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From the laboratory to large scale: Siderite ($FeCO_3$) and calcined clays as supplementary cementitious materials for sprayed concrete applications

Abstract

Siderite ($FeCO_3$) and calcined clays together with other raw materials were tested as new CO_2-friendly SCMs to develop blended binders for shotcrete, aiming to enhance the resulting recipes in terms of strength, durability, and sustainability. Tests were carried out in the lab and real scale. In both cases, promising early-strength results were measured. Future tests will be performed to characterize the impact of siderite and clays on late strength and durability of the developed mix designs.

Introduction

Supplementary cementitious materials (SCMs) are an efficient measurement for significantly lowering the global warming potential (GWP) of concrete and sprayed concrete (shotcrete) while improving qualities such as durability, strength, or workability [1]. However, the steady decline in the availability of commonly used SCMs - such as fly ash and blast furnace slag- raises the need to find new sources of raw materials suitable as SCMs for composite binders.

Our research group has recently discovered the potential use of siderite ($FeCO_3$), mined e.g. at the Austrian Erzberg deposit, as an SCM in concrete and shotcrete applications. Siderite has shown prospects of enhancing important durability properties of shotcrete such as reduction of sintering potential or decreased expansion due to sulfate attack, both of which highly relevant for tunnel applications [2]. Inconveniently, siderite has also shown a significant decrease in early strength in both accelerated and non-accelerated mortar mixes in laboratory tests.

Other already commonly used SCMs, such as ultrafine limestone powder ($CaCO_3$) or ground granulated blast furnace slag (GGBFS) show enhancement of early strength of shotcrete (Limestone), or improvement of durability properties (GGBFS), but each one comes with drawbacks. Limestone as the only supplement seems to increase the leaching potential of calcium in the mixes [3], while the availability of GGBFS is declining as steel industries change to electric furnaces. Substituting GGBFS is of particular importance for future sustainable solutions in concrete and shotcrete, but this is not so easy, as this material comes with great advantages for cementitious systems [4].

Calcined clays greatly enhance the early strength of concrete, and have shown to improve the resistance to chloride attack [5]. The temperature of calcination is an important factor in its reactivity, as different temperatures will impact the reactivity of the clays [5].

In this contribution the behavior of siderite and clay-containing binders in terms of early strength development and their potential use for shotcrete applications is explored.

Materials and methods

Materials

For both laboratory and real-scale tests, CEM I 52.5 R complying with [6] was used. GGBFS, ultrafine limestone powder (UFL), two types of clays calcined at different temperatures, siderite, and waste material from the production of siderite at Erzberg - from here on called barren rock (BR) - were used as binder components. The characterization of the raw materials can be found in Table 1.

An alkali-free, aluminumsulfate-based setting accelerator (SA) was added to every mix. A PCE-based superplasticizer was added to each laboratory and real-scale mixture until a slump of 200 ± 20mm (without hits) was reached.

Tab. 1 Chemical composition of SCMs

Chemical composition						
Oxide (wt%)	Siderite	BR	Clay 1	Clay 2	UFL	GGBFS
SiO_2	5.01	12.38	69.20	49.12	1.10	37.60
TiO_2	0.07	0.14	0.77	0.74	-	0.50
Al_2O_3	1.10	2.51	17.31	17.49	0.10	12.10
FeO	51.73	20.00	-	-	-	-
Fe_2O_3	-	-	2.22	6.60	0.10	0.40
MnO	3.05	1.37	<0.50	0.14	-	1.30
MgO	3.38	5.24	0.07	4.29	1.50	9.40
CaO	3.58	23.61	0.22	5.22	54.60	36.40
K_2O	0.40	0.90	0.76	3.48	-	1.10
Na_2O	-	-	<0.50	0.39	0.10	0.40
P_2O_5	0.06	0.09	0.13	<0.10	-	-
SO_3	0.11	0.20	-	-	-	-
LOI	31.46	33.50	9.05	11.55	42.60	<0.10
ρ(g/cm^3)	3.66	3.10	2.25	2.60	2.72	2.92
Mineralogical composition						
Amorphous			52.86	41.13		97.70
Calcite	3.50	9.90	0.24	1.58	95.50	
Dolomite			1.35	3.42	3.90	
Microcline				1.08		
Kaolinite			10.48	4.62		
Gehlenite						1.60
Phengite			4.79	7.79		
Clinochlore			8.08	8.87		
Biotite			6.20	7.58		
Chamosite			1.24	0.16		
Alite						0.60
Siderite	72.60	8.50				
Ankerite	3.40	47.40				
Quartz	8.20	16.20	4.08	7.93		
Illite	10.10	12.00	6.74	10.26		
Albite			0.11	2.06		
Gypsum			0.22			
Anhydrite			0.15	2.19		
Vermiculite			3.46	1.28		
Phlogopite	2.20	6.00				

For the laboratory tests, standard sand (NS) in compliance with [7] was used as fine aggregate. For the real-scale tests, dolomitic aggregate 0-8mm was used, and 0.13% of air-entraining admixture (AEA) was added. Table 2 summarizes the composition of the mixes.

Methods

For laboratory tests, mortars were mixed following [7] with two slight modifications: a) After the stipulated mixing time, one extra minute was included for the addition and mixing of the superplasticizer, and b) the samples were left to hydrate for 10 minutes before adding the accelerator. The accelerator was mixed for 15 seconds and quickly cast into molds. The 6h and 24h compressive strength tests were carried out according to [7].

For real-scale samples, wet mixes of shotcrete were sprayed into boxes with a PM 500 spraying machine. The early strength was measured with a Sauter FL penetration needle for the first hours of strength development, and with a Hilti BX 3-SCT at 6h and 24h according to [8].

Results and Discussion

Laboratory tests

Figure 1 shows the 6h and 24h compressive strength of the laboratory mixes, which served as a base for the design of the mixes carried out in the real-scale test.

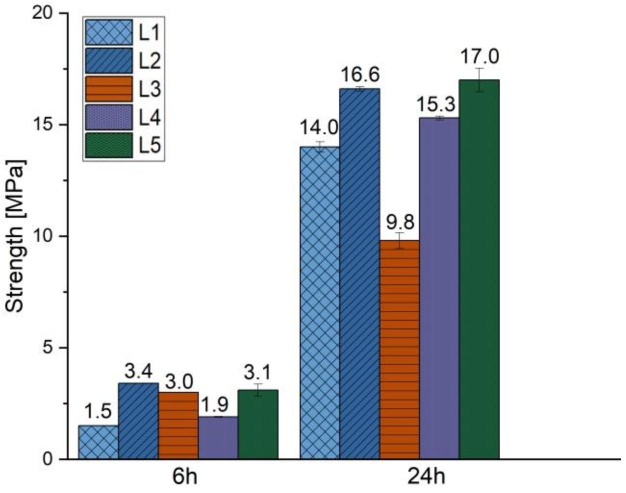

Fig. 1 Early strength results of laboratory (L) mixes

For the mixtures with siderite, mix L1 has the lowest strength at 6h, showing the retardation effect of siderite in cement hydration. Notably, when substituting a percentage of GGBFS with UFL (Mix L2), the 6h strength of the mix duplicates. At 24h, this mix also holds one of the highest values. Despite having only 50% cement, mix L3 portrays one of the highest values of strength at 6h.

Tab. 2 Mix composition of laboratory (L) mixes and real-scale shotcrete (S) mixes with 7% accelerator. S mixes contain 0.13% AEA

Mix	CEM I (%)	GGBFS (%)	UFL (%)	Clay 1 400°C (%)	Clay 1 500°C (%)	Clay 1 600°C (%)	Clay 2 800°C (%)	Siderite (%)	BR (%)	Dolomite 0-8 mm (kg/m^3)	Total binder (kg/m^3)	NS (kg)	w/b	PCE (%)
L1	67	23	-	-	-	-	-	10	-	-	-	1.35	0.5	0.87
L2	67	13	10	-	-	-	-	10	-	-	-	1.35	0.5	0.9
L3	50	17	10	-	5	-	8	10	-	-	-	1.35	0.5	1.44
L4	67	23	-	-	-	-	-	-	10	-	-	1.35	0.5	0.87
L5	67	-	10	-	5	-	8	-	10	-	-	1.35	0.5	1.44
S1	65	-	7	5	-	-	10	13	-	1835	420	-	0.45	3.5
S2*	69.6	-	8.4	11	-	5.2	-	5.9	-	1548.1	314.8	-	0.58	3.5

NS=Normsand, BR=Barren Rock ; *Mixture had 6% of accelerator and macrofiller, which was composed of 210 kg/m^3 of siderite fraction 0.1-1mm and 218.3 "Weißjuramehl" fraction 200µm kg/m

However, at 24 hours the development slowed down, reaching a strength of ~10 MPa. Calcined clays in accelerated binary systems with CEM I showed high early compressive strength in preliminary tests (data not shown). In this case, it seems that calcined clays do not completely compensate for the early strength loss caused by siderite in composite binders.

Mix L4 shows a similar composition to mix L1, but the siderite was replaced by BR. Interestingly, mix L4 shows a similar strength development as L1, with slightly higher values at 6h. Presumably, this happens due to the less reactive nature of the waste material, which would have similar but less pronounced reaction patterns as siderite.

Remarkably, substitution of GGBFS with clays (maintaining 10% usage of UFL) led to similar strength results (L5 versus L2). Considering the future lack of availability of GGBFS, this mixture shows great prospects for future composite shotcrete binders.

Real-scale tests

While both mixes L2 and L5 had the most favorable strength development, L5 was the most interesting since it had no GGBFS and favorable early strengths.

Based on mix L5, mixes S1 and S2 were designed to be tested on a large scale. While, originally, mix L5 contained BR, siderite was used for both shotcrete mixes due to a lack of availability of the BR. Additionally, results from mixes L1 and L4 seemed to indicate that this substitution would not have a big effect on the mixture.

The early strength development of the two shotcrete mixes is shown in Figure 2. In the first hours mix S1 was in the J1 class. After around 2 hours the mix reached the early strength class J2. The early strength of mixture S2 reached class J2 after 15 minutes.

Both mixes show compliance with a J2 curve according to [8]. With these results, a prospect for composite binders without GGBFS is shown. Nevertheless, late strength and durability tests need to be carried out to further study the feasibility of the mixtures. Additionally, the ambient temperature was roughly 30°C, which could artificially increase the strength results. Testing the mixtures at lower temperatures is recommended for future work.

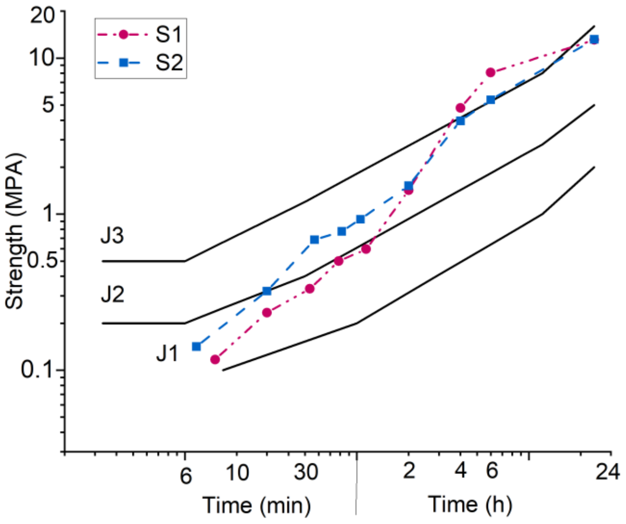

Fig. 2 Early strength development of shotcrete (S) mixes

Conclusions

While siderite has a retardation effect on concrete and consequently decreases its strength at early ages, optimized combinations with other raw materials can mitigate these effects. In the case of siderite-containing binders, limestone seems to best alleviate the inhibition of cement hydration caused by siderite. However, to refrain from using GGBFS without increasing the cement content, calcined clays were crucial in the mixes. To further investigate the viability of the presented shotcrete mixtures, late strength and relevant durability parameters will be assessed. Regardless, achieving acceptable early strengths in composite binders with siderite and calcined clays is an impactful step towards more sustainable solutions for shotcrete.

Finally, laboratory experiments are essential for an in-depth understanding of reaction pathways and for the systematic development of suitable mixes. Nonetheless, their ideal environmental conditions do not replicate real life accurately. Thus, real-scale experimentation can give the most realistic perspective on the suitability of a mixture and both approaches should be used complementarily.

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