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Developing circular concrete: Acid treatment of waste concrete fines

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ABSTRACT

The development of circular concrete, to enable key components to be extracted and reused, is a key requirement to achieve sustainability in the built environment. Current industry practice for end-of-life concrete is best described as down-cycling because recycled concrete aggregate has limited use, with disposal of the associated crushed concrete fines. Acid treatment of waste concrete is being investigated to allow key concrete components to become circular and, in this work, the effect of acetic acid concentration, liquid/solid (L/S) ratio, reaction time and temperature on the leaching of waste concrete fines is reported. An acid concentration of 0.6 mol/L, an L/S ratio of 7 ml/g, and a reaction time of 6 h at ambient temperature allows clean sand to be extracted from concrete fines. This performs identically to new sand in mortar samples. We show for the first time that the dried and ground silica-rich residue produced by acid leaching has pozzolanic properties comparable to commercially available supplementary cementitious materials (SCM) such as blast furnace slag and coal fly ash. The potential for CO_2 sequestration using the Ca^{2+}-rich leached solution to form $CaCO_3$ is calculated. The research shows that acid leaching of concrete fines can produce clean reusable sand, generates a viable SCM and sequester significant amounts of CO_2 by forming precipitated calcium carbonate.

1. Introduction

Waste concrete produced from construction and demolition is a major issue as it is produced in enormous quantities. It is currently predominantly downcycled as it is normally crushed and size sorted, to produce relatively low-grade recycled concrete aggregate. This has high water absorption due to the inherent porosity of cement mortar attached to aggregate particles. In addition, the fine fraction that is generated by crushing concrete has limited use and is often sent to landfill. This represents inefficient management of valuable resources contained in concrete that include aggregate, sand, hydrated cement paste and residual un-hydrated cement particles. Reuse of recycled concrete coarse aggregate has been extensively reported, but few studies have focused on recycling and value extraction from waste concrete fines.

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.

Waste crushed concrete fines have 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, limiting reuse and causing low strength and poor durability (Evangelista et al., 2015; Geng and Sun, 2013; Khatib, 2005; Xiao et al., 2013; Zhu et al., 2013).

Different approaches have been used to improve the performance of waste concrete fines. 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 (Grabiec et al., 2012; Shi et al., 2018; Wang et al., 2020; Zhang et al., 2015; Zhu et al., 2013). 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 (Huang et al., 2020; H. S. Kim et al., 2017; J. H. Kim et al., 2019; Santha Kumar et al., 2019; Santha Kumar and Minocha, 2018).

Concrete fines consist of sand, cement hydration products including portlandite ($Ca(OH)_2$), calcium silicate hydrate (C–S–H) gel, ettringite

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and AFm phases and $CaCO_3$ due to the CO_2 uptake during the service life, demolition and recycling of concrete. Equations (1)–(3) show the effect of acid leaching on $Ca(OH)_2$, $CaCO_3$ and C–S–H gel, where A^- is the conjugate base of the acid. These indicate that acid treatment generates a Ca^{2+}-rich leachate from portlandite and C–S–H gel, and a silica-rich solid residue from leaching C–S–H:

$$2HA + Ca(OH)_2 \rightarrow Ca^{2+} + 2A^- + 2H_2O \quad (1)$$

$$2HA + CaCO_3 \rightarrow Ca^{2+} + 2A^- + CO_2\uparrow + H_2O \quad (2)$$

$$xCaO \cdot ySiO_2 \cdot zH_2O + 2xHA \rightarrow xCa^{2+} + 2xA^- + ySiO_2 + (x+z)H_2O \quad (3)$$

A pozzolanic silica-rich residue has previously been produced by leaching lizardite ($Mg_3Si_2O_5(OH)_4$) using 2 mol/L nitric acid (Benhelal et al., 2018). However, no previous work has reported extracting and characterising the pozzolanic activity of the silica residue produced from waste concrete fines by acid leaching.

Equations (1) and (2) show that acid leaching of cement hydration products produces a Ca^{2+}-rich acidic leachate, that is also likely to contain Al^{3+} and Fe^{3+} ions present in Portland cement (Vanderzee and Zeman, 2018). The addition of an alkali, such as sodium hydroxide (NaOH) or ammonia solution ($NH_3{\cdot}H_2O$) to this leachate increases the pH so that carbonate ions (CO_3^-) form and impurities are precipitated as hydroxides. The alkali Ca^{2+} containing leachate solution is suitable for sequestering CO_2 by forming precipitated calcium carbonate (Sanna et al., 2014). After carbonation, the acid and alkali can be recycled using an electrochemical process (Shuto et al., 2014).

Hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) have been used to treat waste concrete fines (Kim et al., 2017; Santha Kumar and Minocha, 2018; Song and 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 waste concrete fines as a sand replacement after immersion in acetic acid solutions at ambient temperature for 24 h 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 min 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. Also, the valorisation of the silica-rich solid residue from acetic acid treatment of waste concrete fines has not been discussed.

The aim of this research was to optimize acid leaching of waste concrete fines using the process shown in Fig. 1. The optimal conditions for acetic acid leaching of waste concrete fines to produce clean extracted sand are identified and the pozzolanic activity of the dried silica rich residue is assessed. To the author's knowledge, this is the first study considering the reuse of this solid residue as a novel SCM. The potential of the Ca^{2+} rich solution to sequester CO_2 and form calcium carbonate is calculated and the potential for this type of processing to deliver circular concrete discussed.

2. Experimental

2.1. Raw materials

A representative sample of waste concrete was collected from a concrete recycling facility in Shanghai, China, where the waste concrete was crushed, and coarse recycled aggregates separated by size sorting. 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 the oven at 80 °C until the mass remained constant and the material passing a 4.75 mm sieve used as waste concrete fines in subsequent experiments. Standard quartz sand, Portland cement (P.O 42.5 N) and commercially available coal fly ash (CFA), silica fume (SF) and blast furnace slag (BFS) were used. The compositions of these materials were analyzed by titration according to the Chinese standard (Chinese Standard GB/T 176, 2017), and the data is shown in Table 1. The crystalline phases present in waste concrete fines were analyzed by X-ray diffraction (XRD, Bruker AXS D8 Advance) and the thermal stability determined by TG-DSC (Netzsch STA 449).

Table 1
Chemical compositions of materials.

Material	Percentage (%)					
	CaO	SiO_2	Fe_2O_3	Al_2O_3	SO_3	LOI
Waste concrete fines	12.47	63.36	3.31	8.22	0.50	9.7
P.O 42.5 N	49.63	28.60	3.35	8.25	2.22	3.3
BFS	38.68	44.31	1.06	14.76	1.78	−0.5
CFA	15.11	44.70	7.44	25.95	4.02	3.4
SF	1.93	89.91	4.60	1.32	1.65	−0.5
Recycled sand	2.32	85.93	3.10	5.25	–	1.5
Silica-rich residue	3.28	58.79	6.07	18.37	–	10.9

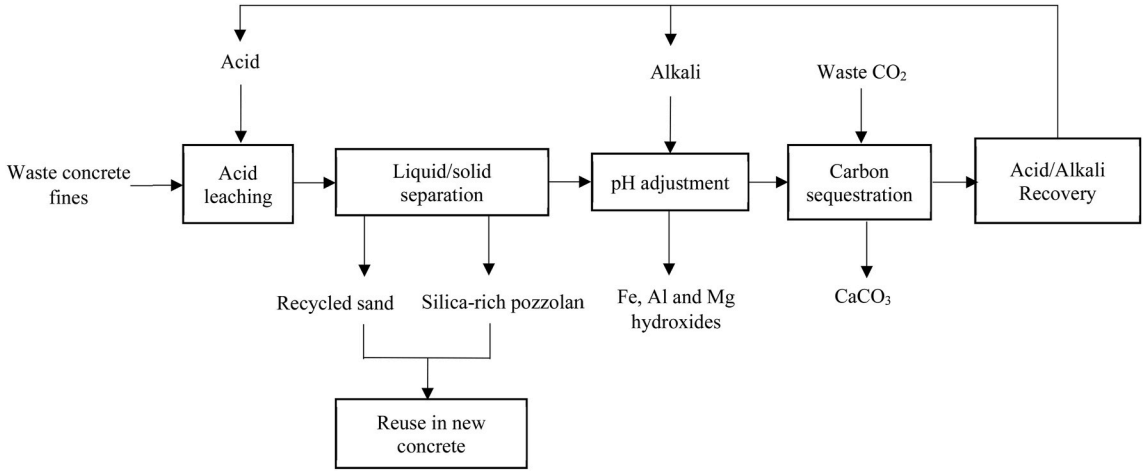

Fig. 1. The flow diagram of acid treatment process of waste concrete fines to extract clean sand and silica-rich pozzolan and sequester CO_2.

2.2. Acid leaching process optimization

Glacial acetic acid (Shanghai Macklin) was diluted with de-ionized water to form acidic solutions with different concentrations, and these were used to leach the waste concrete fines. The effect of acid concentration was investigated by leaching 50 g 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 was investigated by leaching 50 g of waste concrete fines 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) were kept constant.

The effect of temperature was 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 were kept constant at 0.6 mol/L acetic acid and an L/S ratio of 7 ml/g.

During leaching, mixes were magnetically stirred at 300 rpm. Duplicate 1 ml samples of leachate were extracted after 10, 30, 60, 120, 180, 240, 300, 360, 420 and 480 min using a 2 ml syringe. The leachate samples were filtered through a 0.45 μm filter prior to analysis and the concentration of Ca^{2+} ions in solution determined by titration with EDTA and calcein-methylene blue-phenolphthalein (CMP) indicator according to the Chinese standard (Chinese Standard GB/T 176, 2017). The Ca^{2+} extraction was calculated using equation (4),

$$Ca^{2+}\ \text{extraction}\ \ (\%) = 100\% \times \frac{m_{Ca}}{M_{Ca}} \tag{4}$$

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

2.3. 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 (Chinese Standard GB/T 14684, 2011), and the results compared to those for new river sand (i.e. standard sand) and the original waste concrete fines.

A flow table test was used to determine differences in mortar rheology associated with the sand types (Chinese Standard GB/T 2419, 2005). Control mortars containing 1350 g standard sand, 450 g P.O 42.5 N and 225 g 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 0.83, was needed to achieve the same flow when preparing test mortars using dried waste concrete fines.

The test mortar mixes containing the three different sands (waste concrete fines, standard sand, and recycled sand) were made using the water/cement ratios mentioned above and cast into 40 × 40 × 160 mm moulds. Samples were de-moulded after 24 h 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 (Chinese Standard GB/T 17671, 1999), using six replicates tested in a universal strength testing machine (Wuxi Jianyi Model TYE 300).

2.4. Properties of silica-rich residue

The slurry produced using the optimal acid leaching conditions was centrifuged at 3000 rpm for 5 min and then vacuum filtered to separate the leached solid silica-rich residue from the solution. This was thoroughly rinsed with deionized water and dried in a vacuum oven at 50 °C to constant mass. It was then ground using a mortar and pestle until all the material passed a 150 μm test sieve prior to pozzolanicity testing.

The pozzolanic activities of the extracted silica residue and other commercially available SCMs such as BFS, CFA and SF were evaluated using the Frattini test according to the Chinese standard (Chinese Standard GB/T 2847, 2005). In this test, 20 g samples containing 30% SCM and 70% P.O 42.5 N was mixed with 100 ml deionized water in a plastic bottle and stored at 40 °C for 8 days. Samples were identically tested in which the silica-rich residue replaced the BFS, CFA and SF. All sample tests were run in duplicates. The samples were immediately vacuum filtered and the concentration of calcium oxide (CaO) and OH^- determined by titration according to equations (5) and (6):

$$[CaO] = \frac{40 \times T_{CaO} \times V_1}{56.08} \tag{5}$$

$$[OH^-] = 40 \times c_{HCl} \times V_2 \tag{6}$$

where V_1 and V_2 are the volume of EDTA and HCl used in titration, C_{HCl} is the concentration of HCl, T_{CaO} is the mass of CaO that is chelated by 1 ml of EDTA solution, 40 is the volume ratio and 56.08 is the molar mass of CaO. The concentration of CaO and OH^- were plotted on a graph showing the solubility isotherm of $Ca(OH)_2$ at 40 °C. Data points below the solubility curve indicate that the material is pozzolanic.

3. Results

3.1. Properties of waste concrete fines

Table 1 shows the chemical composition of waste concrete fines and the other materials used. The waste concrete fines contain 12.47% CaO by weight and therefore the mass of Ca (M_{Ca}) in 50 g of waste concrete fines is:

$$M_{Ca} = 50 \times \frac{12.47}{100} \times \frac{40.08}{56.08} = 4.46\ g \tag{7}$$

where 40.08 and 56.08 are the molar mass of Ca and CaO, respectively.

Equation (2) shows that 1 mol of CaO reacts with 2 mol 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 4.46/40.08 = 0.11 mol, the theoretical amount of acetic acid required to react with the CaO in the sample is 0.22 mol. 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.

XRD data in Fig. 2 shows that the most abundant crystalline phase in the waste concrete fines is quartz (SiO_2), due to the strong diffraction

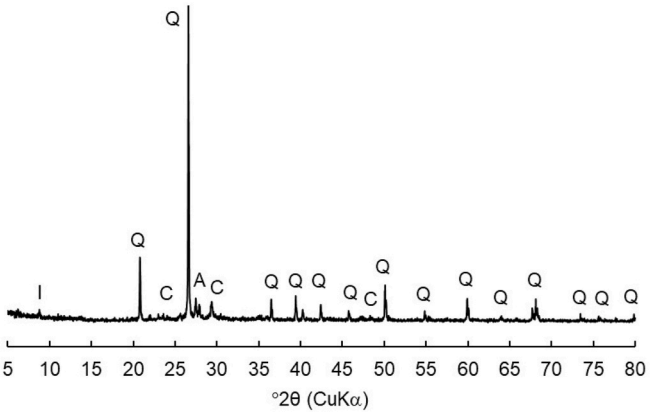

Fig. 2. XRD data of the waste concrete fines. Q: Quartz; C: Calcite; A: Albite and I: Illite.

intensities of siliceous sand compared to cement hydration products. There are additional small peaks associated with calcite ($CaCO_3$), albite [(Na, Ca)Al(Si, Al)$_3O_8$] and illite [(K, H_3O)$Al_2Si_3AlO_{10}(OH)_2$], 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.

The TG-DSC curve in Fig. 3 shows two major mass losses. The first 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 ($CaSiO_3$).

3.2. Effects of acid concentration, L/S ratio, temperature, and time on Ca^{2+} leaching

Fig. 4 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 Ca^{2+} extraction occurred within the first 3 h. Increasing the acid concentration did not significantly increase the rate of extraction. After 6 h, the Ca extraction at 0.4, 0.5, 0.6 and 1 mol/L acetic acid were 73.8, 80.6, 84.2 and 84.3%, respectively. Leaching beyond 6 h also only produced a marginal increase of around 1.0% in leached Ca^{2+}.

The endpoint pH decreased with increasing acid concentration. Acid concentrations of 0.4, 0.5, 0.6 and 1 mol/L resulted 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 resulted in almost the same Ca^{2+} extraction ratio but reduced the endpoint pH. The results show that 0.6 mol/L acetic acid was effective at extracting Ca^{2+} from the cement mortar in crushed concrete fines.

Fig. 5 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 h and dissolution plateaued after 6 h. At 6 h, the calcium extraction at 5, 7 and 9 ml/g L/S ratio were 71.9, 82.0 and 84.2%, respectively. The endpoint pH decreased with increasing L/S ratio. L/S ratios of 5, 7 and 9 ml/g resulted in endpoint pH values of 6.2, 5.0 and 4.7, respectively. The Ca extraction was only slightly increased when the L/S ratio increased 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.

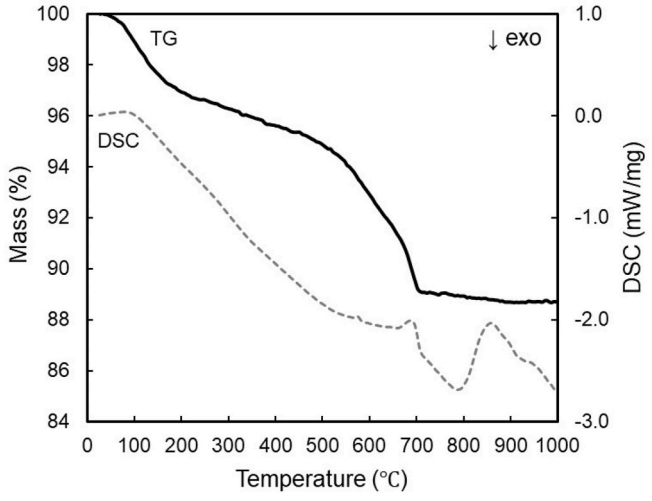

Fig. 3. TG-DSC curve of waste concrete fines.

Fig. 6 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.

3.3. Mortars containing recycled sand

Waste concrete fines from crushed concrete are shown in Fig. 7a). After leaching using 0.6 mol/L acetic acid solution, an L/S ratio of 7 ml/g, and a leaching time of 6 h at 20 °C with 300 rpm stirring the clean dry sand extracted from the fines is shown in Fig. 7b). The chemical composition of the extracted sand is given in Table 1 and this indicates efficient removal of cement paste and production of clean recycled sand from crushed concrete fines.

The physical properties of standard (river) sand, recycled sand and untreated waste concrete fines are compared in Table 2. 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%, compared to crushed concrete fines using the test procedures in Chinese standard GB/T 14684 - 2011. Fig. 8 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. The resulting recycled sand has the same bulk density and void ratio and similar water absorption as standard sand.

Fig. 9 presents 7 and 28-day compressive strength data of mortars containing standard quartz sand (control), recycled sand and waste concrete fines. The mortars containing untreated fines 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 (Sideris and Konsta-Gdoutos, 1996; Wang et al., 2017). The average compressive strengths of mortars with recycled sand were 4.1% and 8.9% greater than the control mortars.

3.4. Pozzolanicity of silica-rich residue

Under the optimum Ca^{2+} leaching conditions approximately 30 wt% of the waste concrete fines formed the silica-rich residue. The chemical composition of this is given in Table 1 and this shows the enrichment of inert aluminate minerals and the coagulation of Al^{3+} with SiO_2 during the acetic acid leaching to form an aluminosilica gel, which gives a higher alumina content (18%) compared to the untreated waste concrete fines. The higher iron oxide content compared to untreated waste concrete fines indicates that Fe accumulates in the leached residue, probably through precipitation as iron hydroxide.

XRD data of the silica-rich residue is shown in Fig. 10. Some peaks of quartz, albite and illite, which are impurities in sand and coarse aggregates are also present. To determine the quantity of amorphous phase in the residue, quantitative XRD with Rietveld refinement using corundum (Al_2O_3) as a reference was completed. A sample containing 20% corundum and 80% silica-rich residue by weight was analyzed. The QXRD data shows that the crystalline phase contained 35.8% corundum (Al_2O_3). The amorphous content of silica-rich residue was calculated using equation (8):

$$C_{Am}\% = 100 - (100 - 35.8) \times \frac{20}{35.8} \times \frac{100}{80} = 55.1 \quad (8)$$

where C_{Am} % denotes the amorphous content. The silica-rich residue was found to contain 55.1% of amorphous phase by weight. The results indicate that the separation of amorphous silica gel from other

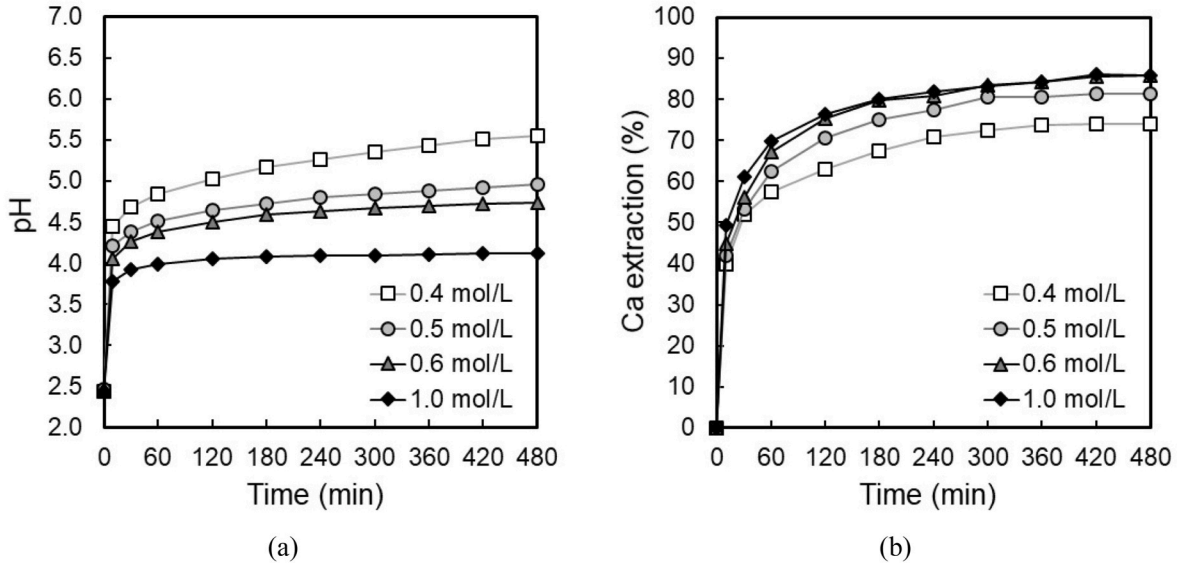

Fig. 4. Variation of (a) pH and (b) calcium extraction with time at different acetic acid concentrations and constant L/S ratio of 9 ml/g and temperature of 20 °C.

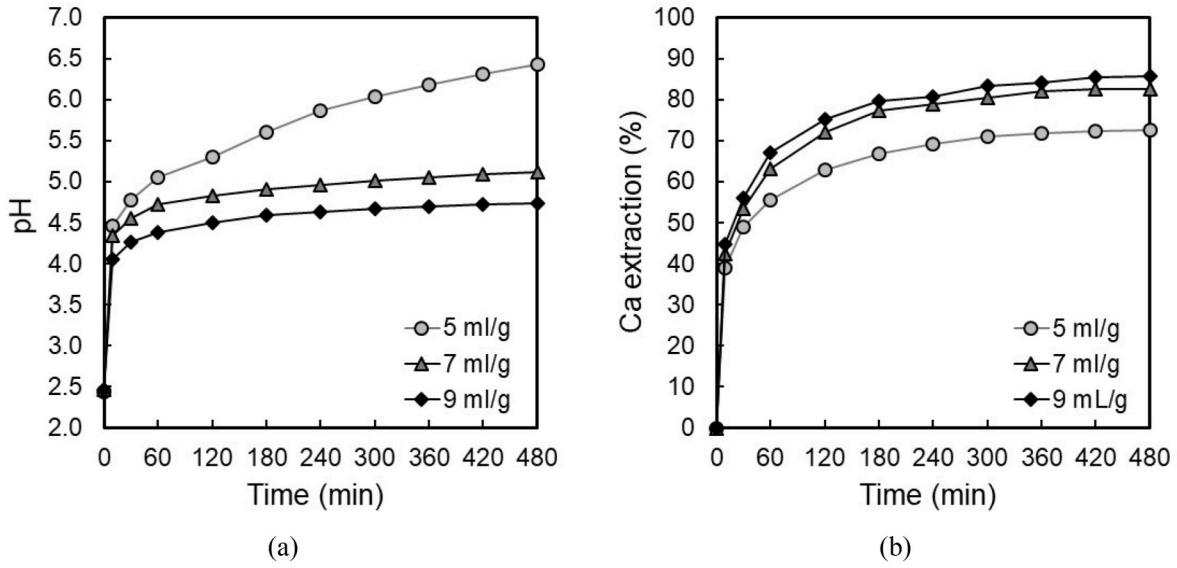

Fig. 5. Variation of (a) pH and (b) calcium extraction with time at different L/S ratios, and constant acetic acid concentration of 0.6 mol/L and temperature of 20 °C.

crystalline impurities could be further improved.

Fig. 11 shows the Frattini test results for samples containing 30% pozzolan and 70% P.O 42.5 N. All the SCMs show pozzolanic activity. Although the silica-rich residue contained impurities, the average Ca^{2+} removal was 88.9% after 8 days curing at 40 °C, This was comparable to that for coal fly ash (93.3%) and indicates the leached silica-rich residue has the potential to be used as a SCM.

4. Discussion

Acetic acid leaching of concrete fines 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 cement hydration products (Ho et al., 2020; M. J. Kim et al., 2017). 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 (M. J. Kim et al., 2017; Kunzler et al., 2011). This probably indicates that the activation energy of the reaction between acetic acid and cement hydration products is low (Chu et al., 2019). 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 h. 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 h 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, approximately 500 g of clean recycled sand was extracted from 1 kg of waste concrete fines. Replacing virgin sand with the recycled sand did not reduce the 7-day and 28-day compressive strengths of new cement mortars. Previous research has used a 1 mol/L acetic acid leachant and a leaching time of 24 h to extract sand from mortar (Santha Kumar et al., 2019). In this work a 400 °C heat treatment stage was necessary to further improve the quality of recycled sand. 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. This saves on chemicals, reduces energy consumption, and eliminated the CO_2 emissions associated with heating.

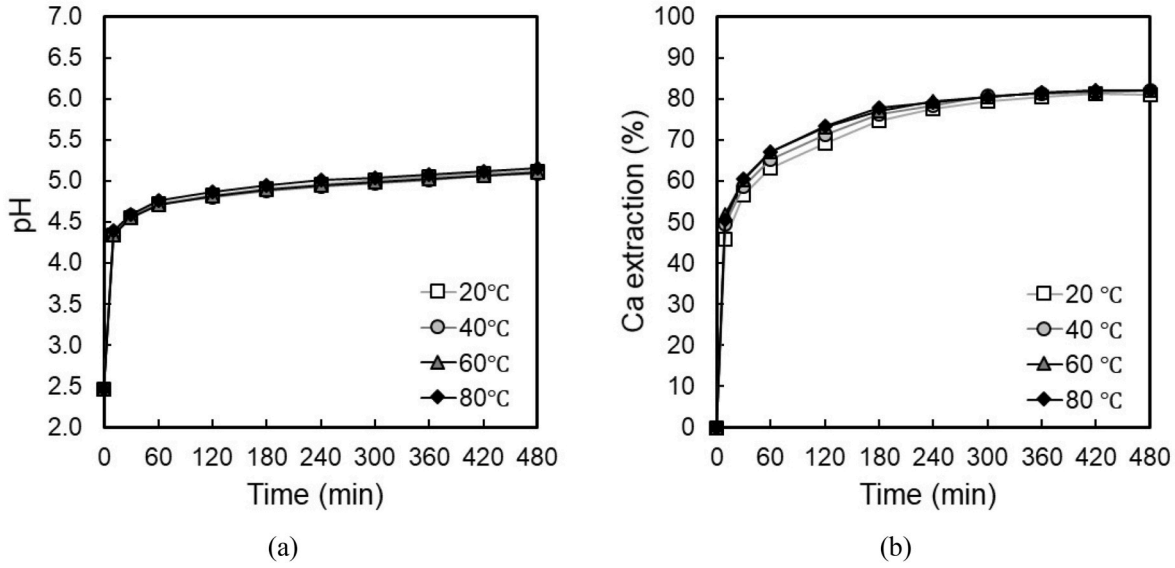

Fig. 6. Variation of (a) pH and (b) calcium extraction with time at different temperatures, and constant acetic acid concentration of 0.6 mol/L and L/S ratio of 7 ml/g.

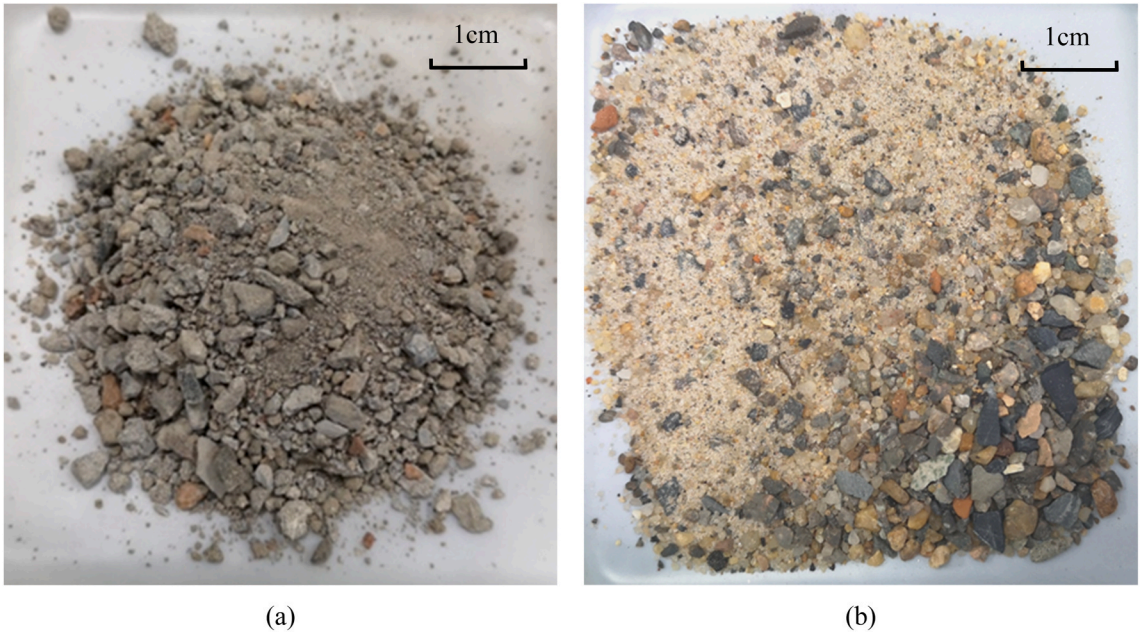

Fig. 7. (a) Waste concrete fines and (b) clean recycled sand extracted using the acid leaching process.

Table 2
Comparison of physical properties of waste concrete fines, standard sand and recycled sand obtained using the methods described in Chinese standard GB/T 14684–2011.

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

The cement industry is associated with significant CO_2 emission. It accounts for 90% of industrial CO_2 emissions and 7% of global CO_2 emissions from all processes (Black and Purnell, 2016). If SCMs such as coal fly ash, blast furnace slag and silica fume are blended with cement clinker there is a reduction in the CO_2 associated with the resulting concrete. However, these commercially available SCMs are generated from fossil fuel combustion in coal-fired power plants and in the steel industry. As these sectors move towards cleaner, low-carbon production, the availability of these SCMs is expected to decrease (Zhou et al., 2017).

This preliminary research has shown that dried milled silica-rich residue produced by acetic acid leaching of waste concrete fines has similar pozzolanic activity to coal fly ash and has the potential to form a novel SCM extracted from waste concrete. There are CO_2 emissions associated with the production and transportation of acetic acid, but other research has shown CO_2 can be utilized as a precursor in the production of acetic acid. If this is applied at a large scale in the future, the production of acetic acid can be carbon neutral or negative (Jourdin et al., 2015; Tu et al., 2021; Wilk et al., 2016). A zero CO_2 emission

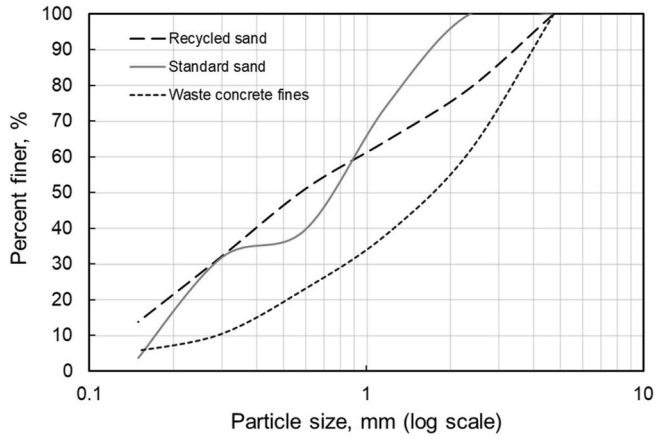

Fig. 8. Particle size distribution of standard sand, recycled sand and waste concrete fines.

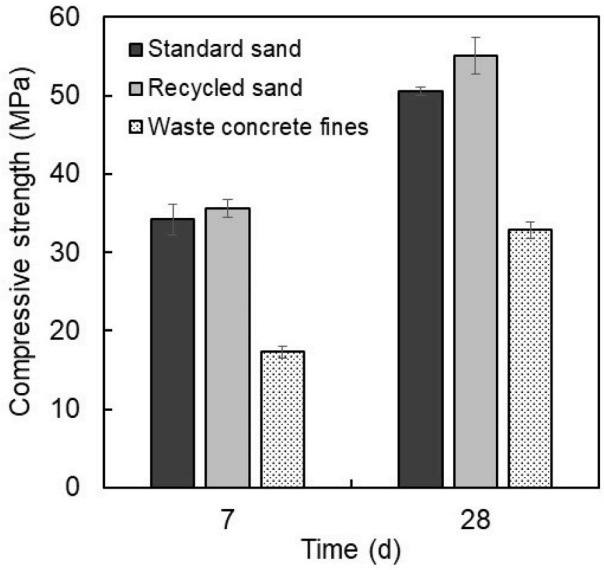

Fig. 9. Comparison of compressive strength of mortars containing standard river sand, recycled sand (from acid leaching) and waste concrete fines.

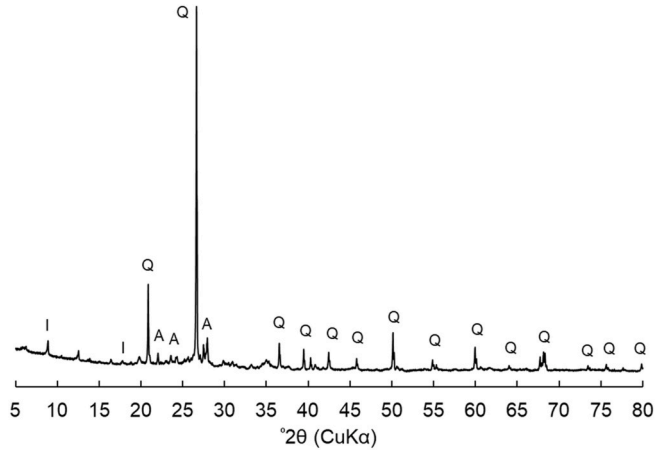

Fig. 10. XRD data of the acid leached silica residue. Q: Quartz; A: Albite and I: Illite.

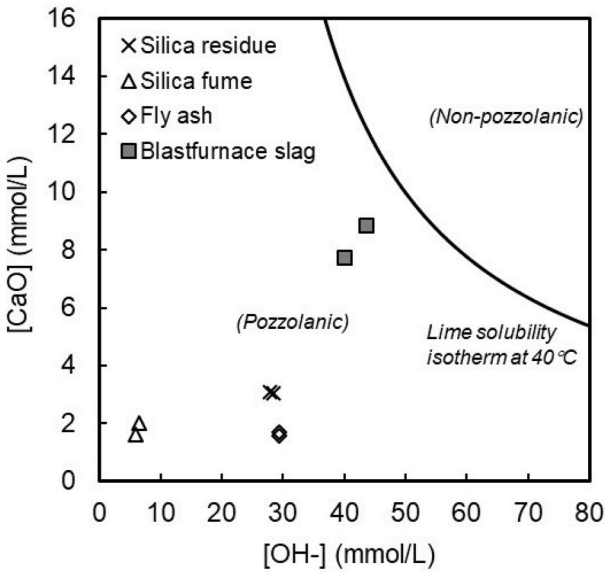

Fig. 11. Frattini test results for pozzolanicity after 8 days at 40 °C.

process that generates a silica-rich residue that is pozzolanic using waste concrete as the primary raw material could contribute significantly to the production of low-carbon concrete and represents a step change in the achievement of circular concrete.

Acid leaching of waste concrete fines also generates a Ca^{2+}-rich leachate which can be used to sequester CO_2 and produce precipitated $CaCO_3$. In this research, the leachate after optimal leaching of 50 g of waste concrete fines contained on average 0.09 mol of Ca^{2+}. According to equation (9), 1 mole of Ca^{2+} reacts with 1 mol of CO_2 under alkaline conditions and potentially, 0.08 g of CO_2 can be sequestered by 1 g of concrete fines in the carbonation process, producing 0.18 g of $CaCO_3$. TG analysis suggests that the waste concrete fines contain approximately 4.2% CO_2 by weight which is released in the acid leaching process and re-sequestered in the carbonation process. This corresponds to 0.04 g of CO_2 per 1 g of concrete fines. Therefore, the net sequestration potential of waste concrete fines is 0.04 g of CO_2 per 1 g of concrete fines.

$$Ca^{2+} + CO_2 + 2OH^- \rightarrow CaCO_3\downarrow + H_2O \quad (9)$$

CO_2 sequestration involves increasing the leachate pH by addition of alkali. The use of NH_3OH to do this produces a waste solution containing ammonium acetate (CH_3COONH_4). Ammonium acetate will decompose during heating to give an equilibrium mixture of ammonia (NH_3), acetic acid, acetamide (CH_3CONH_2) and water. A controlled thermal recycling process has been reported (Rice, 1970). In this process, CH_3COONH_4 solution is heated at atmospheric pressure to temperatures between 175 and 189 °C to extract NH_3 and water. The residue can then be recycled to form a new batch of CH_3COONH_4 solution. This gives recovered acetic acid with 99.6% purity (Rice, 1970).

A major barrier to the large-scale application of an acid treatment process to waste concrete is the high cost on chemicals and waste treatment. Complete recycling of acid and alkali within the process would reduce this cost and improve commercial viability. Ongoing research is investigating the potential of acetic acid and ammonia recovery from waste ammonium acetate solution.

Overall, the proposed process can recycle waste concrete fines and produce clean sand, a novel SCM, and has the potential to sequester CO_2 to produce precipitated $CaCO_3$, with the acid and alkali used in the process being recovered. Further work aims to develop this process that has potential to contribute to the development of low-carbon circular concrete.

5. Conclusions

Clean useable sand and a silica rich supplementary cementitious material can be recovered by acetic acid leaching of waste concrete fines. The optimal leaching conditions use an acid concentration of 0.6 mol/L, an L/S ratio of 7 ml/g, and a reaction time of 6 h at ambient temperature. The chemical, physical and mechanical properties of recycled sand are comparable to new sand. The work also shows, for the first time, that the silica-rich residue produced by leaching can form a novel supplementary cementitious material. Zero waste and improved economics can be achieved by CO_2 sequestration using the Ca-rich filtrate to form $CaCO_3$ and acetic acid/ammonia recovery from the waste ammonium acetate solution.

CRediT authorship contribution statement

Tiejun Ding: Investigation, Formal analysis, Methodology, Writing – original draft, preparation. **Hong Wong:** Supervision, Visualization, Writing – review & editing. **Xiuchen Qiao:** Project administration, Resources. **Christopher Cheeseman:** Conceptualization, Visualization, SupervisionSuspervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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