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PROPERTIES AND CHARACTERIZATION OF MAGNESIUM OXYCHLORIDE CEMENT AS CARBON CAPTURE MATERIAL

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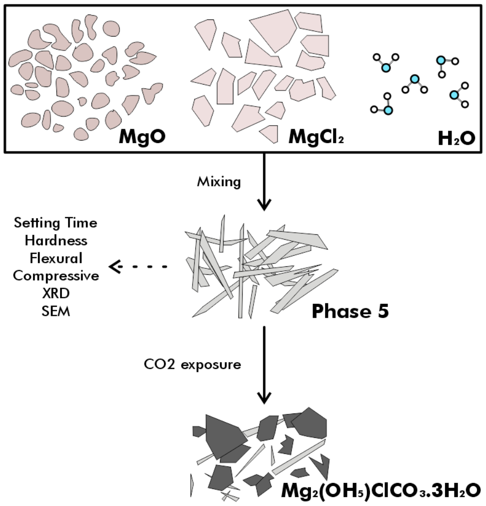
Graphical abstract



Abstract

Greenhouse gas emissions produced by steam-powered electric plants can trigger damage to the atmosphere and increase the average surface temperature below it, resulting in global warming as a manifestation of the operation of power plants. A material is needed to capture carbon dioxide (CO2) gas produced by the power plant. Magnesium oxychloride (MOC) cement, commonly called Sorel cement, has the potential to be used as a carbon capture material. MOC is synthesized from magnesium oxide (MgO), magnesium chloride (MgCl2), and water (H2O). This study aimed to find the optimum ratio of $MgO:MgCl_2:H_2O$ to produce the MOC with highest mechanical properties ranged from 1:1:1, 2:1:1, and 3:1:1. To determine the performance of the resulting MOC, physical, mechanical, X-ray diffraction (XRD), and scanning electron microscope (SEM) characterization tests were carried out. MOC with the highest mechanical properties was exposed to a high CO_2 gas environment to determine its carbon capture performance. The mechanical testing shows that the best ratio of $MgO:MgCl_2:H_2O$ was 3:1:1. This produces a hardness value of 43 VHN, a compressive strength of 57 MPa, a flexural strength of 46 MPa, and a modulus of elasticity of 2 GPa. The MOC 3:1:1 shows a CO_2 gas capture effectiveness of 36% after 7 days, proven by XRD and SEM. The results of the tests carried out show that MOC has the potential to reduce carbon emissions produced by the steam-powered electric plant industry.

Keywords: MOC, carbon capture, carbondioxide gas, mechanical properties, phase 5.

1.0 INTRODUCTION

The electricity consumption in Indonesia reached 255.1 TWh in 2021 and received an increase in sales until April 2022 compared to the same month in the previous year. This shows the high demand for electricity supply, especially after the rise of the Indonesian economy since the pandemic. This need makes the role of electricity suppliers, 66 percent of which is still held by steam-powered electric plants, highly dependent. Even in Indonesia alone, there are 55 power plant locations spread across the archipelago to meet the total electricity demand. Steam-powered electric plants operate by utilizing coal and oil to obtain kinetic energy from steam as a turbine driver connected to a generator [1]. The fuel used in this plant produces waste products in the form of greenhouse gases. These gas emissions can trigger damage to the atmosphere and increase the average surface temperature below it, resulting in global warming as one of the manifestations of the operation of the steam-powered electric plants [2]. Various efforts have been made to reduce the effects of greenhouse gas emissions. one of which is to capture the gas before it can reach the atmosphere. This gas capture technology, especially carbon dioxide, can be referred to as CCUS. Broadly speaking, this technology will convert carbon dioxide in the air into other forms so that it can be stored. However, then the question arises about environmentally friendly storage locations for products that will contain a lot of carbon dioxide. Recently, research on CCUS materials science and engineering has been growing. In 1855, Stanislas Sorel first developed a two-component zinc oxychloride cement by mixing powdered zinc oxide (ZnO) with a solution of zinc chloride ($ZnCl_2$) before working with magnesium compounds. In a matter of minutes, the resulting material has a higher hardness than limestone. A decade later, in 1867, Sorel replaced zinc with magnesium in its formula and also obtained cement with similar beneficial properties, called MOC cement [3]. This new type of cement is stronger and more elastic than Portland cement, and therefore exhibits more shock-resistant behavior. This material has good adhesiveness, and can be colored with pigments. Some of the applications of Sorel are fire protective systems, wall insulation, grinding wheels, mosaic, marble, and ivory substitutes for making billiard balls [4,5]. Sorel cement is a mixture of magnesium oxide (MgO) with magnesium chloride ($MgCl_2$) with the approximate chemical formula $Mg_4Cl_2(OH)_6(H_2O)_8$, or $MgCl_2 \cdot 3Mg(OH)_2 \cdot 8H_2O$, with the weight ratio of MgO and $MgCl_2$ of 2.5–3.5:1.

It is known that MOC, or Sorel Cement, is able to absorb carbon dioxide (CO2) without reducing the quality of the product and has a relatively fast curing time, which makes MOC suitable for quick repairs [6,7]. Even studies reported that its bond with carbon is able to produce an increase in mechanical properties so that it supports the performance of the material in carrying out its functions [8]. MOC can be used in the construction industry as an alternative material for the manufacture of sustainable buildings [9]. Carbonation curing of cement-based materials during the preparation of building materials has attracted attention worldwide [10-13]. The prospect of MOC can help overcome the problem of global warming due to carbon emissions, especially from steam-powered electric plants.

This study aimed to determine the best ratio of MOC raw materials. Mechanical testing, such as hardness, compressive, and flexural tests, was conducted to determine the mechanical properties of each variation. The MOC with the best mechanical properties was exposed to a high-purity CO_2 gas environment, whose capabilities were measured by XRD and SEM characterization.

2.0 METHODOLOGY

Technical-grade MgO, MgCl2, and water were obtained from Bandung, Indonesia. The MOC cement was mixed as a combination of the materials as listed in Table 1.

Table 1 MOC mix design with different MgO and $MgCl_2$ ratio

Code	MgO	MgCl2	H_2O
MOC-1	300	300	300
MOC-2	600	300	300
MOC-3	900	300	300

The materials were mixed according to Table 1. They were then poured into a cubical mold with a size of 50 x 50 x 50 mm. The specimens were cured under moist conditions for 28 days. To determine the fresh properties of MOC paste, setting time was conducted to determine its initial and final setting times (Figure 1).

Figure 1 Vicat apparatus used for setting time test

The hardness of MOC was measured using the Zwick//Roell (Zhµ) Vickers Hardness Instrument. The flexural strength was measured using a Shimadzu Universal Testing Machine instrument. The compressive strength of hardened MOC was measured using the Iber Test conforming to ASTM C-39. The remains were collected for characterization purposes. The XRD measurement was performed using a Philips Diffractometer PW1710 with Cu as the anode. The resulting diffraction pattern was compared to the JCPDS. The SEM measurement was performed with a Hitachi SU3500. The sample was coated with carbon to form a conductive layer. These characterizations were conducted at the Institut Teknologi Bandung, Indonesia.

3.0 RESULTS AND DISCUSSION

3.1 Setting Time Test

The setting time of the MOC paste was conducted using Vicat apparatus and conformed to ASTM C-191. The purpose is to investigate the effect of the MgO/$MgCl_2$ ratio on setting time. Figure 2 shows that MOC pastes set between 45 and 60 minutes after pouring into the Vicat Apparatus Bowl. The ratio of MgO to $MgCl_2$ affects the setting time of MOC, with a higher amount of MgO in MOC-3 compared to others increasing the initial setting time due to the presence of more oxide compounds.

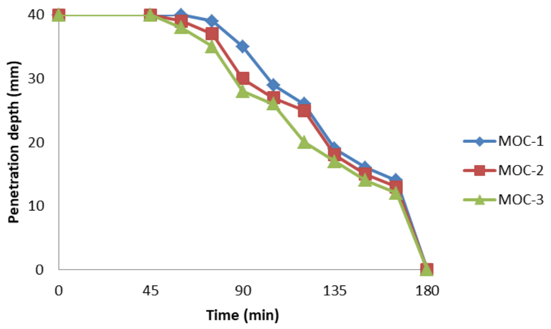


Figure 2 Setting time results from Vicat Apparatus testing of MOC.

The final setting time is determined when the vicat needle is unable to penetrate the slurry after several trials. High MgO content in MOC accelerates the initial setting time. After final setting, MOC-1 has excessive water on the surface, similar to bleeding in hardened concrete. This is a disadvantage of MOC when they contact water [14,15]. Unreacted MgO, when in contact with water, will form a hydrated compound phase, which has a lower mechanical strength than MOC.

3.2 Vickers Hardness Test

The hardness of the MOC paste was determined using a Vicat microhardness apparatus and conformed to ASTM E-384. The purpose is to investigate the effect of the MgO/$MgCl_2$ ratio on hardness. Figure 3 shows that MOC-3 has a higher hardness value than the others. This is due to the higher amount of MgO, which results in more mineral compounds being formed on the hardened material.

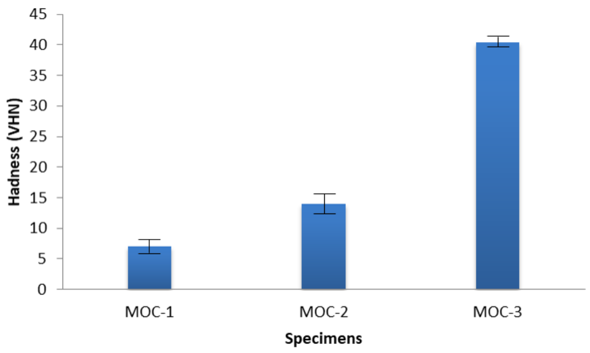


Figure 3 Hardness results from Vickers hardness testing of MOC.

3.3 Flexural Test

The flexural test of MOC was conformed to ASTM C-1161 using the three-point bending method. Figure 4 shows the test result with different MgO:$MgCl_2$ ratios. It shows that an increase in water content in MOC will decrease the flexural strength of the material. MOC-1 and MOC-2 have similar strengths, but MOC-3 specimens have nearly double the flexural strength of previous specimens.

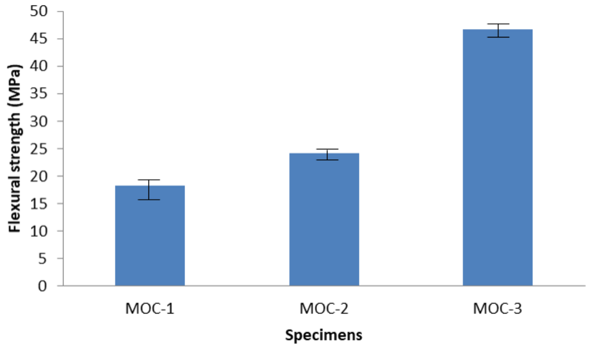


Figure 4 Total of vehicles for each entrance

3.4 Compressive Test

The flexural test of MOC was conformed to ASTM C-109. Figure 5 shows the test result with different MgO:$MgCl_2$ ratios. Similar to the hardness and flexural tests, the highest compressive strength was also achieved by MOC-3. It can be seen that with the increase in curing time, the compressive strength of the samples increases [16].

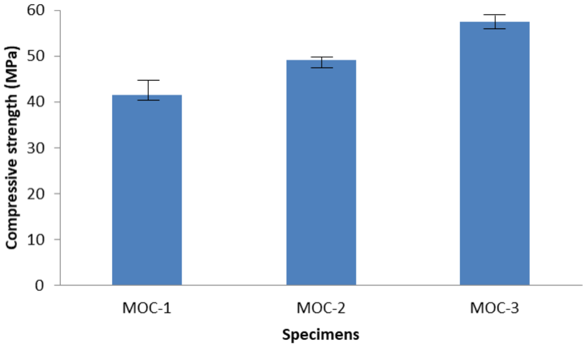


Figure 5 Compressive strength of MOC with different MgO:$MgCl_2$ ratio.

3.5 XRD Characterization

MOC-3, which has the best mechanical properties, is characterized by XRD. The analysis was performed to identify the resulting compound from hardened MOC. Figure 6 shows that Phase 5 ($5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, MOC 5-1-8, JCPDS #070420) is formed after 1 day.

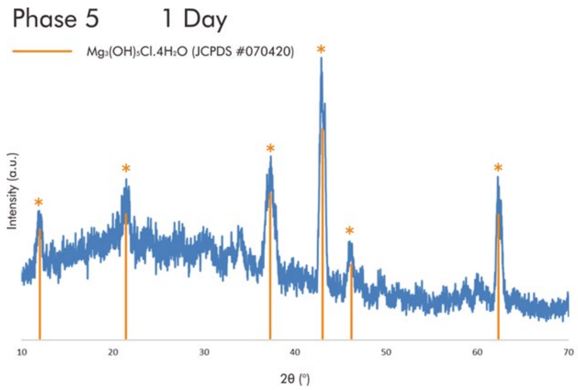


Figure 6 Diffractogram of MOC-3 after 1 days.

There are several phases other than Phase 5 that result from the systems of MgO-$MgCl_2$-H_2O: Phase 2 ($2Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$, MOC 2-1-4) and Phase 9 ($9Mg(OH)_2 \cdot MgCl_2 \cdot 5H_2O$, MOC 9-1-5), which are stable at elevated temperatures (±100°C). Phase 5 and Phase 3 ($3(3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, MOC 3-1-8) are also stable at elevated temperatures until they react with H_2O and CO_2. To measure the carbon capture capabilities of MOC-3, after 24 hours of casting, the sampel was demolded and exposed to high-purity carbon dioxide (CO_2) gas continously for 7 days (Figure 7). The relative humidity was 92%. It was then characterized using XRD. Analysis from XPowder shows the formation of magnesium chloride carbonate, $Mg_2(OH_5)ClCO_3.3H_2O$ (JCPDS #070278), according to Figure 8. The formation of it shows that MOC has the environmental advantage of storing gas in the form of carbonates, which act as a CO_2 sink [17].

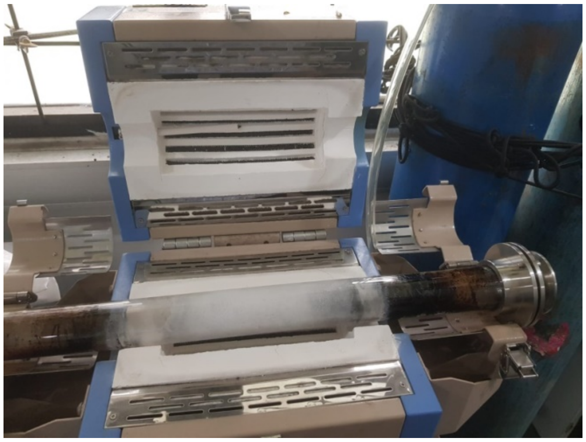


Figure 7 Exposure of MOC-3 to CO_2 gas for 7 days.

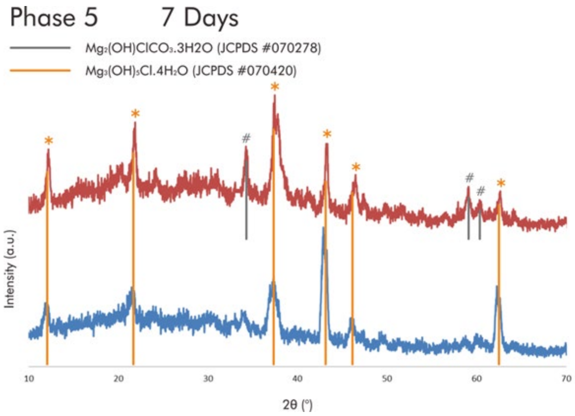


Figure 8 Diffractogram of resulting specimens after 7 days of CO_2 exposure.

The resulting Phase 5 from XRD characterization can be used to calculate the effectiveness of MOC carbon capture performance using the molarity approach presented in Figure 9. It shows that the amount of CO_2 captured was 36%

$$5Mg(OH)_2 \,.\, MgCl_2 \,.\, 8H_2O + 4CO_2 \rightarrow 2[Mg_2(CO_3)(OH)Cl.3H_2O] + 2MgCO_3 + 6H_2O$$

$$457 \quad + \mathbf{176} \rightarrow \quad \mathbf{345} \quad + \mathbf{144} \quad + 108$$

$$CO_2 \text{ captured} = \left(\frac{176}{345+144}\right) \text{ x } 100\% = \mathbf{36\ \%}$$

Figure 9 Carbon capture performance calculation of MOC.

From the XRD characterization of MOC before and after carbon dioxide exposure, it is also shown that there is a crystallinity difference of two diffractograms. There is a more amorphous phase before the exposure, followed by a more crystallinity peak appearance. This is due to the formation of Phase 5 and magnesium chloride carbonate in the sample after exposure.

3.6 SEM Characterization

The morphology of MOC-3 after 1 day (Figure 9) and 7 days of CO_2 exposure (Figure 10) was analyzed using SEM. Figure 10 shows the morphological images of MOC as needle-like or rod-like figures. This shape has a high specific area and unique structure [18]. CO_2 then mineralized and covered the surfaces of MOC, as shown in Figure 11.

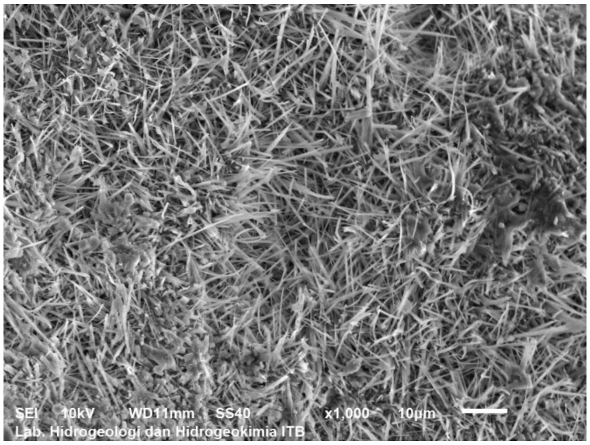


Figure 10 SEM Images of MOC-3 after 1 days.

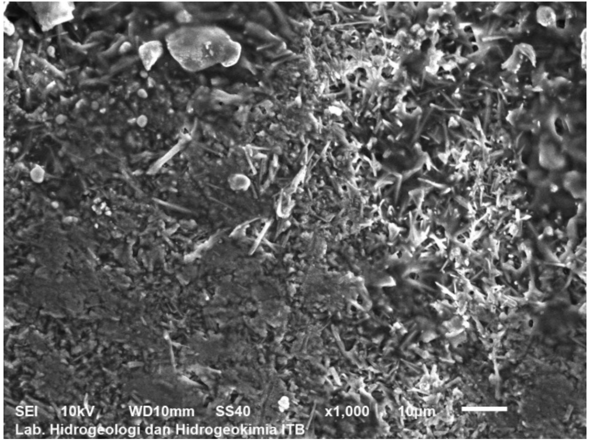


Figure 11 SEM Images of MOC-3 after 7 days of CO_2 exposure.

The process of the aforementioned CO2 sink is called mineral carbonation. Magnesium has been reported as the only element that can be carbonated, aside from calcium [19]. Carbonation of MOC is beneficial for MOC as well as the environment since the material is tougher because it has a denser microstructure [20-23].

4.0 CONCLUSION

This study shows that MOC-3 with a MgO:$MgCl_2$ ratio of 3:1 had the fastest initial setting time and best mechanical properties compared to MOC-1 and MOC-2. This is due to the formation of Phase 5 in the material. The carbon capture capabilities of MOC were tested with XRD characterization, which shows that after 7 days of exposure to carbon dioxide, MOC-3 can capture the gas up to 36%. SEM images show that the carbon dioxide was mineralized on MOC surfaces. It shows that MOC is a potential material for reducing carbon content.

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