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Admixture impact on rheological properties of a calcined clay binder for cemented paste backfill

S Dhers *Master Builders Solutions, Germany*

D Freimut *Master Builders Solutions, Germany*

Z Martic *Master Builders Solutions, Switzerland*

R Salter *Master Builders Solutions, Australia*

Abstract

Calcined clays appear to be one of the most promising supplementary cementitious materials to reduce the CO_2 footprint of cement, in particular the limestone calcined clay combination known as limestone calcined clay cement (LC^3). New and improved admixtures with tailored properties are necessary to ensure a broad implementation of LC^3 in the mining industry, to reach net zero. This study investigates the time-dependent rheological behaviour of cemented paste backfill (CPB) that contains calcined clay as a binder, using three admixtures, amongst which one is part of the Intelligent Cluster System (ICS) for low-clinker concrete technology. Yield stress and plastic viscosity have been reported and highlights the impact of the admixtures. A cradle-to-gate lifecycle assessment comparison between CEM I and the LC^3-35 binder (LC^3-35, containing 40% calcined clay, 20% limestone) is also detailed in this work. This study evidences the readiness of calcined clay binders for CPB, using the adequate high-performing admixtures.

Keywords: *cemented paste backfill, superplasticiser, calcined clay, LC^3, rheology, compressive strength*

1 Introduction

Mining is a crucial part of our societies, notably for several industries such as electronics and energy. However mining also generate significant amounts of waste, particularly in the accumulated volume of tailings, for example with the annual production of tailings exceeding 1.5 billion tonnes in China (Fall et al. 2016; Wei et al. 2022). Mine backfill is a way to dispose of tailings in a safer manner for the environment and can be done using different disposal techniques such as cemented hydraulic fill or cemented rockfill (Belem & Benzaazoua 2008). One of the most interesting is backfilling technique is called cemented paste backfill (CPB) which consists of a mix design comprising tailings, binder and water. Each component of CPB plays a significant role, and to ensure a good placement, curing and mechanical strength, a superplasticiser is usually of crucial importance and has a significant impact on the overall performances of the CPB mixture (Ouattara et al. 2018).

CPB is therefore one of the main axes to improve the overall sustainability of a mining operation and as such, is becoming increasingly significant, with Ordinary Portland Cement (OPC) remaining the most used binder due to its robustness and availability (Yan et al. 2020). However, in terms of sustainability, the CO_2 footprint of OPC shows a high global warming potential (GWP) value between 100 and 200 kg CO_2 per m^3 of concrete, on top of which the binder cost of OPC can reach up to 75% of the operating CPB costs (Hassani et al. 2007; www.oekobaudat.com).

In order to reduce both the costs linked to the binder and to lower the carbon footprint of the backfill mix design, one of the most prominent strategies is reducing the clinker content of the binder. To achieve this goal, the use of supplementary cementitious materials (SCMs) is one of the most promising paths (Scrivener et al. 2018, 2019a; Zieri & Ismail 2019). Traditional SCMs like fly ash and ground granulated blast furnace slag (GGBFS) are waste by-products of CO_2-emitting sectors, which will show limited availability in the future, which is where calcined clays have shown great promises. The calcination of clay do not release CO_2 directly (unlike clinker) and require a much lower calcination temperature, around 800°C (versus 1,350°C for clinker) (Diaz-Loya et al. 2019; Hache et al. 2020). LC^3 is the combination of clinker, calcined clay and limestone, which has been shown to reduce the CO_2 footprint of the binder by up to 50% (Scrivener et al. 2019b).

In this study, the time-dependent rheological behaviour of CPB containing calcined clay as a binder was investigated, using a formulation known as LC^3-35, containing only 35% OPC in the mix design. Three different admixtures have been tested, to demonstrate both the importance of admixtures in such low-CO_2 CPB mix design, and the readiness of these binders for CPB in combination with the right admixture.

2 Material and methods

2.1 Materials characterisation

Tailings samples used in this study were produced from an operational Australian copper mine and were milled in a laboratory ball mill for 30 minutes. The cement used in this study is a CEM I 52.5R obtained from a German cement producer (named CEM I in the study). The calcined clay used in this study originate from India (CC). Gypsum was used in the LC^3 composition to adjust sulfation.

A Mastersizer 3000 Malvern Panalytical was used for particle size distribution measurements (Figure 1) and a NOVATouch from 3P-Intruments was used for BET measurements. The reactivity of the calcined clay was measured following the R^3 test methods developed by and now part of the ASTM C1897 standard (Avet et al. 2016). A summary of these parameters is found in Table 1.

The mineralogical composition of the calcined clay samples weas measured with a D8 equipment from Bruker and quantified with external standard using Rietveld refinement. A summary of the main elements detected is given in Table 2.

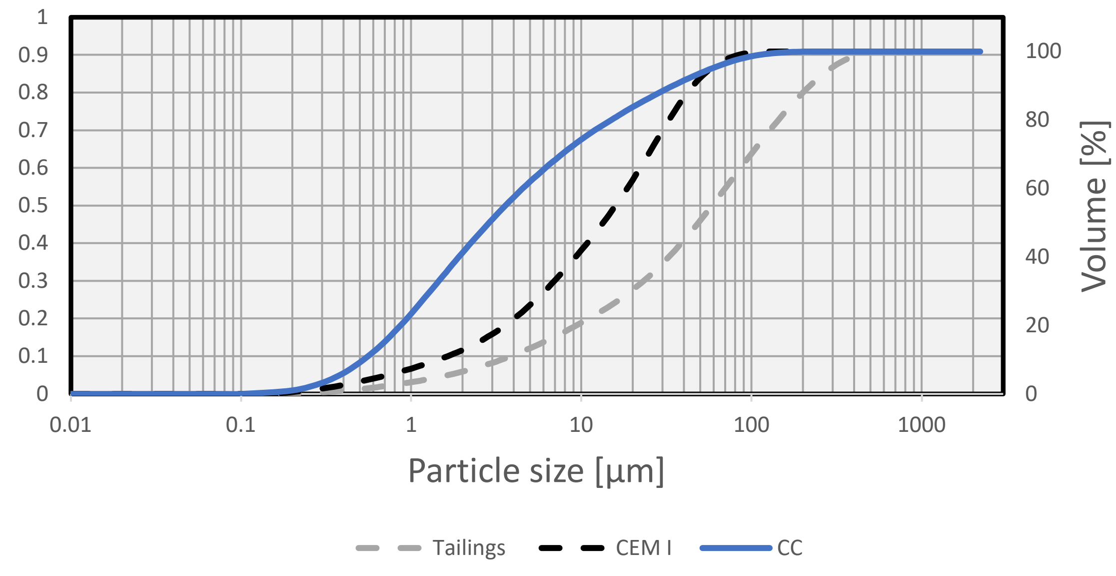

Figure 1 Particle size distribution of tailings, cement and calcined clay used in this study

Table 1 Particle size and specific surface area of OPC, limestone, gypsum and calcined clay samples used in this study, with R^3 test result for calcined clay

	d10 (mm)	d50 (mm)	d90 (mm)	BET (m^2/g)	R^3 (J/g of SCM at seven days)
CEM I	0.89	7.77	26.50	1.49	—
Tailings	3.3	48.5	219.2	0.97	—
Limestone	1.2	10	50	1.88	—
Gypsum	2	10	63	1.68	—
CC	0.5	3	36	9.41	648

Table 2 Quartz, clay minerals and amorphous content measured by quantitative XRD in the tailings and the calcined clay

	Tailings	Calcined clay
Quartz	41.9	14.0
Illite	—	1.5
Kaolinite	—	4.2
Feldspar	11.4	—
Dolomite	16.5	—
Mica	19	—
Amorphous content	—	71.7

2.2 Admixtures

All admixtures (SP1, SP2 and SP3) are pure polymers and were supplied by Master Builders Solutions. SP1 is a high range water reducer based on PCE chemistry with carboxylate anchor groups. SP2 is a different chemistry than PCE, with a polymer containing phosphate anchor groups. SP3 is a polymer with a delayed action, which is part of the new MasterCO_2re brand of superplasticisers for low-CO_2 concrete, using the Intelligent Cluster System (ICS) technology.

2.3 Sample preparation

Samples were casted using an IKA mixer (30 s stirring, 30 s rest, then 1 minute stirring) in 20 × 20 × 20 mm cubes (or transferred to the rheometer for rheology measurements, see Section 2.4). Samples for strength measurements were stored in a climate chamber at 80% rH and 30°C. A typical mix design (total 404.86 g) is described here: 78% solid content, including 95% tailings (= 300 g) and 5% binder (= 15.79 g), with 22% water including 0.2% of admixture SP1 (= 0.2 g, equivalent of 500 ml/tonne of backfill mix) or 0.4% for SP2 and SP3. The water used in this study is distilled water. Two binders were used in this study, a CEM I obtained from Germany, and an LC^3 binder named LC^3-35, containing 35% CEM I, 40% calcined clay, 20% limestone and 5% gypsum.

2.4 Rheology testing

The rheological behaviour of CPB slurries was measured using an Anton Paar HAAKE viscometer MCR 502 rheometer. Rotational tests were carried out in an annular vane-in-cup geometry to reduce the risk of wall slippage during measurements. The measuring device was a vane stirrer with six blades, a length of 16 mm and an equivalent diameter of 22 mm. The cup had gear diameter d = 28.52 cm and a bigger diameter

D = 29.85 cm. The mixed sample (according to the procedure described in Section 2.3) was put in the rheometer and a linear ramp up from 1 to 100 s^{-1} over one minute and a linear ramp down from 100 to 1 s^{-1} in one minute, and this ramp was done at 7.5 minutes and repeated every 15 minutes over 2 hours, with a pre-breaking of the structure of 20 s^{-1} for one minute followed by a one minute rest before starting the ramp measurements.

The Bingham model was used to describe accurately all the CPB systems studied using the down ramp (as demonstrated by good correlation coefficients), described by the equation:

$$\tau = \tau_0 + \eta\alpha \quad (1)$$

where:

τ = shear stress (Pa)

τ_0 = yield stress (Pa)

η = plastic viscosity (Pa.s)

α = shear rate (s^{-1}).

2.5 Lifecycle assessment and global warming potential

The cradle-to-gate lifecycle assessment (LCA) of the CBP recipes was performed with OneClick LCA program using global Ecoinvent 3.8 data. To provide a comprehensive benchmark against real-case scenarios, we assessed one additional CBP formulation using CEM I as the binder without any chemical admixtures versus the LC^3-35 mix design. The primary objective is to demonstrate the ecological optimisation possibilities of CBP using calcined clay as part of the binder composition, to reduce GHG emissions in mining (Song et al. 2017). The functional unit is defined as 1 tonne of backfill. Generic global datasets are used (www.oekobaudat.com). For calcined clay, the values were taken out of reference as an average 100 km (Scrivener et al. 2019b). The transportation distance for OPC, other SCM and admixtures are set to 1,000 km for both transportation scenarios, based on the remote location of a typical mineral mine.

2.6 Cost calculations

Raw material cost of clay is considered zero, as in this scenario it is assumed that it would be property of the mine. The transportation cost for 100 km clay averaged at a cost of USD 23/tonne (Scrivener et al. 2019b). On top of which USD 50/tonne were added for calcination costs. For OPC and GGBFS we assume the price of raw material and transportation together on the same level, USD 250/tonne. Limestone and gypsum were assumed, for both raw material and transportation cost, to be at USD 50/tonne.

3 Results and discussion

3.1 Yield stress

The yield stress of the paste mixes with and without admixtures as a function of time are shown in Figure 2. Time points are collected starting at 7.5 minutes, and then measurements are done from 15 to 120 minutes every 15 minutes. The first observation is that the yield stress obtained when using LC^3-35 is higher than CEM I, which has been demonstrated in the literature (Bahhou et al. 2021; Dhers et al. 2023), evidencing here the increase rheology and decreased workability of this type of binder in CPB.

All three admixtures lower the yield stress of the calcined clay binder significantly, from 204 Pa for the LC^3-35 reference, to values as low as 117 Pa for SP3. Over the first hour, the admixtures can be ranked in terms of increase performance from SP1 to SP2 to SP3, whereas between 1 and 2 hours SP2 shows an increase in yield stress that follows the increase of LC^3-35 without admixture. Between 1 and 2 hours, SP1 is staying constant and SP2 is increasing that follows the increase of LC^3-35 without admixture, giving a ranking of admixtures as follows on performances: SP2, SP1 and SP3.

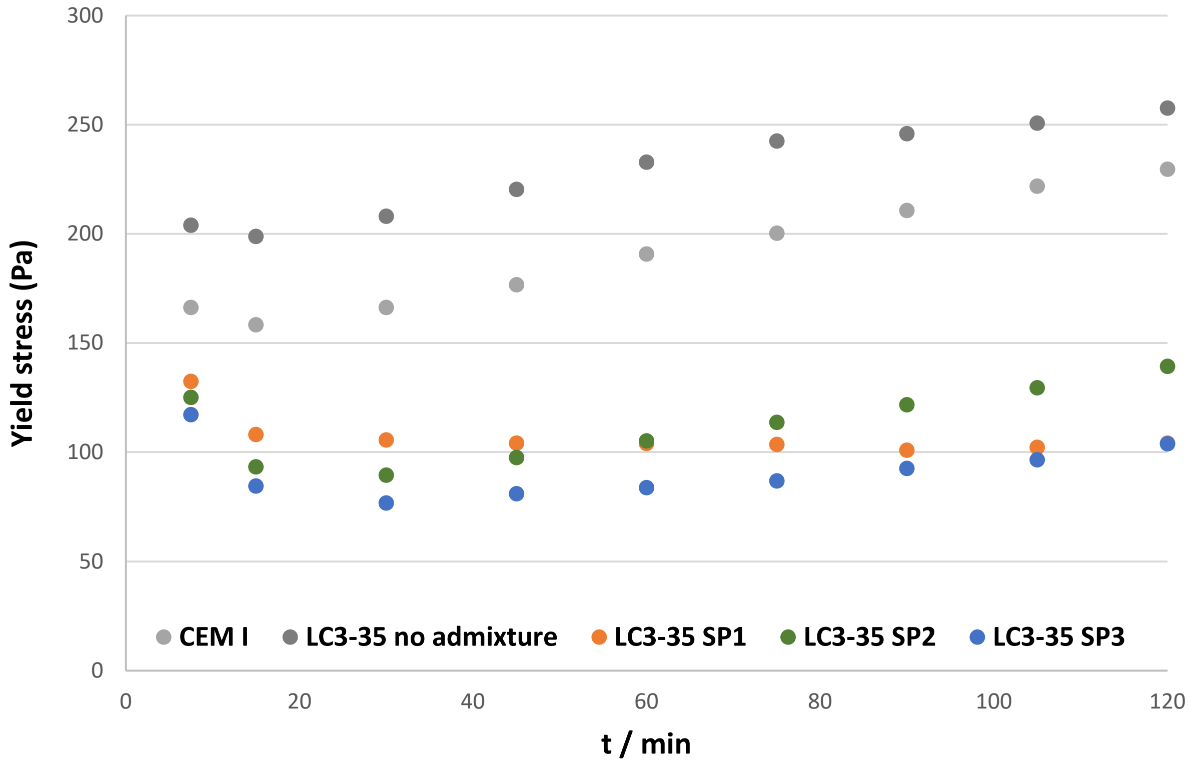

Figure 2 Yield stress measured over 120 minutes with CEM I (light grey), with LC^3-35 using no admixture (dark grey), with LC^3-35 using admixtures SP1, SP2 and SP3 (respectively orange, green, and blue)

In Table 3, the reduction in yield stress is reported as an average percentage reduction over the measurement time, i.e. the average of the reduction in percent obtained for each nine points measured over 2 hours. Two different references are taken, CEM I and LC^3-35, both without admixture, to underline two comparisons: first, how a backfill mix design with LC^3-35 as a binder and a high-performing admixture would compare to a pure CEM I backfill mix design. Second, the gain obtained by using high-performing admixtures in an LC^3-35 backfill mix design. Note that the average difference in percent between the two references without admixture is 20%, which gives an idea of the loss of workability obtained from using the LC^3-35 mix design.

As evidenced in Figure 2, the difference in percent shown in Table 3 highlights the strong contribution of all three admixtures to lowering the yield stress, regardless of the reference taken, CEM I or LC^3-35. SP1 and SP2 showed similar values for both references with a slightly better reduction for SP1, respectively 43 and 53% versus 41 and 51%. However, SP2 showed better performances over the first hour (Figure 2), whereas SP1 is performing better than SP2 between 1 and 2h. On the other hand, SP3 outperforms both admixtures in both references, with 9% more than SP1 compared to CEM I, and 7% more compared to LC^3-35.

Table 3 Reduction in yield stress, in percent, obtained using superplasticisers SP1, SP2 and SP3 (the values given here are an average of the reduction obtained for each time point from 7.5 to 120 minutes)

Difference in percent/superplasticiser	SP1	SP2	SP3
CEM I (average reduction over time)	**43%**	**41%**	**52%**
LC^3-35 (average reduction over time)	**53%**	**51%**	**60%**

3.2 Plastic viscosity

The plastic viscosity for CPB samples with different binders as a function of time is presented in Figure 3. The impact of the admixtures is particularly visible up to 1 hour, with the reduction in plastic viscosity being highest at the first time point, 7.5 minutes, with a lowering in LC^3-35 from 2.1 to 1.6 Pa.s using SP2 and SP3, and 1.5 Pa.s when using SP1. In the first hour, SP1 shows the lowest plastic viscosity of all three admixtures, with SP3 showing a reduction that levels with the plastic viscosity of CEM I. Between 1 and 2 hours, SP2 show an increase in plastic viscosity whereas both SP1 and SP3 shows a similar plastic viscosity as the reference mix LC^3-35 without admixture.

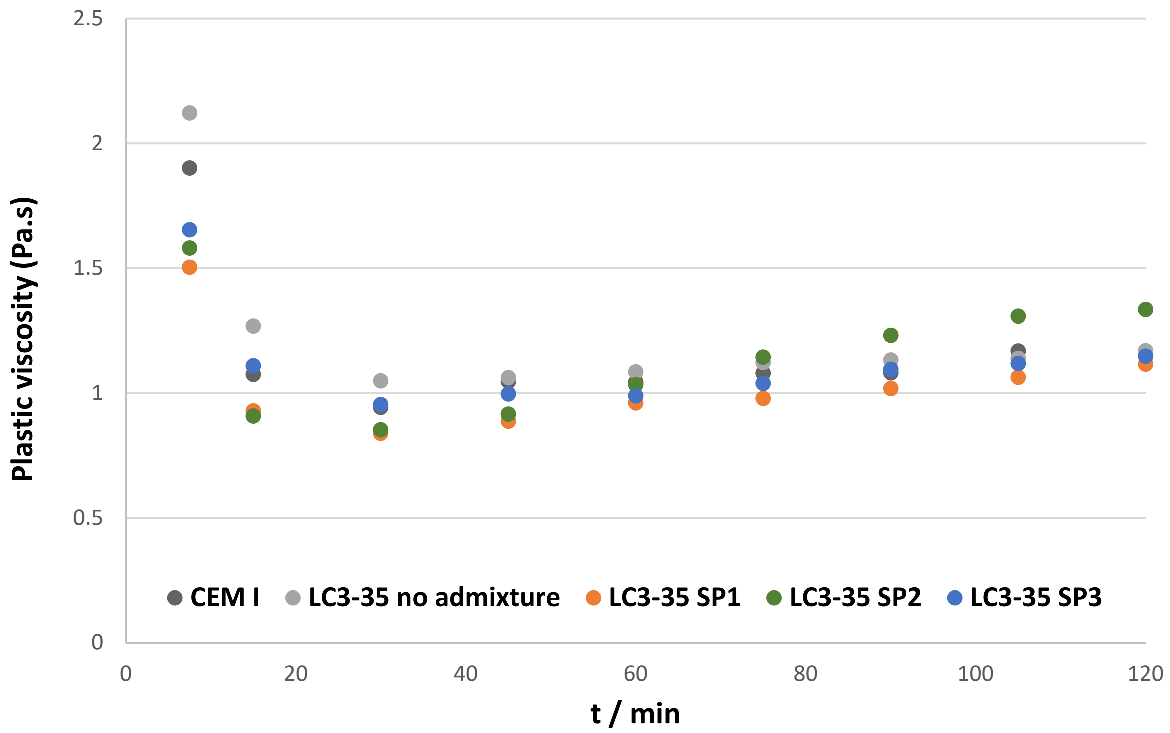

Figure 3 Plastic viscosity measured over 120 minutes with CEM I (light grey), with LC^3-35 using no admixture (dark grey), with LC^3-35 using admixtures SP1, SP2 and SP3 (respectively orange, green, and blue)

Overall, the reduction in plastic viscosity is substantial using admixtures and is most prominent in the first 30 minutes. Coupled with a high lowering of the yield over the time period studied of 2 hours, the benefit of superplasticiser is clear and does appear essential to enable low CO_2 binder such as the LC^3-35 system studied here to be brought in CPB.

3.3 Lifecycle assessment study: ecological and economical comparison

The results of the LCA study and the resulting GWP parameters are presented in Table 4. The changing parameters are in the A1 and A2 phases, while the GWP of the A3 phase is considered the same for both scenarios (the A3 phase includes the energy and fuel required for mixing and pumping of CBP). In these calculations, it is assumed that the mine imports all materials except for calcined clay, which belongs to the mine, and is calcined on the mine facility. The values given here for GWP and cost reductions are intended to serve as an estimation, giving a general trend while keeping in mind that every region and mine operates differently, clearly requiring a more in-depth analysis for each case. With that in mind, the results obtained in this LCA study are still quite striking.

The reduction in GWP going from CEM I to LC^3-35 is calculated to be 45 down to 19 kg CO_2e/1 tonne CBP, highlighting the significant impact that incorporating calcined clay into the binder would have on the carbon footprint of the backfill operation of the mine (Table 4). The cost reduction is also substantial, from USD 13.3 to USD 8.2 per tonne of backfill paste, leading to an impressive savings of USD 5.1 per tonne. Capex costs are not included and a case-by-case return on investment has to be made, however, based on the literature reference (Scrivener et al. 2019b) used for cost calculations, the return on investment should be around five years for cement, which should be significantly lower in the case of backfill due to larger volumes.

Table 4 Summary of the global warming potential (GWP) obtained for the LCA study as well as cost calculations, for both binders, CEM I and LC^3-35

	Lifecycle phase	CEM I	LC^3-35
GWP-fossil (kg CO_2e/1 tonne CBP)	**A1**	45.5	18.9
	A2	5.0	2.5
Costs (USD/1 tonne CBP)	–	13.3	8.2

Another way to look at the data generated during this LCA study in Table 4 is to normalise to the pure CEM I mix design and express these results in percent, as shown in Table 5. It is then even more apparent that the savings made by using this LC^3 binder in CPB are remarkable, with 59 % for GWP on A1, and 52 % for GWP in A2 (Table 5, top), and a costs savings of 39% depending on the variant (Table 5, bottom). It is important to note that the distance of the calcined clay to the mine can have a significant impact particularly on cost, which could give an even higher reduction in final cost of the binder (Scrivener et al. 2019b).

Table 5 Global warming potential (GWP) and cost savings (presented in % difference to the pure OPC reference) for LC^3-35

	Lifecycle phase	CEM I	LC^3-35
GWP saving (%)	**A1**	0	59
	A2	0	52
Costs saving (%)	–	0	39

4 Conclusions

The present work highlights the readiness of calcined clay and LC^3 technologies for use in backfill mining. The significant reduction in yield stress obtained with all three superplasticisers shows the impact of admixture in this type of binders for CPB. This rheological study demonstrated and emphasised the imperative need for high-performance admixtures when dealing with low CO_2 binders that will bring new challenges, amongst which lower workability and increased rheology. On the other hand, this work also demonstrated potential savings of more than 50% in GWP and close to 40% in cost. LCA studies are becoming the standard for sustainability, and further work should include the incorporation of more parameters, such as the ecotoxicity of tailings or the impact of admixture on the flowability of CPB, yielding a higher productivity and a reduction of maintenance costs.

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