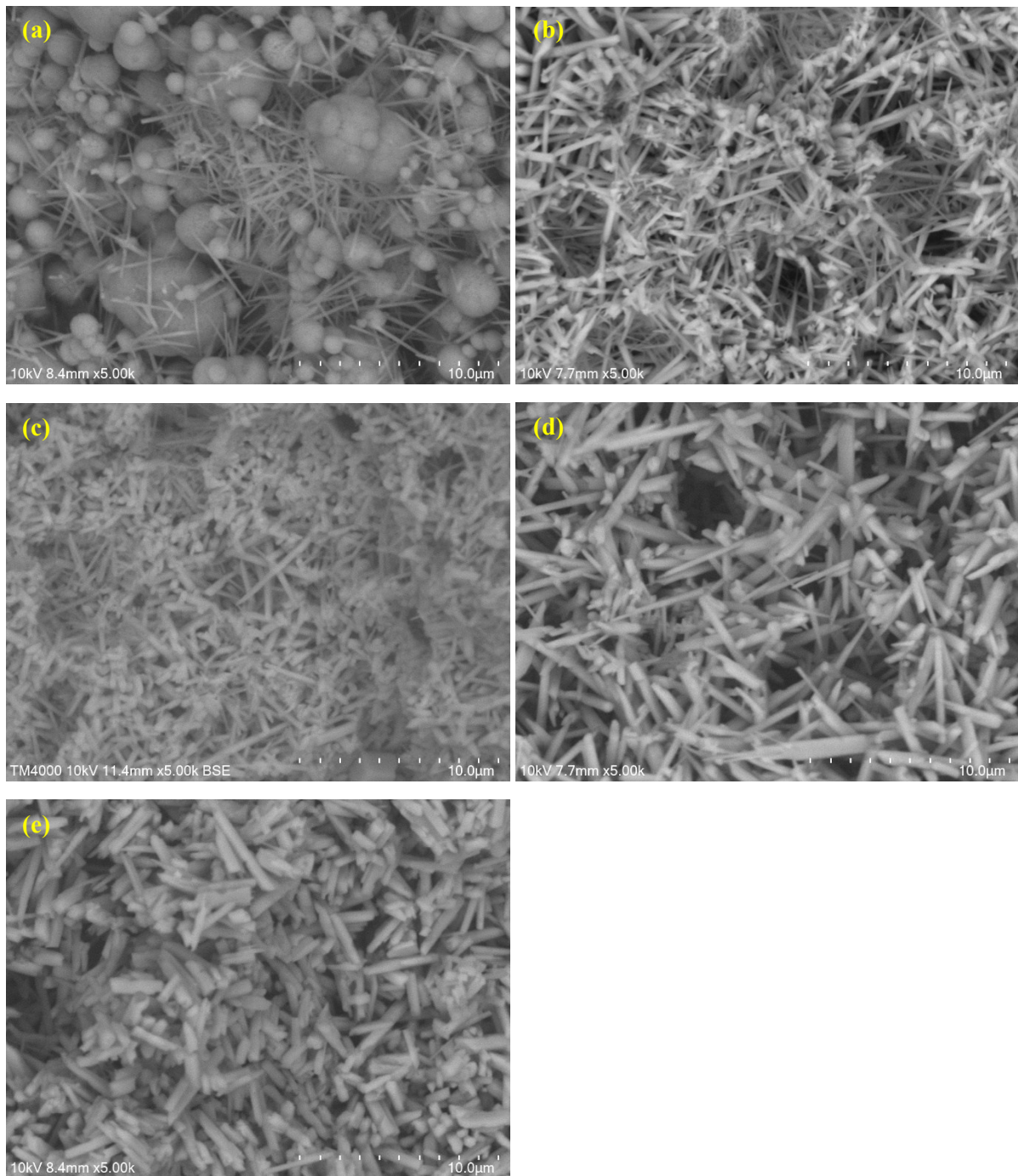


Figure 7.12 SEM images at 5000 times magnification of the morphology of the fracture surfaces of P-0.7 cured at (a) 5 hours, (b) 1 day, (c) 3 days, (d) 7 days and (e) 28 days.

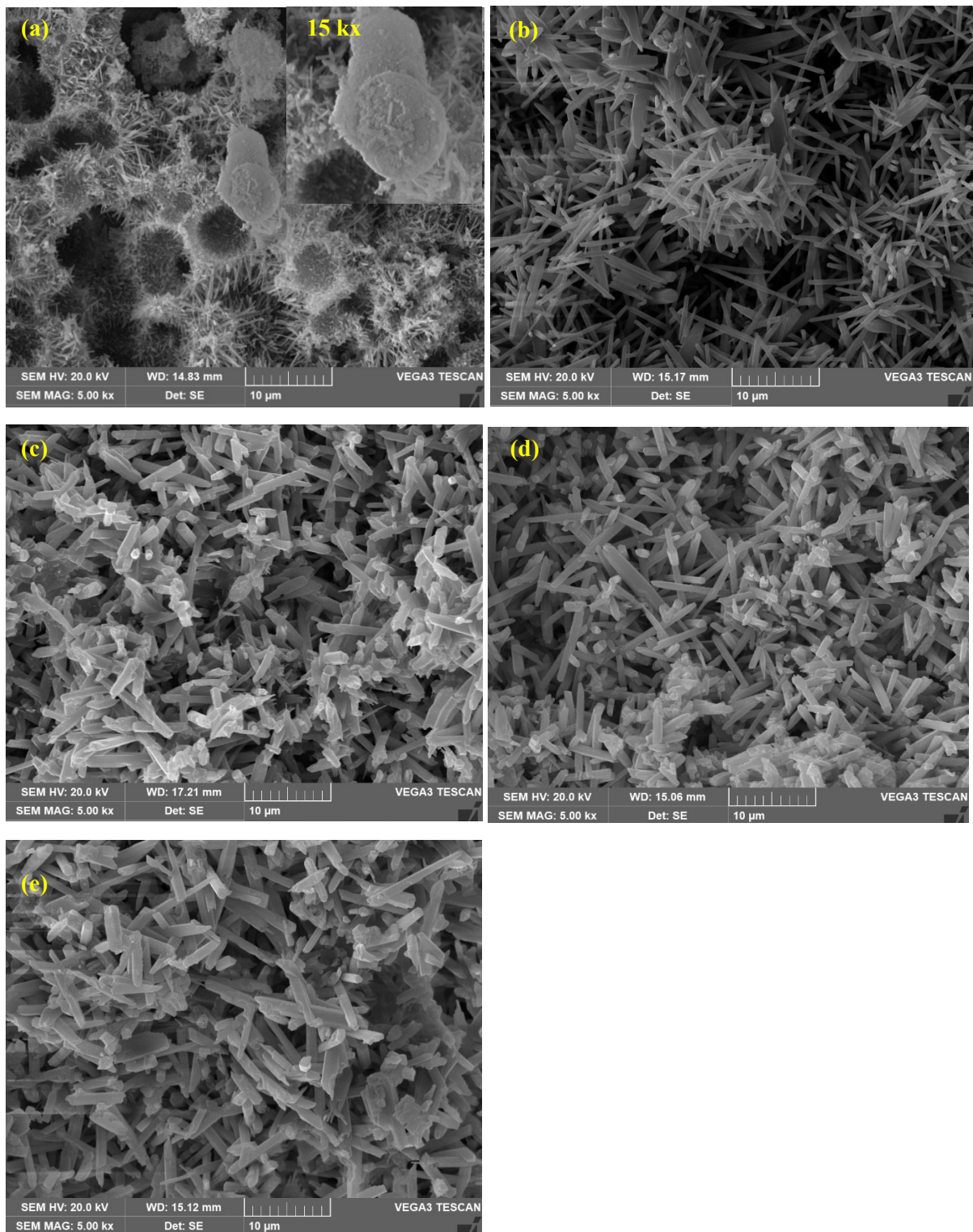


Figure 7.13 SEM images at 5000 times magnification of the morphology of the fracture surfaces of P-1.0 cured at (a) 5 hours, (b) 1 day, (c) 3 days, (d) 7 days and (e) 28 days.

7.3.5 Mechanical performance of aragonite binder

The variation of the compressive strength of aragonite binder with different L/S ratios and after different curing periods is given in Figure 7.14. After 5 hours, all the four pastes have set and developed enough strength to be demoulded. P-1.0 has the highest strength (3.05 MPa) due to the accelerated polymorphic transformation and interlocking aragonite whiskers. This is followed by P-0.5 (2.56 MPa) due to the better packing because of the lower L/S ratio. For P-0.5 and P-0.6, the compressive strength increases during the first 3 days and then remains unchanged with only minor fluctuations until 28 days. This is because the increase in aragonite length and width within 3 days promotes the interlocking and gives better strength (Hargis et al., 2021). In contrast, P-0.7 and P-1.0 displays a continuous increase in compressive strength up to 28 days. This is probably because the increase in width of aragonite prisms further strengthens the interlocking structure. Generally, reducing the L/S ratio increases the compressive strength of the CaCO_3 paste cubes. A lower L/S ratio means there is less liquid phase in the paste, resulting in less porosity and better degrees of interlocking. The highest strengths for P-0.5, P-0.6, P-0.7 and P-1.0 are 23.6, 17.9, 13.3 and 4.2 MPa, respectively.

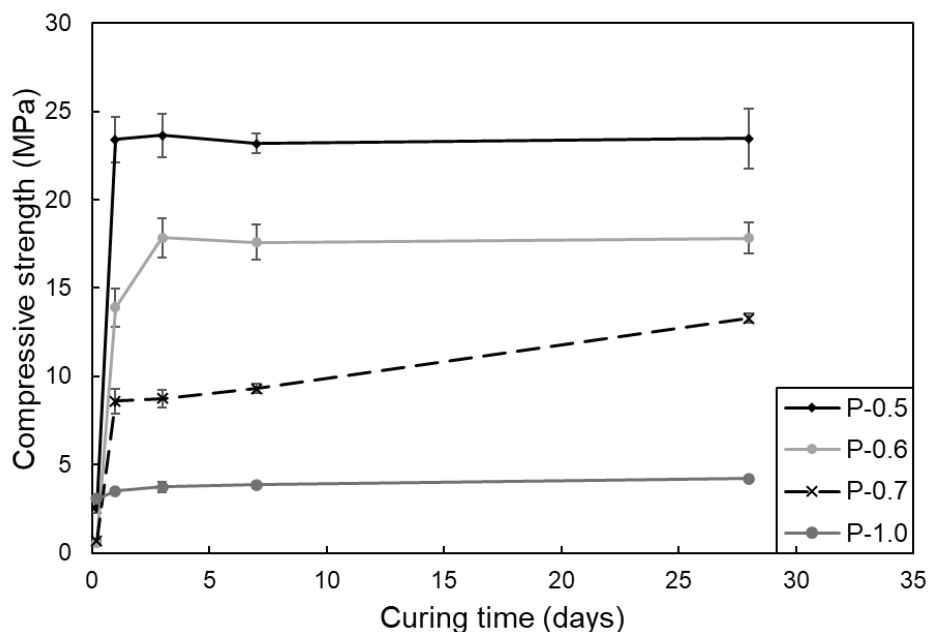


Figure 7.14 Compressive strength of the aragonite binder with different L/S ratios and curing time.

7.3.6 Thermal conductivity of aragonite binder

The thermal conductivity of aragonite board was measured on P-0.6, P-0.7 and P-1.0 cured for 3 days and the results are presented in Table 7.1. A curing age of 3 days is chosen because the strength gain is achieved within 3 days. P-0.6 board had a thermal conductivity of 0.554 W/mK. Increasing the L/S ratio to 0.7 and 1.0 reduced the thermal conductivity to 0.372 and 0.177 W/mK, respectively. This is due to the increased level of connected porosity, and air is a good insulator. Increasing the L/S ratio achieves higher thermal insulation performance but reduces the compressive strength of the aragonite paste. The compressive strength of P-0.6 (13 – 18 MPa) conforms the standard requirement for damp-proof clay bricks (≥ 5 MPa) (BS 3921:1985, 1985), while P-1.0 (3 – 5 MPa) is lower than clay bricks, but comparable to other materials such as gypsum board and foam concrete with density lower than 1000 kg/m³ (Zhang, 2013; Morrison et al., 2016; Raj, Sathyan & Mini, 2019).

Table 7.1 Thermal conductivity of aragonite paste board samples.

Sample	Thermal conductivity (W/mK)
P-0.6-3d	0.554±0.009
P-0.7-3d	0.372±0.008
P-1.0-3d	0.177±0.005

7.4 Discussion

7.4.1 Polymorphic transformation and strength developing mechanism

According to the experimental results, the underlying mechanism of the polymorphic transformation follows the dissolution-reprecipitation route. It is divided into four stages, as illustrated in Figure 7.15. In the first stage, the nanosized grains of vaterite gradually dissolve, releasing Ca²⁺ and CO₃²⁻ into solution and leaving defects on the particle surface. In the second stage, due to the stabilisation effect of Mg²⁺, the Ca²⁺ and CO₃²⁻ re-precipitate as poorly crystalline CaCO₃ and then crystallise into aragonite whiskers on the surface of vaterite and form bridges between vaterite particles. In the third stage, the vaterite particles completely dissolve, generating hollow cores with small aragonite whiskers pointing outwards and resulting in a sea-urchin like structure. This is similar to the previously reported ‘morning star’ structure, but the aragonite whiskers in this study have a higher aspect ratio because of Sr²⁺

(Wagterveld et al., 2014). Finally, the aragonite whiskers continue to increase in length and develop a strength-giving interlocked fibrous structure like a bird's nest. They also increase in width to form hexagonal prisms. Water provides the medium for the dissolution of vaterite and the reprecipitation of aragonite and increasing the amount of water results in a faster polymorphic transformation rate (Figure 7.7).

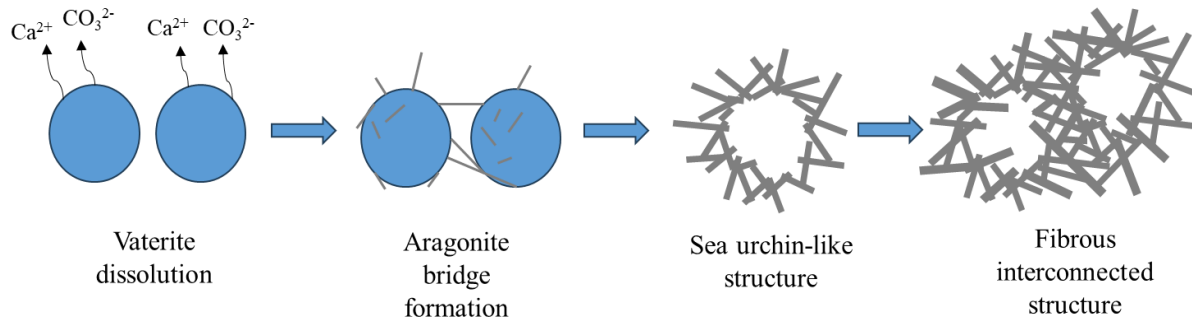


Figure 7.15 Polymorph transformation and strength development mechanism of the aragonite binder.

7.4.2 Potential application of aragonite binder

Compared to cementitious binder, aragonite binder has lower compressive strength but higher thermal insulation property. Compared to commonly used insulators such as silica aerogels, aragonite binder has higher thermal conductivity but higher strength (Pedroso et al., 2020). This indicates its engineering potential as a load-bearing insulation material. Foam concrete is a widely used as a lightweight load-bearing thermal insulating material which is fabricated by introducing air content using a foaming agent. The density, compressive strength and thermal conductivity of foam concrete are $300 - 1800 \text{ kg/m}^3$, $3 - 12 \text{ MPa}$ and $0.2 - 0.8 \text{ W/mK}$, respectively (Raj, Sathyan & Mini, 2019). Figure 7.16 compares the compressive strength and thermal conductivity of 3-day cured aragonite binder and 2-day cured foam concrete varied with bulk density. These results indicate that aragonite binder has similar density, comparable compressive strength and improved thermal insulation properties compared to foam concrete. Particularly, P-0.7-3d has comparable compressive strength and better thermal insulation to foam concrete with similar density, which provides a balanced trade-off between the improvement of thermal insulation and the loss of compressive strength. Also, the aragonite binder is chemically stable. No obvious changes in the appearance and crystal phase composition are observed after immersing all the paste samples in tap water for 1 month.

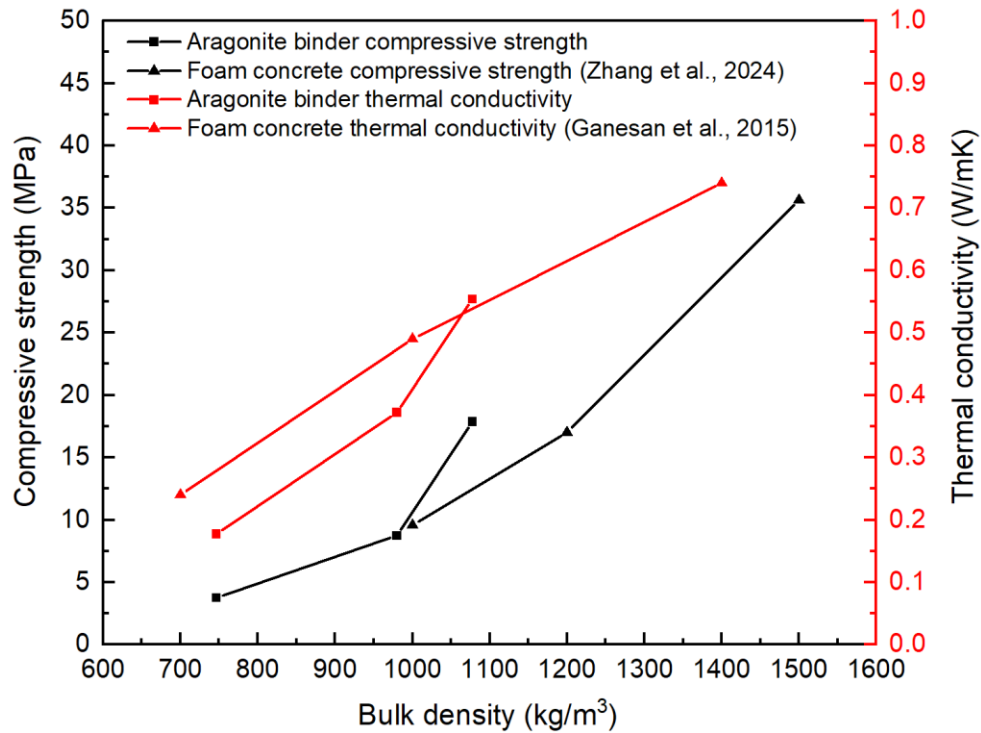


Figure 7.16 Variation of compressive strength and thermal conductivity with bulk density of 3-day cured aragonite binder and 2-day cured foam concrete (Ganesan et al., 2015; Zhang et al., 2024).

In this study, 0.75 kg of vaterite is extracted from 1 kg HCP and the carbonation efficiency is 92 %. The carbonation efficiency is comparable to the reported value of 89.3 – 91.4 % in literature (Mehdizadeh, Mo & Ling, 2023). This yield can be improved by increasing the carbonation time and the ammonia dosage (Mehdizadeh, Mo & Ling, 2023). According to literature data, 1.39 billion tonnes of end-of-life cement paste is generated each year (Driver et al., 2024). 1.04 billion tonnes of vaterite can be produced per year if all the waste concrete is subjected to direct carbonation. Waste concrete can be used as the feedstock material with a lower yield lower due to the less amount of Ca compared to cement paste. When Mg-rich cements/concretes, such as the ones containing slag, are used as feedstocks to produce vaterite, the dissolved Mg^{2+} will be removed upon increasing the pH to 10.5 by adding ammonia (Vanderzee & Zeman, 2018). Therefore, Mg-richer cements or concretes will have minimal effect on the quality of the product. The Mg^{2+} and Sr^{2+} needed in the curing process can come from seawater, which will reduce the corresponding chemical cost of aragonite binder, and further research needs to explore the viability of this. Overall, the aragonite binder extracted from waste concrete has the potential to be applied as a load-bearing thermal insulation material as alternative to foam concrete.

7.5 Conclusions

99.1 % pure vaterite is produced by carbonating the Ca^{2+} -rich solution from acetic acid leaching of HCP with 100 % CO_2 at 1 L/min flow rate for 30 minutes. This can be blended with different amounts of a solution containing 0.1 mol/L MgCl_2 and 0.1 mol/L SrCl_2 and activated at 60 °C and this transforms the vaterite into a fibrous interlocking structure consisting of aragonite whiskers within 3 days. The properties of aragonite binder are mainly controlled by the L/S ratio. The higher the L/S ratio, the faster the polymorph transformation, the lower the density and mechanical performance, and the better the thermal insulating performance. Aragonite binder cured at 3 days with different L/S ratio have low density (750 – 1180 kg/m³), good strength (4.0 – 23.6 MPa) and low thermal conductivity (0.177 – 0.554 W/mK) which is comparable to foam concrete. Therefore, the aragonite binder can form a novel lightweight load-bearing thermal insulating material and contribute to the development of circular concrete.

8 Scale-up potential, cost and sustainability analysis

In this chapter, a scale-up process for indirect carbonation of waste concrete fines (< 4.75 mm) is proposed. The mass balance is calculated based on laboratory data reported in previous chapters and magnified to corresponding mass per 1 tonne of waste concrete fines. A primary estimation of process cost and benefit, energy consumption and CO₂ emissions are conducted under this scale and compared to other indirect carbonation processes in the literature. Then, approaches to improve the economic competitiveness and carbon negativity of this process, including acid and alkali recovery and developing high-value products are summarised.

8.1 Process flow and mass balance

Figure 8.1 shows a schematic scale-up process for the indirect carbonation of waste concrete fines. Because this process uses acetic acid and ammonia which are corrosive chemicals, parts of the plant in contact of the reactants should be made of materials that are resistant to acidic and alkaline environment, and the liquid and vapor of the reactants should be separated from the equipment which are not directly in contact to them. Perfect separation of cement paste and fine aggregates and idealised reaction and transport with no losses of reagent and product are assumed in this process. Because of the larger particle size and lower CaO content which reduce the efficiency of the reaction, the coarse fraction (> 4.75 mm) of waste concrete should be separated, and the resulting fine fraction < 4.75 mm is used in this process. Acetic acid and waste concrete fines are fed to a cylindrical reactor with stirring and reacted at 60°C for 1 hour. After leaching, the adhered cement paste is dissolved, and clean recycled sand and aggregates are recovered by gravitational sedimentation. The SR and Ca²⁺-rich leachate are separated by a filter press. The SR is heated to 900 °C for 1 hour in a furnace and crushed into powders to be used as a viable SCM. The Ca²⁺-rich leachate is pumped to a cylindrical reactor and stirred with ammonia solution. The purification residue is separated from the solution by a filter press. The solution is transferred to the cylindrical carbonation reactor. Pure CO₂ gas is introduced from the bottom of the reactor through a gas diffuser to increase the utilisation efficiency. The reaction lasts for 30 minutes and the precipitated vaterite is extracted by gravitational sedimentation.

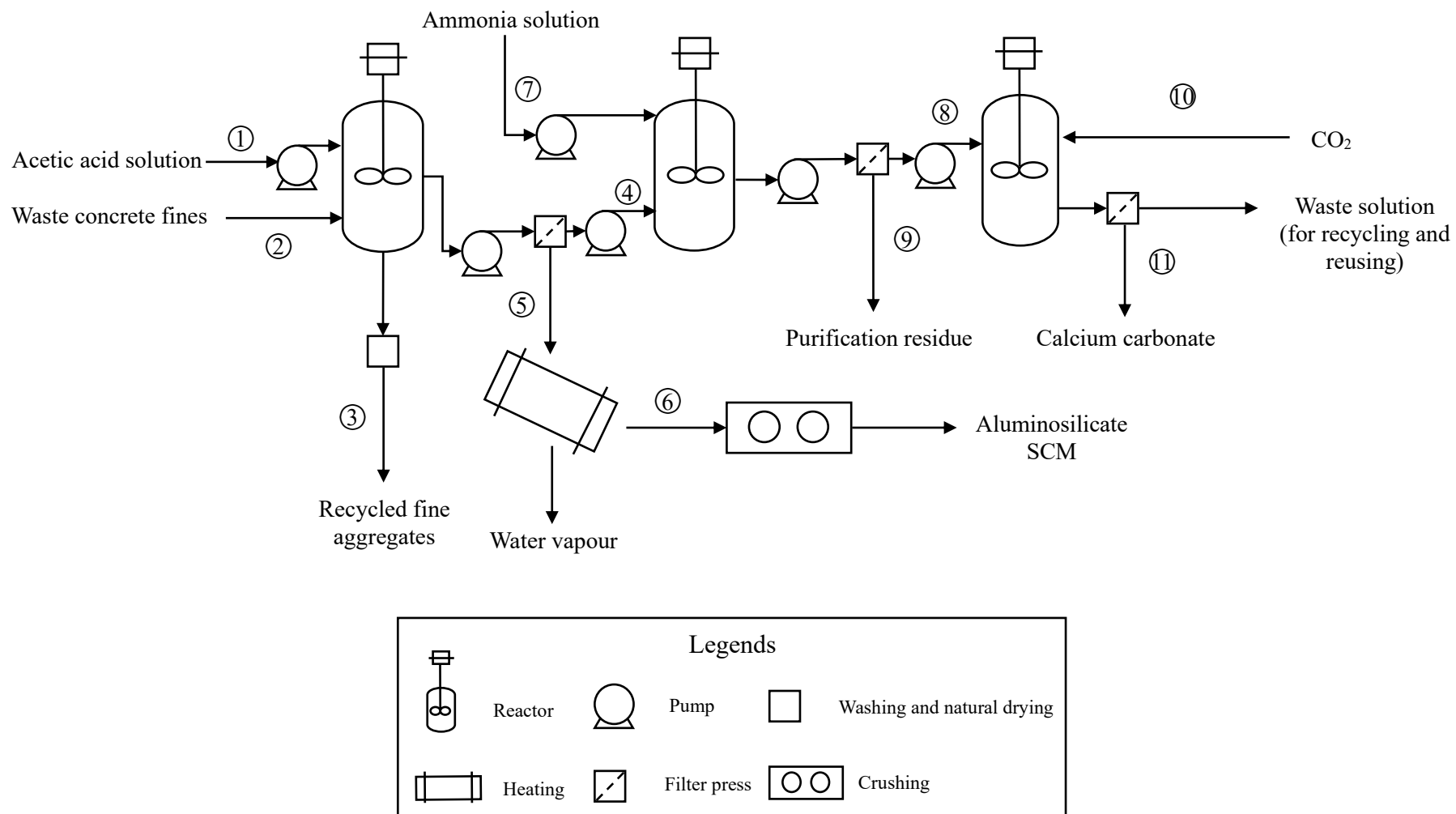


Figure 8.1 Process flow diagram of a pilot-scale indirect carbonation process of waste concrete fines.

Table 8.1 Stream table for the indirect carbonation process of waste concrete fines.

Stream number	1	2	3	4	5	6	7	8	9	10	11
Component	Acetic acid solution	Waste concrete fines	Recycled fine aggregates	Ca ²⁺ -rich solution	Silica-rich residue	SCM	Ammonia solution	Purified Ca ²⁺ -rich solution	Purification residue	Carbon dioxide	Calcium carbonate
Acetic acid (kg)	424										
Water (kg)	4400			4400	24		290	4666			
Hydrated cement paste (kg)		400		296 (dissolved)				286.4 (dissolved)			
Fine aggregates (kg)		600	600								
Aluminosilicate gel (kg)					80	80					
Ammonia (kg)							96.7				
Mg-, Al- and Fe-hydroxides (kg)									9.6		
CO ₂ (kg)										132	
Vaterite (kg)											300
Ammonium acetate (kg)											
Density (kg/m ³)	1004	2110	2660	1040	2040	2400	910	1030	3000	1.98	2540
Temperature (°C)	RT	RT	60	60	60	900	RT	RT	RT	RT	RT

Chapter 4 and 5 have shown the optimal acid leaching condition and the consumption of acetic acid depend on the particle size and chemical composition of waste concrete. Therefore, the exact mass balance of a whole indirect carbonation process is case specific. Here an estimated mass balance based on the selected composition of waste concrete fines and chemical consumption in this research is made, as presented in Table 8.1. According to sections 4.4.1 and 5.3.2, around 60% of the waste concrete fines are fine aggregates. Assuming all the impurities (bricks, ceramics and soil) are separated and removed beforehand, 40% of the waste concrete fines is cement paste. Therefore, 1 tonne of waste concrete fines contain 400 kg of cement paste and 424 kg of glacial acetic acid are needed. As the optimal liquid to cement paste ratio is 11, the total volume of acetic acid solution is 4400 litres making a concentration of 1.6 mol/L. After the Ca^{2+} extraction, 600 kg of clean reuseable aggregates and 104 kg of untreated SR can be produced. 900 °C heat treatment of untreated SR produces 80 kg of aluminosilicate SCM. Ca^{2+} -rich solution are generated from the acid leaching step and used for purification, where 440 litres of 25 % ammonia solution (386.7 kg) are added and 9.6 kg of purification residue are produced. Finally in the carbonation stage, 300 kg of vaterite are produced and 132 kg of CO_2 are sequestered. Wastewater containing ammonium acetate ($\text{CH}_3\text{COONH}_4$) is generated. Overall, the total input mass is 1942.7 kg, and the total mass of the products is 989.6 kg. The difference is because (i) the acetate and ammonia end up in the wastewater (ii) the release of chemically bound water from cement hydration products in acid leaching reactions (equation 2.1 – 2.4) (iii) the formation of new water in the acid leaching (equation 2.1 – 2.5) and carbonation reactions (equation 2.9) and (iv) the release of physically and chemically bound water in the SR during heat treatment. Therefore, 24 kg of water is released during heating and the rest 929.1 kg is contained in the wastewater after carbonation.

Although the lab-scale experiments are done at pure CO_2 , industrial flue gas containing 15 – 20 % CO_2 such as cement kiln exhaust gas could be used in real application. This can reduce the cost associated with purchasing and transporting the compressed CO_2 and recycle a waste gas into a value-added product. Previous research has found that gas-liquid carbonation using flue gas is technically feasible, except that it decreases the carbonation rate and the absorbed CO_2 amount within the same time as using pure CO_2 (Meijssen et al., 2023). Therefore, a higher gas flow rate and longer carbonation time would be needed if flue gas is used.

8.2 Economic and sustainability analysis of indirect carbonation of waste concrete fines

In this section, the economic and climate change mitigation performance of the proposed process is evaluated. The key assumptions made in the calculations are:

1. The pre-processing cost to produce waste concrete fines is estimated to be 7.7 % of the price of natural fine aggregates (Wijayasundara et al., 2016).
2. Inflation rate is not considered.
3. The capital cost, labour cost and transport cost are not considered, and this may lead to an underestimation of costs.
4. The electricity price is fixed and does not change over time.
5. The production scale and equipment parameters of the indirect carbonation process of waste concrete fines for estimating the energy cost follows those proposed by Said et al., as shown in Table 8.3 (Said, Laukkanen & Järvinen, 2016).
6. The specific heat capacity of SR is the same as class-F coal fly ash ($720 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) (Bentz et al., 2011).

8.2.1 Cost and benefit analysis

Table 8.2 summarises the cost of chemicals and revenue of the products. Waste concrete fines and CO_2 can be sourced from demolished buildings and industrial flue gas, which are low cost. The price of acetic acid is £ 585/tonne in Europe (ChemAnalyst, 2024). The price of concentrated ammonia is £ 100/tonne (EChem, 2019). Given that 424 kg of acetic acid and 386.7 kg of ammonium hydroxide are used to treat 1 tonne of waste concrete fines, the total materials cost is £ 286.7.

According to a typical British construction materials seller, the price of virgin sand and aggregates is around £ 40/tonne (Great Yarmouth Aggregates, 2024). The prices of pulverized fly ash and silica fume are £ 45/tonne and £ 117 to £ 623/tonne (depending on its purity and density), respectively (Black & Purnell, 2016; HSA, 2024). As the heat-treated SR from waste concrete fines has better performance than fly ash but lower SiO_2 purity than the densified silica fume, a price of £ 120/tonne is estimated. The price of precipitated CaCO_3 is £ 150 to £ 400/tonne depending on the quality (Vanderzee & Zeman, 2018). Compared to calcite, the vaterite produced in the indirect carbonation of waste concrete fines is

more reactive and porous, so it has value-added applications such as drug carriers (Trushina et al., 2022). Therefore, the value of vaterite is estimated to be at the higher end of precipitated CaCO_3 , so a price of £ 400/tonne is estimated. Therefore, the total revenue of these products is £ 153.6.

Besides the income by selling waste concrete products, this process also generates environmental revenue by diverting the waste concrete from landfill. Because waste concrete is categorised as a non-hazardous and low-polluting waste, it applies to the lower landfill tax rate of £ 3.3/tonne (HM Revenue & Customs, 2024). £ 3.3 is saved by recycling 1 tonne of waste concrete fines.

Table 8.2 Cost of the chemicals and revenues of the products.

Item	Raw materials				Products				Total
	Waste concrete fines	Acetic acid	Ammonia solution	CO ₂	Recycled sand and aggregates	Avoided landfill tax	Aluminosilicate SCM	Vaterite	
Price (£/tonne)	3.1	585	100	0	40	3.3	120	400	
Weight (kg)	1000	424	386.7	132	600		80	300	
Cost (£)	3.1	248	38.7	0*	-		-	-	289.8
Revenue (£)	-	-	-		24	3.3	9.6	120	156.9

* Using industrial flue gas.

Table 8.3 Parameters used to estimate the energy consumption of the plant (Said, Laukkanen & Järvinen, 2016).

Parameters	Value
Volume of the reactor	200 L
Pump head, Z	5 m
Flow rate, V	0.00025 m ³ /s
Power number of the impellers, N_p	1.27
Stirring speed for acid leaching, purification and carbonation, N	300 rpm
Impeller diameter, D	0.3 m

To estimate the energy cost, the power consumptions of pumping and stirrers are estimated using equation 8.1 and 8.2 (Said, Laukkanen & Järvinen, 2016):

$$P_1 = \rho \cdot g \cdot Z \cdot V \quad \text{Eq. 8.1}$$

$$P_2 = \rho \cdot N_p \cdot \left(\frac{N}{60}\right)^3 \cdot D^5 \quad \text{Eq. 8.2}$$

where P_1 is the power consumption of the pumping, P_2 is the power consumption of the stirring, ρ is the density of fluid (kg/m³), g is the standard gravity (9.8 m/s²), Z is the pump head (m), V is the flow rate (m³/s), N_p is the power number of the impellers, N is the stirring speed (rpm) and D is the diameter of the impeller (m). The values are given in Table 8.1 and 8.3.

Table 8.4 summarises the estimated energy consumption of this process, normalised to a treatment capacity of 1 tonne. The total power consumption of the pumping and stirring reactor is calculated to be 3.7 and 35 kWh, respectively. The energy consumption of filter press is 60 kWh/tonne of material, so extracting 104 kg of SR, 9.6 kg of purification residue and 300 kg of vaterite requires 30 kWh in total (Zebratube, 2024).

The energy consumption for optimal heat treatment of 1 tonne of SR at 900°C is calculated by equation 8.3:

$$E = 1000kg \times 720 J \cdot kg^{-1} \cdot K^{-1} \times (900^\circ\text{C} - 20^\circ\text{C}) = 6.34 \times 10^8 J = 176 kWh \quad \text{Eq. 8.3}$$

This is equal to 18.3 kWh/tonne of waste concrete fines. The waste heat can be used to maintain the temperature of the Ca²⁺ extraction reactor at 60°C. The crusher consumes 2.5 kWh/tonne of material as reported in similar research (Iizuka et al., 2017). Therefore, the power consumption of crushing 80 kg of SCM is 0.2 kWh. Overall, treating 1 tonne of waste concrete fines consumes around 87.2 kWh of power. Given the price of electricity in the UK is £ 0.22/kWh, the energy cost is £ 19.2 (Warren, 2024).

Table 8.4 The estimated power consumption from one batch operation of the pilot plant.

Operation unit	Quantity	Normalised power consumption (kWh/t waste concrete fines)
Pumping	6	3.7
Stirring	3	35
Filter press	2	30
Heating	2	18.3
Crushing	1	0.2
Total		87.2

Overall, the net profit of this pilot-scale process is $(156.9 - 289.8 - 19.2) = \text{£ } -152.1/\text{tonne}$ of waste concrete fines.

8.2.2 CO₂ footprint

The CO₂ footprint of this process consists of emissions associated with producing acetic acid and ammonia solution and burning fossil fuels. The CO₂ emissions of acetic acid and ammonia gas produced by conventional routes are 1 tonne CO₂/tonne and 1.9 tonnes CO₂/tonne, respectively (Budsberg et al., 2020; Shi et al., 2024). 424 kg of acetic acid is used. The concentration of ammonia in 25 % ammonium hydroxide is 0.25 kg/L, hence 386.7 kg of ammonium hydroxide contains 96.7 kg of ammonia gas. Thus, the materials CO₂ footprint is 607.7 kg. The CO₂ emissions of fossil fuel combustion is 0.33 kgCO₂/kWh (Cancio Díaz et al., 2017). Therefore, the CO₂ emission from the energy consumption is 28.8 kg. Given 132 kg of CO₂ emission is avoided by carbonation sequestration, the net CO₂ sequestration of this pilot-scale process treating 1 tonne of waste concrete fines is -504.5 kg.

8.3 Comparison to other indirect carbonation process of cementitious waste

Based on the estimation in sections 8.2, the Ca extraction, economic and CO₂ emission reduction performances of the proposed process are compared to other indirect carbonation processes of waste concrete in the literature in Table 8.5 (Meijssen et al., 2023; Mehdizadeh, Mo & Ling, 2023). Some key assumptions used are as follows:

1. Because there was no economic and carbon emission analysis in the referenced literature, the material cost and benefit are calculated based on the mass of feedstocks and products reported. The price and carbon footprint of ammonium chloride are £ 125/tonne and 1.3 tonnes CO₂/tonne, respectively (Driver et al., 2024; CarbonCloud, 2024). The price and carbon footprint of ammonium nitrate are £ 194.6/tonne and 2.9 tonnes CO₂/tonne, respectively (ChemAnalyst, 2023; Meijssen et al., 2023).
2. Because of the lack of energy consumption data in the referenced literature, the value is estimated to be the same as that of the process in this thesis reported in section 8.2.1. These processes did not include a heat treatment of the leaching residue, so the corresponding energy consumption is excluded.
3. The presented values in Table 8.5 are normalised to treating 1 tonne of cementitious waste.
4. Other assumptions are the same as in this thesis.

Table 8.5 Comparison of indirect carbonation of waste concrete processes in this thesis and in the literature.

Ref.	This thesis		(Mehdizadeh, Mo & Ling, 2023)		(Meijssen et al., 2023)
Feedstock	Waste concrete fines		Hydrated cement paste		Recycled concrete aggregates
Feedstock cost (£)	3.1		3.1		3.1
Chemicals	Glacial acetic acid	25 % ammonia solution	Ammonium chloride	25 % Ammonia solution	Ammonium nitrate
Mass (kg)	424	386.7	1070	92.9	100
Chemical cost (£)	286.7		143		19.5
Ca extraction ratio	96 %		65.7 %		30 %
Carbonation efficiency	92 %		91.4 %		100 %
Recycled aggregates (kg)	600		-		987.5
Aluminosilicate SCM (kg)	80		- *		-
CaCO ₃ (kg)	300		615		25
Avoided landfill tax (£)	3.3		3.3		3.3
Product benefit (£)	153.6		246		49.5
Energy cost (£)	19.2		15.2		15.2
Net profit (£)	-152.1		88		15
Emitted CO ₂ (kg)	636.5		1457.9		312.7
Avoided CO ₂ (kg)	132		270		11.3
CO ₂ sequestration (kg)	-504.5		-1187.9		-301.4

*In this literature, the pozzolanic reactivity of the NH₄Cl leaching residue was not tested.

The results indicate that although the proposed process has higher Ca extraction ratio, comparable carbonation efficiency and produces purer products, the economic feasibility is weak compared to other indirect carbonation processes of cementitious waste. This is predominantly due to the high cost of chemicals, especially acetic acid. Also, it should be noticed that the net CO₂ sequestration of all three processes is negative. This derives from the high carbon footprint of the chemicals used. Moreover, the cost and CO₂ emissions to treat 1 tonne of waste concrete fines are higher than the previously reported CO₂ mineralisation processes by direct carbonation (Driver et al., 2024). To improve the economic viability and carbon negativity of the indirect carbonation of waste concrete fines, several approaches can be adopted, and this will be discussed in section 8.4.

8.4 Economic and sustainability potential

8.4.1 Reducing the materials cost and CO₂ emissions

One way to reduce the materials cost is recovering the acid and alkali from the wastewater. Bipolar membrane electrodialysis (BMED) method is effective in recovering the acid and alkali used in the indirect carbonation process. It has two configurations with anion exchange membrane (AEM) or cation exchange membrane (CEM), as shown in Figure 8.3. Using acetic salts improves the recovery ratio by a factor of 2 and reduces the power consumption by approximately 70 % compared to chloride salts (Shuto et al., 2015). Therefore, BMED is suitable for the efficient recovery of the acetic acid and ammonia. In addition, a controlled thermal recycling process has been reported. In this process, ammonium acetate (CH₃COONH₄) solution is heated at atmospheric pressure to temperatures between 175 and 189 °C to extract NH₃ and water. The residue can then be recycled to form a new batch of CH₃COONH₄ solution. This gives recovered acetic acid with 99.6 % purity (Rice, 1970). Besides economic benefits, a zero-waste and environmentally friendly process is achieved by recovering the acetic and ammonia.

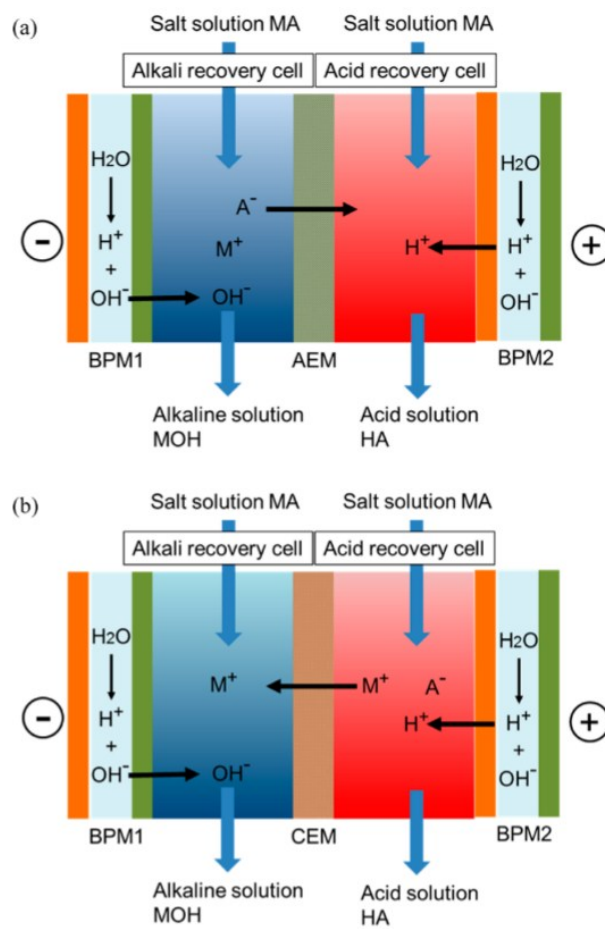


Figure 8.2 Illustrations of BMED cells with (a) anion exchange membrane-bipolar membrane (AEM-BPM) and (b) cation exchange membrane-bipolar membrane (CEM-BPM) configurations (Shuto et al., 2015).

Another way to reduce the materials cost is modifying the leaching process. According to Table 8.5, using ammonium salts can significantly lower the materials cost compared to acetic acid. Additionally, the leaching process can use small amount of acid as done by Meijssen et al (2023). Although the leaching efficiency and vaterite yield are lower, the net profit will be improved. The low Ca leaching efficiency could be compensated by cyclic leaching (Mehdizadeh, Mo & Ling, 2023; Driver et al., 2024).

The carbon emission associated with the acetic acid and ammonia can be reduced by developing sustainable and low-carbon acetic acid and ammonia sources. Conventional route for production of acetic acid is predominantly methanol carbonylation. This method relies on petroleum-derived products, needs high temperatures (150 – 250 °C) and expensive catalysts and generates chemical wastes. Alternative sustainable and cost-effective acetic acid production processes have been emerging recently,

and the market for sustainable bio-derived acetic acid is developing. Acetic acid can be produced from the catalytic reforming of biogas (CH_4 and CO_2) generated in the anaerobic digestion of organic waste (Martín-Espejo et al., 2022). It can also be sourced from microbial fermentation and microbial electrosynthesis of biomass (Mutyalu & Kim, 2022). Such processes can deliver low-carbon acetic acid with a carbon footprint of 0.18 tonnes CO_2 /tonne (Budsberg et al., 2020). Moreover, recent improvements in conventional acetic acid production have developed a heterogeneous catalysis process using recoverable rhodium/iridium catalyst which reduces the carbon footprint to 0.04 tonne CO_2 /tonne (Dimian & Kiss, 2020). Several sustainable production routes of ammonia are also available. By utilising N_2 from cryogenic distillation and H_2 from low-temperature electrolysis as raw materials, the carbon footprint of ammonia is reduced to 0.22 tonnes/tonne (Liu, Elgowainy & Wang, 2020). Besides, the CO_2 emissions from combustion of fossil fuels can be mitigated by using sustainable energy sources including wind and solar power (Zajac et al., 2021). Generally, if sustainable acetic acid and ammonia are used, the materials CO_2 footprint is reduced to 38.2 kg. If the power is supplied by clean energy, the associated CO_2 emission is zero (Zajac et al., 2021). Consequently, this indirect carbonation process will achieve a net CO_2 sequestration of 93.8 kg/tonne of waste concrete fines. In this scenario, the carbon footprint of the aluminosilicate SCM will be reduced from 504.5 kg/tonne to -1172.5 kg/tonne. At a 20% clinker replacement ratio, the carbon footprint of the composite cement is 423.9 kg/tonne, which is 48.5% less than 100% CEM I. This is higher than the CO_2 emissions reduction (10 – 20%) resulted from the same replacement level of conventional SCMs (Yang et al., 2015). Therefore, this process is anticipated to be more economic viable and able to produce low-carbon construction materials in the future.

8.4.2 Improving the product value

The product revenue can be increased by generating high-value products. The major products of the indirect carbonation process of waste concrete fines are recycled sand and aggregates, accounting for around 70 wt% of the products. The cheap price of sand and aggregate is an obstruction to the practical application of this process. However, the price of sand and aggregates has increased by 52.7 % since 2015 and this is anticipated to keep increasing due to inflation and the depletion of natural resources (Statista, 2022). Also, as the SR is rich in aluminosilicate, it is a potential feedstock for synthesising zeolites. Zeolites are microporous aluminosilicate minerals which can be used as pollutant absorbents,

soil enhancers and catalysts. The price of zeolite minerals is £ 430 – 570/tonne (Procurement Resource, 2023). Zeolitic minerals have been successfully synthesised through hydrothermal treatment of fly ash and blast furnace slag (Hu et al., 2021; Liu et al., 2021, 2020; Monasterio-Guillot et al., 2020). Preliminary investigations on synthesising hierarchical analcime-type zeolite using the silica-rich residue generated in the acetic acid leaching of cement paste has been attempted and the results are reported in Appendix B. If this can be applied to the quartz sand and SR extracted from waste concrete fines, the process profit will be significantly improved. This research has successfully developed an load-bearing aragonite insulation material from vaterite with comparable properties to foam concrete. As the current price of foam concrete is cheap (around £ 30/tonne), the aragonite binder from waste concrete fines is less competitive in this case (Ahmadi, Reisi & Sajadi, 2023). Therefore, producing vaterite suitable for higher-value applications such as medicine is key in improving the revenue of this process.

Although several prerequisites need to be achieved before practical application, this process turns a large stream of waste into resources for new materials and contributes to waste upcycling and circular concrete. Indirect carbonation process has wider benefits because it also applies to other types of wastes such as municipal solid waste incineration bottom ash (MSWIBA). Besides Ca extraction, the chelating effect of acetic acid can improve the dissolution of heavy metal ions from MSWIBA, which is another bonus (Cao et al., 2025). Compared to direct carbonation, this process also has merit. Clean sand and aggregates, a viable SCM without adverse effect on the concrete workability and pure vaterite are extracted from waste concrete fines. CaCO_3 cannot be separated in direct carbonation. To produce SCM with good workability, direct carbonation process of waste concrete fines uses 45 % MEA solution at an L/S ratio of 10 mL/g as the reaction medium (Mao et al., 2024). For a treatment capacity of 1 tonne, 4.5 tonnes of MEA is needed. The price of MEA is around £ 900/tonne (Intratec, 2019). Therefore, the materials cost is £ 4050. 500 kg fine aggregates and 690 kg of SCM can be produced at 100% carbonation degree, generating a revenue £ 102.8. Assuming the energy cost in these two processes are similar, the net cost of direct carbonation is much higher. In addition, the production of MEA has a higher carbon footprint than the production of ammonia, bringing penalties on the CO_2 saving potential of direct carbonation (Luis, 2016).

9 Conclusions and research recommendations

9.1 Conclusions

This research has investigated an indirect carbonation process to develop circular concrete. Acetic acid leaching of waste concrete, ammonia purification and carbonation of the Ca^{2+} -rich solution recover clean sand, a viable aluminosilicate SCM and vaterite. The optimal acetic acid concentration, liquid/solid ratio, temperature and time are determined. The properties and performances of recycled sand are assessed. The pozzolanic reactivity of the aluminosilicate SCM and the optimal heat treatment to reduce its water absorption and improve the mortar flowability are investigated. A novel aragonite binder is developed via the polymorphic transformation of vaterite. The cost, benefit and CO_2 saving potential of this process are estimated. The conclusions addressing the objectives of this thesis are as follows:

- Increasing the acetic acid concentration increases leaching of Ca, Al, Fe and Si from cement hydration products. Increasing L/S ratio improves the extraction of Al, Fe and Si. Higher temperature results in less dissolution of Al, Fe and Si. Increasing time improves the precipitation of dissolved silica and reduces the Si extraction. The optimal leaching conditions are determined by the particle size and old cement paste content of waste concrete. For waste concrete fine aggregates (0 – 4.75 mm), the optimal conditions use an acid concentration of 0.6 mol/L, an L/S ratio of 7 ml/g, and a reaction time of 6 hours at ambient temperature. For cement paste (0 – 300 μm), the optimal conditions are an acid concentration, L/S ratio, temperature, and time of 1.6 mol/L, 11 mL/g, 60 °C and 1 hour, respectively. These optimal conditions enable the extraction of clean recycled sand and aluminosilicate SCM from waste concrete.
- The chemical and physical properties of recycled sand are comparable to new sand. Total replacement of virgin sand by recycled sand achieves 7-day and 28-day mortar compressive strengths of 35.6 and 55.1 MPa, respectively, which are higher than mortars with 100 % standard sand.

- This research has demonstrated how it is possible to produce a silica-rich SCM by acetic acid leaching of cementitious materials. The silica-rich residue derived from cement paste has high amorphous content (98.4 %), larger particle size ($D_{50} = 40.6 \mu\text{m}$) and higher specific surface area ($155 \text{ m}^2/\text{g}$) than that derived from waste concrete fine aggregates. The pozzolanic reactivity of the silica-rich SCM derived from cement paste is 40% higher than coal fly ash. 0.5 w/b mortars containing 20 % CEM I replacement of the silica-rich residue from cement paste have a 28-day compressive strength of 63.6 MPa. The pozzolanic reactivity of the silica-rich SCM derived from waste concrete fine aggregates is comparable to coal fly ash. 0.5 w/b mortars containing 20 % CEM I replacement of the silica-rich residue from waste concrete fine aggregates have a 28-day compressive strength of 42.3 MPa.
- The viability of the aluminosilicate residue produced by acid leaching of cement paste to form supplementary cementitious materials can be improved by thermal treatment. The optimum heat treatment temperature is around 900°C . At this temperature, the specific surface area of aluminosilicate residue is reduced by 99%. The resulting SCM has a comparable specific surface area and pozzolanic reactivity to other commercially available SCMs. Higher temperatures result in crystallisation of cristobalite, anorthite and hematite and reduced pozzolanic reactivity, while lower temperatures result in insufficient reduction in surface area. Mortars with 20% cement replacement of optimally heat-treated aluminosilicate residue have good workability and higher compressive strengths than mortars containing coal fly ash and comparable to mortars containing SF and GGBFS. The results indicate that acid treatment of waste concrete combined with indirect carbonation of the leachate and thermal treatment of the aluminosilicate residue, when combined with associated recovery of clean sand and aggregate represents a potential way to achieve circular concrete.
- 99.1 % pure vaterite is produced by carbonating the Ca^{2+} -rich solution from acetic acid leaching of cement paste with 100 % CO_2 at 1 L/min flow rate for 30 minutes. It activated in 0.1 mol/L MgCl_2 and 0.1 mol/L SrCl_2 at 60°C to transform to a fibrous interlocking structure consisting of aragonite whiskers within 3 days. The higher the L/S ratio, the lower the density and mechanical performance, and the better the thermal insulating performance. P-1.0-3d has the lowest thermal conductivity (0.177 W/mK), a low density (750 kg/m^3) and compressive

strength (4 MPa) comparable to gypsum board. Therefore, the aragonite binder can form a novel lightweight thermal insulating material and contribute to the development of circular concrete.

- Based on laboratory data, the economic analysis shows that the indirect carbonation process has a high cost of £ 152.1 for treating 1 tonne of waste concrete fines. The carbon emission of this process is 504.5 kg CO₂/tonne of waste concrete fines due to the high CO₂ footprint related to acetic acid and ammonia. This is lower than the CO₂ emission of cement (823 kg/tonne) but much higher than the direct carbonation process (down to -200 kg/tonne). However, the materials cost can be lowered by acid/alkali recovery and using ammonium salts. With the use of acetic acid derived from an eco-efficient process, sustainable ammonia and low-carbon energy, this process has a potential to achieve a CO₂ sequestration of 93.8 kg/tonne of waste concrete. The profit of this process can be improved by producing high-value products, for example zeolites and vaterite suitable for medical applications.

9.2 Limitations and research recommendations

This research extracts clean recycled sand, a reactive aluminosilicate SCM and aragonite binder via indirect carbonation of waste concrete fines and these are suitable to be used as new construction materials. However, there are some limitations that need to be studied and resolved. The strengths of cement mortar containing recycled sand and optimally engineered SR are primarily investigated, but the application of recycled concrete products in concrete needs to be studied. The purification residue containing Mg, Al and Fe is treated as a waste and not valorised. The effect of carbonation conditions on controlling the properties (particle size, surface structure) of vaterite is not clear. The carbonation uses 100% CO₂ which brings additional materials and transport costs. This research investigated the conversion of vaterite to aragonite in 0.1 mol/L Mg and Sr-containing solution under high temperature. However, this process is still complicated and consumes large amount of chemicals. Several methods of recovering acid and alkali are proposed but not verified. Finally, as the actual concrete incorporates SCMs such as GGBFS and FA, the applicability of this process to waste concrete generated from these needs to be studied.

To unlock the full potential of indirect carbonation in developing circular concrete, in-depth study is needed on the durability of concrete containing recycled sand and aluminosilicate SCM. The recycling of purification residue which is rich in Fe, Al and Mg into value-added products needs to be explored to achieve a zero-waste process. Further research should involve heating the SR at temperatures lower than 900 °C at different times to investigate the optimal balance between reactivity, surface area and energy consumption. The effect of heat treatment on the performance of SR from real waste concrete is also recommended. The performance of composite cement with SR at higher than 20% clinker replacement ratio should be studied. The carbonation with varying parameters such as time, flow rate, temperature and chemical additives and the effects on the physical and chemical properties of vaterite should be studied. As discussed in section 8.1, the lower CO₂ concentration in industrial flue gas will affect the carbonation parameters. Future research should investigate the influence of industrial flue gas on the carbonation rate and carbonation ratio and assess the effect of the gas impurities (SO₂, NO_x) on the carbonation efficiency and product quality. Developing more sustainable and cost-effective curing of aragonite binder is an urgent need. As seawater and desalination brines are huge reservoirs and cheap resources for Mg and Sr salts, the technical feasibility of transforming vaterite to aragonite in these is worth investigating. It has been reported that large amount of seawater extraction can present an issue on the aquatic organisms, for example, they can be extracted with seawater or trapped in the system (Ihsanullah et al., 2021). This can be mitigated by subsurface intakes (Henthorne & Boysen, 2015). If this method is feasible, continuous monitoring and site investigations should be undertaken to evaluate its environment impact. The engineering methods for controlling the pore shape and size distribution of the aragonite board need to be developed. As the thermal insulation of porous material decreases when the humidity level increases (Koh & Brouwers, 2024), the change in thermal conductivity of aragonite binder under different environmental conditions and methods to maintain high thermal conductivity are necessary for the successful application of this material. Due to its large porosity, the aragonite binder is subject to moisture adsorption hence chemical attack in real-world conditions. Investigating the effect of these on the properties of aragonite binder and developing methods to improve its durability are recommended. Finally, the viability of acid and alkali recovery process through BMED or thermal recycling needs to be verified. The acetic acid and ammonia recovery ratio, cost, energy consumption and CO₂ footprint should be assessed.

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Appendix A Determination of chemical compositions in powdered material – titration methods

The titration method for determining the chemical composition of solid samples follows Chinese standard GB176-2017. Before titration, around 0.5 g of the sample is fused with 7 g of sodium hydroxide (NaOH) in a silver crucible and heated at 700 °C in a muffle furnace for 20 minutes. After fusion, the crucible is immersed in 100 mL of boiling deionised water in a 300 mL glass beaker to dissolve the fused sample. After the sample dissolves completely, the crucible is extracted and washed with deionised water. Then, 25 mL of 35% hydrochloric acid (HCl) and 1 mL of 65% nitric acid (HNO₃) is added. The resulting acidic solution is cooled to room temperature and transferred to a 250 mL volumetric flask. Finally, deionised water is added until the volume mark is reached. This is the stock solution used in subsequent titration experiments.

To measure the CaO content, CMP indicator is prepared by mixing 1 g of calcein, 1 g of methyl thymol blue, 0.2 g of phenolphthalein and 50 g of potassium nitrate (KNO₃) in an agate mortar. 25 mL of the stock solution is transferred to a 300 mL glass beaker by a glass pipette. Deionised water is added until the total volume is around 100 mL. 5 mL of 33% triethanolamine solution is added to shield the Al³⁺ and Fe³⁺ from reacting with EDTA. Around 0.01 g of CMP indicator and 200 g/L KOH solution are added until green fluorescence occurs. Then, the solution is titrated with 0.015 mol/L EDTA solution until the green fluorescence disappears and the solution turns red. The CaO content is calculated using equation A.1:

$$W_{CaO}(\%) = \frac{T_{CaO} \times V_{EDTA}}{m_0} \quad Eq. A.1$$

Where W_{CaO} is the weight percentage of CaO, T_{CaO} is the mass of CaO (mg) can be reacted with 1 mL of 0.015 mol/L EDTA solution, V_{EDTA} is the volume of EDTA used in the titration and m_0 is the mass of sample.

To measure the SiO₂ content, 50 mL of stock solution is pipetted to a 300 mL plastic beaker. 15 mL of 65% nitric acid is added. After the solution is cooled down to room temperature, potassium chloride

(KCl) is added until the solution is saturated with KCl. 2 g of excess KCl and 10 mL of potassium fluoride (KF) solution are added afterwards. The solution is let stand for 20 minutes to give enough time for the precipitation of potassium fluorosilicate (K_2SiF_6). Then, the precipitate is extracted by gravity filtration and excess KCl is washed off with small amount of 50 g/L KCl solution. The filter paper containing the remaining K_2SiF_6 precipitate is placed in a plastic beaker, meanwhile 10 mL of 50 g/L KCl in 50% ethanol solution and 1 mL of phenolphthalein indicator solution are added. 0.15 mol/L sodium hydroxide (NaOH) solution is then added until the filter paper turns red. 200 mL of boiling water is added to induce the hydrolysis of K_2SiF_6 to hydrofluoric acid (HF). Finally, the solution is titrated with 0.15 mol/L NaOH solution until the colour turns red. The SiO_2 content is calculated using equation A.2:

$$W_{SiO_2}(\%) = \frac{5 \times T_{SiO_2} \times V_{NaOH}}{m_0 \times 1000} \times 100 \quad \text{Eq. A.2}$$

Where W_{SiO_2} is the weight percentage of SiO_2 , 5 is the volume ratio, T_{SiO_2} is the mass of SiO_2 (mg) can be reacted with 1 mL of 0.15 mol/L NaOH solution, V_{NaOH} is the volume of NaOH solution used in the titration and m_0 is the mass of sample.

To measure the Fe_2O_3 content, 25 mL of the stock solution is pipetted to a 300 mL glass beaker. Deionised water is added until the total volume is around 100 mL. 12.5% ammonia solution and 17.5% HCl are added to adjust the pH to around 1.8. Then the solution is heated to 70°C and 10 drops of sulfosalicylic acid sodium salt indicator were added. 0.015 mol/L EDTA solution is used to titrate the sample solution until the colour changes from red to yellow. The Fe_2O_3 content is calculated using equation A.3:

$$W_{Fe_2O_3}(\%) = \frac{T_{Fe_2O_3} \times V_{EDTA}}{m_0} \quad \text{Eq. A.3}$$

Where $W_{Fe_2O_3}$ is the weight percentage of Fe_2O_3 , $T_{Fe_2O_3}$ is the mass of Fe_2O_3 (mg) can be reacted with 1 mL of EDTA solution, V_{EDTA} is the volume of EDTA used in the titration and m_0 is the mass of sample. To measure the Al_2O_3 content, 200 mL of deionised water is added to the solution resulted from the titration of iron. The pH of the solution is adjusted to 3.0 using 12.5% ammonia solution and heated to

boiling. Then, 10 drops of EDTA-Cu solution and 3 drops of 0.2 g/L 1-(2-pyridylazo)-2-naphthol (PAN) indicator in ethanol solution are added. The solution turns red. Finally, the solution is titrated with 0.015 mol/L EDTA solution until the colour turns yellow. The Al_2O_3 content is calculated using equation A.4:

$$W_{Al_2O_3}(\%) = \frac{T_{Al_2O_3} \times V_{EDTA}}{m_0} \quad Eq. A.4$$

Where $W_{Al_2O_3}$ is the weight percentage of Al_2O_3 , $T_{Al_2O_3}$ is the mass of Al_2O_3 (mg) can be reacted with 1 mL of EDTA solution, V_{EDTA} is the volume of EDTA used in the titration and m_0 is the mass of sample. To measure the SO_3 content, around 0.5 g of the solid sample is mixed with 40 mL deionised water and 10 mL 17.5% HCl solution and boiled for 5 minutes to extract the sulphate. The solution is separated by gravity filtration and heated to boiling. 10 mL of preheated 100g/L barium chloride ($BaCl_2$) solution is slowly added to precipitate barium sulphate ($BaSO_4$). Then, the mixture is let stand for 24 hours before the $BaSO_4$ is collected by gravity filtration using an ashless filter paper and washed by deionised water. The precipitate and the filter paper are heated under $950^\circ C$ in a muffle furnace for 30 minutes. The filter paper is burned off and only $BaSO_4$ is left. The weight of $BaSO_4$ is recorded and the SO_3 content is calculated by equation A.5:

$$W_{SO_3}(\%) = \frac{0.343 \times m_1}{m_0} \times 100 \quad Eq. A.5$$

Where W_{SO_3} is the weight percentage of SO_3 , 0.343 is the content of SO_3 in $BaSO_4$, m_1 is the mass of the precipitate after heating and m_0 is the mass of sample.

The loss on ignition (LOI) of solid samples is determined by calculating the mass change of samples after drying under $80^\circ C$ and heating under $1050^\circ C$ for 1 hour, using equation A.6:

$$LOI(\%) = \frac{m_{80} - m_{1050}}{m_{80}} \times 100 \quad Eq. A.6$$

Where m_{80} is the mass of sampled dried under $80^\circ C$ and m_{1050} is the mass of sample heated under $1050^\circ C$.

Appendix B Production of hierarchical analcime-type zeolite using the aluminosilicate residue from acid leaching of hydrated cement paste

In this appendix, hydrothermal reaction is used to transform the aluminosilicate residue from the acetic acid leaching of hydrated cement paste (HCP) into hierarchical analcime-type zeolite materials. The possibility of improving the economic viability of the indirect carbonation of waste concrete by generating a high-value product zeolite, is investigated. This appendix reports the current results of an ongoing work in collaboration with Dr. Priyanka Katiyar's group at Shiv Nadar University in India.

Introduction

Indirect carbonation of waste concrete produces clean sand, an aluminosilicate SCM and vaterite. This approach has the potential to produce circular and low-carbon concrete. However, these products have low economic value and cannot offset the high cost generated by the chemicals used as discussed in chapter 8. Therefore, obtaining high-value products from this process needs to be pursued. Zeolites are crystalline aluminosilicate minerals which are built from corner-sharing $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedra. The structure of zeolite is microporous (pore size < 2 nm) with high level of porosity and connected channels, making it suitable for high-value applications such as contaminant adsorption, ion exchange and catalysis (Monasterio-Guillot et al., 2020). During catalysis, the micropores in zeolite limits the diffusion rate of large molecules and can cause pore blockage which reduces the lifespan of the catalyst. Hierarchical zeolites are zeolites materials with a larger pore size, normally mesoporous (pore size 2 – 50 nm). The mesopores can improve the access of larger molecules to the active sites, making hierarchical zeolites more efficient in catalysis and more durable than microporous zeolites (Feliczak-Guzik, 2018).

Zeolite is synthesised from hydrothermal reaction, where the aluminosilicate precursors are reacted with NaOH solution in an autoclave under relatively high temperature (100 – 200°C). Tetraethylammonium hydroxide (TEAOH) is widely used as an organic structure directing agent for synthesising zeolite and refining the pore structure (Liu et al., 2019; Pescarmona et al., 2002; Torres & Cardoso, 2008). From

the chemical composition shown in Table 5.1, the SR is rich in silica and alumina. This makes it a possible precursor to zeolites. Most zeolite synthesis from waste materials use external Si or Al sources to adjust the Si/Al ratio (Guo et al., 2017; Kuwahara et al., 2008; López-Delgado et al., 2020). Less research has investigated the synthesis of hierarchical zeolite from totally waste materials as the Si and Al sources. Kanda et al. synthesised zeolite materials from calcareous waste concrete powder by hydrothermal reaction with 1 – 4 mol/L NaOH under 120 – 180°C for 3 – 18 hours. Although analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) phase was formed, the product also contained impurities such as albite and hematite (Kanda & Harada, 2022). Also, the pore structure of the product was not investigated. Therefore, this work aims to synthesise a hierarchical analcime-type zeolite with refined pore structure. To avoid the influence of impurities in real waste concrete fines, SR extracted from hydrated cement paste is used in the hydrothermal synthesis with TEAOH as the template.

Experimental

The SR is produced from the optimal acetic acid leaching of HCP described in section 4.4.1. It contains some residual Ca due to adsorption by the highly porous aluminosilicate gel (Table S1). It has been reported that a high content of Ca in the starting material may inhibit the crystallisation of zeolite (Kuwahara et al., 2008; Wajima, 2020). Therefore, the SR-cp is mixed with dilute HCl solution (0.1 mol/L) at a liquid/solid ratio of 5 at 60°C for 1 hour to reduce the Ca content. The resulting Ca-depleted SR (CdSR) is collected by vacuum filtration through hardened ashless filter paper (Whatman 541), washed with deionised water by 3 times and dried in a 60°C oven for 24 hours. This is the starting material in the hydrothermal synthesis.

Table S1 Chemical compositions of the materials determined by XRF (in oxides).

Sample	Na ₂ O (%)	CaO (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	SO ₃ (%)	MgO (%)	K ₂ O (%)	TiO ₂ (%)	LOI (%)	Si/Al molar ratio
SR	-	5.8	47.7	14.0	4.1	0.2	0.4	0.6	0.7	23.8	2.9
CdSR	-	3.1	47.7	14.2	4.5	0.1	0.4	0.5	0.8	25.9	2.9
Reference	12.2	3.9	40.7	19.1	6.6	0.2	0.6	0.2	0.9	13.0	1.8
Product	10.1	4.0	45.1	20.7	7.5	0.2	0.5	0.2	1.0	6.4	1.9

In the hydrothermal synthesis, 10 g of CdSR is mixed with 100 mL of 2 mol/L NaOH solution and 2 g of TEAOH (Sigma Aldrich) in an autoclave reactor with PTFE lined vessel (Cambridge Energy Solutions, UK). The autoclave reactor is stored in a 150°C oven (Carbolite Gero AX 60) for 24 hours. After the hydrothermal reaction, the resulting mixture is vacuum filtered to collect the solid. The solid is calcined under 550°C for 3 hours in a muffle furnace (Carbolite Gero HTF 17/5) to remove the TEAOH and generate the final product. Same procedure is conducted without TEAOH and calcination to produce the reference material. The zeolite samples and synthesis conditions are listed in Table S2.

Table S2 Zeolite samples and synthesis conditions.

Sample	NaOH solution	TEAOH (g)	Temperature (°C)	Time (h)	Calcination
Reference	2 mol/L, 100 mL	0	150	24	No
Product	2 mol/L, 100 mL	2	150	24	550°C, 3h

The chemical compositions of the materials are determined by XRF (Malvern PANalytical Zetium). The phase compositions of the materials are measured by XRD (Malvern PANalytical Empyrean). Quantitative analysis is conducted on powder mixes of 80% sample and 20% internal standard (corundum Al₂O₃). The results are analysed using Rietveld Refinement in HighScore Plus software. The specific surface area and pore structure of the materials are determined by N₂ adsorption and desorption (Micromeritics 3Flex 3500). The cumulative and distributive pore size are calculated based on the adsorption isotherm using the Dollimore-Heal model. The morphology of the materials is observed using FE-SEM (Zeiss Sigma 500VP).

Results and discussion

The chemical compositions of CdSR, reference and product are presented in Table S1. The Ca content of SR reduced from 5.8% to 3.1% after the HCl leaching. In diluted HCl solution, the silica and alumina are not dissolved, and the Si/Al molar ratio of the SR remains the same. After the hydrothermal reaction, the Si/Al molar ratio reduced from 2.9 to around 2. The Si/Al molar ratio in the product (1.9) is closer to that in analcime (2) than the reference (1.8), indicating there is a templating effect of the TEAOH.

The XRD patterns of the materials and phase compositions determined by QXRD are shown in Figure S1 and Table S3, respectively. CdSR is predominantly amorphous with 1.9% crystalline quartz. After hydrothermal reaction, quartz is consumed, and the crystallinity significantly increases as indicated by Table S3. The crystalline phase of the product contains solely analcime, while that in the reference also contains gismondine ($\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{16}\cdot 9\text{H}_2\text{O}$), sodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}$) and some poorly crystalline phases indicated by the wide signal at $7.7^\circ 2\theta$. Moreover, the product has a higher crystallinity (75.4%) than the reference (43.2%). These demonstrate that using TEAOH improves the crystallisation of analcime-type zeolite.

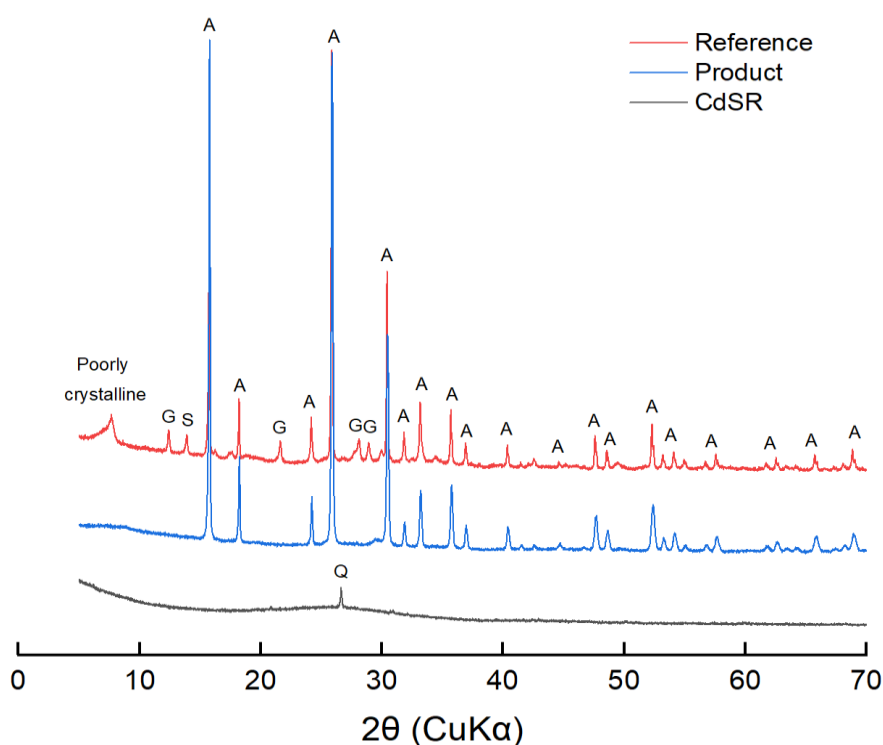


Figure S1 XRD patterns of CdSR, reference and product.

Table S3 Phase compositions of CdSR, reference and product determined by Rietveld refinement.

Sample	Phase (%)					Crystallinity (%)
	Analcime	Gismondine	Sodalite	Quartz	Amorphous	
CdSR	-	-	-	1.9	98.1	1.9
Reference	33.5	8.2	1.5	-	56.8	43.2
Product	75.4	-	-	-	24.6	75.4

The BET specific surface area of the CdSR, reference and product are 243.3, 27.3 and 19.5 m²/g, respectively. CdSR predominantly contains amorphous aluminosilicate gel which is highly porous. The specific surface area of the product is close to the value for analcime synthesised from coal gangue reported in literature (Jin et al., 2022). Hydrothermal reaction increases the crystallinity hence reduces the specific surface area. Incorporating TEAOH in the hydrothermal synthesis changes the pore structure. In Figure S2, all the adsorption-desorption isotherms of CdSR, reference and product are Type IV isotherms which is representative for mesoporous materials according to the IUPAC classification (Schlumberger & Thommes, 2021). However, there is a difference in the shapes of the hysteresis. The hysteresis of product conforms to IUPAC type H2(b) and those of CdSR and reference have a steep stepdown between 0.4 and 0.5 P/P₀, which conform to IUPAC type H5 (Schlumberger & Thommes, 2021). This suggests that the product has a narrow pore size distribution with wide pore necks, while the CdSR and the reference contains both open and restricted mesopores with small pore necks (Schlumberger & Thommes, 2021). The cumulative pore volume and pore size distribution of the three materials are presented in Figure S3. Figure S3a shows CdSR has the highest cumulative pore volume (0.46 cm³/g), followed by the reference (0.11 cm³/g) and the product (0.09 cm³/g). In Figure S3b, the CdSR and reference contain mainly micropores and mesopores together with minor amount of macropores (> 50 nm). The pore size distribution of the reference shows it is rich in micropores and narrow mesopores (< 4 nm) with a peak at around 2.5 nm. These small-sized pores are related to the amorphous aluminosilicate gel. By applying TEAOH in the hydrothermal synthesis, the micropores, narrow mesopores and macropores are reduced and more mesopores in the range of 7 – 40 nm are formed in the product. This confirms the pore size refining effect of TEAOH.

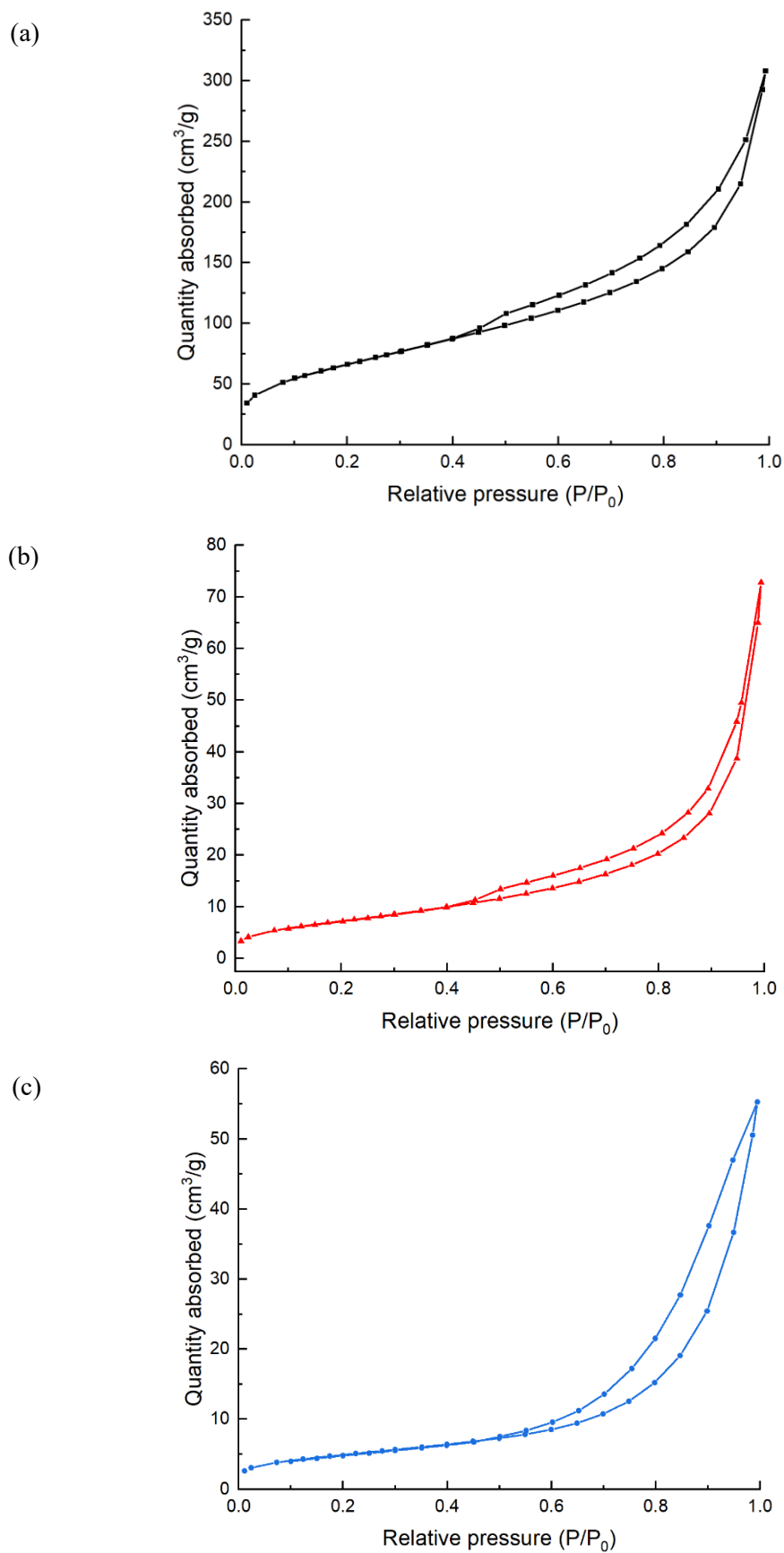


Figure S2 The absorption-desorption isotherms of (a) CdSR (b) reference and (c) product.

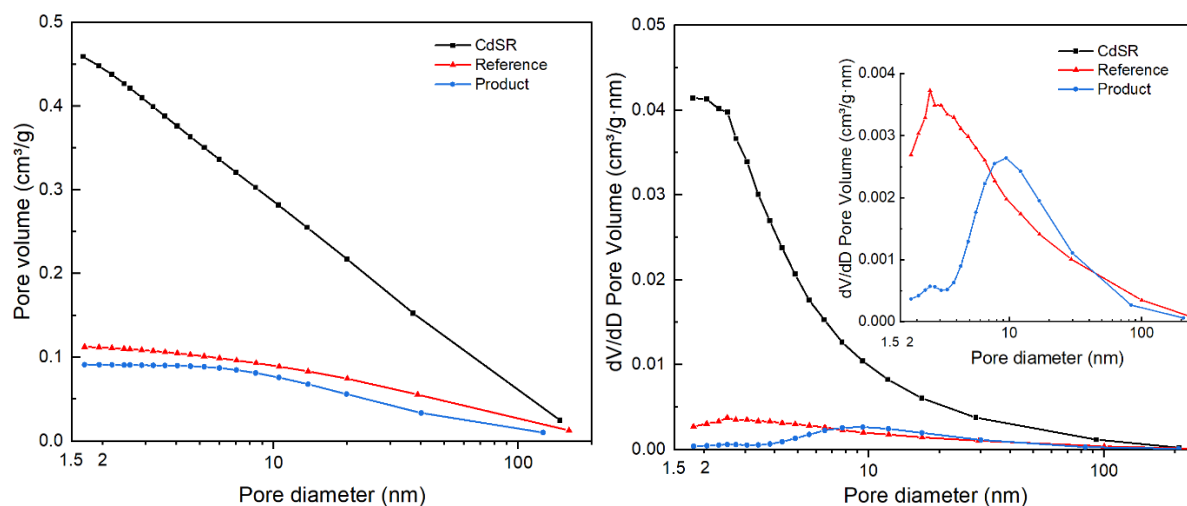


Figure S3 (a) cumulative pore volume and (b) pore size distribution of CdSR, reference and product.

The morphology of the reference and the product are compared in Figure S4. Without TEAOH, the reference is in irregular shape with rough and porous surfaces (Figure S4a). In contrast, the product synthesised with TEAOH contains purer crystal with particle size between 12 and 15 μm and a well-defined multi-faced polyhedron shape. This is similar to the analcime synthesised from other industrial waste and natural minerals (Jin et al., 2022; Novembre & Gimeno, 2021).

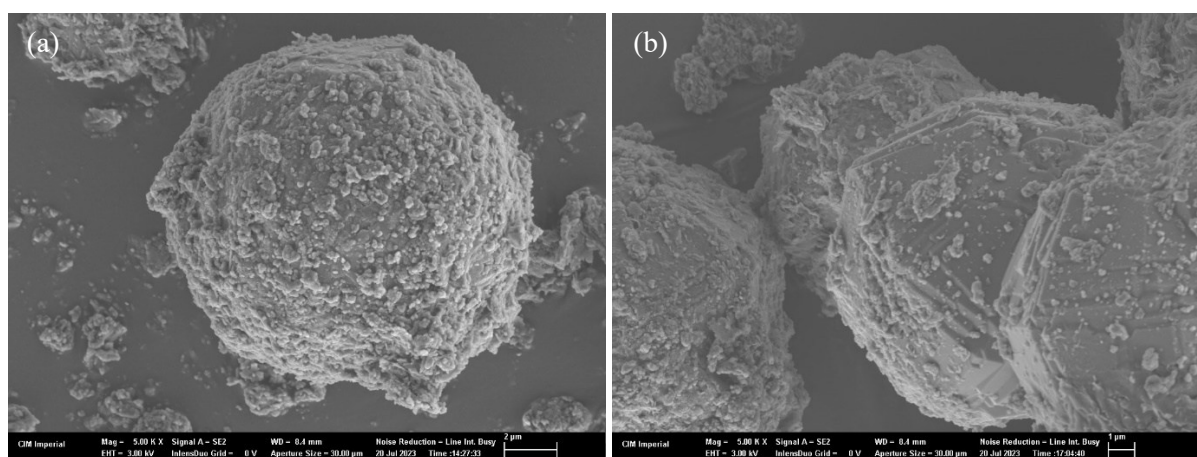


Figure S4 SEM images of (a) reference and (b) product.

Limitations and recommendations

This work verifies the technical viability for valorising waste concrete through the synthesis of hierarchical zeolite from the aluminosilicate residue generated in indirect carbonation of hydrated cement paste. However, some limitations are noticed which needs to be resolved by future research.

- The SR from acetic acid leaching of HCP is further treated by diluted HCl, but the Ca content is not fully removed, resulting in a Ca content of 4% in the product. Besides, the product contains Fe. The relationship between residual Ca and Fe contents and the properties of the zeolite synthesised from SR is not clear. If a Ca- and Fe- free feedstock produces zeolite with higher crystallinity and better pore structure, more concentrated acetic acid or stronger acid can be used to leach waste concrete. This needs to be investigated by further research.
- The effects of NaOH concentration, TEAOH/CdSR ratio, NaOH/CdSR ratio, synthesis duration and temperature on the properties of the product are not clear. The synthesis conditions of the product need to be optimised in future research.
- Ongoing research on the application of the product from this work as a catalyst in the pyrolysis of food waste is being conducted by Dr. Priyanka Katiyar's group in Shiv Nadar University and the results will be reported elsewhere.

Conclusions

This study has successfully synthesised hierarchical analcime-type zeolite without external Si and Al sources. Hydrothermal reaction with TEAOH improves the crystallinity of the product, promotes the crystallisation of analcime and refines the pore structure by generating more 7 – 40 nm mesopores. The results shed light on extracting high-value products from cementitious waste materials.

Appendix C Publications arising from this research

Journal papers

1. Ding, T., Wong, H., Qiao, X., Cheeseman, C. (2022). Developing circular concrete: Acid treatment of waste concrete fines. *Journal of Cleaner Production*, 365, 132615. <https://doi.org/10.1016/j.jclepro.2022.132615>.
2. Ding, T., Wong, H., Yio, M., Cheeseman, C. (2024). Production of amorphous aluminosilicate and vaterite from acid leaching of hydrated cement paste. *Journal of Sustainable Cement-Based Materials*, 1–12. <https://doi.org/10.1080/21650373.2024.2397484>.
3. Ding, T., Zhang, S., Yio, M., Wong, H., Cheeseman, C. (2025). Engineering aluminosilicates extracted from waste concrete to form a viable supplementary cementitious material. *Construction and Building Materials*, 462, 139981. <https://doi.org/10.1016/j.conbuildmat.2025.139981>.
4. Ding, T., Gao, Z., Chan, J. T. C., Wong, H., Yio, M., Cheeseman, C. (2024). Thermal insulating aragonite board from waste concrete. (In preparation).