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INFLUENCE OF ADDITIVES ON THE FRACTURE MECHANICAL PROPERTIES OF REACTIVATED CEMENT PASTE

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Abstract: Since the production of cement is very CO_2-intensive alternative binders are on the rise. The reactivation of cement has proven to be possible. Attempts are being made to find out, how it can be used as a binder or clinker supplement. A problem to solve is that, so far, the mechanical strength is not as high as the one of the original binder. Reasons for that are a new chemical composition with a different variety of strength giving phases and the morphology of the reactivated grains. The new powder shows high inner porosity and a much bigger specific surface area. This work aims to increase the mechanical strength of reactivated cement by using two types of additives. First, milling agents that are added during the milling process. In this study ground blast furnace slag (GBFS), copper slag (CuS) and electric arc furnace slags (EOS) were used. Further additives are added during the mixing of cement and water. Microsilica (MS), concrete plasticizer, superplasticizer and retarder have been chosen. Parameters that were tested are compressive strength, porosity and fracture toughness. While GBFS gives the highest compressive strength, chemical admixtures increase the strength of reactivated cement paste as well. The fracture toughness is a stable value whereas porosity and strength vary for reactivated cement.

1 INTRODUCTION

Cement production takes a big part in worldwide industrial CO_2-emissions with a yearly outlet well above 1.5 million tons over the past 10 years [1]. This corresponds to about 8 % of the yearly worldwide emissions [2]. In the quest for more sustainability, these figures must decrease. One approach to reduce the carbon footprint is the recycling of cement regained from concrete waste. Research in this field started in the early 2000s and has increased over the years.

A recycling process seems possible, because hydrated cement exposed to heat shows dehydration of the CSH-phases and the recovery of Belite as a strength-giving phase [3, 4]. During rehydration new hydration phases form. One of the current challenges regarding reactivated cement is its loose and porous particle morphology [5]. Reactivated cement grains tend to have a less dense crystalline structure [6]. While in most cases the particle size of reactivated material is bigger, the specific surface area is nonetheless much higher due to the porous structure [5, 7]. That porosity causes an immediate reaction on the outer surface but also inside the grain as soon as it is mixed with water [8]. This in turn leads to a high water demand and shorter setting times which means reduced workability. All these factors result in a generally higher porosity in the reactivated cement stone [5, 7, 9]. A review by Zanovello et al. includes a collection of results of the compressive strength of reactivated cements and the corresponding porosity. As the porosity is in general higher for cements and mortars that include reactivated material, the compressive strength decreases accordingly. The strength-porosity correlation commonly known for ordinary Portland cement therefore also applies to reactivated material [10].

Overall, the compressive strength is in a range where reactivated cement is too weak to be used individually. This has led to a series of studies about reactivated cement as a supplement for clinker [11, 12]. While this seems promising, supplementing more than 15 % leads to reduced strength. That means the mechanical strength of reactivated cement in general needs to be improved. In many studies chemical admixtures have been used to delay the hardening and improve the workability. The selection of these was mostly without strategy. Carrico et al. used a polycarboxylate based superplasticizer [13, 14] as well as Real et al. and others to meet the required consistency for working with reactivated cement [10, 15]. So far one study has been conducted where a variety of additives was strategically tested. In 2019 Zhang et al. investigated the effects of retarder on setting and hardening behavior of reactivated cementitious materials showing that the setting time, the microstructure and the mechanical properties can vary under the influence of different retarders during hydration [16].

Another approach to increase the mechanical strength is to adjust the microstructure by using slags as milling agent and additionally use the effect as a pozzolanic material. Zhang et al. found out, the greater hardness of slag particles helps to break up the microagglomerates of the cement particles and increases grinding efficiency. A greater grinding fineness leads to more hydrate phases that are formed on the outside of the cement particles [8]. Slags are already used as a clinker supplement due to their pozzolanic reaction [17–19]. Slags can also improve the strength of reactivated cement [8, 17]. Pozzolanic materials that have been studied so far in the context of cement recycling are fly ash [20–22], ground blast furnace slag [8, 20, 22], and lime stone [20].

In all studies mentioned above, a big variety of parameters has been looked at with many different foci. Our study is a groundwork for a fracture mechanical approach on the use of additives for reactivated cement. Therefore, a selection of additives, one group used as a milling agent and a second group used as admixtures, has been tested for porosity, compressive strength and fracture toughness. Based on these results, a large-scale study on the influence of additives can be designed.

At 28 d ground blast furnace slag gives the highest compressive strength due to a decrease in porosity. Chemical admixtures increase the strength, more likely due to improving the workability. The fracture toughness is a stable value indicating that the overall quality of the chemical bonding in the matrix is good.

2 EXPERIMENTAL PROGRAMS

In this study ordinary Portland cement CEM I 52.5 R (VCe) (Portlandzementwerk Wittekind Hugo Miebach Söhne KG) was used to produce reactivated cement and tested as a reference material.

For the preparation of reactivated cement, in a first step VCe was mixed according to the mixing and densification steps as described in DIN EN 196-1 with a water/cement ratio (w/c ratio) of 0.5 [23]. After 1 d curing in a covered mold, the hardened specimens were stored in water for 27 days. After a total of 28 d hydration the cement stone was mechanically crushed in a jaw breaker. Then, the crushed cement stone underwent a heat treatment at 650 °C for 1 h with a heating ramp of 5 °C/min. Following the thermal treatment, the reactivated material was milled in a planetary mill down to a maximum grain size of 250 µm, resulting in the reactivated cement powder (RVCe).

For the reactivated cement different additives were used that were added during the preparation of the samples. Table 1 shows the recipes of the mixtures prepared. If slag was used as an additive, slag particles ≤ 250 µm were added before the milling process.

Table 1: Mixture recipes

Cement	Additive	Amount	w/c ratio
CEM I 52.5 R (VCe)	-		0.5
RVCe	-		0.75
RVCe	Ground blast furnace slag (GBFS)	50 m.-% RVCe	0.45
RVCe	Copper slag (CuS)	50 m.-% RVCe	0.45
RVCe	Electric arc furnace slag (EOS)	50 m.-% RVCe	0.45
RVCe	Microsilica (MS) + Super-plasticizer	5 m.-% RVCe + 1.5 m.-% water	0.75
RVCe	Concrete Plasticizer MC-TechniFlow 41	1.5 m.-% water	0.65
RVCe	Super-plasticizer MC-PowerFlow evo 303	1.5 m.-% water	0.65
RVCe	Retarder Centrament Retard 371	1.5 m.-% water	0.65

Slags that were tested were ground blast furnace slag (GBFS), copper slag (CuS) and electric arc furnace slag (EOS). Additives that were added during mixing were micro silica (MS), retarder, concrete plasticizer, and superplasticizer.

2.1 Sample Preparation

There is an individual processing time for each recipe when mixed with water. RVCe in general reacts faster than VCe. Therefore, mixing durations as proposed in the standard only work for reference samples from VCe [23]. For RVCe the mixing and densification times had to be shortened but care must be taken to ensure proper homogenization. The freshly mixed paste was poured into molds and densified on a vibrating table. After 1 d hardening in the mold and 27 d of curing in water the subsequent tests were conducted at 28 d.

2.2 Compressive Strength and Porosity

Commonly the flexural and compressive strengths are tested on prisms sized 40 x 40 x 160 mm. In this study that process was changed. Each prism was used for compressive strength and porosity testing by sawing it into three equal parts as presented in Figure 1. For statistical validation 3 prisms were tested, generating 6 compressive strength results and 3 porosities per mixture.

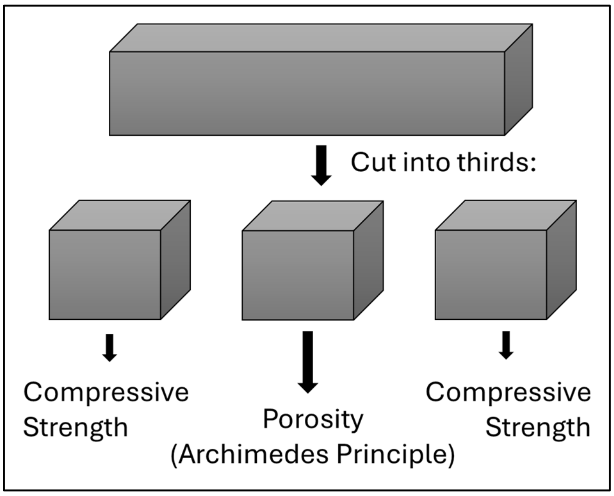

Figure 1: Prism testing

Strength testing was conducted according to the standard [23]. Porosity was calculated with the mass of the 28 d old saturated samples outside water, under buoyancy and the mass of the dry sample by application of Archimedes' principle [24].

2.3 Fracture Toughness

For fracture toughness testing the geometry of the compact-tension specimen were used as shown in Figure 2 originally known from metallurgy. The molds for compact-tension (CT) specimen are made from silicon and already include the holes for fixation. The notch was cut with a circle saw after demolding. Five specimens of each mixture were tested. A detailed description of the testing procedure can be found in [25].

Figure 2: Compact-tension (CT) specimen for fracture toughness testing (48 x 50 x 8 mm)

The CT sample is fixed into an ARCO-CT device (Advanced Rigid Crack Opening on CT-samples, Rödel & Isaia GmbH, Mühltal, GER), an extra rigid frame. The load is applied to the sample over the fixation to open the notch and create a progressing crack. The displacement is controlled via a piezo transducer. Once the crack propagates, the toughness can be calculated with the failure load and the geometry of the specimen [26].

3 RESULTS AND DISCUSSION

A rich experimental program regarding the fracture mechanical properties of reactivated cement should give an idea about what process or mixture gives the highest mechanical strength and ideally give reasons for that. Figure 3 shows the compressive strength results from this study. The addition of GBFS has the effect of increasing the compressive strength of reactivated cement by nearly 90 %. With a strength of 34.5 MPa the mixture reaches one of the official strength classes set for cement [27]. All other slags as well as microsilica do not have a significant influence on the strength, even though, testing at one age only, in this case 28 d, does not allow assumptions about the individual pozzolanic reactions. More sample ages and a longer testing period are needed for proper comparison of mixtures and the correlated strength increase based on pozzolanic reactions. The chemical admixtures all significantly increase the mechanical strength. The addition of retarder generates the highest strength, all results are in a similar range.

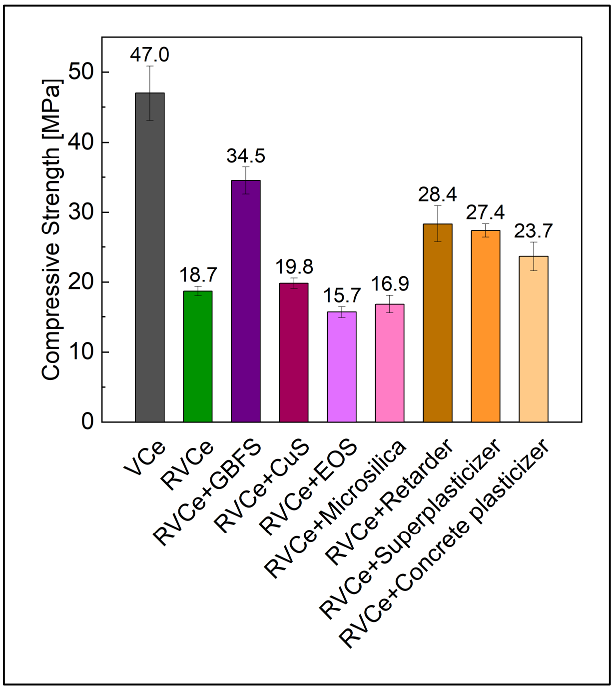

Figure 3: Compressive strength results.

The compressive strength itself gives no answers about why certain additives have an influence on the mechanical properties of RVCe. Figure 4 shows the strength results in correlation with the porosity.

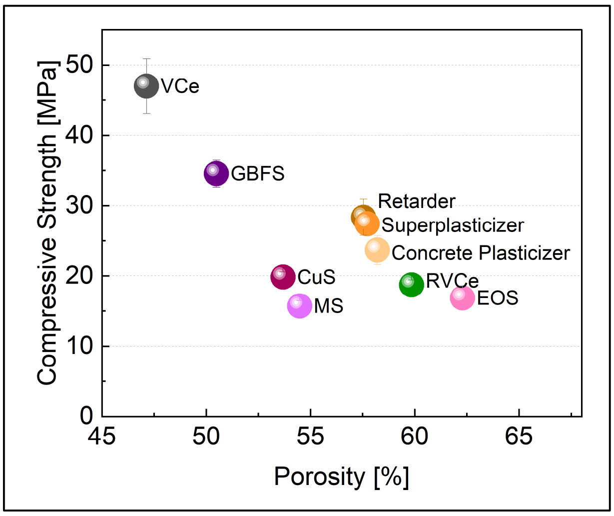

Figure 4: Compressive strength – porosity results.

The overall behavior fits with literature where increasing porosity leads to a decrease in strength [10]. It is very prominent that the addition of GBFS decreases the porosity. To what extent there are other processes that increase the mechanical strength cannot be answered. The fact that copper slag and micro silica decrease the porosity significantly without having an influence on the strength and even slightly decreasing it indicates that there are more processes contributing to GBFS strength. These processes could be amongst others a pozzolanic reaction or a milling effect changing the microstructure of grains and hardened cement paste.

The results of the chemical admixtures as well show that porosity is not the only factor influencing strength. When added to RVCe the resulting strength increases whereas the total porosity is still close to that of RVCe without additives. A more detailed analysis of the defect structure is needed in this case. It might be that, due to the better workability, the pores are distributed more equally in the volume. In addition, the rapid hardening can result in predetermined breaking points where two layers of material were never fully mixed. The use of retarders and superplasticizers might reduce this effect.

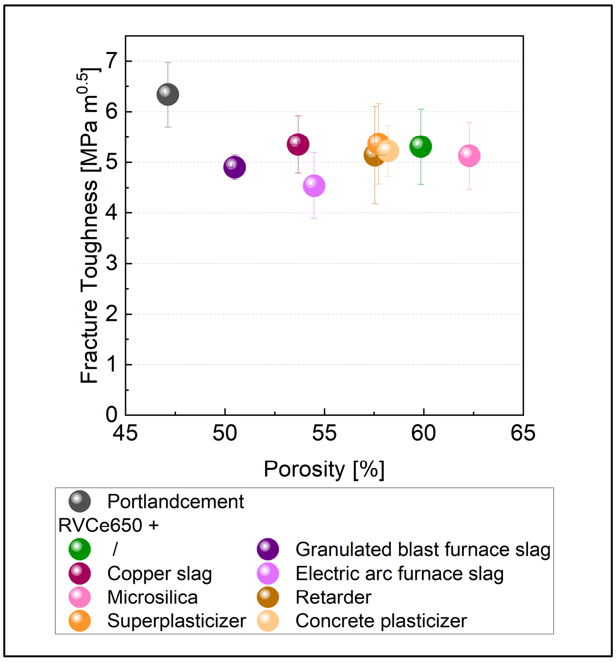

Figure 5: Fracture toughness – porosity correlation.

A parameter giving insights on the microstructure is the fracture toughness. Figure *5* shows the results in combination with the porosity determined on prisms. The strength comprises the defect structure and the fracture toughness of a tested volume. To have fracture toughness results in the same range for all additives and pure RVCe indicates an overall good quality of the chemical bonds in the volume and that improvements are needed specifically on the defect structure. That means future studies should aim for less porosity but also an even pore size distribution and fewer cracks.

4 CONCLUSIONS

This study is a basic work for more detailed research on the influence and combination of additives. It can be used as a guide for what additives are most promising but also what parameters must be tested for a meaningful study. It can be concluded that,

- GBFS increases strength by decreasing porosity. Other strengthening processes are not excluded.
- Copper slag and micro silica decrease the porosity without increasing the strength.
- Chemical admixtures increase the strength without decreasing the porosity. This is most likely based on the defect structure.

In future works, the additives and their mode of action must be investigated in more detail. It is also important to try out combinations e.g. slag and plasticizer. Additional information about the sieve line, the microstructure of grains and hardened cement paste should be obtained by scanning electron microscopy or the pore size distribution by mercury intrusion porosimetry and computer tomography.

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