- Technical Paper -

Experimental investigation on the effect of mixing dry ice and γ-C_2S in concrete

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ABSTRACT
With the aim to reduce the carbon footprint resulting from concrete consumption, this study investigates the performance of concrete using γ-C_2S as a replacement for cement clinker. To promote a further reduction in carbon emissions, CO_2 is supplied while mixing concrete in the form of dry ice pellets to facilitate its storage into concrete. Various mixing methods have been investigated, such as adding dry ice at the same time as water, along with post and pre-mixing of γ-C_2S and dry ice. The results show that mixing of dry ice directly into concrete leads to loss in slump and compressive strength. However, pre-mixing dry ice and γ-C_2S with sand and gravel mitigates the loss in fresh properties and the required compressive strength could be obtained despite reducing the amount of cement clinker in concrete.
Keywords: Carbon dioxide utilization, Compressive strength, Dry ice, Sustainable concrete, Workability

1. INTRODUCTION

Manufacturing of cement leads to evolution of large volumes of CO_2 gas into the atmosphere due to the decarbonation of limestone and the burning of fossil fuels. The evolved CO_2 gas harms the environment and contributes to climate change and global warming. In order to mitigate the damage to the environment, and reduce the emission of greenhouse gases, researchers have increased their focus on reducing emissions from cement production together with developing innovative ways to fix exhaust CO_2 from factories into concrete allowing its recycling and removal from the environment [1].

One approach to reducing CO_2 generated from concrete consumption is by replacing cement clinker with supplementary cementitious materials (SCMs) such as fly ash, blast furnace slag (BFS), calcined clay etc. Energy and CO_2 minimum cement (ECM) [2] and Limestone Calcined Clay Cement (LC3) [3] are some of the products which have achieved significant CO_2 reduction per unit of concrete produced.

Apart from SCMs, special admixture such as γ-C_2S has also been successfully used to replace cement. Unlike its counterpart β-C_2S which is present in cement clinker, γ-C_2S does not hydrate on mixing with water. Instead, it can readily absorb CO_2 in the presence of water to produce thermodynamically stable calcium carbonate and silica gel. The γ-C_2S proposed to be used in this study has a significant advantage in that it is produced using calcium hydroxide which is obtained as a by-product of manufacturing calcium carbide from acetylene gas [4]. The amount of CO_2 evolved during the production of γ-C_2S is only 124.5 kg/ton compared to 766 kg/ton produced from cement. Further, 1 ton of γ-C_2S has the potential to absorb around 500 kg of CO_2, thereby promoting carbon negativity. Hence replacement of cement with γ-C_2S has the potential to reduce the carbon footprint left by the construction industry.

Another approach to reducing the overall carbon footprint of construction is to upcycle CO_2 gas in concrete through carbonation curing of casted structural

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components. CO_2-SUICOM is one such product in which cement is replaced with BFS and γ-C_2S to reduce greenhouse emissions and has attained carbon negativity on carbonation curing [1]. Apart from storing CO_2 in concrete through carbonation curing, CO_2 has also been recycled by mixing concrete in an environment of CO_2 gas. The calcium ions present in cement react with the carbonic acid generated by mixing CO_2 gas in water and precipitates nano-calcite which impinges on top of cement particles. Generation of nano-calcite has shown to accelerate hydration, formation of C-S-H and achieve target compressive strength even after 7-8% binder reduction [5, 6]. An alternative technique to fix CO_2 into the concrete while mixing is in the form of dry ice which is the solid form of CO_2. Previous studies on mortar with varying dosages of dry ice have shown that adding 0.6% by weight of cement content of dry ice reduces the setting time and increases the compressive strength [7]. Thus, the addition of CO_2 into concrete alters the rate of hydration reaction. However, intensive studies investigating the impact of dry ice addition on fresh properties and strength development in concrete are still lacking.

The objective of this study is to develop and propose an appropriate concrete mixing method to facilitate the reduction in the amount of CO_2 emitted due to concrete consumption and store CO_2 in concrete using dry ice. To promote real-world applications of the addition of γ-C_2S and dry ice into concrete, two mixing frameworks i.e. post-mixing and pre-mixing of dry ice and γ-C_2S in concrete have been introduced. The influence of the above-mentioned methods on slump flow and compressive strength is investigated. Thermogravimetric analysis has also been conducted to measure the change in the amount of calcium hydroxide and calcium carbonate resulting from the addition of dry ice.

2. EXPERIMENTAL SCHEME

2.1 Materials

Ordinary Portland Cement (OPC) as a binder with γ-C_2S as its replacement was used in this study. The chemical composition for both as measured using the X-ray fluorescence (XRF) analytical technique is shown in Table 1. The XRF result shows that the calcium content is almost identical in both OPC and γ-C_2S. The density and specific surface area for both are shown in Table 2. CO_2 was supplied by directly adding commercially available cylindrical dry ice pellets with 6 mm diameter and around 30 mm length.

Table 1: Chemical composition of OPC and γ-C_2S

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	LOI
OPC	63.8	20.5	5.1	3.1	1.2	2.0	0.3	0.4	2.6
γ-C_2S	63.9	33.9	1.0	0.4	0.1	0.4	0.1	0.1	0.1

Table 2: Physical properties of material used

	Name	Density (g/cc)	SSA* cm^2/g
OPC	Ordinary Portland Cement	3.16	3310
γ-C_2S	Di-Calcium Silicate	2.85	1500
S	Crushed sand	2.61	
G	Gravel	2.65	

*SSA: Specific surface area

2.2 Mixing Method

The three different mixing methods namely (1) Normal (2) Post-mixing (3) Pre-mixing were investigated in this study in an attempt to enhance the compressive strength of concrete mix even after reducing the binder content and increasing the amount CO_2 stored while mixing concrete. The sequence of adding ingredients for each of these mixing frameworks has been shown in Figure 1. Normal mixing method is the standard procedure generally followed while mixing concrete. The post-mixing method involves addition of dry ice together with γ-C_2S after all the other ingredients have been kneaded together to make concrete. The post-mixing framework was selected to investigate the viability of addition of dry ice and γ-C_2S once the ready-mix truck has arrived at the construction site. In the proposed pre-mixing framework, γ-C_2S and dry ice along with sand and gravel are mixed with 70% of water and admixtures following which cement and remaining 30 % of water are added.

2.3 Mix Proportion and Experimental Cases

The experimental cases considered in this study along with mix proportion has been shown in Table 3. The water to powder ratio (W/P) where weight of powder is the sum of weight of cement and γ-C_2S was fixed as 50%. With the intention to produce concrete having same strength but reduced carbon footprint, a

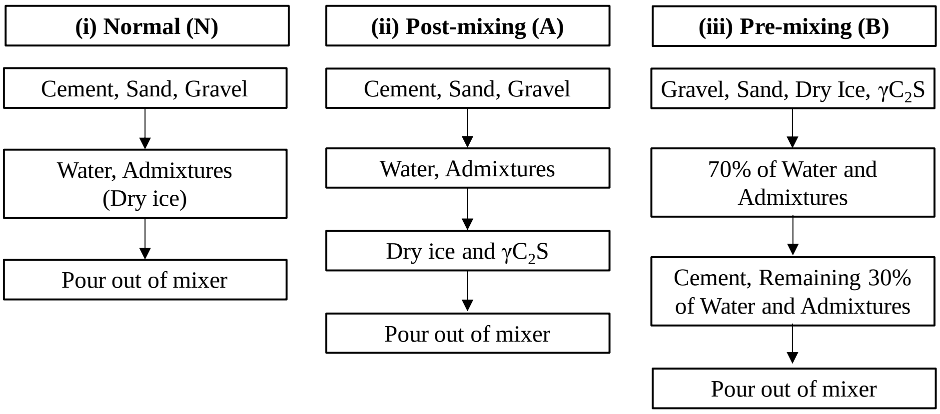


Figure 1: Sequence of mixing of materials for (i) Normal mixing (ii) Post-mixing (iii) Pre-mixing method

reduced binder case namely C2-N, containing 5% less cement was investigated as well for comparison. The cement content of C2-N was reduced from 350 kg/m^3 to 332 kg/m^3 of concrete, was same as that of mixes in which 5% of cement has been replaced with γ-C_2S. The letters "N", "A" and "B" correspond to the normal, post-mixing and pre-mixing sequence of the addition of γ-C_2S and dry ice. The concrete mix was designed for a target slump of 12 cm and target air content of 4.5%. The amount of dry ice (DI) added in this study was 0.6% of the weight of powder in the concrete mix i.e., 2.1 kg/m^3 of concrete. Water-reducing agent (WRA) and air-entraining agent (AEA) were adjusted depending upon mixing method and dosage of dry ice to obtain target air content.

2.4 Tests Conducted

(1) Fresh Properties

Temperature, slump, and air content were measured for all cases to evaluate the impact of the sequence of addition of dry ice and γ-C_2S on fresh properties following JIS A 1156, JIS A 1101 and JIS A 1128 respectively.

(2) Compressive Strength Tests

The compressive strength for each experimental case was measured on cylindrical specimens of diameter 100 mm and height 200 mm after 1, 7 and 28 days of sealed curing under 20°C and 60% relative humidity.

(3) Thermogravimetric Analysis

With the objective to accurately measure the amount of calcium hydroxide and calcium carbonate produced from the reaction of dry ice with cement and γ-C_2S, specimens with the same mix design but excluding sand, gravel and admixture were prepared. The paste was mixed in a small mortar mixer following the same sequence of mixing as shown in Figure 1. The prepared paste was poured into a cylindrical mold of 50 mm diameter and 100 mm height and later sealed. Samples for analysis were acquired from the center of these specimens and hydration was stopped after 1 day of sealed curing using acetone. The thermogravimetric/differential thermal analysis (TG-DTA) was conducted on 10 mg sample under nitrogen gas flow. The mass loss was measured by increasing the

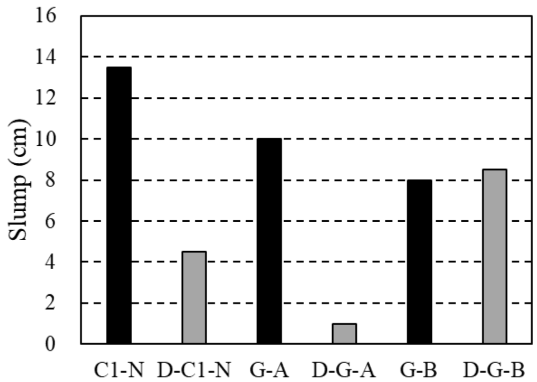
Table 3: Concrete mix design and experimental cases

Name	W/P*	W/C	Dry Ice	Unit Weight (kg/m^3)					Mixing method	Remarks
	(%)	(%)	(%)	W	C	γ-C_2S	Sand	Gravel		
C1-N	50	50	0.0	175	350	—	794	980	Normal	Base case
D-C1-N	50	50	0.6	175	350	—	794	980		Effect of dry ice
C2-N	52.5	52.5	0.0	175	332	—	801	988		Reduced binder
G-A	50	52.5	0.0	175	332	18	793	988	Post- mixing	Replacement of binder with 5% γ-C_2S
D-G-A	50	52.5	0.6	175	332	18	793	988		
G-B	50	52.5	0.0	175	332	18	793	988	Pre-mixing	
D-G-B	50	52.5	0.6	175	332	18	793	988		

*P = Weight of Cement + Weight of γ-C_2S

Table 4: Fresh properties of concrete mixes

Name	Mixing	Slump (cm)	Air Content (%)	Temperature (°C)
C1-N	Normal	13.5	3.9	21.7
D-C1-N		4.5	4.2	21.9
G-A	Post mixing	10.0	4.6	22.1
D-G-A		1.0	3.9	21.8
G-B	Pre mixing	8.0	4.0	22.0
D-G-B		8.5	4.0	21.9



W/C (%)	50	50	52.5	52.5	52.5	52.5
W/P(%)	50	50	50	50	50	50
γ-C_2S(%)	0	0	5	5	5	5
Dry Ice (%)	0	0.6	0	0.6	0	0.6
Method	N	N	A	A	B	B

Figure 2: Effect of mixing method and dry ice addition on the slump

temperature up to 1000°C at a rate of 20°C/min. The CSH dehydration, calcium hydroxide and calcium carbonate content were measured by calculating mass loss between 20°C to 200°C, 405°C to 515°C and 600°C to 850°C respectively.

3. RESULTS

3.1 Slump

The slump flow of concrete is an important parameter to ensure proper concrete placement and assess the quality of concrete mix design. The results of the slump flow have been shown in Table 4 and compared in Figure 2. Comparing the effect of the sequence of mixing only γ-C_2S into concrete i.e. cases C1-N, G-A and G-B, a decrease in slump compared to the normal mixing method was observed. As per the post-mixing method, γ-C_2S was added after all of water and admixtures have been mixed into concrete, since most of the WRA has already been consumed by previously added cement, the remaining amount is not able to prevent the flocculation of γ-C_2S particles to the same extent causing a loss in slump. In the pre-mixing method, γ-C_2S which is a small proportion of the total powder in the mix was initially mixed with water, sand and gravel following which cement which is the remaining 95% of the powder along with the remaining water is mixed. Hence, similar to the post-mixing method, loss in slump was observed in the pre-mixing method as well but since the larger portion of powder i.e. cement was added in the end, the resulting loss in slump is also more compared to the post-mixing method.

Addition of dry ice as per the normal mixing method (D-C1-N) and post-mixing method (D-G-B), led to drastic slump loss with slump being limited to 4.5 cm and 1 cm respectively. Mixing an additional amount of water reducer and air-entraining agent had no effect on the observed slump behavior. However, pre-mixing of dry ice and γ-C_2S followed by the addition of cement aids in the retention of slump flow after adjusting the amount of AEA as shown in Figure 2 for cases G-B and D-G-B. The temperature of the concrete mix for all cases was almost similar ranging from 21.7°C to 22.1°C indicating that the addition of dry ice does not reduce the temperature of concrete, rather the heat evolved from carbonation reaction balances the low temperature of dry ice. Since previous studies have reported the formation of nano-calcite on the mixing of concrete in the presence of CO_2 gas [3]. As per the authors, it is possible that the addition of dry ice following the normal mixing or post-mixing method leads to the formation of calcite particles which impinge on top of unreacted cement and γ-C_2S particles. These impinged crystals could change the shape of the particle making it irregular and hence offering resistance to the flow. The proposed pre-mixing of γ-C_2S and dry ice allows the materials to react and complete the in-situ formation of calcium carbonate. Thus, on the addition of cement in the following step, the cement particles do not react with dry ice and the cement slurry lubricates the carbonated γ-C_2S particles helping in slump flow retention. Hence, the proposed pre-mixing method offers a remedy for the slump loss observed on normal and post-mixing of dry ice in concrete.

Table 5: Compressive strength (MPa) results

Name	Dry Ice (%)	Age of Specimen		
		1-Day	7-Day	28-Day
C1-N	0.0	7.8	32.3	44.4
D-C1-N	0.6	7.1	30.3	42.5
C2-N	0.0	5.3	26.7	37.1
D-G-B	0.6	6.0	31.5	43.6

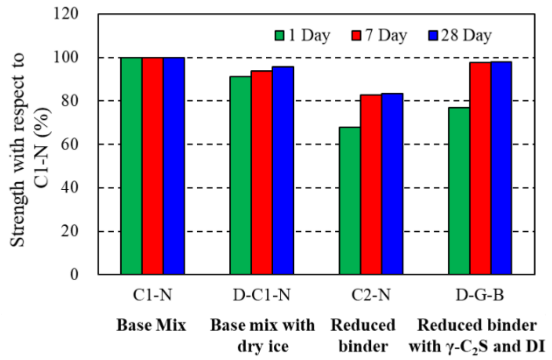


Figure 3: Comparing the compressive strength for all cases with respect to C1-N at corresponding ages

3.2 Compressive Strength

This section discusses the impact of pre-mixing γ-C_2S and dry ice in concrete on compressive strength. The acquired strength data has been shown in Table 5. As discussed in the previous section, since post-mixing of γ-C_2S and dry ice in concrete led to loss in slump, compressive strength test was not conducted for G-A and D-G-A. Considering the C1-N as the base case, i.e. concrete containing only cement with W/C of 50%, the compressive strength for all cases corresponding to the age of the specimen has been expressed as a percentage of the base case in Figure 3. From the results of C1-N and D-C1-N, it can be clearly observed that the addition of dry ice at the same time as water leads to loss in initial as well later age strength. The observed outcome is contrary to the previously published results as compressive strength evolution is sensitive to the dosage of dry ice and the tests were conducted on mortar and not concrete [5]. However, pre-mixing γ-C_2S and dry ice into concrete (D-G-B), the specimens showed 20% lower 1-day strength compared to C1-N but the 28-day strength was almost similar. Comparing D-G-B with C2-N, i.e. reduced binder case, it was observed that on pre-mixing, the 1-day strength improves when compared with the

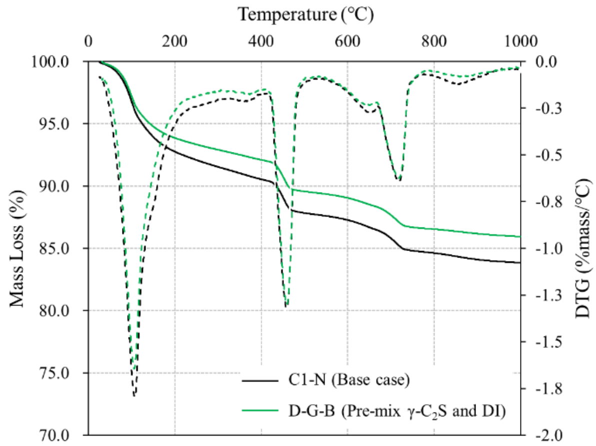


Figure 4: TG-DTA curves for C1-N and D-G-B

concrete mix containing the same cement content. This is in concurrence with the previously observed result that the addition of dry ice accelerates hydration. The in-situ nano calcite formed because of addition of dry ice provides greater number of nucleation sites for cement hydration thus resulting in higher early strength. Further, the 7-day and 28-day strength results also showed an improvement of around 20%. Since nano calcite has also shown to react with C_3A and C_3S present in cement, increasing their reactivity, this improves their contribution to compressive strength. The enhancement in strength despite reduction in binder could be attributed to this possibility as well. Hence on pre-mixing γ-C_2S and dry ice (DI), almost similar strength was obtained despite a reduction of cement content from 350 kg/m^3 to 332 kg/m^3. Considering that the amount of CO_2 evolved on the manufacturing of cement and γ-C_2S is 766 kg/ton and 124.5 kg/ton respectively, the amount of CO_2 evolved with respect to mix C1-N and D-G-B is 268.1 kg/m^3 and 256.5 kg/m^3 of concrete. Hence, pre-mixing γ-C_2S and dry ice supports a reduction of about 11.6 kg of CO_2 per m^3 of concrete. Since cement is primarily responsible for CO_2 emission, emissions resulting from only cement and γ-C_2S have been compared.

3.3 Thermogravimetric analysis

To understand the impact of the addition of dry ice on the hydration process, the amount of calcium hydroxide and calcium carbonate for C1-N i.e. base case (black color) and D-G-B (green colour) were measured using TG-DTA as shown in Figure 4. The plot shows mass loss with a solid line and the rate of mass loss per unit temperature with a dotted line. From the plot, it could be observed that after 1 day the peak of DTG corresponding to CSH dehydration (20℃ to 200℃) in D-G-B is lower than that of C1-N, indicating that the amount of hydration product is lower. Further the DTG peak of calcium hydroxide (CH) (405°C -515°C) and calcium carbonate (CC) (600°C - 850°C) does not have any significant difference for both cases. Since the amount of dry ice added is only 0.6% by weight of cement, even though it clearly has an effect on fresh properties and compressive strength of the concrete mix, the difference in the amount of calcium carbonate could not be accurately detected using TG-DTA. As per JIS R 5210:2009, the addition of components such as limestone, flyash, etc. by up to 5% of cement is allowed, hence the high amount of calcium carbonate shown by sample containing only cement (C1-N) and no dry ice could be due to the addition of limestone by the manufacturer. The similar trend shown by mass loss and DTG curves for both cases indicates that the hydration mechanism on the addition of dry ice does not change significantly.

4. Conclusion

Following the discussions from the previous sections, it could be concluded that the pre-mixing of γ-C_2S and dry ice is a viable method for enhancing compressive strength while ensuring workability as per industry standards. In the current study, the separate effect of post-mixing and pre-mixing of dry ice and γ-C_2S on fresh properties and compressive strength of concrete has been investigated. The following points could be concluded from the study.

(1) Addition of dry ice into concrete either at the same time as water or post-mixing leads to a drastic loss in slump. However, the proposed pre-mixing method offers a remedy, such that the loss in workability could be prevented.
(2) Compared to normal mixing, using the pre-mixing method, target compressive strength could be obtained even after a 5% reduction in cement content in the mix design. Thus it promotes a reduction in carbon footprint.
(3) Even though the addition of dry ice has a clear effect on concrete properties any significant change in the mechanism using TG-DTA could not be detected. Hence, a more sensitive and detailed analysis is required.

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