

ROLE OF OLIVINE AGGREGATE IN LIME AND CEMENT MORTARS FOR THE SEQUESTRATION OF ATMOSPHERIC CO₂

ZAKONITOSTI OLIVINSKEGA AGREGATA V APNU IN CEMENTNIH MALTAH ZA ZAJEMANJE ATMOSFERSKEGA CO₂

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Construction industry is majorly criticised due to a great liberation of carbon dioxide (CO₂) into the atmosphere. Researchers have identified various techniques to capture the atmospheric CO₂. Nevertheless, the recognised methods have both merits as well as demerits. Thus, scientific communities are working on simple and easily exhibited ways of capturing atmospheric CO₂. One such technique is the conversion of gaseous CO₂ into stable calcium/magnesium carbonates. The present study was conducted to identify the carbon-capturing efficiency of olivine aggregate in cement and lime mortars. Olivine aggregate has a tendency to change its mineral structure under alkaline environment and it is able to interact with atmospheric CO₂ to form a stable carbonate. Analytical techniques (XRD, TGA) were conducted to elucidate the formation of hydrated phases formed in both lime and cement mortars. The study concluded that the addition of olivine sequestered atmospheric CO₂ and converted it into magnesium carbonate. Out of the lime and cement mortar, lime mortar captured a greater amount of CO₂ and produced stable compounds.

Keywords: carbon capture, carbon sequestration, olivine aggregate

Gradbena industrija se v glavnem kritizira zaradi velike svobode do izpustov ogljikovega dioksida (CO₂). Raziskovalci so do sedaj iznašli različne tehnike za zajemanje atmosferskega CO₂. Vendar pa imajo vse te do sedaj ugotovljene metode oziroma postopki določene prednosti in pomanjkljivosti. Tako znanstvena skupnost še naprej dela na poenostavitvah poti za zajemanje atmosferskega CO₂. Ena od takšnih možnih tehnik je pretvorba plinskega CO₂ v trdno obliko kot so karbonati na osnovi kalcija in magnezija. Predstavljena je študija s katero so poizkušali ugotoviti učinkovitost agregatov olivina ((Mg,Fe)₂SiO₄) v cementnih in apnenih maltah. Agregati olivina (pesek z delci velikosti pod 65 μm) imajo sposobnost reagiranja z atmosferskim CO₂ in tendenco pretvorbe svoje mineralne strukture v alkalnem okolju v trdni karbonat. S pomočjo analitičnih metod (XRD, TGA) so razložili nastanek hidratne faze, ki nastaja tako v apneni kot tudi v cementnih maltah. Ugotovili so, da dodatek olivina izolira atmosferski CO₂ in ga pretvori oziroma veže v magnezijev karbonat. Apnene malte vežejo večjo vsebnost atmosferskega CO₂ kot cementne in tvorijo trdne spojine.

Ključne besede: zajemanje atmosferskega ogljika, odstranjevanje atmosferskega ogljika, olivinski agregat

1 INTRODUCTION

The significant growth in the urbanization and industrialization of the world has triggered a drastic alteration in the climate of Earth and that may be the major reason behind the global warming. The intergovernmental panel on climate change (IPCC), funded by the UN (United Nations) concluded that the increase in global warming occurred due to the rise in the atmospheric CO₂ concentrations produced by humans.¹ The burning of fossil fuels like natural gas, coal and oils leads to a greater liberation of CO₂ into the atmosphere, which further significantly impacts the environment. According to the Kyoto Protocol, the CO₂ emissions from fossil fuels have been raised by 2.7 % annually over the previous ten years and are already 60 % higher than the levels in the reference year 1990.²

To control the global CO₂ emissions, carbon capture and utilization (CCU) is one of the effective solutions.² It comprises the sequestration of atmospheric CO₂ and its transformation into a valuable commodity either directly or after conversion. Direct utilization of CO₂ is found in the pharmaceutical industry, enhanced oil recovery, and food and drink industries.³ The conversion of CO₂ into a product is found in the biofuel and chemical industry and mineral carbonation.⁴ In case of mineral carbonation, CO₂ interacts with metal oxides of calcium and magnesium bearing compounds, producing stable calcium/magnesium carbonates. Its major shortcomings are mining, transportation and production of metal oxides, requiring a lot of energy, which may not be economical.²

At the same time, concrete is the most widely used material on Earth after water and it is primarily composed of cement, aggregates and water.⁵ The production of cement necessitates the use of fossil fuels at temperatures varying in a range of 1400–1500 °C and could en-

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danger the environment due to the liberation of CO₂.⁶ In general, the manufacture of one tonne of cement emits an equivalent quantity of CO₂ into the atmosphere, accounting for 7 % of the world CO₂ emissions.⁷ The construction sector also relies on non-renewable resources to generate aggregates, which account for around 60–75 % of the total concrete volume.⁸

Knowing from the past, lime mortars were the key materials used over the centuries for the ancient structures. The hardening of lime mortars occurs through the process called carbonation. It involves an interaction of calcium hydroxide with atmospheric CO₂ to form a stable compound, calcium carbonate (CaCO₃).⁹ Hence the carbonation is also called the natural way of sequestering atmospheric CO₂ from the environment and converting it into a stable product and this technique is similar to the mineral carbonation in the CCU technique.

In recent years, researchers have identified another important mineral, called olivine that could help to convert atmospheric CO₂ into stable carbonates. In general, olivine is a naturally occurring mineral with varying proportions of magnesium to iron, combined with silicates. It is usually identified in mafic and ultramafic igneous rocks. Based on the amounts of magnesium and iron, they are named as forsterite (MgSiO₄) and fayalite (Fe₂SiO₄). Fasihnikoutalab et al.¹⁰ studied the role of olivine aggregate in the stabilization of soils. The study concluded that an addition of olivine aggregates improved the unconfined soil strength by 120 % when compared with the reference one. They also stated that the precipitation of magnesite was found, which could be the reason behind the improved strength. Westgate et al.¹¹ discussed the role of olivine aggregate in lime mortars. The research confirmed that fine-sized olivine aggregates underwent dissolution in the lime alkaline environment and stable magnesium carbonate precipitated in comparison to references mortars. The authors also explained that the added olivine aggregate plays a dual role, replacing fine aggregates and helping the sequestration of carbon dioxide from the atmosphere. Thus, in the current study the authors attempted to examine the carbon-capture ability of both lime and cement mortar with olive aggregates. Analytical techniques like XRD and TGA were conducted to identify the hydrated phases developed in the mortars.

2 EXPERIMENTAL PART

2.1 Binder

Natural hydraulic lime and cement are chosen as binders for the proposed study. Both binders are procured from commercial suppliers from Vellore, India. Hydraulic lime conforms to class A according to IS 712: 1984;¹² the chemical composition is presented in **Table 1**. The lime exhibits nearly 24 % of clay impurities, hence it is categorised as eminently hydraulic in nature. Ordinary Portland cement (OPC) of grade 53 is used.

Table 1: Oxide composition

Oxide components	Percentage of oxides	
	Lime	Cement
CaO	63.2	66.67
MgO	0.161	0.87
SiO ₂	19.94	18.91
Al ₂ O ₃	4.315	4.51
Fe ₂ O ₃	1.833	4.94

2.2 Aggregates

Two types of aggregates are selected for the study, namely river sand and olivine aggregate. The river sand is procured locally and the gradation of aggregates is done through a sieve analysis.¹³ Olivine is procured from Industrial Minerals & Refractories, Tamil Nadu, India. The obtained olivine aggregates are ground into fine particles of a size not exceeding 65 µm.

2.3 Mix proportions

Two sets of samples are prepared to investigate the role of olivine aggregate in both lime and cement mortars. Set 1 comprises lime sand (LS), lime olivine (LO) and Set 2 includes cement sand (CS), cement olivine (CO). For both sets of mortars, a 1:3 binder-to-aggregate ratio is adopted with 0.65 (lime) and 0.45 (cement) as the binder-to-water ratios. Initially, one part of binder (lime/cement) and three parts of aggregate (fine aggregate/olivine aggregate) are weighed separately and mixed thoroughly to attain a uniform state. The grinding of two sets of mortars are done in a separate paddle mixer. Many researchers have discussed the chemical incompatibility of lime and cement mortars. Hence, while mixing the mortars, proper care should be taken to avoid intermixing. After preparing the mortars as per IS 6932 (Part VII): 1973¹⁴ (Hydraulic lime) and IS 2550 : 1981¹⁵ (Cement mortars), the mortar mix is shifted into moulds with a size of 50 mm × 50 mm in three layers with proper compaction to ensure the voids are reduced. Cement mortar is demoulded after 24 h and kept at a temperature of 27 ± 2 °C and 75 % relative humidity and lime mortar is demoulded after 3 d and cured at the same conditions.

2.4 Analytical techniques

After the curing period, the core portion of the cube is crushed thoroughly and passed through a 45 micron sieve. The sieved (passed) material is examined with analytical tests, X-ray diffraction (XRD) and TGA (thermal gravimetric analysis). The XRD of the samples is carried out using BRUKER D8 Advance (Germany) with Cu K_α radiation (0.15406 nm), a Lynxeye detector (silicon-strip detector technology), and a Ni filter, detecting the crystalline phases present in the mortars. TGA is conducted to identify the weight loss of various hydrated phases developed in both lime and cement mortars.¹⁶

3 RESULTS

3.1 XRD of aggregates

The crystalline phases of fine aggregate and olivine sand are compared with the XRD analysis as shown in **Figures 1a** and **1b**. The majority of the peaks observed in fine aggregate indicate quartz followed by feldspar and zirconium. Quartz is a highly stable compound and it acts as an inert material in lime and cement mortars. On other hand, olivine is a natural mineral with variable quantities of magnesium to iron, combined with silicates. XRD interpolation confirms that the selected olivine aggregate is a magnesium-rich forsterite mineral. Fasihnikoutalab et al.¹⁷ discussed the dissolution mechanism of olivine mineral in an aqueous solution. These authors also stated that olivine is a good candidate for CO₂ sequestration because it originates from basalt rocks and it is a neosilicate mineral. The mechanism involves the dissolution of atmospheric CO₂ in pore water and the formation of carbonic acid, which keeps the pH at around 5.7 and stimulates the dissolution of olivine aggregate so that finally magnesium-bearing compounds are formed. The prime factors that affect the dissolution of olivine aggregate are pH, CO₂ concentration, temperature and grain size. The dissolution mechanisms of olivine aggregates in the aqueous state are included in Equations (1), (2) and (3).

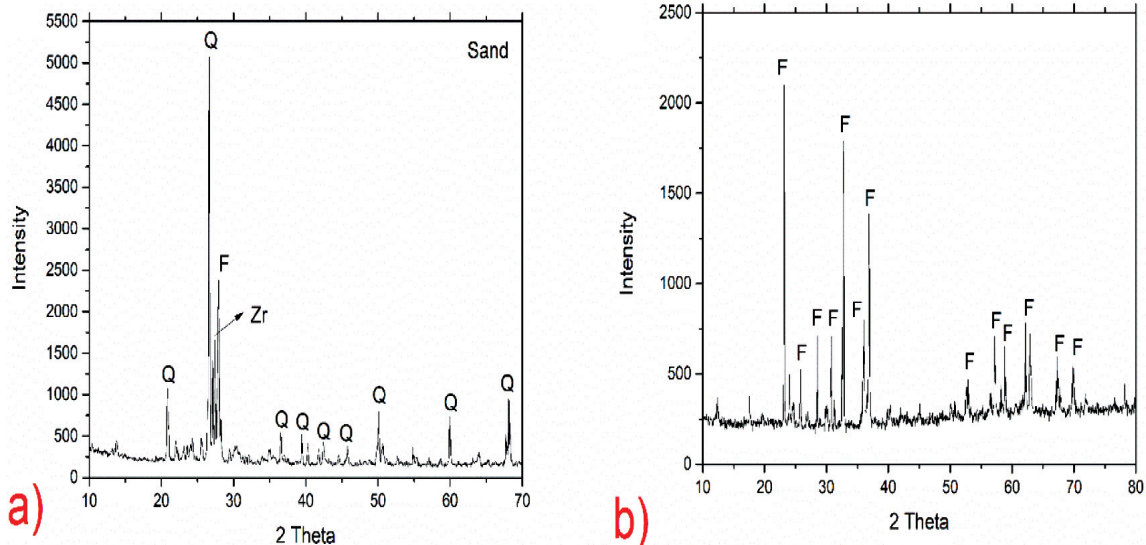
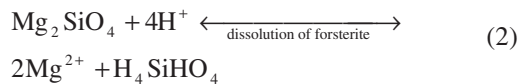
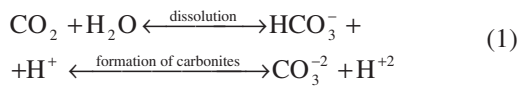


Figure 1: a) sand, b) olivine aggregate

3.2 XRD analysis

Figures 2a and **2b** depict the XRD patterns for LS (lime + sand), LO (lime + olivine), CS (cement + sand) and CO (cement + olivine) mortars for 28 d. The examination was initiated by comparing the crystalline phases of reference lime mortars with lime/olivine aggregate mortar. The significant peaks recognized in reference mortars (**Figure 2a**) are calcite, portlandite, quartz, and traces of tobermorite and gismondine. The dominant calcite peaks are due to the conversion of portlandite to calcite through the process called carbonation. In general, carbonation is a natural phenomenon, in which atmospheric CO₂ reacts with calcium hydroxide in the presence of pore water to form a stable compound, calcium carbonate. Cultrone et al.¹⁸ stated that carbonation is a slow process, prolonged from months to years. Hence, the presence of portlandite could be the reason behind it. The traces of tobermorite and gismondine are also identified due to the presence of clay impurities in the binder. In case of the LO mortar, **Figure 2a** depicts the majority of calcite peaks, followed by aragonite, magnesite, dolomite, tobermorite, gismondine and brucite. As discussed before, the ground form of forsterite aggregate undergoes dissolution in water and converts into Mg and Si ions. The magnesium ions interact with atmospheric CO₂ and form magnesite and dolomite. Magnesium ions can act as catalysts for the precipitate aragonite phase in the lime mortars.¹⁹

Now the discussion will focus on the cement reference mortar and cement/olivine mortar. For the reference mortar (**Figure 2b**), the major peaks observed indicate quartz, calcite, ettringite, aragonite and portlandite. The occurrence of calcite is due to the presence of free portlandite, which occurred during the hydration of cement. Tobermorite peaks are observed due to the interaction of alite and belite with water. In comparison with reference mortars, cement/olivine mortar shows greater

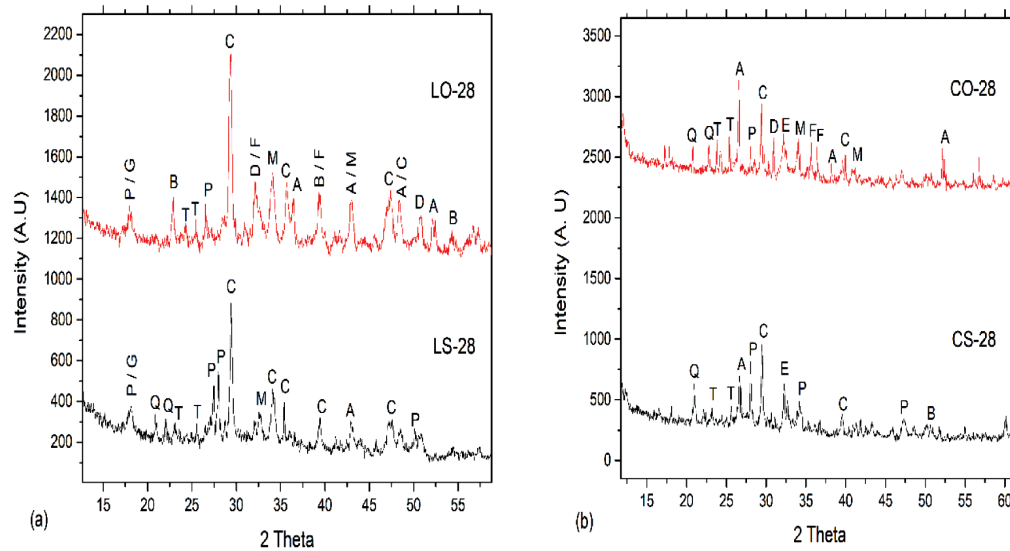


Figure 2: a) LO, LS, b) CO, CS; P: portlandite; G: gismondine; B: brucite; T: tobermorite; C: calcite; M: magnesite; A: aragonite; D: dolomite; Q: quartz; E: ettringite

intensive peaks of aragonite, dolomite, calcite and traces of brucite. The reason behind the domination of crystalline phases compared to amorphous phases could be the natural carbonation of mortars (CS, CO) (a temperature of 28 °C and RH of 65 %). Cizar et al.²⁰ discussed the competition of hydration and carbonation in hydraulic mortars under standard conditions. These authors concluded that hydration is followed by a carbonation process. Based on the above discussion, the final conclusion is that lime mortars have a natural CO₂ sequestration ability, but an addition of olivine improves the sequestration process, which is evident due to the greater intensity peaks observed in the mortars with added olivine. The olivine mortars also show the major strength giving compounds due to the presence of magnesium ions.

3.3 TGA analysis

Combined TGA and DTA graphs of lime and cement mortars are depicted in **Figures 3a** and **3b**; the weight losses of both mortars are presented in **Table 1**. In the temperature range below 120 °C, weight losses of 0.27 % and 0.3 % are observed for lime and olivine mortars, representing a low level of hygroscopic water. Weight losses of 4.36 % and 4.44 % (120–420 °C) are identified in lime reference and lime/olivine mortars. This could be due to the weight loss of the clay impurities present in lime, while the slight increase in the weight loss of olivine mortars could be attributed to the presence of brucite. In the temperature range of 400–600 °C, weight losses of 2.62 % and 2.96 % are observed in LS and LO mortars. The weight loss in both

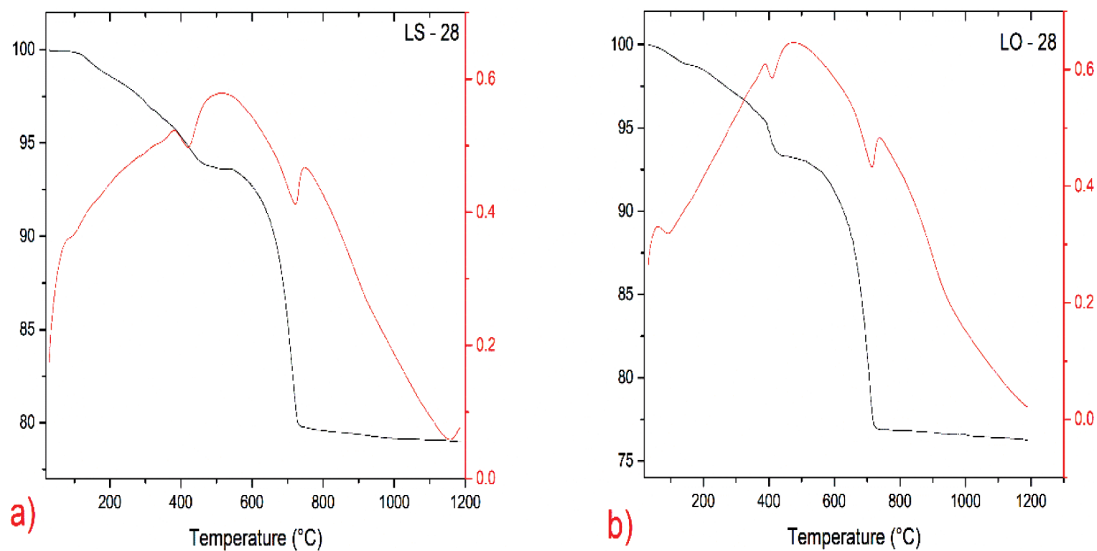


Figure 3: a) LS – 28, b) LO – 28

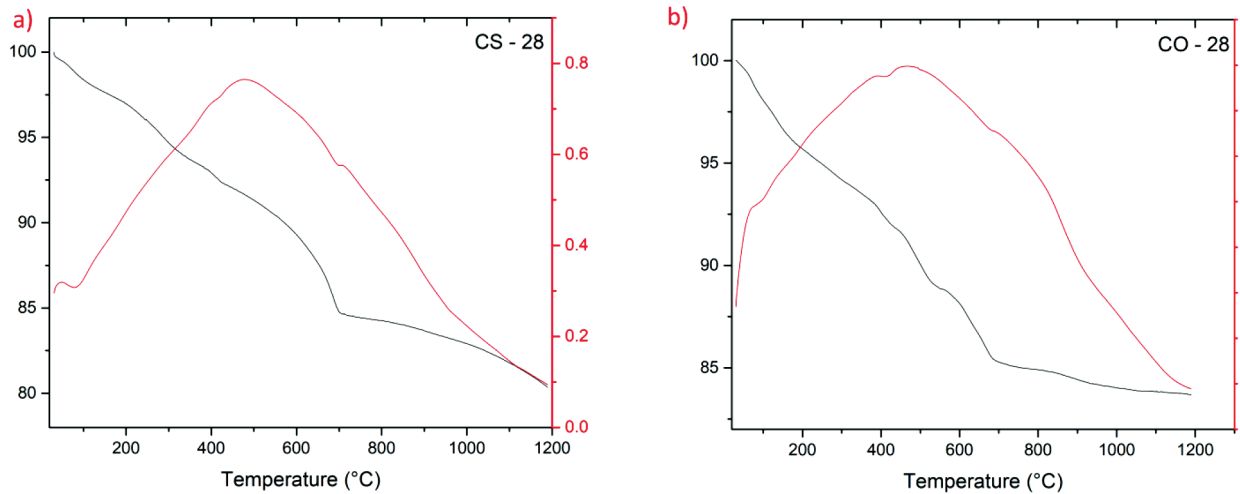


Figure 4: a) CS – 28, b) CO – 28

Table 2: Percentage of weight loss

Description	< 120 °C	120–420 °C	400–600 °C	600–800 °C
LS – 28	0.27	4.26	2.62	13.11
LO – 28	0.3	4.34	2.92	15.37
CS – 28	2.14	5.47	4.23	3.27
CO – 28	2.27	5.52	4.61	5.01

mortars is due to the decomposition of uncarbonated portlandite present in the samples. In addition, the greater weight loss in LO mortar is due to the decomposition of magnesite. The fall in weight at 600–800 °C is due to the release of CO₂ from the polymorph of calcium carbonate (aragonite, calcite) in LS mortars.¹⁶ The greater weight losses in LO mortars are due to the formation of dolomite along with calcium carbonate polymorphs. The XRD results also depict the presence of additional minerals like brucite, magnesite and dolomite in the lime/olivine mortar.

Significant mass losses of 7.6 (CS) and 7.7 % (CO) are observed in the range of 120–420 °C due to the loss in the surface water, dehydration of C-S-H and decomposition of ettringite and brucite (Table 2). The weight losses in cement olivine mortars are greater than in lime mortars due to a greater decomposition of calcium silicates and aluminates along with brucite. DSC depicted an exothermic reaction in the temperature range of 400–600 °C, which can be attributed to the dehydration of portlandite and magnesite. A weight loss of 5.01 % is found in CO mortars compared to 3.27 % in CS mortars in the temperature range of 600–800 °C. The increase in the weight loss of CO mortars is due to the decomposition of calcium carbonate along with dolomite. DSC curves show endothermic reactions in the same temperature range. The decomposition of calcium carbonate is shifted before 800 °C, which can be due to the formation of metastable calcium carbonates (Figures 4a and 4b). Hence, the increased weight loss in both LO and CO mortars is due to the interaction of finely ground forsterite compounds with atmospheric CO₂, confirming that

olivine-based mortars have a greater ability to capture atmospheric CO₂.

4 CONCLUSIONS

An addition of olivine aggregates greatly improves the properties of both lime and cement mortars. The strength gains in both mortars are due to the formation of magnesium-bearing compounds magnesite and dolomite, which is confirmed with analytical techniques, XRD and TGA. These compounds are formed due to the interaction of carbonate ions with dissolved magnesium ions in both mortars. During the process of hardening of olivine mortars (lime, cement), olivine sequesters atmospheric CO₂ and forms a stable compound. Hence, the adoption of olivine aggregate in binding mortars is highly advisable as it improves the properties of both mortars and reduces the carbon footprint on the environment, acting as a carbon capture and sequestration unit.

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