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Keywords

SCDA, Portland cement, chemical accelerators; Viscosity Enhancing Agents; fracture onset; cost analysis

RESEARCH ARTICLE

Influence of admixtures on the performance of soundless chemical demolition agents and implications for their utilization

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Abstract

Soundless Chemical Demolition Agents (SCDAs) are an environmentally friendly and safer alternative to traditional rock fragmentation methods. Admixtures are used to change the rheological properties and performance of SCDAs. This study aimed to investigate the effect of various concentrations of chemical accelerators (chloride salts) and viscosity enhancing agents (VEAs: Xanthan gum, Guar gum, and Gellan gum) on the fracture onset compared to an unmodified SCDA (BRISTAR 100®). All experiments were conducted on Portland Type 1 (OPC 1) cement blocks. The flowability of the mixtures was determined by mini-slump tests. Results show that 4wt% $MgCl_2$ and 3wt% $CaCl_2$ have accelerated the fracture onset by 47.4% and 61.2%, respectively. VEAs have a decelerating effect, which is mitigated by the addition of the aforementioned chloride salts. Combining 4wt% $MgCl_2$ with 0.2wt% Xanthan gum reduced the fracture onset time by 66.8%. A cost analysis shows that the initial price of the SCDA mainly determines a potential cost reduction by using admixtures. For a low-cost SCDA, the focus is likely to shift to saving time. This study can serve as a basis for future studies to further improve performance and cost as well as diversify the range of applications for SCDAs.

Keywords: SCDA, portland cement, chemical accelerators, viscosity enhancing agents, fracture onset, cost analysis

1. Introduction

Rock fragmentation by drilling and blasting is the most traditional and economically viable method compared to other fracturing mechanism options [1]. However, the use of explosives entails various issues that need to be properly addressed, e.g., dust, noise, fly rock, and toxic gases, which pose a potential danger to nearby residential areas and ecosystems [2–4]. Massive amounts of these pollutants are emitted annually by the mining industry. Some toxic gases, mainly nitrogen oxide and carbon monoxide gases, are harmful to the health of humans and wildlife, for example, by affecting the respiratory system [5].

Industrial mining activities, especially rock blasting, have generated significant environmental problems worldwide [6–10]. Green Mining Projects were launched, which set out basic principles for mining industries following the Organization for Economic Co-operation and Development (OECD) recommendations. The principles include preventing and minimizing environmental impacts and prioritizing the health and safety of all stakeholders during mining operations [11–14]. However, environmental management in mining industries has remained a low priority compared to profitability [11]. Many potential alternatives to traditional mining methods are considered not cost-effective because they lead to a considerable increase in production costs [15–17].

Over the past decades, Soundless Chemical Demolition Agents (SCDAs) have been developed and researched as an environmentally friendly and safer substitute for explosives as their utilization is free of

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dust, noise, and toxic gases [15,18]. Unlike explosives, SCDAs are nearly nonhazardous to use and therefore do not require a highly qualified workforce [15–17]. The disadvantage of this method, however, is the expenditure of time. Reaction rates are low, which slows down fragmentation and leads to increased production costs compared to the use of explosives [19]. Consequently, SCDAs are rarely used in mining except for specific applications (e.g., dimension stone).

To overcome inherent shortcomings, previous studies have been investigating approaches to enhance SCDAs [20–24]. Their chemical composition was changed in two different ways: 1) higher amounts of CaO (lime) and 2) admixtures. Tricalcium aluminate ($3CaO \cdot Al_2O_3$) and Alite ($3CaO \cdot SiO_2$) were added to increase the proportion of CaO, leading to an improved expansion rate. However, the higher amount of CaO generates excessive heat and steam which may result in a blowout, especially at higher ambient temperatures [25]. The addition of inorganic salts (accelerators) and viscosity enhancing agents (VEAs) to SCDAs affect rheological characteristics and reaction rate. VEAs retard the hydration process of SCDAs, which can prevent blowouts [20,22,26,27]. Therefore, De Silva et al. [22] proposed combining the VEA (0.1wt% Welan gum) with a chemical accelerator (2wt% $CaCl_2$) which resulted in a significantly faster fracturing onset compared with the unmodified SCDA.

In addition to mining and geotechnical processes, SCDAs are also used in (re-) construction. OPC 1 is a common type of cement widely used in construction. OPC 1 provides high compressive strength, which makes it suitable for constructions requiring high strength and durability, such as foundations, columns, beams and slabs, high-rise buildings, roads, and expressways. Over time, buildings may need to be repurposed, renovated, or partially demolished. SCDAs can serve as an alternative to the conventional methods for demolition work, providing the possibility to preserve the original construction materials if desired [18]. Additionally, SCDAs can safely be used in residential and metropolitan areas (no noise, no dust, no toxic gases, etc.).

There are still few studies about the influence of different types and concentrations of chemical accelerators and VEAs on the expansive onset and cost of SCDAs. Previous studies indicated that the addition of chemical accelerators ($CaCl_2$) in combination with VEAs (Welan gum) to SCDAs accelerate the onset of expansive pressure [22,23,28]. In this study, various chemical accelerators (NaCl, $MgCl_2$, and $CaCl_2$) and VEAs (Xanthan gum, Guar gum, and Gellan gum) were tested regarding their effect on the performance of the SCDA. The performance of each modified SCDA was tested on OPC 1 cement blocks, characterized by the time until the appearance of the first crack on the surface. The results were compared to the performance of an unmodified SCDA (BRISTAR 100®). Mini-slump flow tests were conducted to determine the flowability of unmodified and modified SCDA with regard to their application in the field. In addition, we performed a cost analysis to examine the potential for cost savings through the use of admixtures.

2. Materials and methods

2.1. Soundless cracking demolition agent (SCDA)

Since the introduction of SCDAs in the 1960s, many researchers have studied their chemical composition and their expansion mechanism [16]. SCDAs can exert pressures ranging from 120 to 150 MPa on borehole walls. Mixing an SCDA with water starts the hydration process causing an expansion (BRISTAR 100® Manuals). The chemical reaction producing calcium hydroxide is shown in Equation (1) [18]:

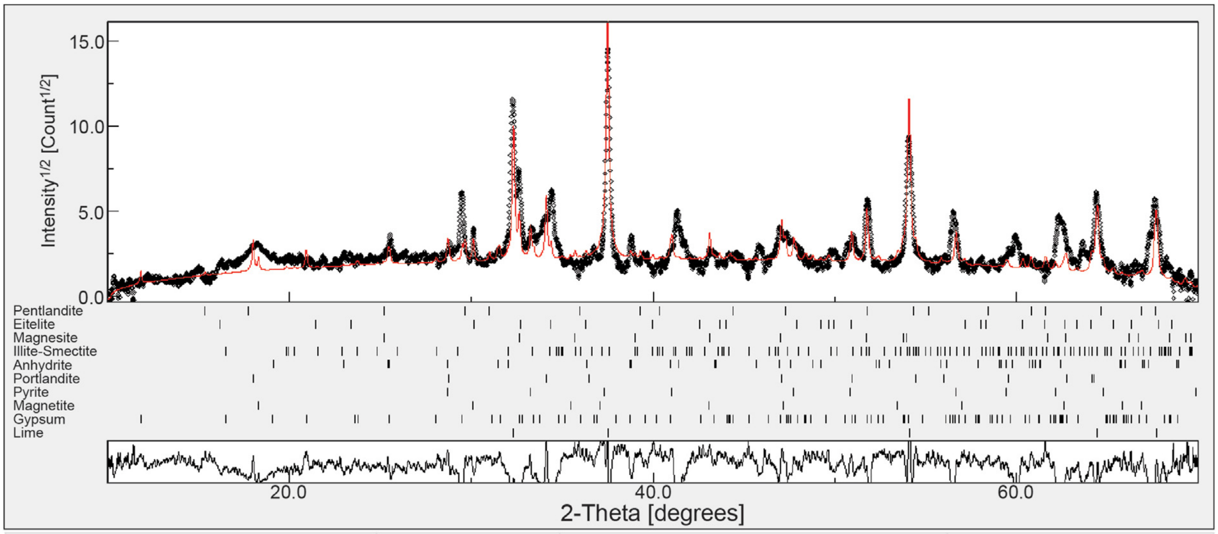
$$CaO + H_2O \rightarrow Ca(OH)_2 + 15.2\ \text{kcal/mol} \quad (1)$$

The manufacturers of SCDAs offer a variety of products suitable for different ambient conditions. In this study, BRISTAR 100® was used. This SCDA is suitable for ambient temperatures ranging from 15 to 35 °C (BRISTAR 100® Manuals).

Understanding the distribution and concentration of calcium oxide (CaO) hydration within a mass of SCDA, according to Natanzi et al. [29], could significantly improve understanding of expansive pressure generation and, as a result, ensure more predictable SCDA application and aid in geometric optimization of installation [29]. In this study, the chemical composition of BRISTAR 100® was analyzed by X-ray diffraction with MAUD program for quantitative analysis (http://maud.radiographema.eu/) (Fig. 1). According to our analysis, BRISTAR 100® mainly consists of lime (CaO), magnesite ($MgCO_3$), and hydrated lime or portlandite ($Ca(OH)_2$). Other components are, for example pyrite (FeS_2), gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), and clay minerals (Fig. 1).

2.2. Chemical accelerators and viscosity enhancing agents (VEAs)

Admixtures can influence the hydration process of SCDAs. Inorganic salts act as accelerators. Their



Component	[wt%]	Component	[wt%]
Lime (CaO)	60.4	Anhydrite ($CaSO_4$)	3.0
Magnesite ($MgCO_3$)	11.0	Illite-Smectite	2.1
Portlandite ($Ca(OH)_2$)	9.4	Eitelite ($Na_2Mg(CO_3)_2$)	1.6
Pyrite (FeS_2)	5.5	Pentlandite ($(Fe,Ni)_9\ S_8$)	1.3
Gypsum ($CaSO_4 \cdot 2H_2O$)	4.6	Magnetite (Fe_3O_4)	1.1

Fig. 1. Mineral composition of BRISTAR 100£ based on XRD data. For quantitative analysis with MAUD Program, Goodness of Fit (GOF) is 1.78% and Rwp value is 7.25%.

accelerating effect is controlled by the mobility of anions: the higher the anion mobility, the greater the accelerating effect on the cement hydration [28]. Anions are ranked according to their effectiveness [22]:

$$Cl^- \approx Br^- > SCN^- > I^- > NO_3{}^- > ClO_4{}^-$$

Chlorides are considered the most effective chemical accelerators in cementitious systems. While Viscosity Enhancing Agents (VEAs) retard the hydration process; a combination with chloride salts can mitigate this effect. The rheological properties of VEAs are affected by the nature and concentration of cations, generally declining in the presence of inorganic salts [30,31]. The addition of 2wt% $CaCl_2$ in combination with 0.1wt% VEA (Welan gum) has been shown to be beneficial for the performance of SCDAs, accelerating the onset of expansive pressure [22]. The addition of both admixtures allowed for the development of an expansive pressure of over 20 MPa after only eight hours, while the unmodified SCDA took more than 24 h [22]. In this study, NaCl, $MgCl_2$ and $CaCl_2$ (99% purity) were used as chemical accelerators. Gellan gum, Xanthan gum, and Guar gum, which are commonly used as thickening agent in the food industry, were used as VEAs.

2.3. Portland Type 1 cement blocks

The performance of each modified SCDA was tested on cement blocks (5 × 5 × 5 cm) containing a central hole with a diameter of 1 cm and a depth of 2–4 cm. The blocks were made of Portland Type 1 cement. The chemical composition of OPC 1 cement consists of: CaO (63.30–63.70wt%), SiO_2 (19.70–19.90wt%), Al_2O_3 (4.60–5.00wt%), Fe_2O_3 or Fe_3O_4 (2.57–3.47wt%), SO_3 (2.5–2.7wt%), MgO (1.39–3.59wt%), K_2O (0.45–0.69wt%) and Na_2O (0.09–1.55wt%) [32,33]. The cement mixture was poured into a cube mold. To avoid micro-cracks in the cement blocks, instead of drilling, a solid cylinder with a diameter of 1 cm was inserted into the center of each yet uncured cement block. The production date of the cement blocks and the date of the experiments were monitored in order to guarantee similar conditions. After removing the mold, the cement blocks were kept at room temperature (28°C) for 7–10 days. The average compressive strength after seven days is approx. 30 MPa (Supplementary data Fig. 1).

2.4. Experimental parameters

2.4.1. Hole depth and amount of chloride salts and VEAs

The OPC 1 cement blocks (5 × 5 × 5 cm) containing a central hole with a diameter of 1 cm and a depth of 2–4 cm were tested with unmodified BRISTAR 100® to investigate the effect of various hole depths on the performance of the SCDA.

Various admixtures were tested regarding their effect on the performance of SCDAs, particularly the time until the occurrence of the first crack (Table 1). BRISTAR 100® was modified by adding 1–4wt% of NaCl, $MgCl_2$, or $CaCl_2$ (chemical accelerators) and/or 0.1–0.3wt% of Gellan gum, Xanthan gum, or Guar gum (VEAs). Each cement block was quality-checked before the experiments and hole depths were measured. The SCDA mixtures were poured slowly into the hole. While pouring, a small thin stick of wood was used to prod the mixtures within the hole to remove air bubbles and ensure the holes were completely filled. All experiments were recorded with a digital camera (GoPro 7, time lapse with 60 s interval). The time span between pouring the SCDA mixtures into the hole and the appearance of the first crack is recorded (in hours). The fracturing onset was observed for 15 h at maximum. Each experiment was conducted at least four times at room temperature (28°C).

2.4.2. Flowability

To investigate the effect of various concentrations of VEAs on the rheological properties of SCDAs, mini-slump flow tests were performed to determine the flowability of each mixture [34,35]. Yield stress is important in quantifying flowability and a significant factor in many industrial processes (e.g., pumping, spreading, and coating) [36–38]. The mini-slump flow test is based on measuring the spread of a mixture placed into a cone-shaped mold [39]. The cone was placed into the center of the metal plate, and immediately after mixing, the modified SCDA was filled into the cone. The cone was then vertically lifted to let the mixture flow freely. Finally, the diameter was measured at two right-angle positions after the mixture stopped flowing, and the average diameter of the measurements is recorded. Each modified mixture was tested two times.

Table 1. Experimental program of the SCDA mixtures.

Admixture	Concentration	Hole depth [cm]	Samples per configuration	Date Tested
Unmodified	–	2, 3, 4	5, 11, 13	07/20–07/28/2021
NaCl	1wt%, 2wt%, 3wt%, 4wt%	4	5, 5, 4, 5	07/20–07/28/2021
$MgCl_2$	1wt%, 2wt%, 3wt%, 4wt%	4	6, 6, 6, 6	07/20–07/30/2021
$CaCl_2$	1wt%, 2wt%, 3wt%, 4wt%	4	6, 4, 6, 6	07/20–07/31/2021
Gellan gum	0.1wt%, 0.2wt%, 0.3wt%	4	5, 5, 5	07/23–07/28/2021
Xanthan gum	0.1wt%, 0.2wt%, 0.3wt%	4	6, 6, 4	07/24–07/31/2021
Guar gum	0.1wt%, 0.2wt%, 0.3wt%	4	6, 4, 6	07/24–07/31/2021
$MgCl_2$ + Xanthan gum	3wt% $MgCl_2$ 0.1wt% Xanthan gum	4	4	07/21–07/31/2021
	3wt% $MgCl_2$ 0.2wt% Xanthan gum	4	4	07/21–07/31/2021
	4wt% $MgCl_2$ 0.1wt% Xanthan gum	4	4	07/21–07/31/2021
	4wt% $MgCl_2$ 0.2wt% Xanthan gum	4	4	07/21–07/31/2021
$MgCl_2$ + Guar gum	3wt% $MgCl_2$ 0.2wt% Guar gum	4	4	07/21–07/24/2021
	4wt% $MgCl_2$ 0.2wt% Guar gum	4	4	07/21–07/24/2021
$CaCl_2$ + Xanthan gum	2wt% $CaCl_2$ 0.1wt% Xanthan gum	4	4	07/21–07/23/2021
	3wt% $CaCl_2$ 0.1wt% Xanthan gum	4	4	07/21–07/23/2021
$CaCl_2$ + Guar gum	2wt% $CaCl_2$ 0.2wt% Guar gum	4	4	07/21–07/23/2021
	3wt% $CaCl_2$ 0.2wt% Guar gum	4	4	07/21–07/23/2021

3. Results

3.1. The influence of the cement block hole depth on the fracturing onset of SCDA

To investigate the correlation between hole depth and fracture onset, the SCDA was tested on cement blocks with different hole depths (2–4 cm). The time span between pouring the SCDA mixtures into the hole and the appearance of the first crack on the surface is shown in Fig. 2. The results show that deeper holes are favorable for fracture onset. The average time span was 9 h 45 min for a hole depth of 4 cm, 10 h 38 min for 3 cm, and 12 h 33 min for 2 cm hole depth (Fig. 2 and Supplementary data Fig. 2).

The results, however, did not only differ with regard to the fracture onset. While the OPC 1 blocks with a hole depth of 3–4 cm exhibited wide open fractures that went down the side of blocks, the blocks with a hole depth of 2 cm showed smaller cracks that only stayed on the top surface of the blocks. The blocks with a hole depth of 4 cm did ultimately break apart completely (Supplementary data Fig. 2).

3.2. The influence of chloride salts on the fracturing onset of SCDA

To investigate the effect of chloride salts on the performance of SCDAs, the amount of 1–4wt% of NaCl, $MgCl_2$, or $CaCl_2$ was added to BRISTAR 100® (Fig. 3). The results show that higher concentrations (3–4wt%) of NaCl decelerated the fracturing onset of the SCDA. However, the addition of 1–2wt% NaCl, did slightly accelerate the process compared to unmodified BRISTAR 100® (Supplementary data Fig. 3). Increasing concentrations (1–4wt%) of $MgCl_2$ led to an earlier fracture onset. A concentration of 4wt% $MgCl_2$ proved to be the fastest mixture in the $MgCl_2$ series, with an average time span of 5 h 8 min until the appearance of the first fracture, followed by 3wt% $MgCl_2$ with 7 h 58 min (Fig. 3 and Supplementary data Fig. 4).

The results for increased concentrations of $CaCl_2$ were also remarkable, exceeding those of $MgCl_2$, except for 4wt% $CaCl_2$. The addition of 1–3wt% $CaCl_2$ significantly accelerated the fracture onset. The fastest mixture in the $CaCl_2$ series was the mixture with 3wt% $CaCl_2$ with an average time span of 3 h 47 min until the appearance of the first fracture, followed by 2wt% $CaCl_2$ with 5 h 39 min. However, the results for the SCDA with 4wt% $CaCl_2$ varied between 2 h 23 min and more than 15 h until fracture onset (Supplementary data Fig. 5). This variation indicates that higher concentrations of $CaCl_2$ lead to a highly volatile hydration reaction. A rapid temperature increase further accelerated the hydration process. The volumetric expansion of the modified SCDA seemed to occur within the first few minutes after being mixed with water. In addition, the mixture's viscosity increased significantly, and the mixture solidified after a short period of time which made it difficult to fill the holes. Consequently, a concentration of 4wt% $CaCl_2$ had no beneficial effect on the performance of the SCDA.

3.3. The influence of VEAs on the fracturing onset of SCDA

To investigate the effect of VEAs on the performance of SCDA, BRISTAR 100® was mixed with

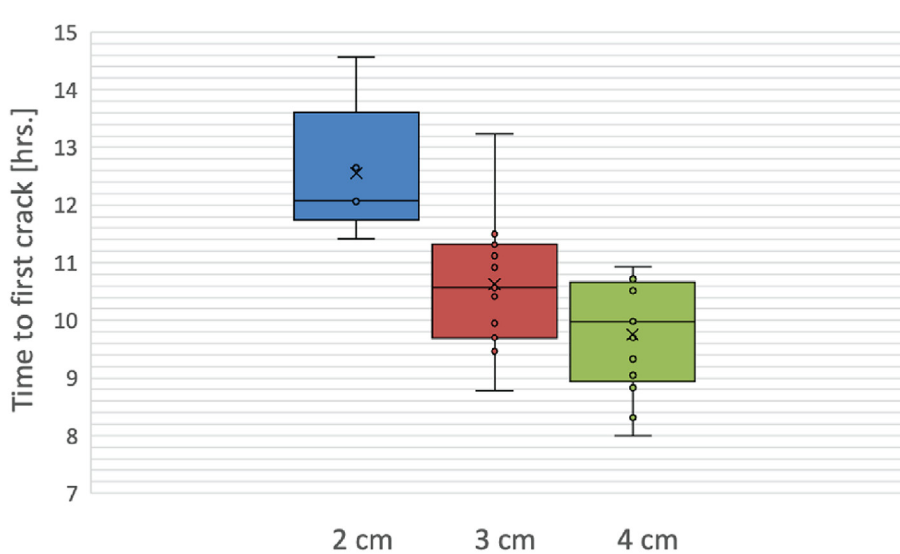


Fig. 2. Fracture onset of unmodified BRISTAR 100£ for OPC 1 blocks with different hole depths (2, 3, and 4 cm).

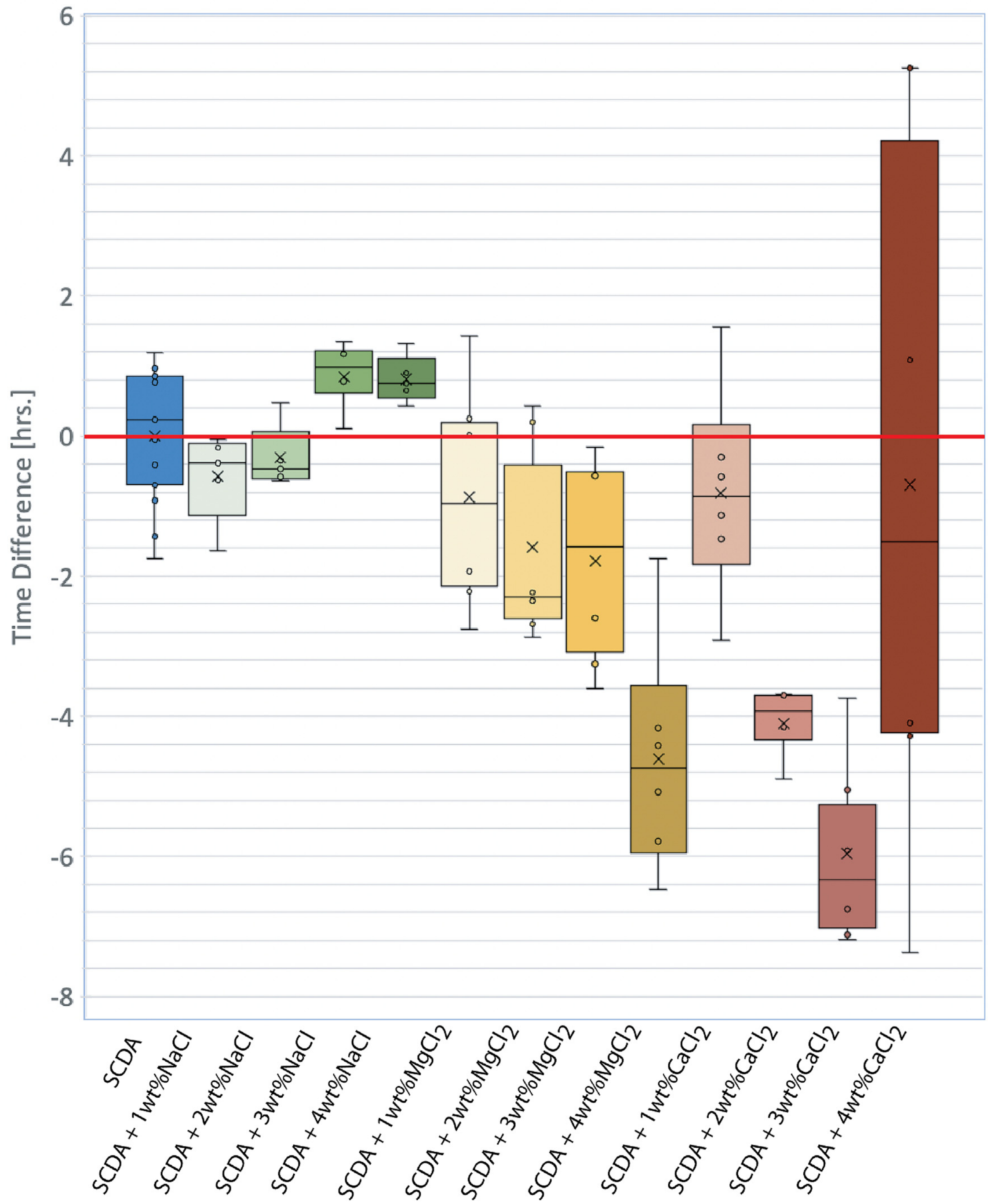


Fig. 3. Effect of chloride salts on the fracture onset of unmodified BRISTAR 100£ . The red line represents the average fracture onset for OPC 1 blocks with a hole depth of 4 cm (9 h 45 min).

varying concentrations (0.1–0.3wt%) of Gellan gum, Xanthan gum or Guar gum. The time until fracture onset for the various mixtures compared to unmodified BRISTAR 100® are shown in Fig. 4. Higher concentrations of VEAs generally prolong the time span until the appearance of the first crack on the block surface. The fastest fracture onset was achieved with 0.1wt% Xanthan gum (8 h 50 min, almost one hour faster than unmodified BRISTAR 100®) with higher concentrations having a retarding effect. The addition of 0.1–0.2wt% Guar gum also had a slight accelerating effect. The mixture with 0.2wt% Guar gum has the mean fracture onset time of 9 h 42 min. Gellan gum did not influence on the performance of the SCDA, except for the mixture with 0.3wt% Gellan gum which had a

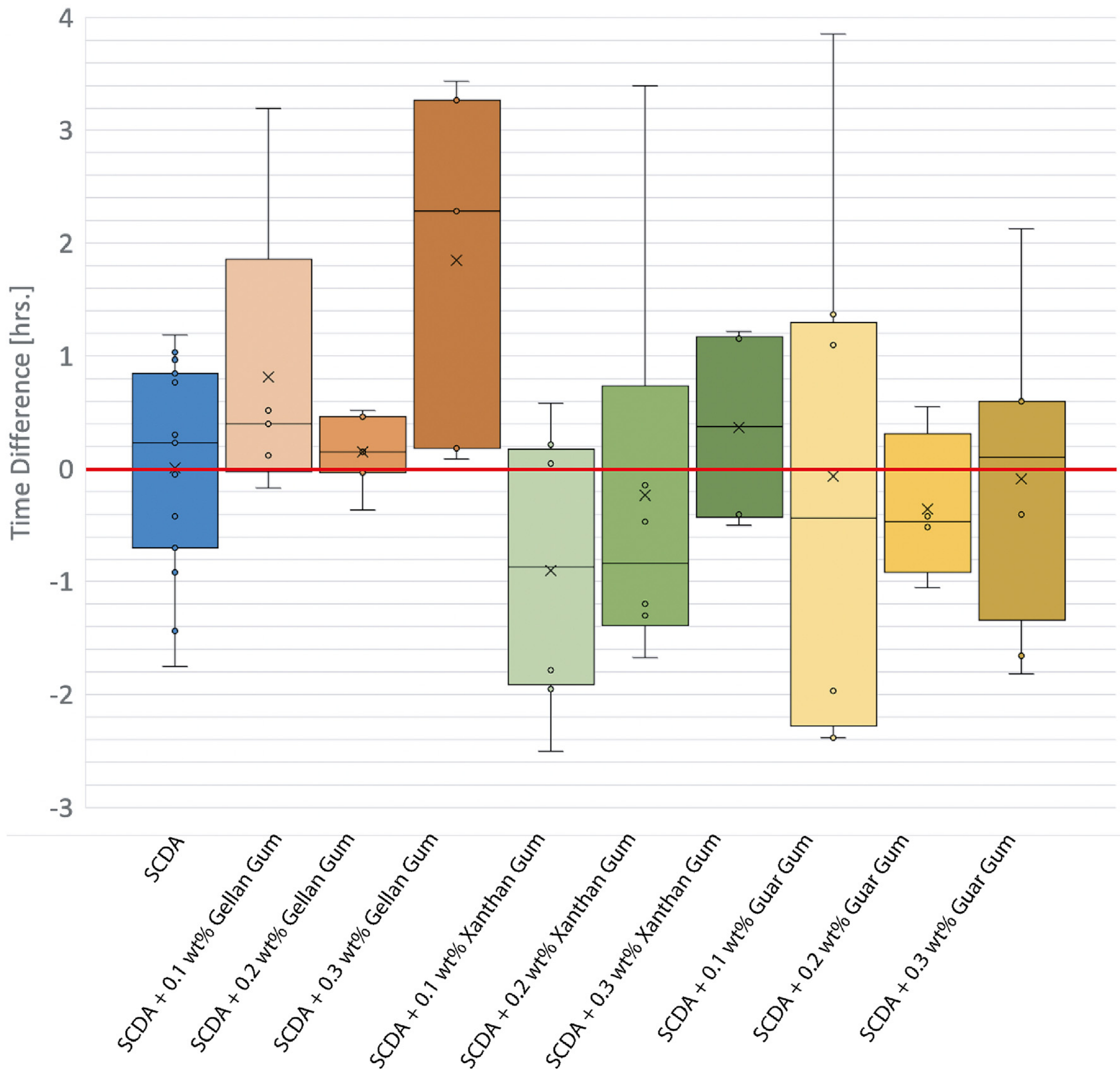


Fig. 4. Effect of viscosity enhancing agents on the fracture onset of unmodified BRISTAR 100£ . The red line represents the average fracture onset for OPC 1 blocks with a hole depth of 4 cm (9 h 45 min).

significant retarding effect (Fig. 4). Overall, the VEAs do not affect the fracture onset to the same extent as chloride salts.

3.4. The influence of chloride salts in combination with VEAs on the fracturing onset of SCDA

Based on the experimental results, with $MgCl_2$ and $CaCl_2$ having shown to accelerate the fracture onset, the two fastest concentrations for each chloride salt (3–4wt% $MgCl_2$ and 2–3wt% $CaCl_2$) were mixed with VEAs (0.1–0.2wt% Xanthan gum or Guar gum) to test their combined effect on the performance of the SCDA. The results of the $MgCl_2$ and $CaCl_2$ series are shown in Fig. 5.

The $MgCl_2$ series (Fig. 5) showed that a combination of the SCDA with 4wt% $MgCl_2$ and 0.2wt% Xanthan gum significantly increased the performance. First cracks appeared after 3 h 14 min, accelerating the fracture onset by 6 h 31 min. The mixture with 4wt% $MgCl_2$ and 0.2wt% Guar gum also showed a substantially accelerated fracture onset with 4 h 3 min. The average time until the occurrence of the first crack for a mixture with 4wt% $MgCl_2$ without a VEA was 5 h 8 min. The modified SCDA with 3wt% $MgCl_2$ also showed an accelerated fracture onset. The mixtures with 3wt% $MgCl_2$ and 0.2wt% Xanthan or Guar gum had average times until the appearance of first cracks of 6 h 19 min and 6 h 13 min, respectively (a time saving of approx. 3 h 30 min).

The $CaCl_2$ series (Fig. 5) showed that combining the SCDA with 3wt% $CaCl_2$ and 0.1wt% Xanthan gum significantly increased the performance. First

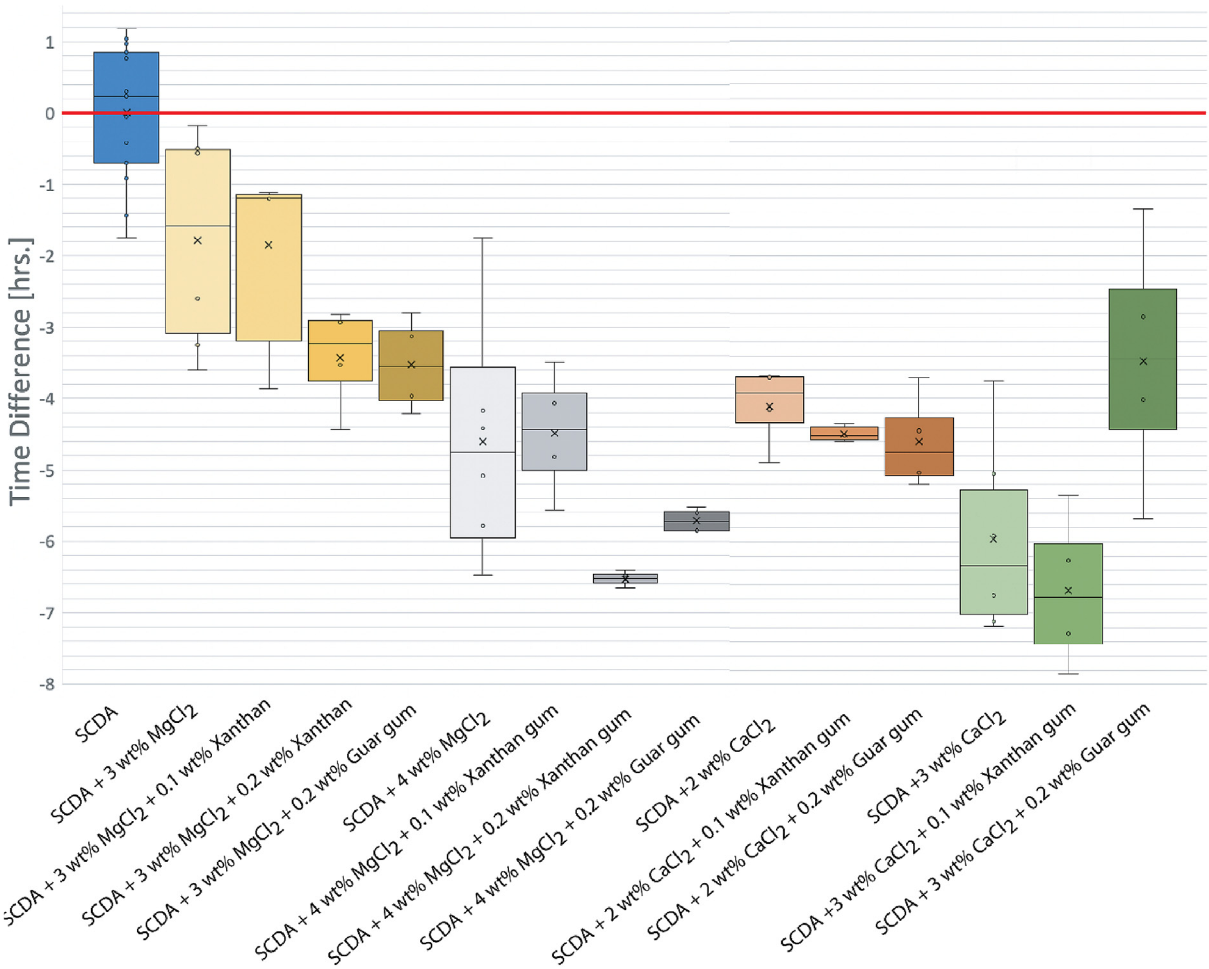


Fig. 5. $MgCl_2$ and $CaCl_2$ series compared to unmodified BRISTAR 100£ . The red line represents the average fracture onset for OPC 1 blocks with a hole depth of 4 cm (9 h 45 min).

cracks appeared after 3 h 4 min, accelerating the fracture onset by 6 h 41 min. The mixture with 3wt% $CaCl_2$ and 0.2wt% Guar gum showed a substantially decelerated fracture onset within 6 h 35 min. The average time until the occurrence of the first crack for a mixture with 3wt% $CaCl_2$ without a VEA was 3 h 47 min and 5 h 39 min for 2wt% $CaCl_2$. The addition of 0.1wt% Xanthan gum and 0.2wt% Guar gum to the mixture with 2wt% $CaCl_2$ lead to a slightly accelerated fracturing onset, with an average of 5 h 15 min and 5 h 9 min, respectively.

3.5. The influence of different concentrations of VEAs, $MgCl_2$, and $CaCl_2$ on the flowability of SCDA

The mini-slump test showed that higher concentrations of the VEA affect the viscosity of the SCDA, reducing the diameter of spread (Fig. 6A). The same applied to the addition of chloride salts (Fig. 6B). The addition of 0.1wt% of the VEAs, especially Gellan gum, resulted in a significant decrease of the flowability. The diameter of spread was reduced from 32.6 mm (unmodified SCDA) to 25.3 mm for Gellan gum, followed by Xanthan gum (26.5 mm) and Guar gum (27.8 mm). Higher concentrations (0.2–0.3wt%) of the VEAs further decreased the flowability, however, to a lesser extent, especially for Gellan gum. At a VEA concentration of 0.3wt%, all modified mixtures performed similarly with diameters of spread of 24.5 mm (Gellan gum), 24.3 mm (Xanthan gum), and 24.8 mm (Guar gum).

The effect of chloride salts on the flowability of an SCDA is similar to VEAs (Fig. 6). The addition of 1wt% of $MgCl_2$ or $CaCl_2$ resulted in a significant decrease of the diameter of spread. $CaCl_2$ had a stronger effect on the flowability than $MgCl_2$, reducing the diameter of spread from 32.6 mm to 26 mm, while the latter exhibited a value of 27 mm. Higher concentrations (0.2–0.4wt%) of the chloride

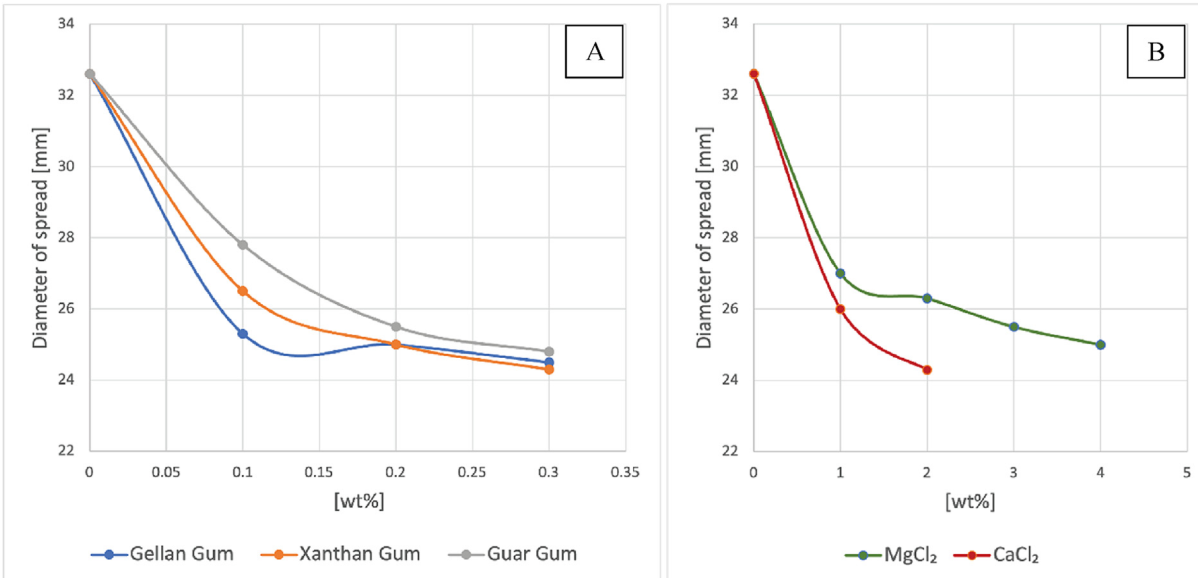


Fig. 6. (A) Diameter of spread for a modified SCDA with various concentrations of VEAs. (B) Diameter of spread for a modified SCDA with various concentrations of chloride salts.

salts further decreased the flowability. At a concentration of 0.2wt%, the diameter of spread was reduced to 24.3 mm ($CaCl_2$) and 26.3 mm ($MgCl_2$). The mini-slump test for 3–4wt% of $CaCl_2$ failed as the mixture got stuck in the cone. The diameter of spread for $MgCl_2$ further decreased to 25.5 mm (3wt%) and 25 mm (4wt%).

The yield stress of each mixture for which a mini-slump test was conducted was calculated using Equation (2) [39]:

$$\tau_0 = 225\ \rho g \Omega^2 / 128 \pi^2\ R^2 \tag{2}$$

The yield stress is described as a function of the density of the mixture ρ, the volume of the mini-slump cone Ω, and the mini-slump spread diameter R; g is the acceleration due to Earth's gravity (9.81 m/s^2). The density of each mixture was calculated based on their formulation and the density of each component. The calculated values for density and yield stress of each mixture are shown in Table 2.

4. Discussions

4.1. Discussing the effect of hole depth and different admixtures on SCDA fracturing onset

In this study, we aimed to investigate the effect of various admixtures on the performance and cost of

Table 2. Density, diameter of spread and yield stress of BRISTAR 100£ and various mixtures.

Mixture	Density [g/ cm^3]	Diameter of spread [mm]	Yield stress (τ_O) [Pa]
unmodified BRISTAR 100®	1.3448	32.6	5.5
BRISTAR 100® + 0.1wt% Gellan gum	1.3421	25.3	19.6
BRISTAR 100® + 0.2wt% Gellan gum	1.3394	25.0	20.8
BRISTAR 100® + 0.3wt% Gellan gum	1.3367	24.5	23.0
BRISTAR 100® + 0.1wt% Xanthan gum	1.3448	26.5	15.6
BRISTAR 100® + 0.2wt% Xanthan gum	1.3448	25.0	20.9
BRISTAR 100® + 0.3wt% Xanthan gum	1.3448	24.3	24.1
BRISTAR 100® + 0.1wt% Guar gum	1.3444	27.8	12.3
BRISTAR 100® + 0.2wt% Guar gum	1.3439	25.5	18.9
BRISTAR 100® + 0.3wt% Guar gum	1.3434	24.8	21.7
BRISTAR 100® + 1wt% $CaCl_2$	1.3476	26.0	17.2
BRISTAR 100® + 2wt% $CaCl_2$	1.3505	24.3	24.2
BRISTAR 100® + 1wt% $MgCl_2$	1.3481	27.0	14.2
BRISTAR 100® + 2wt% $MgCl_2$	1.3514	26.3	16.3
BRISTAR 100® + 3wt% $MgCl_2$	1.3547	25.5	19.0
BRISTAR 100® + 4wt% $MgCl_2$	1.3581	25.0	21.1

SCDAs. However, all results should be considered preliminary due to the inherent limitations of the experimental setup (e.g., temperature and humidity control, scaling). Our results are nevertheless consistent with previous studies. The experimental results showed an improved performance of the SCDA in connection to an increased hole depth within the OPC 1 blocks. Holes with a depth of 4 cm exhibited an earlier fracture onset than holes with a depth of 3 cm or 2 cm. A hole depth of 3 cm or 4 cm equals 60% or 80% of the sample height (5 cm). Many manufacturers and researchers recommend 70% of height for the whole depth, which critically relates to both the quantity of material in the whole and the pressure distribution with respect to the confining geometry [19,40,41]. Shallower holes produce fewer, shorter, and narrower cracks which may be insufficient for a complete demolition [42]. However, this can be useful if a destruction is not desired, e.g., if the original construction materials are to be preserved [18].

Chloride salts have been shown to act as chemical accelerators for the hydration process, in some cases reducing the time until the occurrence of the first crack by 61.2%. While NaCl (Na^+ cations) had no beneficial effect, $MgCl_2$ (Mg^{2+} cations) and $CaCl_2$ (Ca^{2+} cations) both accelerated the fracture onset, resulting in a time gain of several hours. However, high concentrations of these chloride salts may render the rection volatile [22]. Adding 4wt% $CaCl_2$ causes a rapid increase in the temperature, which further accelerates the hydration reaction [22]. These results indicate that rheological properties and chemical reaction rates depend on the nature and concentration of the cations.

The mini-slump test clearly showed the effect of chloride salts and VEAs on the flowability of the mixtures. Higher concentrations of the admixtures led to increased yield stress values. Yield stress is important in quantifying flowability and a significant factor in many industrial processes (e.g., pumping, spreading, and coating). At high concentrations of $CaCl_2$ (3–4wt%) the mixture exhibited a significantly reduced flowability and got stuck in the cone. Even though the modified SCDA with 3wt% $CaCl_2$ proved to be the most successful formula in the $CaCl_2$ series regarding fracture onset, its reduced flowability could potentially cause problems when filling the boreholes. The rheological parameters of polysaccharide solutions decline in the presence of inorganic salts [30], indicating that they also depend on the nature and concentration of the cations [31].

The results of this study show that the addition of VEAs to the SCDA generally had no accelerating effect on the fracture onset. Higher concentration even slowed down the process, clearly demonstrated by the Xanthan gum series (Fig. 4). These results indicate that the addition of VEAs retards the hydration process resulting in a slower volumetric

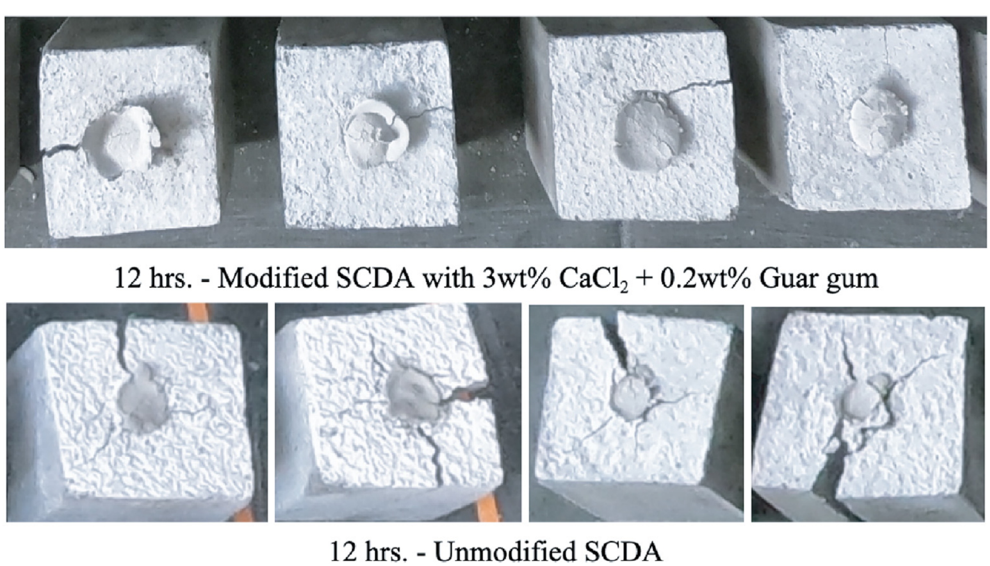


Fig. 7. Comparison of the fracture development between BRISTAR 100 (unmodified SCDA) and a mixture with 3wt% $CaCl_2$ and 0.2wt% Guar gum 12 h after the start of the experiment.

expansion, leading to a relatively low rate of expansive pressure generation [20–22]. However, this can be counteracted by adding chemical accelerators (chloride salts), which successfully accelerated the fracture onset in combination with the VEAs. As previously mentioned, inorganic salts lead to a decline of the rheological parameters of the VEAs. Ca^{2+} cations have a stronger effect on the yield stress than Na^{+} cations [31]. According to the results of this study, a mixture with 3wt% $CaCl_2$ and 0.1wt% Xanthan gum yielded the greatest time gain (Fig. 5). First cracks appeared on average after only 3 h 4 min. (6 h 41 min faster than the unmodified SCDA). A mixture with 4wt% $MgCl_2$ and 0.2wt% Xanthan gum had a slightly slower fracture onset, with an average time of 3 h 14 min (Fig. 5).

Although VEAs generally do not accelerate the fracture onset, they appear to have a stabilizing effect leading to more consistent results, especially in combination with chloride salts. In this context, Xanthan gum appears to be more effective than Gellan gum or Guar gum. The various gums differ with regard to, for example molecular weight, degree of substitution, network structure, temperature resistance, and pH stability. Xanthan gum has higher thermal stability than Guar gum which may explain the more consistent results [43]. Mixtures with higher concentrations of $CaCl_2$ (Ca^{2+} cations) seem to benefit more from this apparent stabilizing effect of Xanthan gum than mixtures with higher concentrations of $MgCl_2$ (Mg^{2+} cations).

Table 3. Prices of SCDAs and various admixtures.

SCDA	BRISTAR 100® (high import tax*)		BRISTAR 100® (standard**)		SCDA (local product***)	
Price per kg [USD]	13		5		0.2–0.6	
Admixture	NaCl	$MgCl_2$	$CaCl_2$	Gellan gum	Guar gum	Xanthan gum
Price per kg [USD]	0.60	0.69	0.60	39.72	4.48	5.87

* e.g., Thailand, **e.g., Japan, ***based on Chinese prices.

Table 4. Prices and percentual price changes for various SCDA mixtures. (F) Fastest (f) second fastest (bold) cheapest mixtures.

Mixture	High Import Tax		Standard		Local Product	
	Price per kg [USD]	Price change [%]	Price per kg [USD]	Price change [%]	Price per kg [USD]	Price change [%]
unmodified BRISTAR 100®	13.0000	–	5.0000	–	**0.6000**	–
BRISTAR 100® + 0.1wt% Gellan gum	13.0267	0.21	5.0347	0.69	0.6391	6.52
BRISTAR 100® + 0.2wt% Gellan gum	13.0534	0.41	5.0694	1.39	0.6782	13.03
BRISTAR 100® + 0.3wt% Gellan gum	13.0802	0.62	5.1042	2.08	0.7174	19.57
BRISTAR 100® + 0.1wt% Xanthan gum	12.9929	−0.05	5.0009	0.02	0.6053	0.88
BRISTAR 100® + 0.2wt% Xanthan gum	12.9857	−0.11	5.0017	0.03	0.6105	1.75
BRISTAR 100® + 0.3wt% Xanthan gum	12.9786	−0.16	5.0026	0.05	0.6158	2.63
BRISTAR 100® + 0.1wt% Guar gum	12.9915	−0.07	4.9995	−0.01	0.6039	0.65
BRISTAR 100® + 0.2wt% Guar gum	12.9830	−0.13	4.9990	−0.02	0.6078	1.30
BRISTAR 100® + 0.3wt% Guar gum	12.9744	−0.20	4.9984	−0.03	0.6116	1.93
BRISTAR 100® + 1wt% NaCl	12.8760	−0.95	4.9560	−0.88	**0.6000**	–
BRISTAR 100® + 2wt% NaCl	12.7520	−1.91	4.9120	−1.76	**0.6000**	–
BRISTAR 100® + 1wt% $CaCl_2$	12.8760	−0.95	4.9560	−0.88	**0.6000**	–
BRISTAR 100® + 2wt% $CaCl_2$	12.7520	−1.91	4.9120	−1.76	**0.6000**	–
BRISTAR 100® + 1wt% $MgCl_2$	12.8769	−0.95	4.9569	−0.86	0.6009	0.15
BRISTAR 100® + 2wt% $MgCl_2$	12.7538	−1.89	4.9138	−1.72	0.6018	0.30
BRISTAR 100® + 3wt% $MgCl_2$	12.6307	−2.84	4.8707	−2.59	0.6027	0.45
BRISTAR 100® + 4wt% $MgCl_2$	12.5076	−3.79	4.8276	−3.45	0.6036	0.60
BRISTAR 100® + 3wt% $MgCl_2$ + 0.1wt% Xanthan gum	12.6263	−2.87	4.8716	−2.57	0.6080	1.33
BRISTAR 100® + 3wt% $MgCl_2$ + 0.2wt% Xanthan gum	12.6164	−2.95	4.8724	−2.55	0.6132	2.20
BRISTAR 100® + 3wt% $MgCl_2$ + 0.2wt% Guar gum	12.6137	−2.97	4.8697	−2.61	0.6105	1.75
BRISTAR 100® + 4wt% $MgCl_2$ + 0.1wt% Xanthan gum	12.5005	−3.84	4.8285	−3.43	0.6089	1.48
BRISTAR 100® + 4wt% $MgCl_2$ + 0.2wt% Xanthan gum **(f)**	12.4933	−3.90	4.8293	−3.41	0.6141	2.35
BRISTAR 100® + 4wt% $MgCl_2$ + 0.2wt% Guar gum	**12.4906**	**−3.92**	**4.8266**	**−3.47**	0.6114	1.90
BRISTAR 100® + 2wt% $CaCl_2$ + 0.1wt% Xanthan gum	12.7449	−1.96	4.9129	−1.74	0.6053	0.88
BRISTAR 100® + 2wt% $CaCl_2$ + 0.2wt% Guar gum	12.7350	−2.04	4.9110	−1.78	0.6078	1.30
BRISTAR 100® + 3wt% $CaCl_2$ + 0.1wt% Xanthan gum **(F)**	12.6209	−2.92	4.8689	−2.62	0.6053	0.88
BRISTAR 100® + 3wt% $CaCl_2$ + 0.2wt% Guar gum	12.6110	−2.99	4.8670	−2.66	0.6078	1.30

Some mixtures exhibited an accelerated fracture onset, but were ultimately less destructive. Even though a modified mixture with 3wt% $CaCl_2$ and 0.2wt% Guar gum showed first cracks more than 3 h earlier than the unmodified SCDA, after 12 h, more (and wider) fractures were produced by the unmodified SCDA (Fig. 7). However, the results of this study should be considered preliminary. Further tests with an improved experimental setup and on a larger scale are required for verification.

4.2. Cost

The cost of using SCDAs varies from country to country (Table 3). Due to high import taxes, for example, BRISTAR 100® retails in Thailand for ~13 USD per kg, while the retail price in Japan is ~5 USD per kg. Alternative products from China have a retail price between 0.2 and 0.6 USD per kg. If their utilization is associated with high cost, they are likely to be rarely used, especially in mining.

Reducing the cost of SCDAs is essential to diversify their range of applications and to make them more attractive to the mining industry. Initially, governments could reduce import taxes or allow for the import of cheaper alternative products from abroad. Ultimately, however, it should be the goal of each country, its mining industry and associated research institutions to develop a product based on local resources, which could further reduce cost.

Admixtures will not only affect the performance of SCDAs but also the total cost. The approximate prices for admixtures and various mixtures are shown in Tables 3 and 4. For BRISTAR 100® the use of admixtures reduces the cost by up to ~4%. This

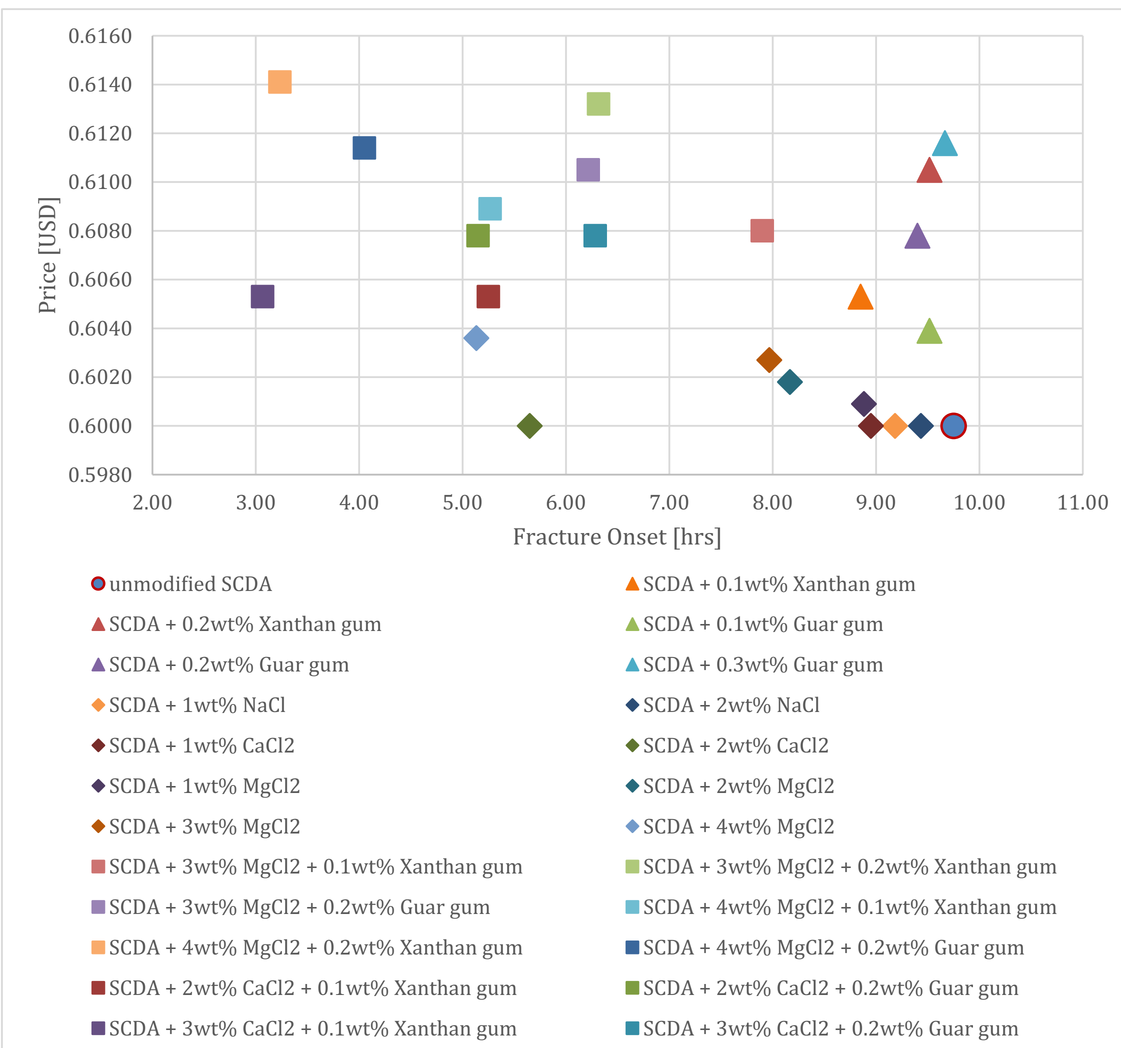


Fig. 8. Price vs. Fracture Onset for various modified mixtures compared to an unmodified SCDA (local product).

cost reduction is due to the low cost of the admixtures, which replace equivalent parts of the SCDA. The potential for cost reduction is directly related to the initial cost of the SCDA. The cheaper the SCDA, the fewer costs can be saved by using admixtures. In the case of a local product, with an initial price of the SCDA at or below the price of the admixtures, the total will likely increase. Finding the right balance between cost savings and time savings is likely to become more important (Fig. 8).

Traditional methods using ammonium nitrate-based explosives (ANFO, heavy ANFO, slurries, etc.) are significantly cheaper (1 kg of ANFO costs ~0.6 USD in Thailand) than SCDAs for rock fragmentation. In Thailand, the estimated cost of producing 1 m^3 of rock by drilling and blasting is ~1.52–1.82 USD (50–60 THB) (personal communication). The use of BRISTAR 100® would increase the cost to over 12.13 USD (400 THB) which is almost three times higher than the maximum acceptable costs of 4.55 USD (150 THB, personal communication) per m^3 of rock. Under normal circumstances, SCDAs are not competitive for rock fragmentation. However, in the special case of a mining operation located near or within a nature reserve (ongoing study), when pollution and noise are prohibitive for ANFO, utilization of SCDAs can be a viable alternative, especially at reduced cost.

5. Conclusions

In this study, a series of experiments were conducted to investigate the effect of various admixtures (chloride salts and VEAs) on the performance and cost of an SCDA (BRISTAR 100®). In agreement with previous studies, our results show that hole depth and admixtures affect the performance of the SCDA regarding fracture onset, fracture width, and fracture length. Increased concentrations of $MgCl_2$ and $CaCl_2$ accelerated the fracture onset by up to ~60%, while NaCl had no beneficial effect. However, higher concentrations of $CaCl_2$ (4wt%) rendered the reaction volatile. The addition of VEAs, especially Xanthan gum, appears to have a stabilizing effect on the reaction, which lead to more consistent results. The addition of VEAs to an SCDA, on the other hand, results in a later onset of fracture. The flowability of the SCDA is affected by chloride salts and VEAs, resulting in higher yield stress values. For example, a mixture of 3wt% $CaCl_2$ and 0.1wt% Xanthan gum successfully accelerated fracture onset (time gain 6 h 30 min), but the reduced flowability could cause problems when filling boreholes. The price of an SCDA varies by country. High costs would certainly limit their use to specific applications. This study suggests that the use of admixtures has the potential for both saving cost and time. The cost-saving potential of admixtures is largely determined by the SCDA's initial price. The development of a low priced, local product would shift the focus to time savings.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical statement

The authors state that the research was conducted according to ethical standards.

Funding body

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Authors contribution

Nattamon Maneenoi (BSc. exchange student) and Raphael Bissen: Investigation, Formal analysis, Visualization, writing original draft preparation, Writing-review & editing. Raphael Bissen & Sakonvan Chawchai: Supervision, Conceptualization, and essentially intellectual contributor, funding acquisition, Writing, review & editing.

APPENDIX 1.

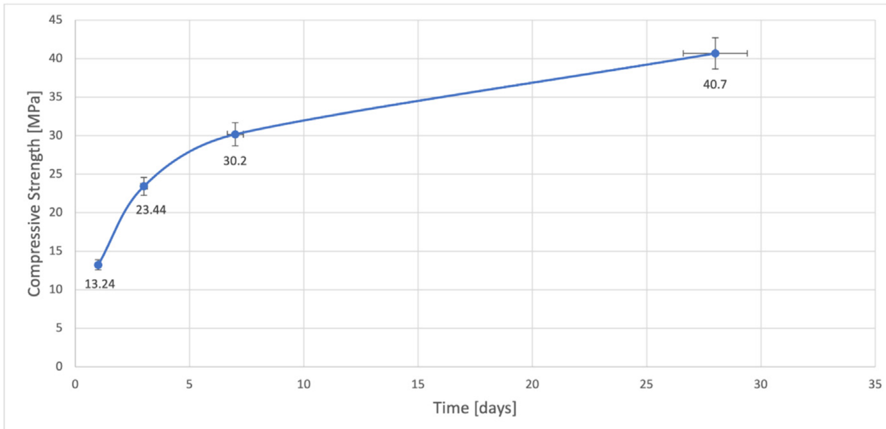

Fig. S1. Compressive Strength [MPa] of OPC 1 blocks vs Time [days].

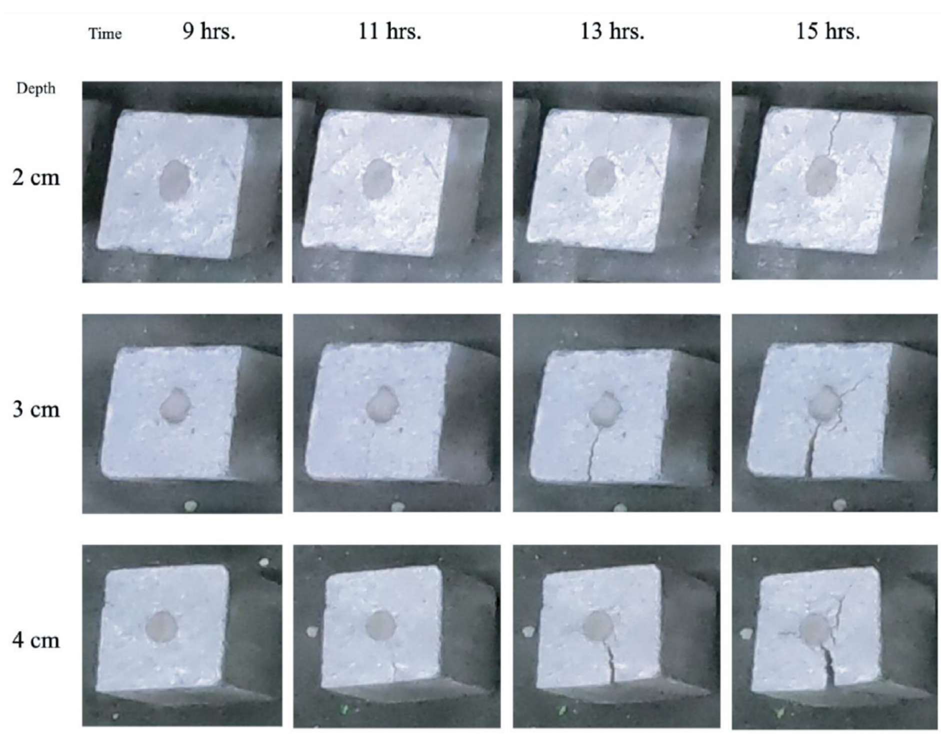

Fig. S2. Evolution of fracturing for OPC 1 blocks with hole depths of 2, 3, and 4 cm after 9, 11, 13, and 15 hrs. The holes were filled with unmodified BRISTAR 100£ . After 15 hrs. the blocks with a hole depth of 3 and 4 cm exhibited wide open fractures, while the blocks with a hole depth of 2 cm showed only small cracks. The blocks with a hole depth of 4 cm did ultimately break apart completely.

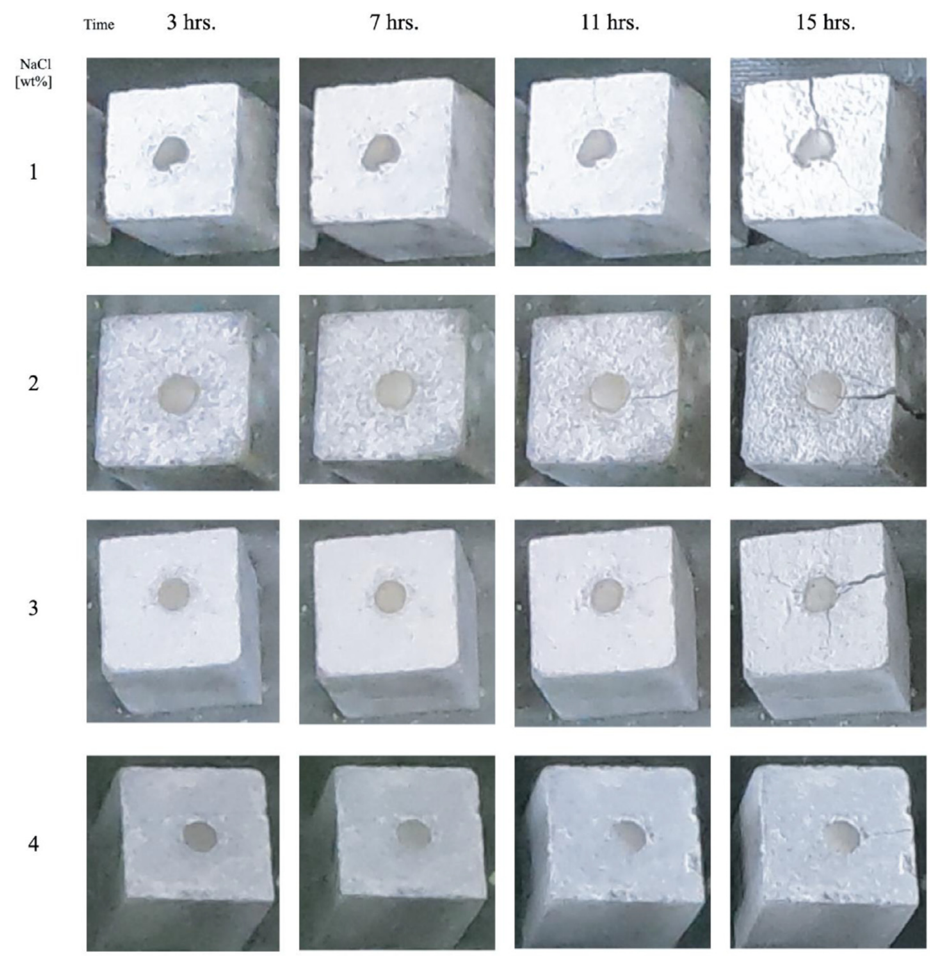

Fig. S3. Evolution of fracturing for OPC 1 blocks with a hole depth of 4 cm after 3, 7, 11, and 15 hrs. Modified BRISTAR 100£ with 1, 2, 3, and 4wt% NaCl.

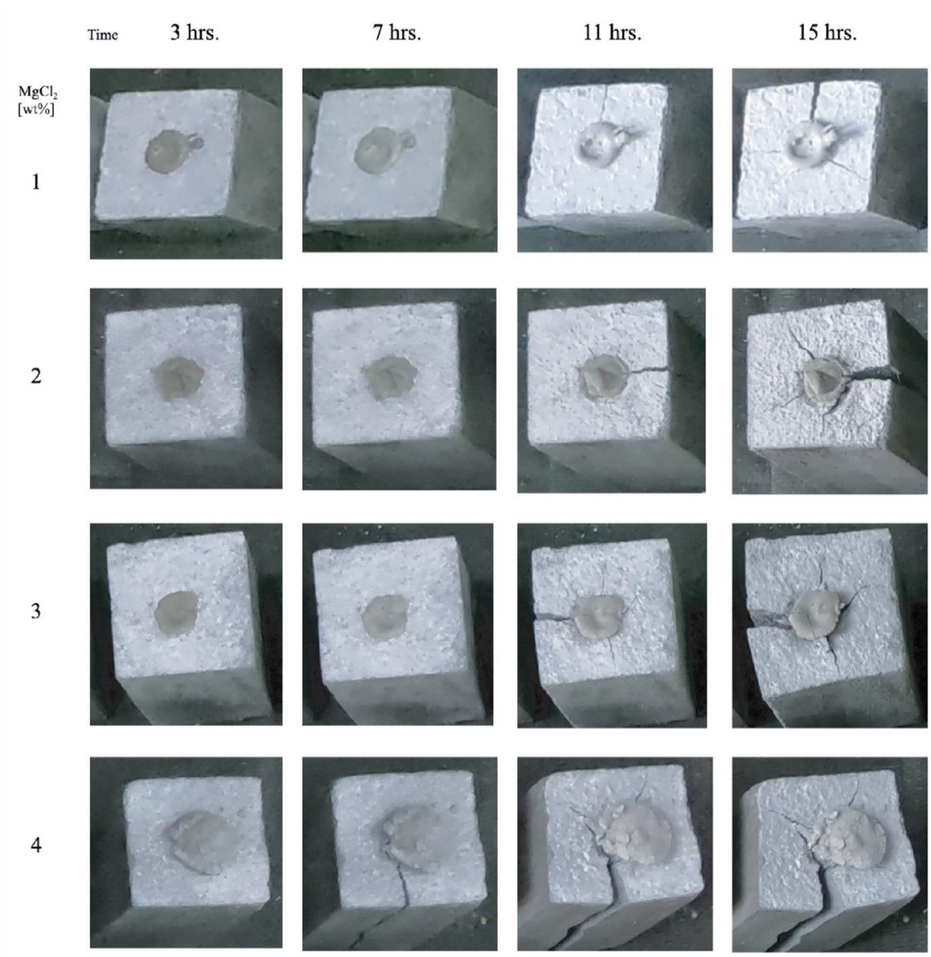

Fig. S4. Evolution of fracturing for OPC 1 blocks with a hole depth of 4 cm after 3, 7, 11, and 15 hrs. Modified BRISTAR 100£ with 1, 2, 3, and 4wt% MgCl2.

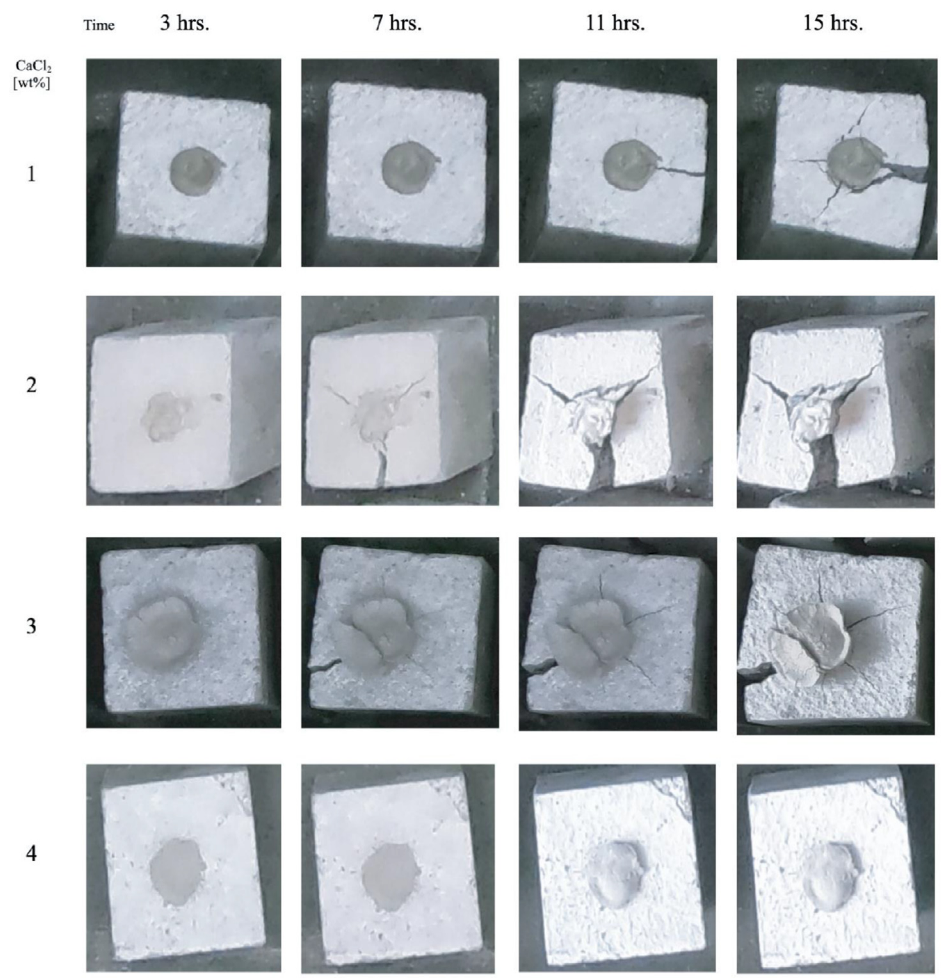

Fig. S5. Evolution of fracturing for OPC 1 blocks with a hole depth of 4 cm after 3, 7, 11, and 15 hrs. Modified BRISTAR 100£ with 1, 2, 3, and 4wt% CaCl2.

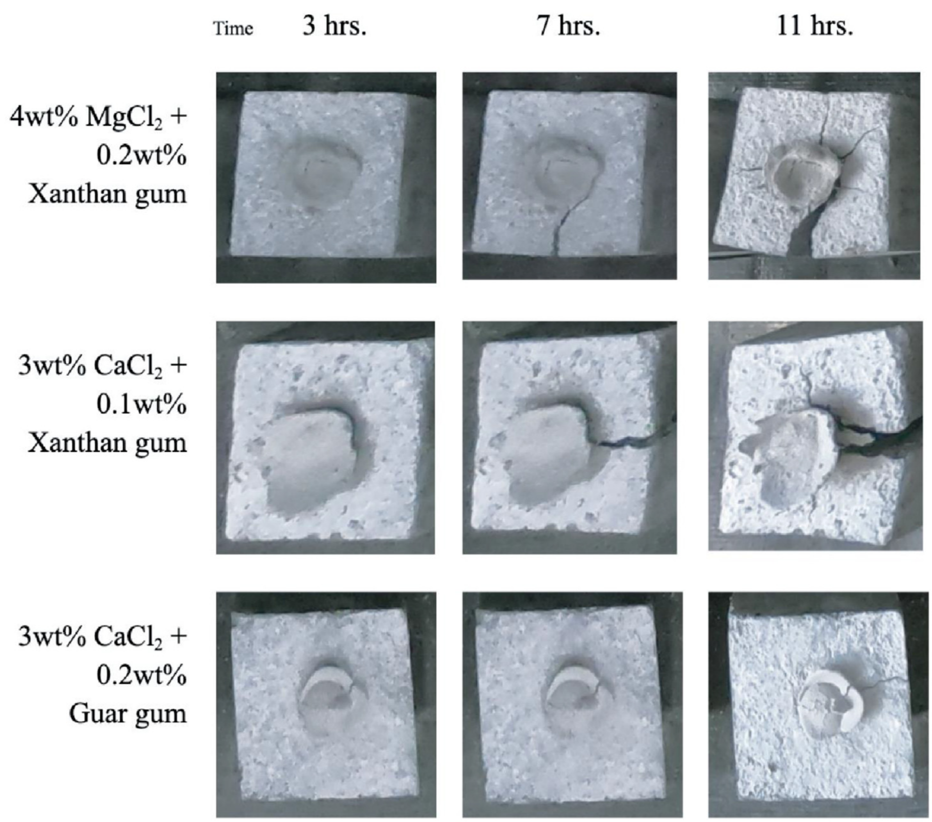

Fig. S6. Evolution of fracturing for OPC 1 blocks with a hole depth of 4 cm after 3, 7, and 11 hrs. Modified BRISTAR 100£ with varying concentrations of MgCl2, CaCl2, Xanthan gum, and Guar gum.

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