Utilisation of copper slags as supplementary cementitious materials in cemented paste backfill

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Abstract

In the Abitibi mining district of Canada, several underground mines rely on cemented paste backfill (CPB) for ground support, enhancing operational productivity and profitability. However, the rising cost of binding agents and the substantial carbon footprint associated with their production make CPB an increasingly expensive technique. To address this, the mining industry is actively seeking ways to reduce binder costs, primarily by partially replacing general use (GU) Portland cement with industrial byproducts, known as supplementary cementitious materials (SCMs). This study aims to evaluate the potential of copper slags (CS) from the Horne Smelter in Rouyn-Noranda, Quebec (Canada), as SCMs by enhancing their pozzolanic activity through mechanical, chemical and hybrid activation methods. Initial findings demonstrate that mechanical activation through grinding for a period of 40 to 80 minutes (at a fixed speed of 180 rpm) combined with chemical treatments using sodium sulphate (Na_2SO_4) at concentrations between 0.1 and 0.5 N, and alkaline activators such as lime kiln dust (5 to 15% substitution rate), effectively improve the hydration and hardening of cementitious pastes. These treatments have yielded uniaxial compressive strength (UCS) values at 28 days comparable to 100% GU binders, with UCS ratios ranging from 0.8 to 1.11. This improvement is likely due to stimulation of the reactivity of the SiO_2 glass in CS, which promotes the production of a higher volume of hydrates, notably calcium silicate hydrate, thereby reducing the overall porosity of the CPB. The valorisation of CS as SCMs in CPB reduces binder costs and promotes the sustainable use of industrial waste, aligning with modern environmental policies.

Keywords: *copper slags, cemented paste backfill, supplementary cementitious materials, pozzolanic activity, uniaxial compressive strength*

1   Introduction

Cemented paste backfill (CPB) consists of mine tailings from mineral processing, wet filtered tailings (with solids mass concentration [C_w] between 78 and 85%), binding agent and mixing water, designed to achieve a paste consistency with 70% $\leq C_w \leq$ 85%. The resulting CPB uniaxial compressive strength (UCS) required for secondary ground support generally ranges between 0.2 and 5.0 MPa after 28 days of curing time (Belem & Benzaazoua 2008a, 2008b; Belem et al. 2003). The mixture's consistency should yield an Abrams cone slump between 152 and 254 mm (6 and 10 inches) for efficient pipeline transport (Belem et al. 2003). Binders used in CPB can be general use (GU) Portland cement, used alone or blended with a supplementary cementitious material (SCM) such as ground granulated blast furnace slag (GGBFS), fly ash types F (FA-F) and C (FA-C), metallurgical slags, recycled glass, silica fume, or metakaolin (Behera et al. 2021; Benzaazoua et al. 2010; Peyronnard & Benzaazoua 2012).

If the required strength is for short-term needs, i.e. between 3 and 14 days, GU Portland cement alone or blended with FA-C can be used, provided the tailings do not contain dissolved sulphate. However, when long-term strength is targeted or the tailings contain dissolved sulphate, SCMs such as GGBFS or FA-F can be blended with GU cement. Indeed, the blend of GU Portland cement and GGBFS has provided optimal mechanical performance for mine backfill in various cases, particularly in Quebec's Abitibi region, where a

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blend of 20% GU and 80% GGBFS (20GU/80GGBFS) is commonly used with great success. However, binder costs can account for up to 75% of backfilling operation expenditure, largely influenced by the price of cementitious materials (~CAD260 per tonne for GGBFS, CAD195 per tonne for GU and CAD120 per tonne for FA-F (Gélinas 2023; Ouffa et al. 2023). By 2050, SCMs are expected to fulfill around 20% of global cement production needs (Singh & Singh 2019). Additionally, GU cement production emits significant CO_2 (approximately 0.8 tonne per tonne of cement produced), raising environmental concerns, especially as mines are increasingly located in remote areas, adding to both costs and carbon footprint.

To minimise costs, binder formulations can be optimised by incorporating locally available aluminosilicate materials such as copper slags (CS) from nearby smelting facilities. This article aims to establish a process for valorising CS from the Horne Smelter, near the Abitibi mining regions, as an SCM while concurrently mitigating associated environmental impacts.

Research indicates that mixtures with up to 30% CS substituting GU can achieve acceptable UCS values, with performance often comparable to Portland cement (Chen et al. 2017; Peyronnard & Benzaazoua 2012; Zhu et al. 2022). However, CS has limited pozzolanic activity, necessitating simple yet effective treatments to enhance its reactivity. For example, CS granulated through high-pressure water cooling after fusion at around 1,400°C (GCS) become largely amorphous (up to 98%), which is beneficial for pozzolanic reactivity. The reactivity of pozzolanic materials, such as CS, depends on their chemical composition and amorphous phase structure. Glassy materials like GCS typically exhibit low polymerisation, granting them pozzolanic properties that make them suitable as SCMs (Feng et al. 2020; Nazer et al. 2016).

High-energy mechanical grinding (for between 0.5 and 2 hours) can improve CS reactivity by increasing surface area and creating structural disarray, thereby accelerating hydration through particle size reduction (< 60 µm) (Lan et al. 2020; Song et al. 2019). Additionally, sodium sulphate (Na_2SO_4) serves as a common chemical activator, facilitating the dissolution of the silica network as sulphate ions react with alumina within the slags. Studies have shown that a Na_2SO_4 content of 1 to 6% enhances compressive strength, reaching up to 23.3 MPa after three days of curing time and 36.1 MPa after 28 days of curing time (Abdullah et al. 2012; Chen et al. 2021; Wang et al. 2019). Furthermore, Feng et al. (2020), Feng et al. (2019) and Zhu et al. (2022) have demonstrated that an optimal lime (CaO) content stimulates CS hydration, increasing the release rate of reactive silica and providing additional Ca^{2+}, which reacts with calcium hydroxide (CH) from cement hydration to form a higher quantity of calcium silicate hydrate (C-S-H).

In this article, lime kiln dust (LKD), with a CaO content exceeding 65%, is utilised as a promising alkaline activator. The use of these activation methods is justified by their low cost, effectiveness and availability, allowing for further reduction in GU Portland cement consumption. Consequently, the operating costs of mines using backfill can potentially be reduced while concurrently reducing the social and environmental impact of the CS being generated by smelters.

2 Methodology

This section aims to present the raw materials used in this paper, along with the techniques used for their characterisation. The process begins with activation tests on the CS, including mechanical grinding to optimise the fineness of the CS. Following this, chemical activation is applied using various agents such as anhydrous Na_2SO_4 and LKD, and partial replacement by Type GU Portland cement.

The design of experiments (mixture designs) is then implemented to formulate simulated CPB mixes (SCPB), utilising fine pure silica (Sil-Co-Sil 106®) as the skeletal structure of the CPB simulating mine tailings. The properties of these formulations, particularly the UCS, are assessed after curing times of 7 and 28 days.

2.1 Materials used

Three different types of slags obtained from the Horne Smelter (copper metallurgy) were used as target activation materials: (i) fresh slag-mud waste (CS2), which is a mix of pure slag in slurry form combined with mud from the sulphuric acid plant; (ii) aged slag-mud waste (CS3), consisting of the same type of slag as CS2

but having been deposited for some time; and (iii) aged slag (CS4), which is slag from reverberatory furnaces air-cooled onsite. Currently, the Horne Smelter uses these as backfill material onsite.

GU Portland cement, supplied by Lafarge Canada Inc., was used as a binder for partial substitution with CS. Additionally, LKD, a byproduct of lime manufacturing (rich in CaO), was used to hopefully promote the chemical activation of CS due to its alkalinity. This product was supplied by Graymont Inc.'s Bedford Plant (Quebec, Canada). Finally, sulphate activation of the CS is achieved with Na_2SO_4, which has a purity level of 98.5% (in fine powder form). This product was supplied by Avantor Inc. (Ohio, USA).

2.2 Materials characterisation

2.2.1 Physical characterisation

The material relative densities were determined using a Micromeritics AccuPyc 1330 helium pycnometer, following the American Society for Testing and Materials (ASTM) C128 Standard.

The specific surface areas (SSA) were determined using nitrogen (inert gas) adsorption isotherms following the Brunauer, Emmett and Teller (BET) theory (Brunauer et al. 1938). The BET SSA was measured using the GEMINI surface analyser from Micromeritics, following the BET theoretical model. An alternative and more efficient method is the Blaine SSA measurement. The Blaine air permeability apparatus determines the cement fineness in terms of SSA, expressed in cm²/g or m2/kg of cement. The Blaine SSA was measured using the Humboldt Blaine air permeability apparatus, following the ASTM C204 Standard.

The particle size distribution (PSD) analysis for fine and very fine materials was performed using the Malvern Mastersizer 3000 laser diffraction particle size analyser, measuring particle size between 0.05 and 900 μm. For coarse material such as the CS4 sample, particle size analysis was performed by sieving with a series of standard opening sieves (1.25, 2.5, 5, 10, 14, 20, 28, 40, 56 and 80 mm, and above), in compliance with CSA-A23.2-09 and ASTM C-136 Standards (ASTM 2006).

Table 1 present the physical characterisation results of Sil-Co-Sil 106 sand, slags, binder and additive used.

The PSD curves (Figure 1) reveal that the proportion of particle diameters smaller than 20 μm ($P_{20μm}$) also denoted as ultrafine particles (< 20 μm) in Sil-Co-Sil 106 silica sands achieves 47%, thereby classifying these simulated backfills as 'medium' according to the Golder Paste Technology classification (Landriault 1995). In addition, a minimum proportion of 15% ultrafine particles is desirable to ensure effective backfill pipeline transport, although exceeding this proportion ($P_{20μm} > 60\%$) may reduce mechanical strength (Landriault 1995). The specific gravity (SG) or relative density (D_R) of Sil-Co-Sil 106 is 2.63. In general, the SG is a critical parameter in designing mix formulations as it directly influences the volume of binder required for preparing CPB. The binder dosage is determined as the binder-to-tailings or silica sand ratio and therefore does not take into account the SG variable, which depends on the origin of tailings (Belem & Benzaazoua 2008a). Overall, the physical properties of Sil-Co-Sil 106 are like those of hard rock mine tailings.

Among the key parameters for CS, Type GU cement and LKD, the particle fineness (SSA) provides the most significant indication of cementitious reactivity. The SGs of the tested materials range from 2.63 to 3.46, BET SSA from 747.8 to 6,182 m²/kg and Blaine SSA from 414.6 to 794.8 m²/kg.

Special attention should be given to CS3 and CS2, which exhibit high BET SSA of 6,182 and 3,968.4 m²/kg, respectively, providing a notable advantage in reactivity and reducing grinding costs. Conversely, CS4 consists of coarse material, with 97% of particles between 10 and 40 mm in diameter and a relatively narrow PSD ($C_U = 1.66 < 2$). Therefore, further grinding is required to refine CS4 for effective use as an activated cementitious material.

Table 1   Physical properties of the materials used

| Parameter	Copper slag			Binder and additive		Silica sand
	CS2	CS3	CS4	LKD	GU	Sil-Co-Sil 106
Specific gravity (SG)	3.44	3.44	3.46	2.72	3.11	2.63
BET SSA (m²/kg)	3,968.4	6,182	–	747.8	1,652.3	937.5
Blaine SSA (m²/kg)	648.7	794.8	–	517.6	538.3	414.6
$C_U = D_{60}/D_{10}$	6.77	8.44	1.66	8.65	7.06	16.74
$C_C = D_{30}^2/D_{60} \times D_{10}$	0.94	0.97	1.02	0.84	1.46	1.28
D_{10} (µm)	3.42	1.76	14,350	5.16	3.05	1.87
D_{30} (µm	8.63	5.04	18,740	13.92	9.78	8.67
D_{60} (µm)	23.14	14.86	23,890	44.61	21.53	31.3
D_{90} (µm)	51.03	37.84	33,450	67.86	157.46	51.14
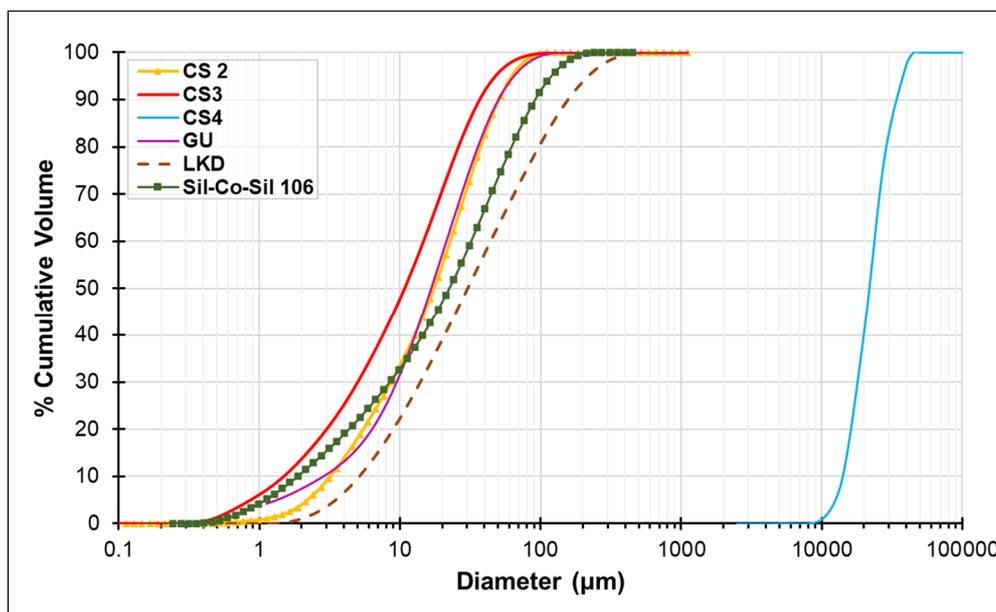
Figure 1   Particle size distribution curves of the materials used

2.2.2   Chemical and mineralogical analysis

Chemical composition was obtained via X-ray fluorescence (XRF) analysis using the Bruker ED-XRF Ranger S2 spectrometer. This chemical analysis was complemented by mineralogical analysis using X-ray diffraction (XRD). Samples were exposed to an X-ray beam, with diffracted rays measured based on the 2θ deviation angle to determine the internal structure and quantify the mineral phases present. This analysis was performed using a Bruker AXS Advance D8 diffractometer in θ/2θ mode, covering diffraction angles from 5° to 70°.

The results of the chemical analysis (XRF) for the materials are presented in Table 2. The Sil-Co-Sil 106, used as the skeleton for SCPB mixtures, achieves a purity of 97.4% in SiO_2 and 1.76% in Al_2O_3, which corresponds to a mineralogical composition of 95.7% quartz, with very low impurities in the form of muscovite (4.2%) as determined by XRD analysis.

XRF analysis results indicate that the copper slags CS2, CS3, and CS4 have a relatively similar chemical composition. They are particularly rich in Fe_2O_3 (about 50%), and contain significant amounts of SiO_2 (ranging from 27.5 to 30%) and notable proportions of Al_2O_3 (7 to 8%) and CaO (1 to 4.3%).

XRD mineralogical analysis reveals that the crystalline phase of these slags is predominant over the amorphous phases. These materials primarily consist of silicates such as fayalite (approximately 43% for CS2 and CS3, with a higher content of 76.4% for CS4). Magnetite is also present in varying proportions from 21.7 to 35% across the three types of slag, while gypsum is significant in CS2 and CS3, achieving 13.8 and 31.1%, respectively. The slags studied exhibit theoretical basicity indices ([CaO + MgO]/SiO_2) below the required values for effective hydraulic reactivity ($0.08 \leq$ [CaO+MgO]/$SiO_2 \leq 0.22$ compared to the requirement of ≥ 1.4) (Pal et al. 2003). This suggests that these slags are highly acidic and may not exhibit inherent hydraulic reactivity. However, the sum of the oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$), which indicates the pozzolanic potential of these slags, shows values exceeding 80%, comparable to class F fly ash ($SiO_2 + Al_2O_3 + Fe_2O_3 > 70\%$ and CaO < 8%).

Calcium-rich materials, such as GU Portland cement and LKD, contain 64.4 and 68.3% CaO, respectively. This high calcium content makes them suitable as alkaline activators for CS.

Table 2   Chemical composition of materials used by the X-ray fluorescence method

Materials	Major oxides (%)								
	Al_2O_3	SiO_2	SO_3	K_2O	Na_2O	CaO	MgO	Fe_2O_3	CuO
CS2	7.45	27.93	5.84	0.66	< 0.01	4.24	1.78	50.5	0.92
CS3	8.67	27.24	5.51	0.73	< 0.01	4.41	1.47	50.24	0.65
CS4	7.14	30.49	2.13	0.72	0.7	1.15	1.16	43.96	0.98
LKD	3.17	6.2	4.22	0.93	< 0.01	68.34	< 0.01	0.79	< 0.01
GU	4.1	15.6	4.47	1.1	0.42	64.66	2.01	2.76	< 0.01
Sil-Co-Sil 106	1.76	97.4	< 0.01	< 0.01	< 0.01	< 0.01	0.28	0.02	< 0.01

2.3   Simulated cemented paste backfill mixture designs and preparation

The component limits for the binder mixtures were defined based on the scientific literature on the activation of CS for use as a cementitious material (Chen et al. 2021; Feng et al. 2020; Peyronnard & Benzaazoua 2012; Wang et al. 2019; Zhang et al. 2023; Zhu et al. 2022), as well as on preliminary laboratory tests aimed at validating these activation methods while maintaining optimal proportions among the three main components: CaO, SiO_2, and Fe_2O_3-Al_2O_3 (Table 3). These values were then input into statistical software to design the experiments and develop optimal binder formulations. Minitab® 22 Statistical Software was used for this study. It allows the creation of three binary mixture designs, two binary designs with process variables and two ternary mixture designs.

Table 3   Limits of different components in experimental designs

	GU (%)		CS (%)		LKD (%)		Na_2SO^4 (M)		
	Min	Max	Min	Max	Min	Max	Min	Max	No. of Plans
CS/GU	50	90	10	50	–	–	–	–	3
CS/GU + [Na_2SO^4]	20	60	40	80	–	–	0.1	0.5	2
CS/GU/LKD	45	55	30	50	5	15	–	–	2

For the preparation of SCPB, the target solids mass concentration ($C_w = M_{solid}/M_{SCPB}$) was set at 75%, giving a water mass concentration of 25%, with the binder-to-silica ratio B_w (= $M_{binder}/M_{Sil-Co-Sil}$) set at 8%. The formulated binder, including ground CS (Figure 2a), was mixed with the activator (LKD and/or GU) in dry form with a small amount of water in the Eurodib electric mixer bowl (Figure 2b). For sulphate activation, the Na_2SO_4 mass ($M_{Na_2SO_4}$) was part of the liquid phase. To prepare a solution of X molarity, X moles of Na_2SO_4 per litre of solution are needed. Given Na_2SO_4's molar mass of approximately 142 g/mol, $M_{Na_2SO_4}$ = X × 142 g/L.

The mixture was initially stirred manually until reaching a homogeneous slurry. Subsequently, the mixer was set to low speed while gradually adding Sil-Co-Sil, followed by five minutes of mixing with a gradual increase in speed up to 180 rpm to ensure uniformity (Figure 2c). The final mixture was poured into plastic cylindrical moulds with dimensions of 30 mm diameter and 60 mm height (1.2 × 2.36 inches). The plastic moulds were then vibrated to remove air bubbles. Triplicate samples were placed in humidity chambers set at 23 °C and > 95% relative humidity for curing times of seven and 28 days (Figure 2d).
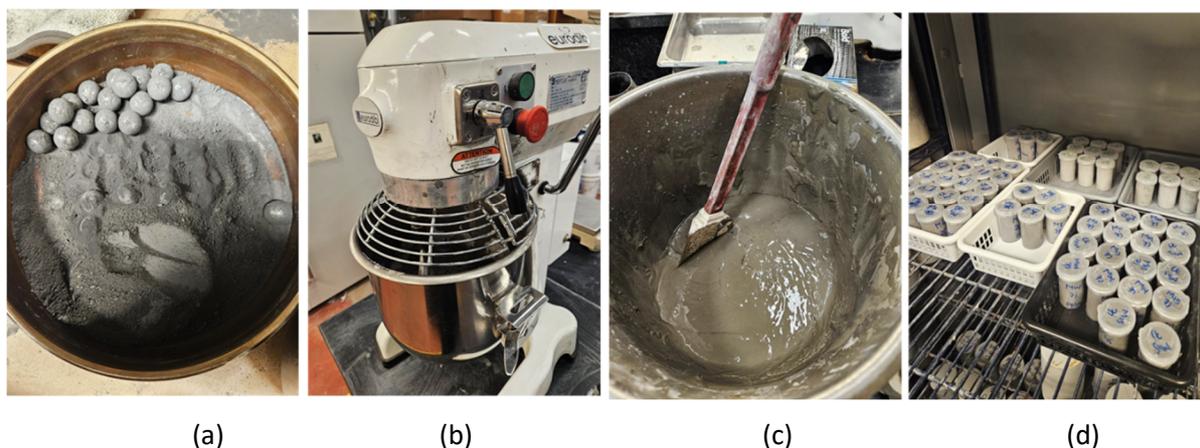

| (a) | (b) | (c) | (d) |

Figure 2   **Preparation of simulated cemented paste backfill (SCPB): (a) Mechanical grinding of copper slags; (b) Mixing process; (c) Homogeneous SCPB; (d) Storage in humid curing chambers**

2.4   Uniaxial compression tests

The UCS value is commonly used to evaluate the mechanical properties of CPB due to the simplicity and cost-effectiveness of its test. Uniaxial or uniaxial compression tests involve placing an SCPB sample between the two platens of the mechanical press and gradually applying an axial load until the sample fails (Figure 3). The UCS measurements were taken at each curing time using a rigid MTS 10/GL mechanical press with a 50 kN capacity. The tests were conducted at a displacement rate of 1 mm/min. Before each test the specimens were carefully demoulded and the ends were squared using single-blade scrapers to ensure even force distribution across the sample's cross-section. The reported UCS value represents the average result obtained from triplicate samples.
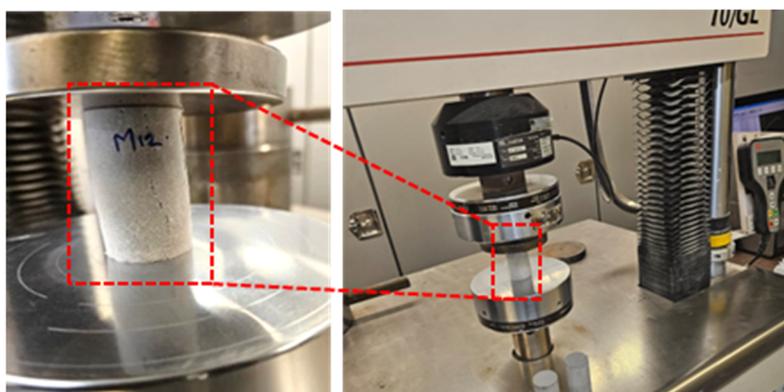

Figure 3   **Uniaxial compression testing of simulated cemented paste backfill using an MTS 10/GL mechanical press**

2.5　Statistical analysis of uniaxial compressive strength prediction models

The aim of the statistical analysis presented in this paper is to understand the contribution of each mixture component to the 28-day curing UCS value (UCS28d) and its trends. Based on multiple regressions, this statistical analysis also aims to explain the interactions between mixture components and their impact on UCS28d. Calculations were conducted using Minitab 22 software. UCS28d prediction statistics are reported with a 95% confidence limit, and p-values are provided with a significance level of α = 0.05. To ensure the reliability of the model, it is essential to calculate performance indicators, such as root mean square error (RMSE), the coefficient of determination (R²) and adjusted R², using the following equations:

$$\text{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\hat{y}_i - y_i)^2} \tag{1}$$

$$R^2 = 1 - \frac{\sum (\hat{y}_i - y_i)^2}{\sum (y_i - \overline{y_i})^2} \tag{2}$$

$$R^2 \text{adjusted} = 1 - \frac{(1 - R^2)(n - 1)}{n - p - 1} \tag{3}$$

where :

$\hat{y}_i$　　=　predicted values

y_i　　=　observed values

$\overline{y_i}$　　=　mean of the observed values

n　　=　number of data points

p　　=　number of predictors.

3　Results and discussions

3.1　Effect of mechanical activation

To assess the effect of mechanical grinding (using a planetary ball set to a fixed speed of 180 rpm) on the hydration activity of CS, SCPB mixtures were prepared using the same parameters mentioned previously, with a binary binder formulation of 50GU/50CS. Generally, the results show a positive correlation between the UCS of the cementitious material and the Blaine SSA of the CS powder (Figure 4).

When the optimal Blaine SSA of CS2 achieves 816.2 m²/kg (optimal fineness), the SCPB strength is 413.2 kPa after seven days of curing time and 992.3 kPa after 28 days of curing time (Figure 4a). With a maximum grinding time of 120 minutes, corresponding to the peak fineness of 905.6 m²/kg, the UCS at 28 days achieves 1,009.2 kPa, representing an increase of 16.9 kPa compared to CS2 ground for 60 minutes.

For CS3, the Blaine SSA quickly (within 40 minutes) reaches its optimum, allowing the UCS to reach 341.6 kPa at seven days and 908.7 kPa at 28 days. Beyond this duration, the UCS slightly decreases due to the agglomeration of particles smaller than 10 μm, leading to a reduction in the Blaine SSA (Lan et al. 2020). However, as these ultrafine particles fragment again during subsequent grinding stages, the UCS slowly increases to a maximum of 452.7 kPa at seven days and 936.6 kPa at 28 days, corresponding to a grinding time of 100 minutes.

For CS4, optimal strength is achieved with an extended grinding time of 80 minutes, achieving a fineness of 482.4 m²/kg and a UCS of 428.9 kPa at seven days and 923.2 kPa at 28 days. Prolonging the grinding time to 100 minutes results in a slight increase in UCS, reaching 446.6 kPa at seven days (a 4.1% increase over the optimal mixture) and 931.1 kPa at 28 days (an increase of 0.88% over the optimal mixture).

Mechanical grinding enhances the activity of CS, primarily due to particles smaller than 30 μm which dominate the hydration process, with those under 10 μm being especially beneficial for early UCS development (Feng et al. 2019; Lan et al. 2020). However, as grinding time increases, so does the cost of mechanical activation. Therefore, optimising this process to enhance the pozzolanic activity of CS through additional chemical activation experiments is essential.
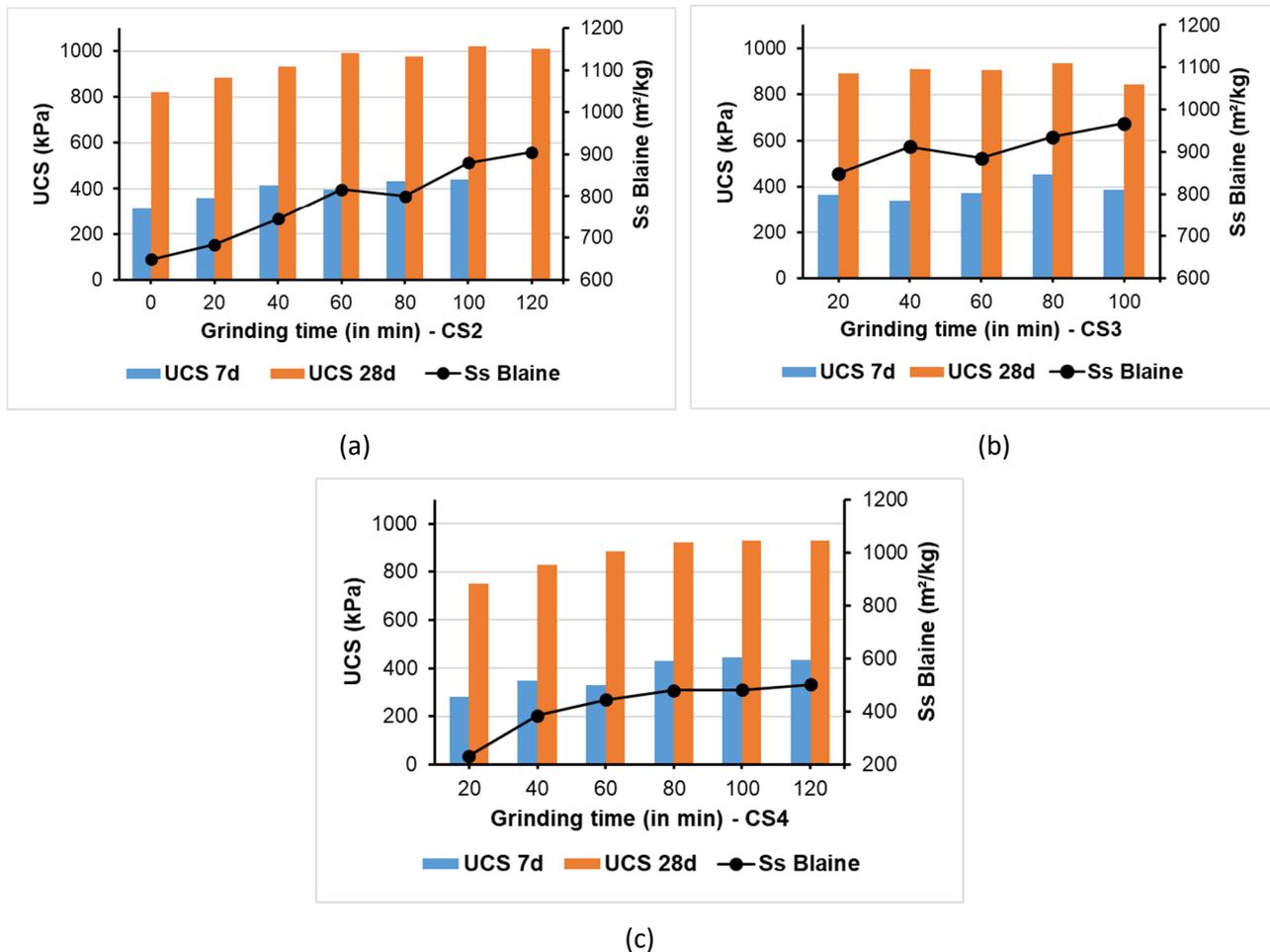

(a)

(b)

(c)

Figure 4   Effect of grinding time on the Blaine specific surface area and strength of copper slags: (a) CS2; (b) CS3; (c) CS4

3.2   Effect of chemical activation

After optimising the mechanical grinding process, an activation step (either alkaline or sulphate) was applied using Type GU cement, LKD or controlled-concentration chemical solutions such as Na_2SO_4. This approach enables us to understand the coupled effects of mechanical-chemical on the pozzolanic reactivity of the copper slags.

3.2.1   Binary mixtures with copper slags-general use Portland cement binder

The results indicate that the UCS of the mixtures decreases as the CS content increases. However, this UCS improves significantly between curing periods of seven and 28 days, especially for CS2 (Figure 5). At 28 days, the enhancement of UCS in mixtures with CS compared to the reference cement (100% GU) confirms the pozzolanic nature of the slags. For example, in a mixture with 30CS/70GU, the UCS at seven days is 542 kPa for CS2, 690.7 kPa for CS3 and 641.3 kPa for CS4, compared to 954.8 kPa for the reference cement (100GU), indicating limited early reactivity of CS2 (primarily exhibiting a filler effect). However, at 28 days the UCS for 70CS2/30GU reaches 1,214.5 kPa, or 80.2% of the reference cement's value (1,513.8 kPa), demonstrating an

intensification of CS2 hydration activity in the medium term. In contrast, CS3 and CS4 show a lesser strengthening effect at this stage.

The strength activity index (SAR) is a widely used indirect method for assessing the reactivity of a pozzolanic material (Brial et al. 2021; Donatello et al. 2010). It involves preparing a reference mortar without pozzolan (in this paper, the 100GU reference binder) and a mortar with 20% pozzolan to be tested (here, the 20CS/80GU binder). A pozzolanic material is considered reactive if the compressive strength of the mortar with pozzolan reaches at least 75% of that of the reference mortar at seven and 28 days, or between 85 and 90% at 90 days, following the ASTM C618 Standard. In this paper, all CS exceeds the 75% SAR threshold except for CS2, which has a SAR of 74.7% at seven days of curing, slightly below the threshold but considered negligible (see Figure 5).

(a)

(b)
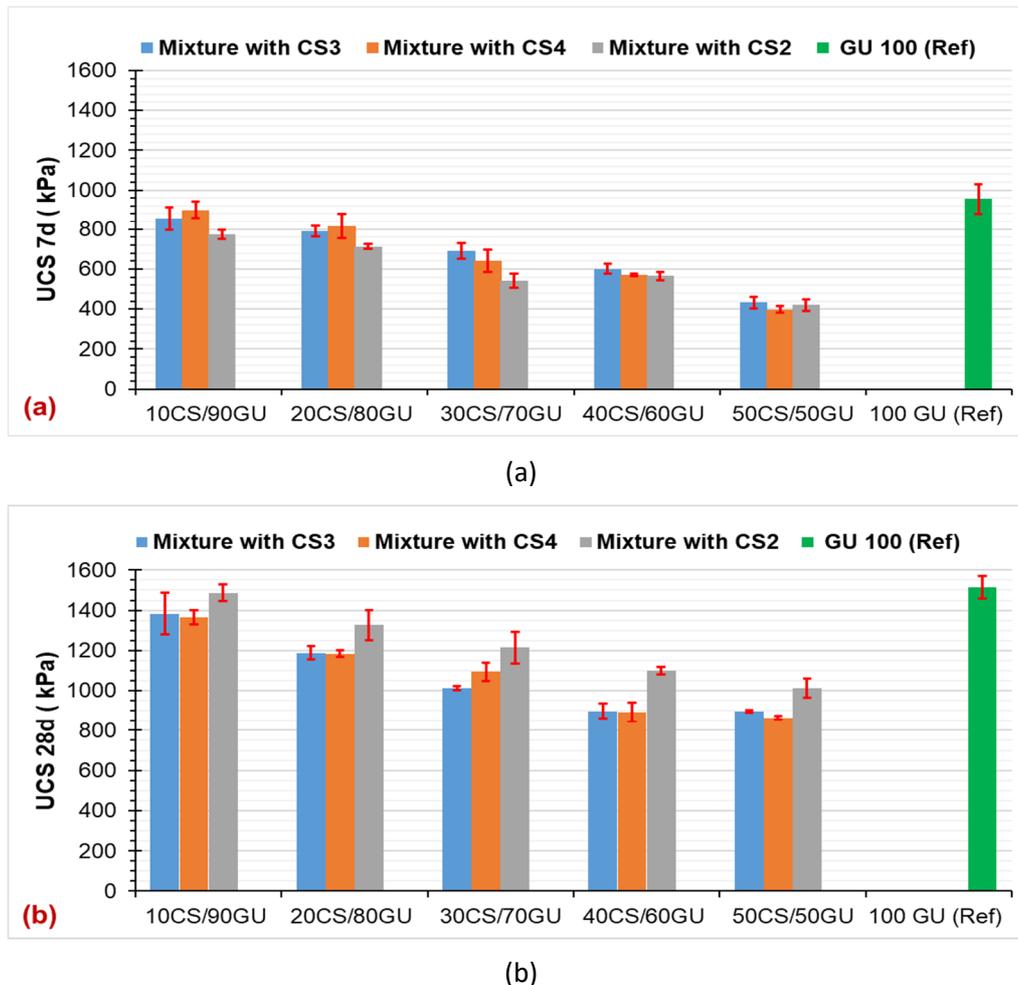
Figure 5 Evolution of uniaxial compressive strength in simulated cemented paste backfill mixtures of copper slag-general use Portland cement binder: (a) at seven days; (b) at 28 days of curing

3.2.2 Binary mixtures with process variable (copper slag-general use Portland cement) and sodium sulphate (Na_2SO_4) binder

At seven days of curing: the 40CS/60GU binder mixtures exhibit similar UCS values regardless of Na_2SO_4 (process variable) concentration, with a slight improvement for CS4 compared to CS3 (Figure 6a). However, these strengths remain lower than those of the 100GU reference binder. A low Na_2SO_4 concentration (0.1 M) enhances the strength of the 40CS3/60GU mixture, achieving 761.4 kPa, which is 79.7% of the UCS of 100GU. For the 40CS4/60GU mixture, a 0.3 M concentration yields an optimal strength of 805.7 kPa (84.4% of 100GU). As the proportion of CS in the mixture increases, a higher Na_2SO_4 concentration becomes necessary to improve the strength. For example, for the 60CS4/40GU binder, the maximum strength achieved is

576.3 kPa with a Na₂SO₄ concentration of 0.5 M. At early ages, an excessive Na₂SO₄ content is not recommended when CS proportion is low, as an excess of Na⁺ ions can cause a salinity effect. However, when the substitution rate of CS is higher, a greater Na₂SO₄ concentration is required to activate hydration and promote reactive SiO₂ dissolution (Chen et al. 2021; Wang et al. 2019).

At a medium curing age (28 days): the 40CS/60GU binder mixtures show a significant increase in compressive strength (Figure 6b). For instance, with an optimal Na₂SO₄ concentration of 0.3 M, the UCS of the 40CS3/60GU binder increases from 710.8 kPa at seven days to 1,368.7 kPa at 28 days, representing a ratio of 92.2% compared to the 100GU reference binder. For the 40CS4/60GU binder, at the same concentration of 0.3 M, the UCS increases from 805.7 kPa at seven days to 1,637.1 kPa at 28 days, yielding a ratio of 108.1% relative to 100GU.

As the CS proportion increases relative to GU, a higher Na₂SO₄ concentration is needed to stimulate CS reactivity. For instance, the 60CS4/40GU mixture achieves a maximum strength of 1,234.8 kPa at 28 days with a Na₂SO₄ concentration of 0.5 M. However, even higher CS proportions show limited hydration progress, even with elevated Na₂SO₄: the 80CS3/20GU binder, for instance, exhibits an increase in strength from 386.84 kPa at seven days to 532.8 kPa at 28 days. Consequently, a 0.3 M concentration of Na₂SO₄ appears to be optimal for stable long-term strength improvement in a 40CS4/60GU mixture. This dosage is advantageous for large-scale sulphate activation, as Na₂SO₄ is a neutral, cost-effective salt with low corrosive properties.
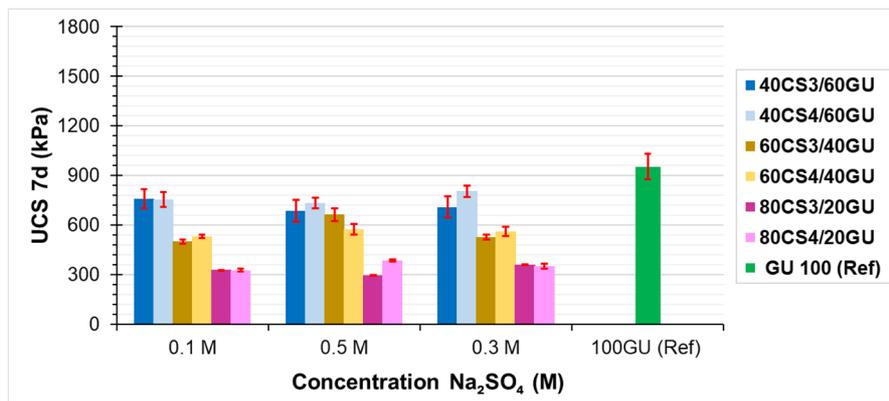
(a)
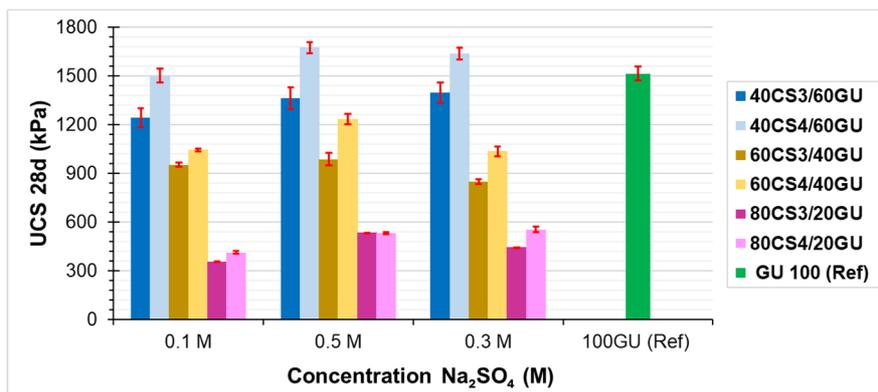
(b)

Figure 6   Evolution of uniaxial compressive strength in simulated cemented paste backfill mixtures of copper slag-general use Portland cement and Na₂SO₄ binder: (a) at seven days; (b) at 28 days of curing

The UCS28d can be predicted for each type of CS using the stepwise regression method (or multiple stepwise regression). The prediction equations are as follows:

$$\text{UCS 28d (CS3)} = 48.1\text{CS3} + 2{,}196\text{GU} + 14.03(1/\text{GU} \times \text{Na}_2\text{SO}_4]) \tag{4}$$

$$\text{UCS 28d (CS4)} = 2{,}485.9\text{GU} + 786.9\text{CS4} - 130.75\left(\frac{1}{\text{GU}}\right) +$$
$$376.7(\text{GU} \times \text{CS4} \times [\text{Na}_2\text{SO}_4]) \tag{5}$$

Both multiple linear regression models proved to be significantly representative. For the CS3 model, an adjusted R² of 96.67%, a *p*-value ≤ 0.03, and a Fisher coefficient of 143.14 confirm an excellent fit and significance of the variables included in the UCS28d (CS3) model. However, the RMSE value of 71.82 indicates slightly lower precision for this model. Regarding the CS4 mixture design, the significance and fit are even better than those for the CS3 model, with an adjusted R² of 99.7% and an RMSE of 6.59, confirming a high level of precision.

3.2.3 Ternary mixtures copper slag-general use Portland cement-lime kiln dust binder

At an early age (seven days of curing): compressive strength is mainly influenced by Type GU content. The higher the CS content, the less cement is involved in paste hydration, resulting in fluctuations in compressive strength despite the partial substitution of GU with LKD for both types of CS (Figure 7a). The UCS reaches a maximum at seven days when the binder consists of 55% GU, 15% LKD and 30% CS, with values of 599.7 kPa for CS3 (62.8% relative to the 100% GU reference binder) and 629.2 kPa for CS4 (65.9% relative to the 100% GU binder). This confirms that CS4's reactivity is enhanced at an early age in the presence of an alkaline activator, like LKD, compared to CS3.
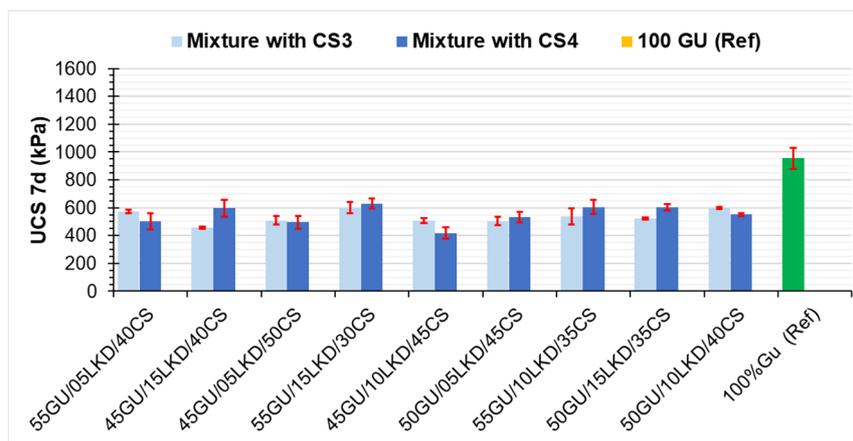
(a)
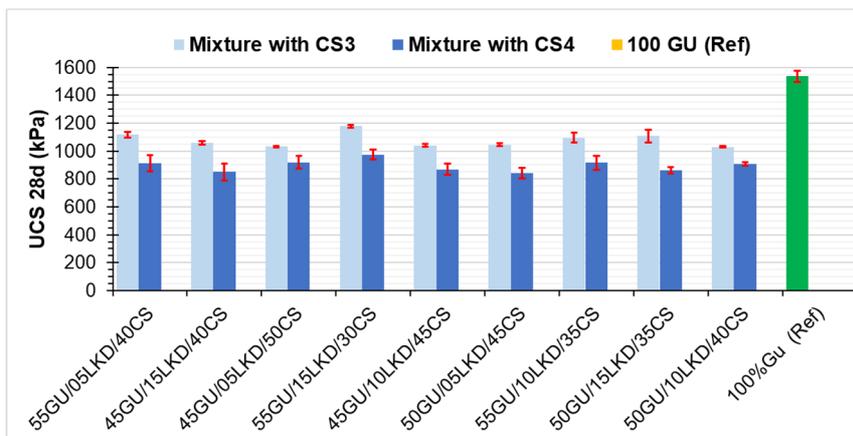
(b)

Figure 7 **Evolution of the uniaxial compressive strength of simulated cemented paste backfill mixes of copper slag-general use Portland cement-lime kiln dust binder: (a) at seven days; (b) at 28 days of curing**

<u>At mid-term (28 days of curing):</u> CS3 shows a significant improvement in strength across all tested mixtures compared to CS4. The 55GU/15LKD/30CS3 binder can be considered optimal, with its UCS increasing from 599.7 kPa at seven days to 1,177.8 kPa at 28 days, reflecting a UCS ratio of 76.7% (Figure 7b). Conversely, a 55GU/15LKD/30CS4 binder demonstrates lower mechanical strength (from 629.2 kPa at seven days to 974.3 kPa at 28 days), indicating a slower pozzolanic reactivity in CS4, which reduces later strength in an alkaline environment rich in CaO.

A 15% LKD content appears sufficient to stimulate long-term hydration activation in CS, especially for CS3, while allowing further reduction of GU in the mix. This is due to the increased release of reactive silica and additional Ca^{2+}, promoting C-S-H formation through pozzolanic reaction with CH from GU hydration (Feng et al. 2020).

The UCS28d can be predicted for ternary CS/GU/LKD mixtures using the stepwise multiple regression method. The prediction equations are as follows:

$$UCS\ 28\ d\ (CS3) = 1,901GU + 301CS3 + 1,0526LKD - LKD \times CS3 \times GU \times 68,224$$
$$- LKD \times CS3\ (LKD - CS3) \times 23,505 \qquad (6)$$

$$UCS\ 28\ d\ (CS4) = 3,882GU - 2,101LKD + 4,699CS4 - 13,694(GU \times CS4) \qquad (7)$$

For CS3, an adjusted R^2 of 91.67%, a Fisher coefficient of 23.25, and a reduced RMSE of 14.35 confirm a strong fit and acceptable statistical significance of the variables in the UCS28d model (CS3). Conversely, the UCS28 model for the mixture containing CS4 shows a slightly lower adjusted R^2 of 72.7%, the same Fisher coefficient of 23.25 and a higher RMSE of 24.05, indicating a reasonably good fit for the adjusted UCS28 (CS4) model, though with slightly lower accuracy than the CS3 model.
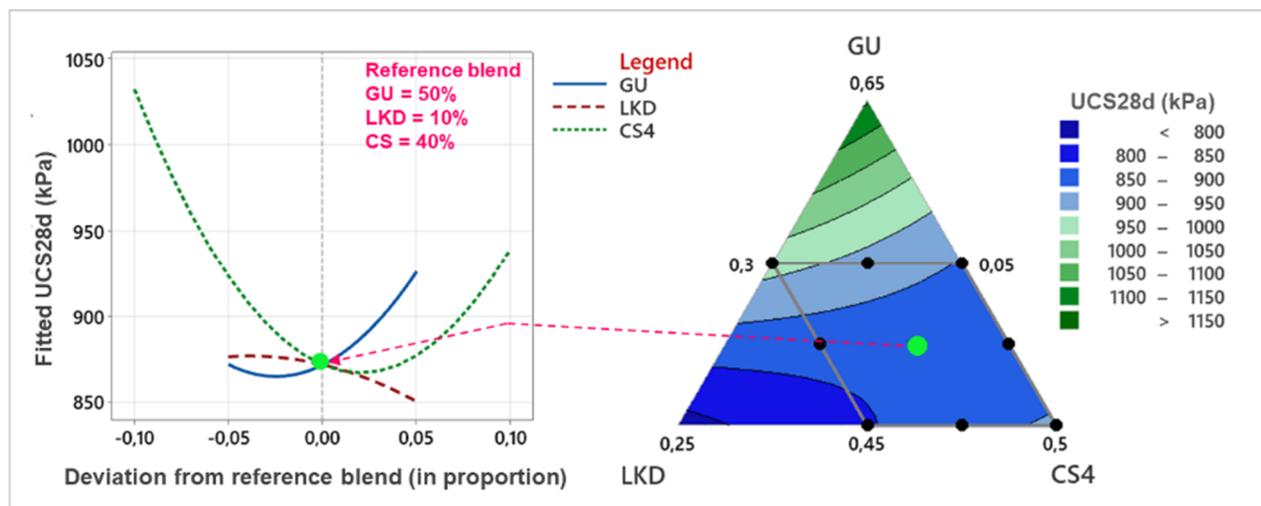
The Cox trace plot and ternary diagram utilise Equations 6 and 7 to examine the effect of each component on the UCS28d response, as shown in Figure 8.

For instance, starting with an intermediate composition such as the 50GU/10LKD/40CS3 binder (Figure 8a), the 28-day strength is primarily influenced by the GU and CS3 proportions. An increase in LKD seems to have a less pronounced effect on UCS28d. Increasing GU consistently enhances UCS28d, while increasing CS3 reduces strength within this ±10% substitution range among components. Conversely, for the 50GU/10LKD/40CS4 binder, strength is influenced non-linearly, with a combined effect from all three components (GU, CS4 and LKD) on UCS. The CS4 trend line shows that an increase in CS4 also results in a reduction in UCS28d.

Therefore, to maximise UCS28d, it is advisable to increase GU content, maintain LKD at moderate levels and minimise the CS proportion, particularly CS4, as its increase leads to a more pronounced decrease in strength compared to CS3.
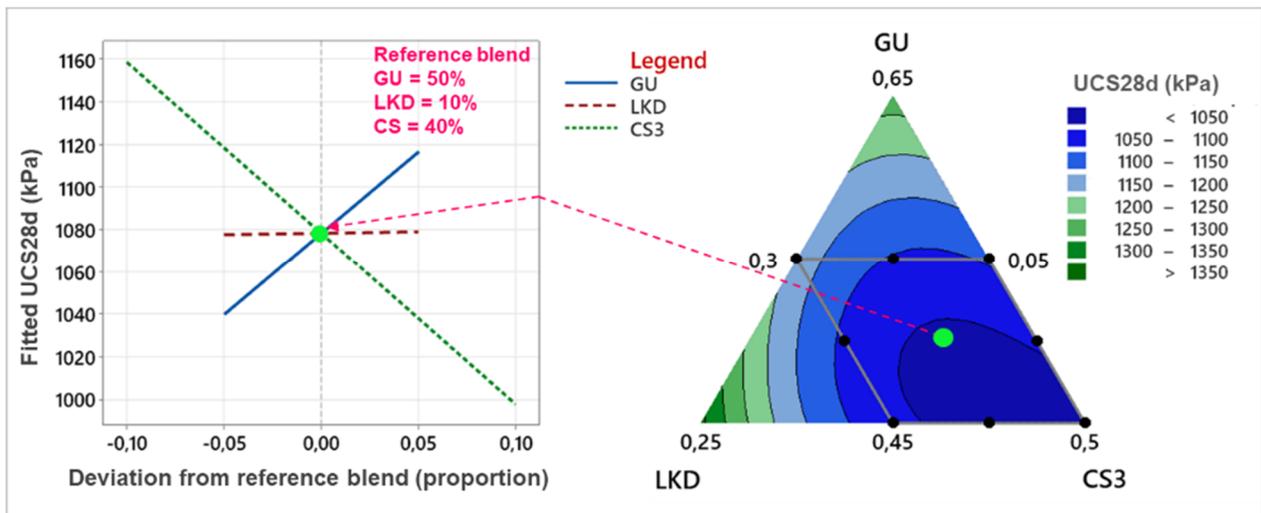
(a)

(b)

Figure 8   Cox trace plot and ternary diagram corresponding to UCS28d (kPa) of the ternary copper slag-general use Portland cement-lime kiln dust binder mixtures: (a) CS3; (b) CS4

4   Conclusion

The following conclusions can be drawn from the results presented :

- Mechanical activation has a positive effect on the Blaine SSA area (fineness) and the reactivity of the CS glass $(Zn_2, Fe_2) SiO_2$, significantly enhancing their mechanical strength, especially for CS2.

- It is possible to replace up to 30% of GU Portland cement with ground copper slags (GCS) without significant impact on UCS28d (ratio ≥ 0.8).

- Sulphate activation with a low concentration of Na_2SO_4 (N = 0.3) effectively achieves high UCS values (ratio = 1.11). This process enhances CS reactivity, promoting the production of an increased volume of hydrates, particularly C-S-H, which reduces the overall porosity of the SCPB. This method is advantageous on a large-scale, as Na_2SO_4 is a neutral, cost-effective and low-corrosivity salt.

- The incorporation of lime kiln dust, rich in free CaO, allows further reduction in the amount of GU Portland cement required for CS reactivity while achieving the UCS28d target for simulated mine backfill. It also contributes to cost reduction and a smaller carbon footprint for backfilling.

- Moving forward, it is essential to evaluate the short- and long-term reactivity (≥ 56 days) of CS in blends with actual mine tailings to validate their industrial application potential, considering the availability of byproducts and strength requirements. Comparative cement and blend quality tests will be conducted following EN196 standards for cement testing (European Committee for Standardization 2016).

Acknowledgement

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