

Development of low-carbon cementitious material using magnesium oxide and fly ash as partial replacement of Portland cement

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Abstract—Magnesium-based binders have shown several potential benefits, such as improved strength and durability, better fire resistance, and a lower carbon footprint compared to traditional cement binders. Generally, high-water demand and low hydration of MgO retards strength of MgO based cement blend. In this study, the effect of hydration agent (Nitric acid) on compressive strength and water absorption of mortar cubes prepared with Portland cement, Magnesium oxide and Fly ash (PC-MgO-FA) have been investigated. Partial replacement of cement with reactive magnesium oxide with incorporation of hydration agent has a positive effect on compressive strength and water absorption. It resulted in increased compressive strength and reduction in water absorption as compared to the compressive strength and water absorption of mortar prepared without hydration agent. The result indicated that the Mix (PC-50%, MgO-30%, FA-20%) with 1M concentration of hydration agent showed 36 MPa at 28 days and water absorption of 2.5%. XRD analysis showed that the formation of hydrated Calcium silicate, Calcium alumino silicate hydrate, Magnesium hydroxide, Magnesium silicate hydrate and Hydrotalcite increased as compared to mortar without hydration agent resulting in increased compressive strength.

INTRODUCTION

Energy conservation completely depends on population growth and available natural energy sources. In last four decades, the global energy consumption has increased by about 92% [1]. Almost 33% of the entire energy consumed, buildings and construction share 30% of greenhouse gas emissions in most of the countries [2,3]. Manufacturing of cement for construction is responsible for almost 6 billion tons of global CO₂ emissions in 2018 [4].

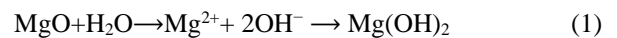
Magnesium oxide has been used as a binder in concrete [5]. Magnesium-based binders have been shown to have lower carbon footprint with several potential benefits such as improved strength and durability, better heat resistance compared to conventional cement binders [6]. Raw magnesium oxide has been extracted from magnesite [7].

Reactive Magnesia (MgO) based cementitious binders have earned importance due to their capacity to replace Portland cement in some sort of applications. [8]. The reactive

magnesium oxide shows an extra advantage that it is produced at relatively lower calcination temperatures as compare the conventional cement (i.e., 700-900°C vs. 1450°C) [9] and it can sequester carbon dioxide (CO₂) to improve its strength in the form of stable and dense products [10,7]. Though MgO has low solubility, when MgO is used as the only binding material then its hydration results into formation of brucite, that contributes to some extent in gaining of strength [11,12].

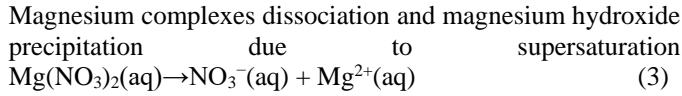
Reactivity of magnesium oxide and specific surface area varies with calcination temperature [13]. The composition of Reactive MgO can vary depending on the specific manufacturing process and raw materials used. It typically contains around 90-95% magnesium oxide, with the remaining 5-10% being made up of impurities such as calcium oxide and silicon dioxide [14]. Reactive MgO has many industrial uses, including in cement manufacturing, as a source of magnesium in fertilizers, and as a component in refractory materials [6].

Hydration reaction of MgO, which forms brucite in eq. 1, is as listed [15],



The product of above-mentioned reaction has more volume than its reactants, therefore this hydration reaction of MgO creates volume change, which, if rigorously studied and controlled, may compensate the shrinkage of composites made of cementitious material [16,17]. The hydration of MgO seems to be quite similar to that of conventional cement, along with the formation of brucite, pozzolanic reactions may form magnesium silicate hydrates (M-S-H) gel [18]. M-S-H gel is capable of exhibiting significant growth in strength [19], when there is presence of amorphous silica-containing chemical admixtures and additive additions, such as fly ash [20,21] or silica fume [22]. Nuclear waste encapsulation can be targeted using a blend of M-S-H based cement binder [15] and castables of refractory industries also have direct application of the same blend [23].

The hydration mechanism of MgO is slow, using hydration agent with varying concentration might accelerate the hydration. Hydrating mechanism depends on pH of solution and also plays a key role in product formation [24,25]. Hydration of MgO is a two-step process which start with dissolution (eq. 2 -4) followed by precipitation process [25,26].



The complex ions of magnesium-nitrate promote enabling of brucite precipitation within the solution [27].

2. MATERIAL AND METHODOLOGY

2.1 Material and mix preparation

The mortar consists of OPC-43 with measured normal consistency of 29.5%, commercially available MgO and industrial waste class F Fly ash. Nitric acid was used as hydration agent to accelerate hydration of MgO. The molar concentration of nitric acid varies and test were performed. MgO reactivity was evaluated with acetic acid test. It was reported by the time measured for complete neutralization of an acidic solution. Shorter time of neutralization of MgO reflect its higher reactivity [16]. The recorded neutralization time of MgO was 218 secs and can be labelled as reactive MgO.

The OPC was kept constant to 50%, the quantity of MgO and class F fly ash 20-30 % individually as listed below in Table-1. Mortar cubes of size 50x50x50 mm, keeping binder to sand ratio of 1:3 was casted with w/b=0.42(using normal consistency) for the determination of water absorption and compressive strength.

Table-1: Mix Designation and proportions

Group	Mixes	W/B	PC (%)	MgO (%)	FA (%)	HA (Conc.)
Control Mix	CM	0.42	100	---	---	---
G1	G-1-1		50	30	20	0M
	G-1-2		50	25	25	0M
	G-1-3		50	20	30	0M
G2	G-2-1		50	30	20	0.5M
	G-2-2		50	25	25	0.5M
	G-2-3		50	20	30	0.5M
G3	G-3-1		50	30	20	1.0M
	G-3-2		50	25	25	1.0M
	G-3-3		50	20	30	1.0M

2.2 Compressive strength

The compressive strength test was conducted by taking mean of 3 samples as per IS:4031(Part-6) [28]. The compressive

strength (CS) test was performed after 7 days,14 days and 28 days.

2.3 Water absorption

The water absorption of mortar cube was done. The initial mass of the samples was noted and then samples were immersed in the water tank for 24 hours.

3. Result and discussion

3.1 Compressive strength

Mortar samples from Group-G1 have very less compressive strength as compared to Group-G2 and group-G3. The M-S-H formation in this group is very minute due absence of accelerating hydration agent (HNO₃) which is evident from Figure-1. Without hydration agent the unreacted MgO was there causing less formation of brucite and hence more porous structure that also can be seen in water absorption. On inclusion of hydration agent, the hydration process gets accelerated and the brucite is formed, which subsequently reacts to form M-S-H phases. Compressive strength of sample varies directly with concentration of hydration agent as it can be seen for 1M concentration the compressive strength for G-3-1 (MgO:30%, FA:20%) has a relatively high compressive strength (36 MPa) after 28 days as shown in Figure-3. No significant M-S-H peaks were seen in Figure-2(a) showing data of group-1 without hydration agent. Figure-2(a) also depicts significant peaks of MgO which imply the reason of reduction of compressive strength. Increased molar concentration of hydration agent forms Brucite at early stage of hydration which lead to the formation of M-S-H as shown in Figure-2(b) and 2(c). The M-S-H peaks were found around at 33°-40°and 58°-60°[29].M-S-H and other phases formation results into a relatively good Compressive strength and less water absorption. Samples containing hydration agent showed high rate of strength gain than the sample without hydration agent. Although the reported compressive strength of G-3-1 at 28 days was 18% lesser than the control mix, however the PC content was cut down to 50% and hence seems to be more sustainable solution.

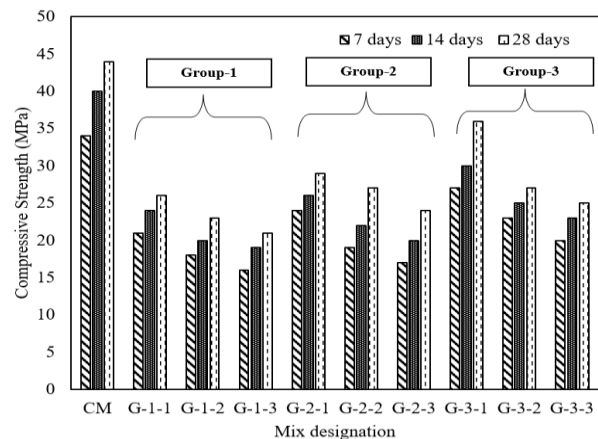


Figure 1: Compressive strength of mixes

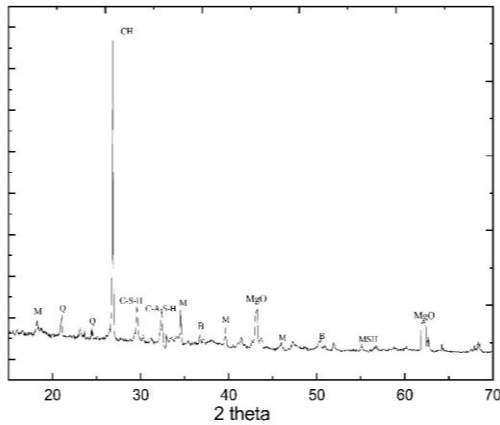


Figure 2(a): G-1-1 mix XRD graph

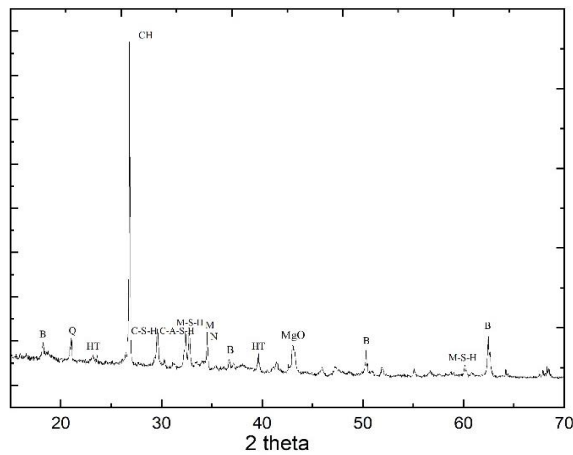


Figure 2(b): G-2-1 mix XRD graph

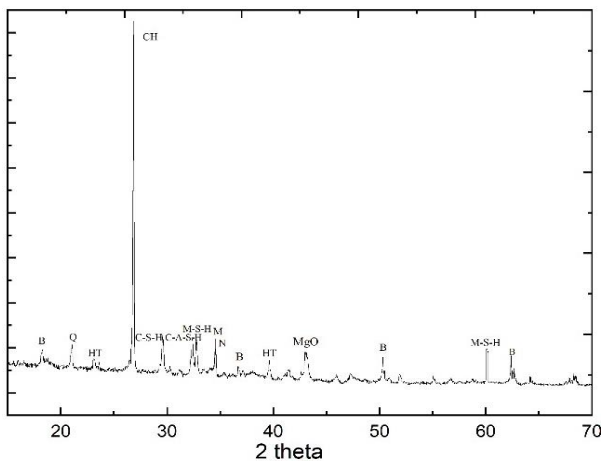


Figure 2(c): G-3-1 mix XRD graph

B= Brucite; Q= Quartz; HT= Hydrotalcite; M= Mullite; N= Nesquehonite

3.2 Water absorption

Water absorption depends on the available pores in the matrix. The reported water absorption of control mix (CM) was 6.8% while the group-2 and group-3 showed a significant reduction of 20% and 50% respectively (Figure-3). For 1M Concentration of hydration agent the water absorption of 2.6% was recorded. XRD results as shown in Figure-2(b) and 2(c) also confirms the phenomena of reduction in water absorption in the blended samples. As the proportion of M-S-H, Brucite, Hydrotalcite, C-S-H, C-A-S-H increases, it resulted into reduction of water absorption. Samples from group-1 without hydration agent have maximum water absorption as shown in Figure-3. Unreacted MgO in group-1 causes higher water demand and have poor water absorption as reported in Figure-2(a).

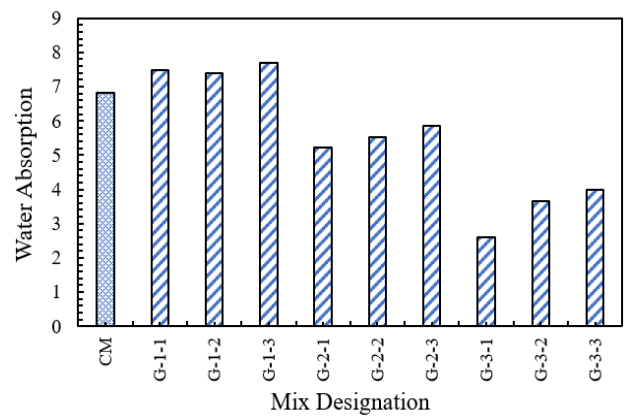


Figure 3: Comparative water absorptions of mixes

4. CONCLUSION

On the basis of observations and discussion, the following conclusion can be derived.

1. The compressive strength of all samples containing MgO and FA were lesser than the control mix, however Group-2 and Group-3 Mixes were found to have significantly less water absorption as compared to control mix indicating better durability.
2. Slow hydration of MgO due to absence of hydration agent in Group-1 mortar series resulted in less compressive strength and increased water absorption as compared to the other mixes with hydration agent.
3. Mix G-3-1 showed the maximum compressive strength of 36 MPa and least water absorption of 2.5% when compared to the other mixes containing MgO and fly ash.
4. The compressive strength increased and water absorption decreased as the concentration of hydration agent increased.

5. ACKNOWLEDGMENT

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