IMPERIAL

Concrete Trials 1

CCUS Innovation 2.0

Key Knowledge Deliverable 3.2

October 2024

Key Knowledge Deliverable Cover Sheet

This Key Knowledge Deliverable (KKD) has been produced by Imperial College London as part of the Department for Energy Security and Net Zero £1bn Net Zero Innovation Portfolio (NZIP) - CCUS Innovation 2.0 programme. The document is reflective of the status of the project at the time of writing. The material presented could have been subject to change as the project matured. These documents should not be considered a full representation of the final project.

Project Description

This project seeks to further develop and scale a new carbon sequestration process which transforms waste CO2 gas from industrial facilities into valuable construction products. Sequestered CO2 through this process is cheaper than conventional approaches that rely on purification, liquification and offshore or geological storage. The CO2 is stored in the form of a stable mineral which ensures they will be no leakage over time.

The patent-pending technology involves taking globally abundant magnesium silicate minerals and splitting this into magnesia and silica components. Through simple chemical processing two products of high purity are created: a) an amorphous silica that can be used as supplementary cementitious material (SCM) to facilitate low-carbon concrete and b) a concentrated magnesium solution in which CO2 from industrial flues can be sequestered to produce other construction materials.

This CCUS Innovation 2.0 award will be used to increase our technology and commercial readiness level by de-risking and facilitating the development of a pilot facility, in order to demonstrate that the technology is economically viable and deployable at scale.

Description of KKD

Report detailing complete test plans for the remainder of WP3, including concrete performance testing and characterisation, the use of commercial admixtures, testing of concrete products for certification and planned mix designs of interest for detailing LCAs/ EPDs.

KKDs to be released in full

- D3.4 – Concrete Trials 3
- D4.4 – Product Optimisation 2

KKDs to be released after redactions

- D1.1 – Flue Gas Recovery and Testing 1
- D1.2 – Dissolution Procurement
- D1.3 – Dissolution Operation
- D1.4 – Flue Gas Recovery and Testing 2 & Carbonation Procurement
- D1.5 – Carbonation Operation
- D2.3 – Reagent Regeneration Procurement
- D2.4 – Reagent Regeneration Operation
- D3.2 – Concrete Trials 1
- D3.3 – Concrete Trials 2
- D4.2 – Process Optimisation
- D4.3 – Product Optimisation 1
- D5.2 – Business Development 2 (Supply Chain)
- D5.3 – Business Development 3 (Business Planning)
- D5.4 - Business Development 4 (Commercial Readiness)
- D6.1 – Year 1 Report
- D6.2 – Year 2 Report

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Introduction

The silica produced from the processes of acid digestion of olivine for CCUS (from Imperial College London) can be of different purity levels depending on the ingredients used. So, two silica samples known as high-grade silica (high content of silica) and low-grade silica (low silica content and high iron content) are distinguished. The delivery report 3.1 has demonstrated the benefits of the post-processing high-grade silica to improve their suitability to be used as SCM. This mainly consists of altering the silica surface properties to reduce specific surface area and remove sulfate impurities. Thus, washing silica for example, to remove as much as impurity has been found useful to improve the workability of the mix design and enhance the hydration. The works reported here aim to assess the inherent characteristics of the post-processed (washing) high- and low-grade silica to optimize their use as SCM and characterise the performance of resulting concretes, benchmarked against Portland cement concretes and blended cement concrete obtained with fly ash.

Methodology

Materials preparation

Ordinary Portland cement class CEM I 52.5R was used with amorphous precipitated silica recovered from olivine as SCM. Two silica grades were produced from the acid dilution of olivine using the Seratech process. The two silica were labelled “Sil” for high grade and “Fe-Sil” for low grade. A conventional SCM consisting of Low calcium fly ash (FA) was used as a reference for comparison purposes. Sand with particle size < 2 mm was used as fine aggregate to prepare mortars.

Experiments and characterization

The paste samples were prepared for studying the hydration reaction using the mix ratio shown in Table 1. The sand was added to the selected mix to prepare mortar samples on selected paste samples as described in Table 1. They were cast in 50 mm cubic molds and stored in a curing room at 99% RH and 20 oC. After demolding the samples were cured under water until further tests were carried out.

Table 1 Mix design

	OPC	Fly ash	Fe-Sil	Sil	w/b	Sand/binder
C0	100	0	0	0	0.55	3
C30	70	30	0	0	0.55	3
CS15	85	0	15	0	0.55	-
CS30	70	0	30	0	0.55	3
CS40	60	0	40	0	0.55	-
CA15	85	0	0	15	0.65	-
CA30	70	0	0	30	0.65	3
CA40	60	0	0	40	0.65	-

Characterisation of the SCM

X-ray diffractometry (XRD, Malvern Panalytical Empyrean) was carried out on raw materials and paste samples to get information on their mineralogical composition. The device operates with Cu Kα1 radiation (λ = 1.54 Å), at 35 kV, 45 mA. The XRD patterns were recorded in the range of 5–70° 2θ. The chemical composition was measured using X-ray fluorescence (XRF, Malvern Panalytical Zetium). The density of raw materials was measured using a Helium pycnometer.

Hydration and pozzolanic reaction

The influence of the silica on the hydration kinetics was investigated by measuring the heat evolution using an isothermal calorimeter at 25 °C (TA instruments, TAM Air) for 7 days. Each paste was prepared using the mix proportion described in Table 1 (except sand). The mixture was stirred for at least 30 seconds using a vortex mixer. 10 g of the paste was weighed in an ampoule and placed in the calorimeter. Thermogravimetric analysis (Netzsch STA 449 F5 Jupiter) was carried out on hydrated samples at 7 days to determine the portlandite (CH) content and assess the pozzolanic reaction. The tangent method was used for the quantification and the final result was expressed as a percentage of the CH content in hydrated Portland cement [1]. The mineralogy was determined using XRD (Malvern Panalytical Empyrean) with CuKα radiation in a 2 theta range of 5-70o and a step size of 0.02 °/min.

Mechanical properties

The compressive strength evolution at 3 and 7 days was measured to assess the contribution of silica to hardened properties. The final value is the average of 3 tested samples.

Results and discussion

Physical and Chemical characteristics of silica

The chemical analysis of the silicas obtained from the process is reported in Table 2. One can observe that high-grade silica (sil) has 73 wt.% of silica content and 4 wt.% of sulfates with low iron and magnesium oxide content of 1.9 and 3.34 wt.% respectively. Whereas the low-grade - silica has only 35 wt.%of SiO_2 and 2.7 wt.% of SO_3, but with high content of MgO (17.45 wt.%) and Fe_2O_3 (16.6 wt.%). Further another significant difference involves the loss of ignition which is 15 and 29.89 wt.% for high and low-grade silica respectively. That LOI refers not only to free water but also includes the majority of the chemical-bound water and water from the decomposition of unreacted olivine minerals. This has been ascertained in the TGA (Fig 1) and is ascribed to the presence of the silanol group in silica [2]. The latter is likely due to the fineness or surface properties of those silica particles which make water molecules tightly fixed. However, still need to understand the high bound water content of low-grade silica as compared to high-grade silica, which might be related to the production process. This also holds for the difference in chemical composition. The density shown in Table 3 stresses that both types of silica have similar density which will assume that their fineness might be the same. Nevertheless, their specific surface area and sorption capacity are yet to be measured to make a strict comparison of their surface properties and give a tentative explanation of the difference in bound water content.

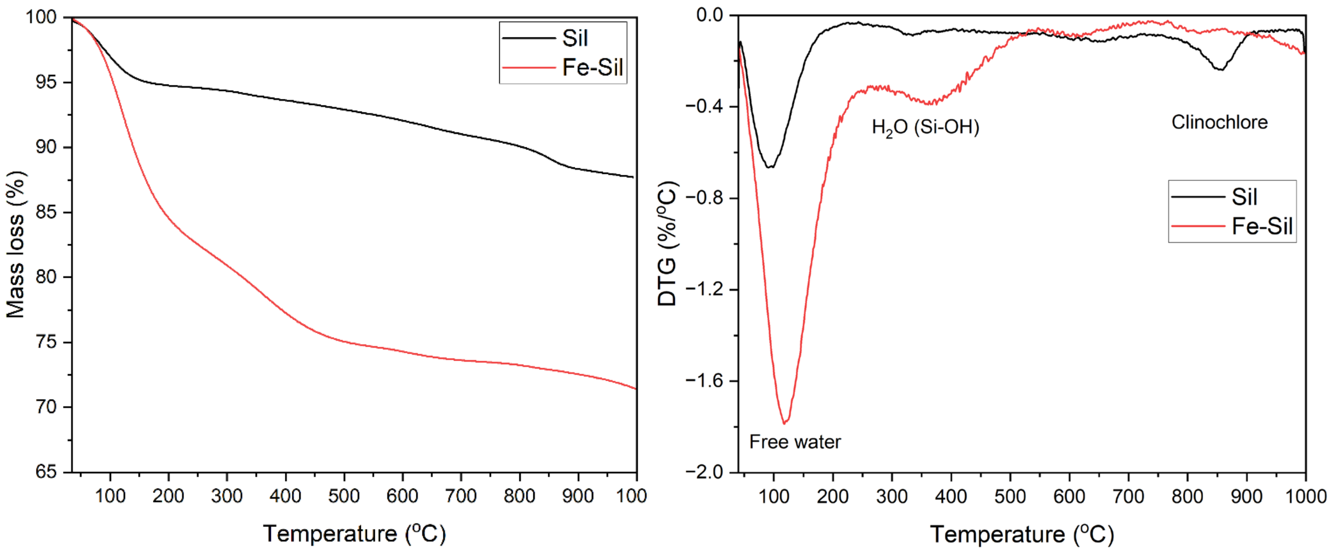
Table 2 chemical composition of low- and high-grade silica

Oxides	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	NiO	MnO	SO_3	Cr_2O_3	LOI	Total
Sil	73.14	1.07	3.347	0.494	1.893	-	-	4	0.849	15	99.79
Fe-Sil	32.17	0.435	17.45	0.126	16.6	0.25	0.15	2.68	-	29.89	99.75

Table 3 Density of raw materials

Materials	Density (g/cm^3)
CEMI (52.5 R)	3.1523
Fe-Silica (Low-grade silica)	2.1244
Silica (High-grade silica)	2.1369
Fly ash	2.3175

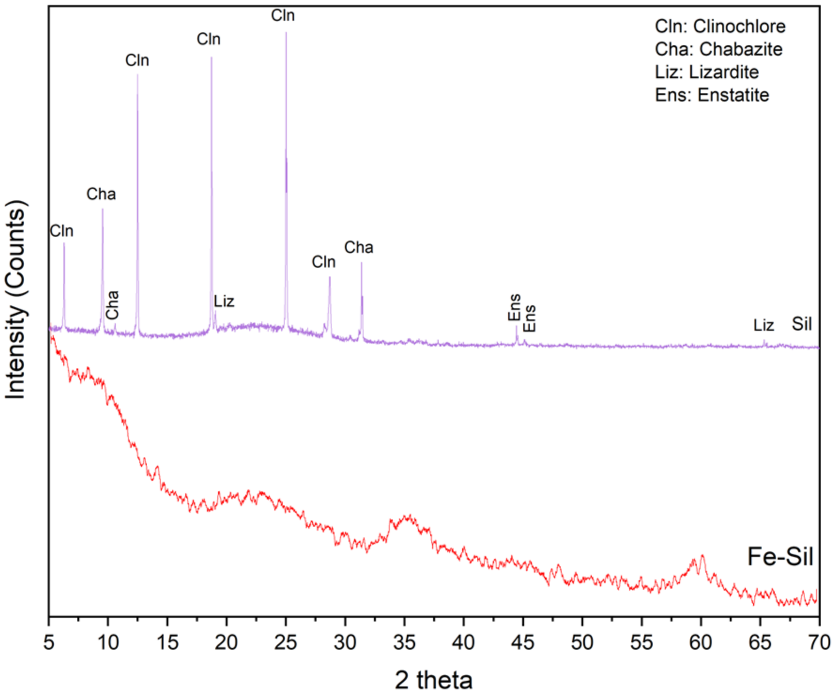
Figure 1 TGA-DTG of high-grade silica and low-grade silica



Mineralogy

Fig 2 shows the mineralogical composition of the silica prepared. The high-grade silica (Sil) is semi-crystalline while low-grade silica (Fe-Sil) is completely amorphous. Sil contains mainly undissolved minerals from olivine consisting of clinochlore, charbazite, lizardite and Enstatite. Despite the presence of these minerals, it is observed a broad hum between 15 and 30 degrees 2 theta characteristics of the amorphous phase.

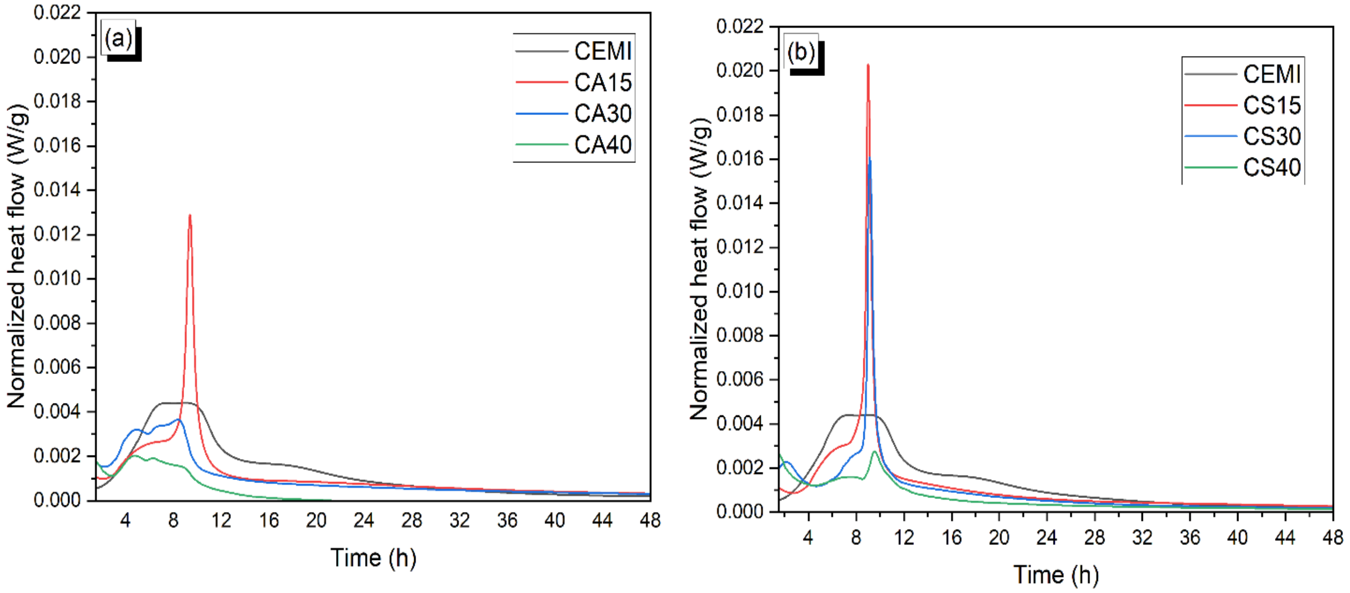
Figure 2 XRD of high-grade silica and low-grade silica



Hydration heat evolution

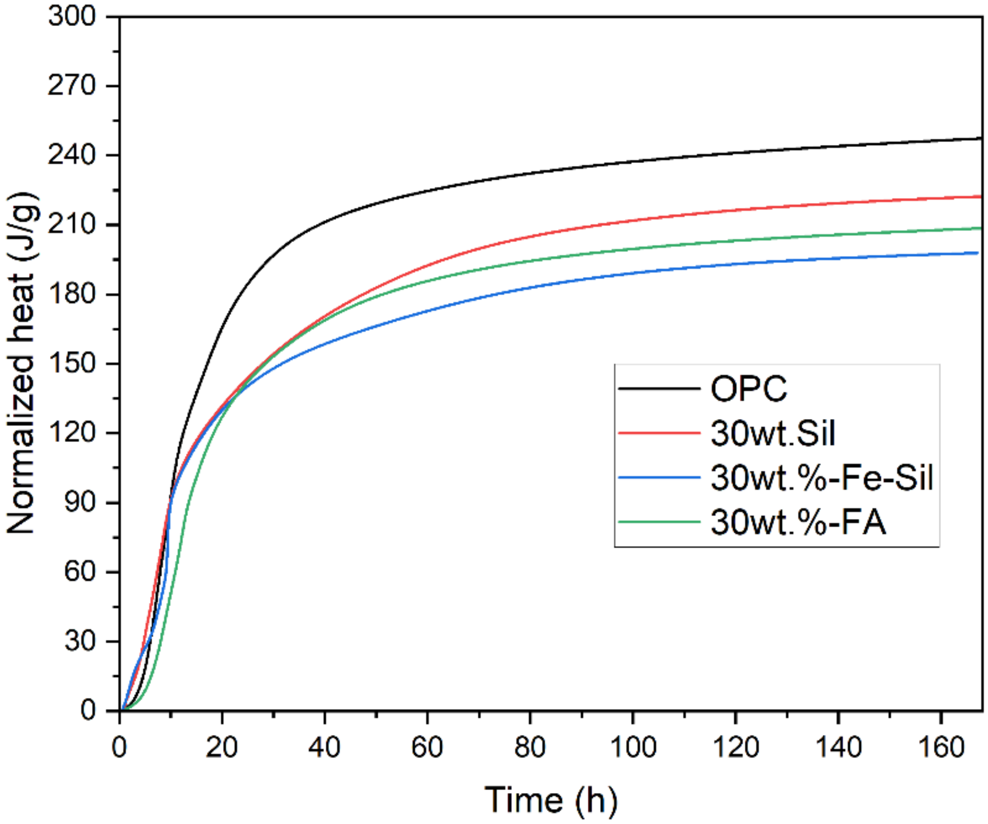
The heat evolution of blended cement containing both types of silica is depicted in Fig 3. The hydration of OPC (CEMI) is added for comparison purposes. The hydration of OPC is characterized by two major peaks with the first corresponding to C3S dissolution followed by the second peak due to C3A reaction. Further, a peak appearing as a shoulder at 16h is due to the AFm formation. In blended cement, it is observed an enhanced C3A reaction ascertained with the strongest peak while the C3S peak is barely visible. That is the rapid formation of CSH that adsorbs sulfate species on its surface inducing an undersulfation of the mix which fosters the dissolution rate of C3A against C3S. The difference in the extent of this acceleration for each silica type can be explained by the difference in sulfate content and the reactivity of both silica types. The excess sulfate from high-grade silica is likely to saturate the bulk system and limit the dissolution rate of C3A with the increased content of silica. But further test is required to better explain this trend.

Figure 3 Influence of silica content on heat evolution a) high-grade silica b) low-grade silica



A comparison of the total heat evolution over 7 days of the hydration of OPC and 30 wt.% replacement of cement with silica and fly ash is shown in Fig 4. This shows the decrease of the heat with silica releasing higher heat than Fe-sil an FA. But all are lower than the heat of OPC. Likely, competition between water adoption by silica and the water availability for subsequent hydration of the cement phase has decreased the degree of reaction. However, previous works demonstrated that low replacement level rather plays the role of filler and enhances hydration [3,4]. This needs to be investigated further to unveil the silica behaviour during hydration.

Figure 4 A comparison of the 7 days cumulative heat evolution of hydration of 30 wt.% replacement with high-grade silica, low-grade silica and Fly ash



Hydration and pozzolanic reaction

X-Ray Diffractometer

Figs. 5 and 6 show the influence of silica type and content on the phase assemblage of the blended cement. The hydrated products identified are ettringite and portlandite. The ettringite peaks are strong in blended cement compared to Portland cement paste. That can be correlated with the enhanced hydration of C3A observed in the calorimetry results. Knowing that higher dissolution of aluminate phases releases more aluminium that is consumed by silica in the presence of sulfate to form ettringite. The portlandite peak is less strong in the blended cement and has almost disappeared from 30 wt.% replacement with high-grade silica and 40 wt.% for low-grade silica onward. That indicates the pozzolanic reaction ongoing between silica and portlandite which leads to an increase in the volume of CSH formed. In addition to hydrated phases, one observed the unreated phases from olivine.

Figure 5 Hydration products of blended cement containing high-grade silica after 7 days.

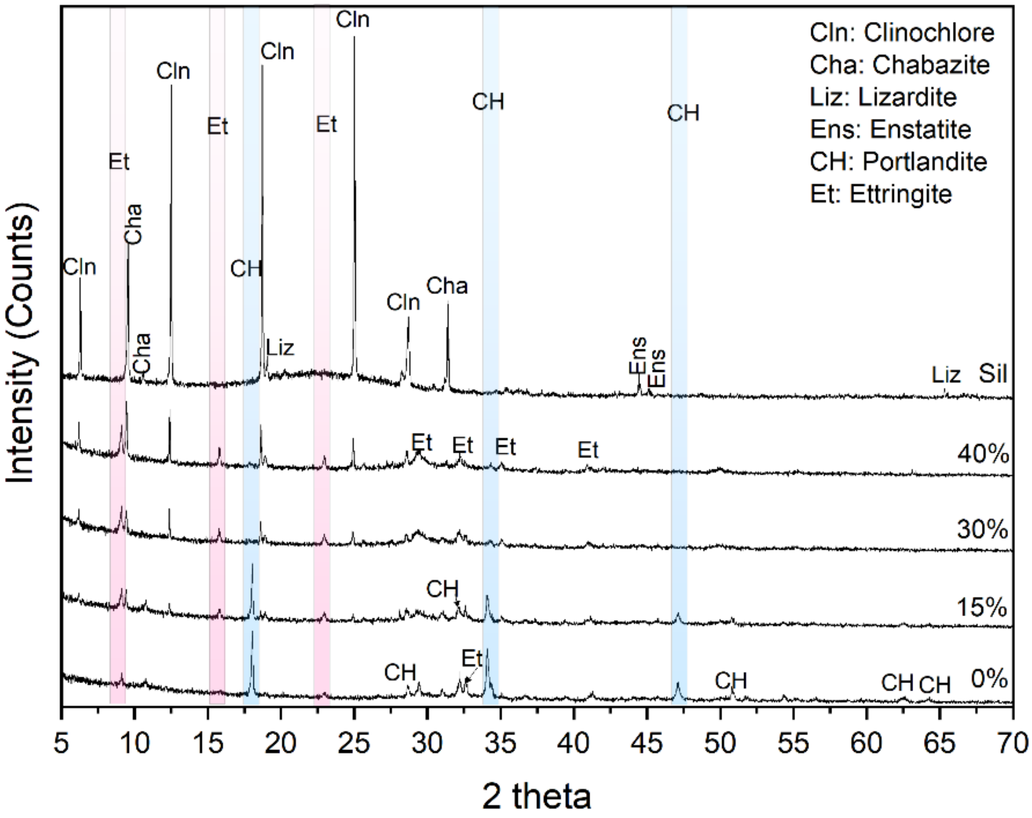
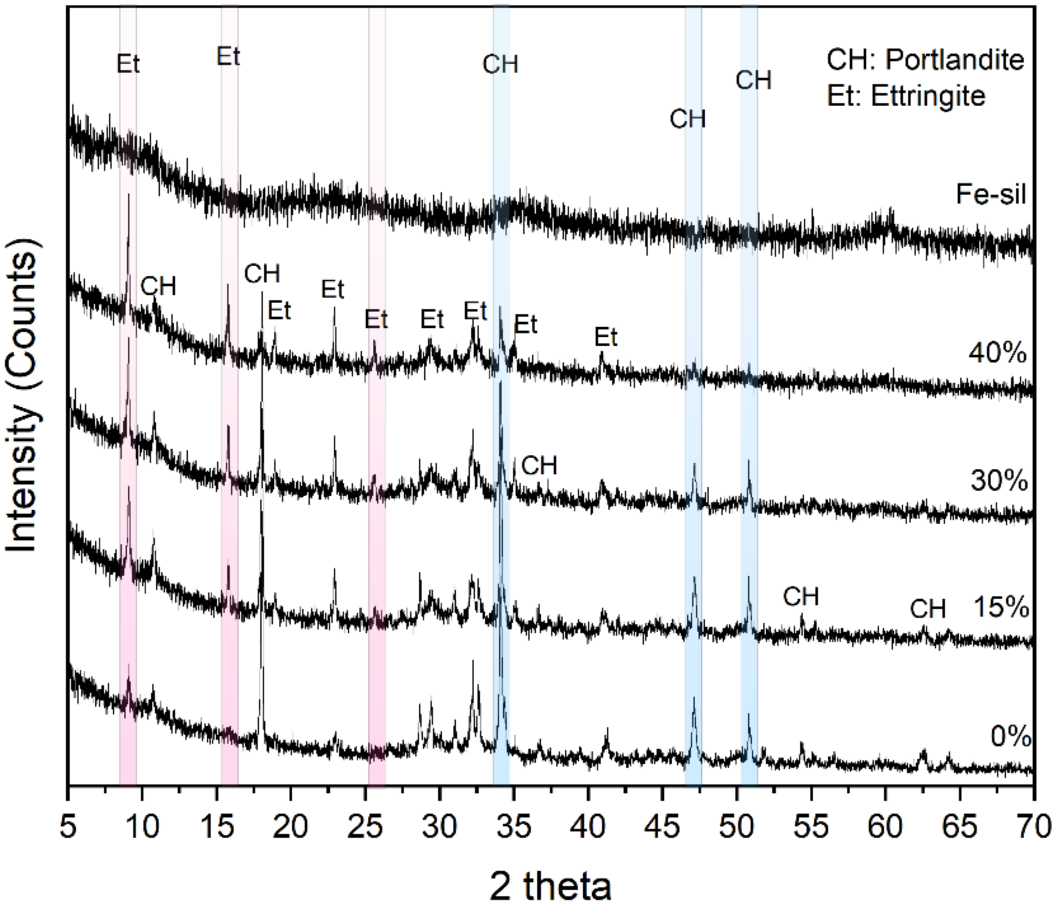


Figure 6 Hydration products of blended cement containing low-grade silica after 7 days.



Thermogravimetry analysis

The derivative of the TG analysis is shown in Fig 7 to better highlight the mass loss changes. The first mass loss is assigned to CSH and ettringite decomposition. The patterns of that peak corresponding to ettringite are becoming well resolved with the silica content. The second mass loss refers to the decomposition of AFm which here stands for the mosulfoaluminate phase. This peak disappears with the increased silica content from 30 wt.% for high-grade silica and is significantly lowered in the case of low-grade silica. This trend also holds for the portlandite content which evolves similarly to AFm. Therefore, the sulfate content of high-grade silica has been beneficial for higher ettringite formation with silica content against AFm formation. Its higher reactivity has accelerated the pozzolanic reaction by consuming a higher amount of portlandite formed. Thus high-grade silica is more reactive than low-grade silica. This is ascertained by the consumption rate of portlandite (CH) in Fig 9. While 100 % of CH produced by the hydration of cement phases is consumed by 30 wt.% of Sil replacement, the maximum consumption rate of 95 wt.% is achieved by 40 wt.% of Fe-Sil replacement.

Figure 7 Differential thermogravimetry analysis of blended cement

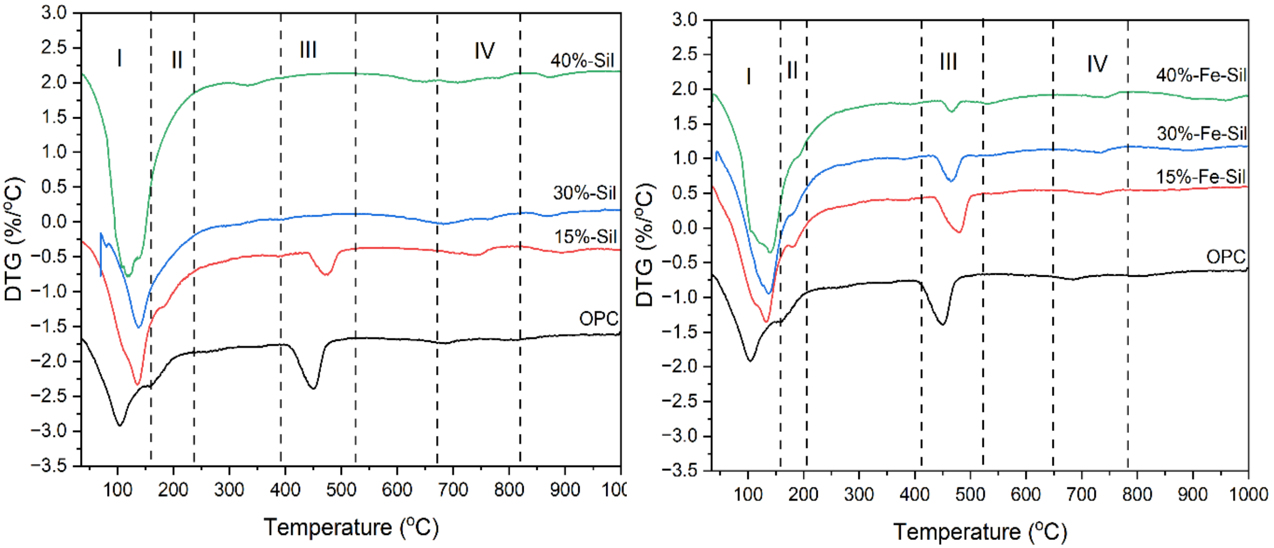


Figure 8 A comparison of TGA-DTG of 30 wt.% replacement of high-grade silica (Sil), low-grade silica (Fe-Sil) and fly ash (FA)

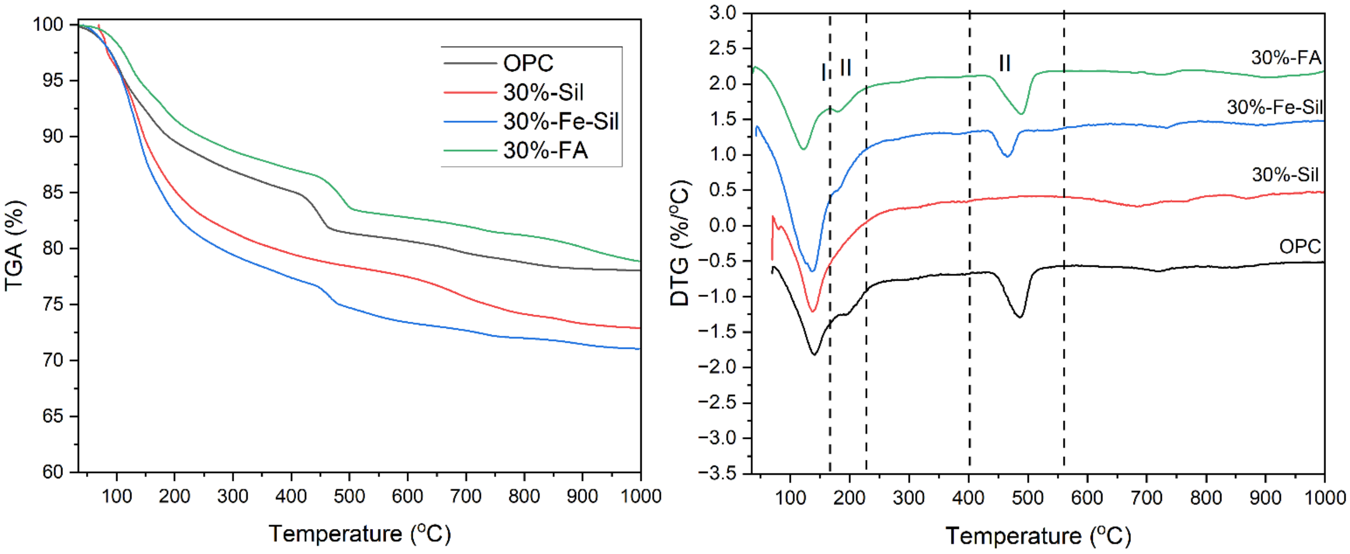
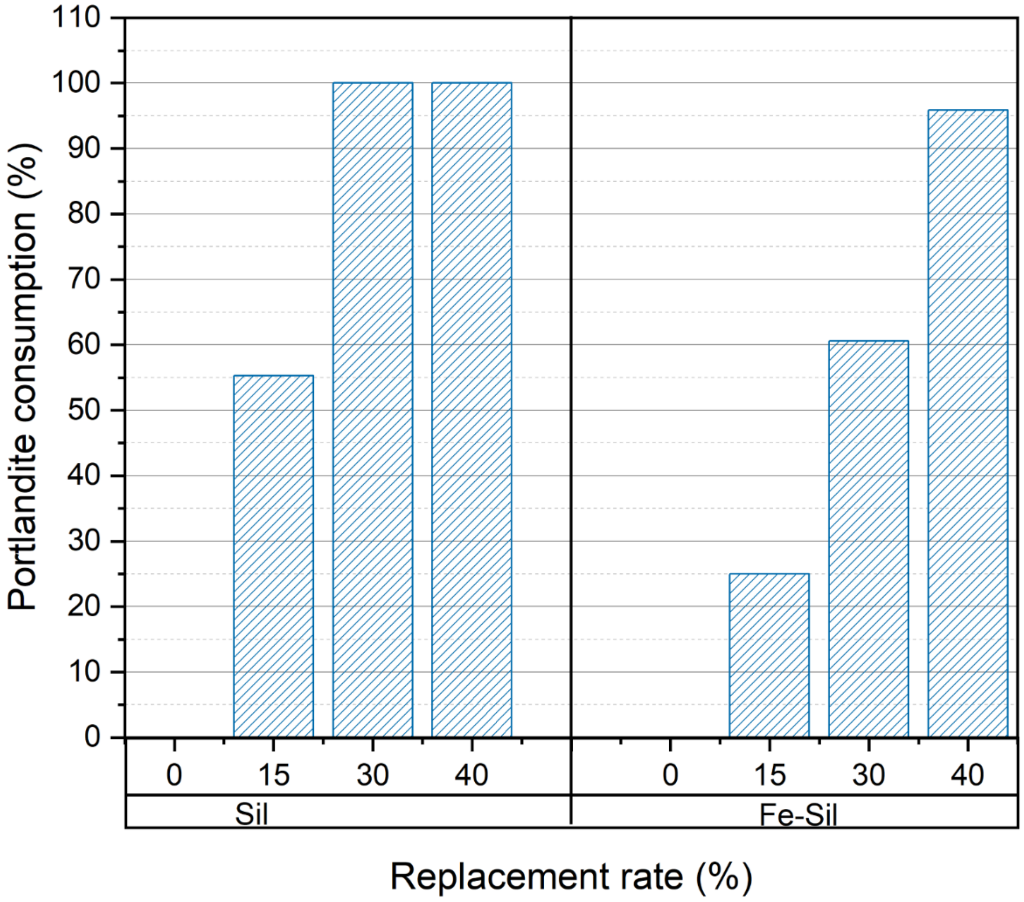


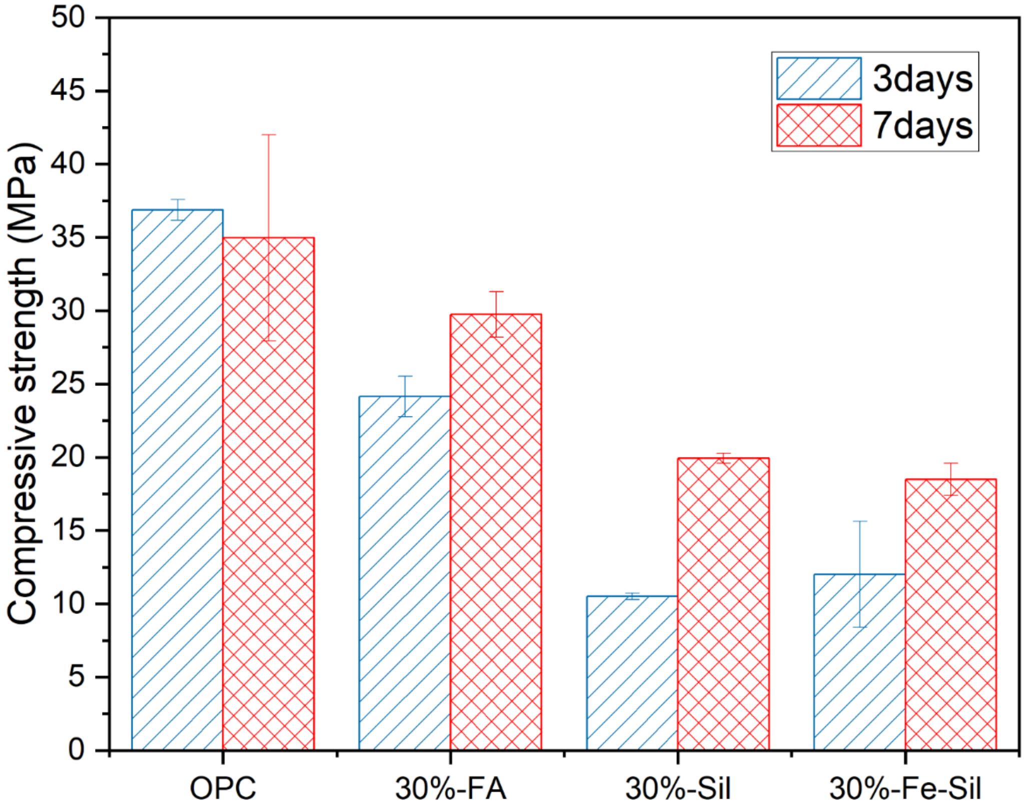
Figure 9 Portlandite consumption rate with the content of high-grade silica (Sil), low-grade silica (Fe-Sil)



Compressive strength evolution

Fig 10 compares the compressive strength evolution from 3 to 7 days of silica and fly ash. Regardless of the sample age, the strength of the blended cement mortar is lower than that of the OPC mortar. Though silica has shown higher reactivity, it developed a lower compressive strength than fly ash-based blended cement. That is likely due to the difficulty of mixing silica with cement at higher replacement levels which require more water. Thus, the samples prepared are not easy to compact. Understanding the mix design processing with silica is the new challenge that is being addressed to optimize its use in concrete.

Figure 10 A comparison of the 3 and 7-day compressive strength of 30 wt.% replacement with high-grade silica, low-grade silica and Fly ash



Conclusion

The olivine derived silica has a higher pozzolanic reactivity than fly ash;

That higher reactivity causes rapid sulfate depletion does not allow the proper dissolution of the silicate phases (C3S) and affects the setting behaviour of the paste;

The high-grade silica is more reactive than low-grade silica;

The lower compressive strength observed is merely due to the difficulty of properly mixing silica rather than it reactivity as SCM.

References

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