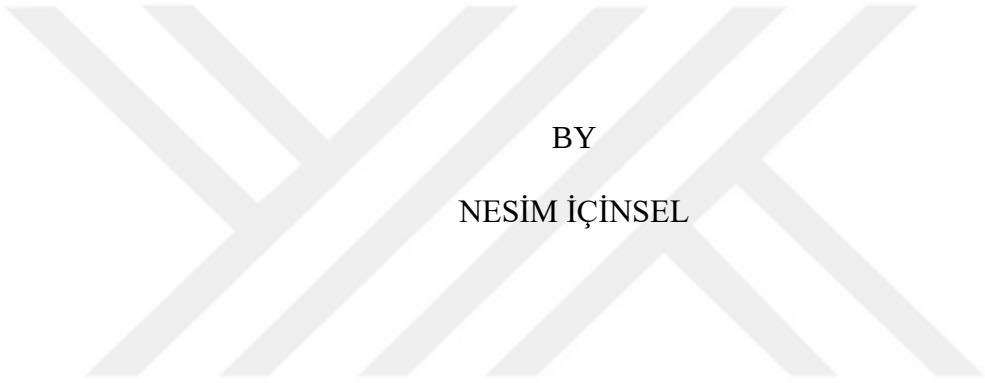


DEVELOPMENT OF MAGNESIUM OXALATE CEMENTS
WITH RECYCLED PORTLAND CEMENT PASTE

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
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NESİM İÇİNSEL

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Approval of the thesis:

**DEVELOPMENT OF MAGNESIUM OXALATE CEMENTS
WITH RECYCLED PORTLAND CEMENT PASTE**

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ABSTRACT

DEVELOPMENT OF MAGNESIUM OXALATE CEMENTS WITH RECYCLED PORTLAND CEMENT PASTE

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Master of Science, Civil Engineering

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In search of lower-carbon-footprint alternatives to portland cement systems, magnesium-based cements are one of the most promising materials to investigate. Even though it is not possible to directly replace the calcium oxide in portland cement with magnesium oxide, magnesium oxide has its distinct mechanisms of forming binders with various materials. Some of the proven magnesium cements use acid-base reactions to create a binder by coupling an acid with magnesium oxide, such as the well-known magnesium phosphate cements. In this study, oxalic acid (an acid that can even be produced from carbon dioxide in the atmosphere) is coupled with magnesium oxide to form a cementitious system. In an effort to control this very reactive system, oxalic acid is blended with recycled portland cement paste. The development of an appropriate mixture design is attempted, and some experiments are carried out to investigate the possibility of forming a stable and serviceable binder. Then the developed binder (magnesium oxalate hydrate) is analyzed to elucidate the mechanism of formation and effects of raw materials, retarders, pozzolans, and mix design on the resulting system. The compressive strength

development of the mortars is evaluated together with their mineralogy and microstructures using x-ray diffractometry, x-ray fluorescence spectroscopy, electron microscopy, and thermogravimetric analysis. A somewhat porous mortar, with low-to-medium strength but with a significantly lower carbon footprint than portland cement mortar could be obtained.

Keywords: Magnesia, Oxalic acid, Recycled cement paste, Acid-base cements



ÖZ

GERİ KAZANILMIŞ PORTLAND ÇİMENTOSU İÇEREN MAGNEZYUM OKSALAT ÇİMENTO HARÇLARININ GELİŞTİRİLMESİ

İçinsel, Nesim
Yüksek Lisans, İnşaat Mühendisliği
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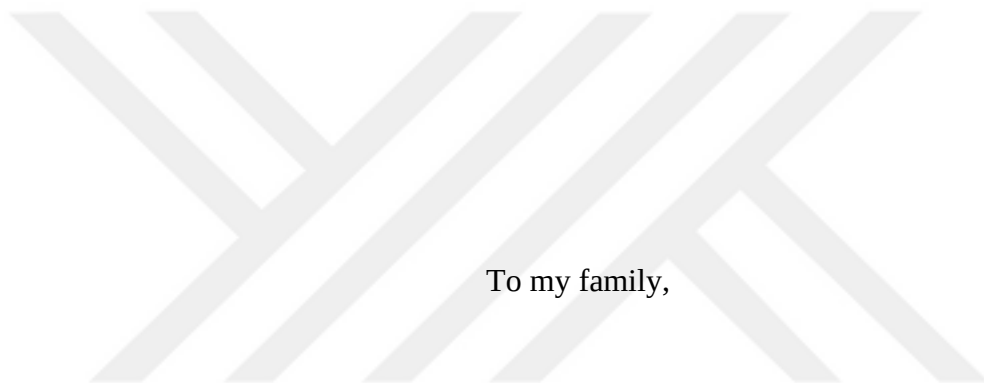
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Portland çimentolu sistemlere, düşük karbon ayak izine sahip bir alternatif arayışında, magnezyum esaslı çimentolar en çok umut veren malzemelerden biridir. Portland çimentosundaki kalsiyum oksit, magnezyum oksit ile doğrudan ikamesi mümkün olmasa da magnezyum oksit çeşitli malzemelerle bir bağlayıcı oluşturabilecek kendine özel bazı mekanizmalara sahiptir. Bazı magnezyum esaslı çimentolar bağlayıcı oluşturmak için magnezyum oksit ile uygun bir asitin tepkimesini içeren asit-baz reaksiyonlarına dayanır. Magnezyum fosfat çimentoları bunların en iyi bilinen örneklerinden biridir. Bu çalışmada, bağlayıcı bir sistem oluşturmak için magnezyum oksit ile oksalik asit (atmosferdeki karbon dioksit ile dahi üretilen bir asit) ana tepkiyenler olarak kullanılmıştır. Reaksiyonları kontrol edebilmek için oksalik asit geri dönüştürülmüş portland çimentosu hamuru ile karıştırılmıştır. Sağlam ve kullanışlı bir bağlayıcı oluşturma olasılığını araştırmak ve karışım tasarımını geliştirmek için bazı deneyler yapılmıştır. Daha sonra ise ortaya çıkan bağlayıcının (magnezyum oksalat hidrat) oluşum mekanizmasını anlayabilmek ve hammaddelerin, geciktiricilerin, pozolanların ve karışım oranlarının sistem

zerindeki etkileri gzlemlemek iin analizler yapılmıřtır. Harların basın dayanımı geliřimi ile birlikte mineralojileri ve mikro yapıları, x-ıřını kırınımı, x-ıřını floresans spektroskopisi, elektron mikroskopi ve termogravimetrik analiz yardımıyla incelenmiřtir. Dřk - orta dayanıma ulařabilen, gzenekli bir yapıya sahip fakat portland imentolu harlara kıyasla olduka dřk karbon ayak izi olan bir har elde edilebilmiřtir.

Anahtar Kelimeler: Magnezyum oksit, Oksalik asit, Geri dnřtrlmř imento, Asit-baz imentoları





To my family,

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing Materials
BA	Boric Acid
C-S-H	Calcium Silicate Hydrate
CP	Recycled Portland Cement Paste
CPOx	Recycled Portland Cement Paste and Oxalic Acid Blend
CP/Ox	Mass Ratio of Recycled Portland Cement Paste-to-Oxalic Acid Dihydrate to be Used to Produce CPOx
d	day
DCP	Recycled Dehydrated Portland Cement Paste
DCPOx	Recycled Dehydrated Portland Cement Paste and Oxalic Acid Blend
DTA	Differential Thermal Analysis
EDX	Energy-dispersive X-ray Spectroscopy
EN	European Norms
HCP	Recycled Hydrated (or Hardened) Portland Cement Paste
HCPOx	Recycled Hydrated Portland Cement Paste and Oxalic Acid Blend
FA	Fly Ash
JIS	Japanese Industrial Standard
kN	Kilo Newton
L/S	Liquid to Solid Ratio
M-S-H	Magnesium Silicate Hydrate
METU	Middle East Technical University
MKPC	Magnesium Potassium Phosphate Cement
MPa	Mega Pascal
MPC	Magnesium Phosphate Cement

MPCBC	Magnesium Phosphate Chemically Bonded Ceramics
MSPPC	Magnesium Silicon Potassium Phosphate Cement
MOC	Magnesium Oxychloride Cement
MOSC	Magnesium Oxysulfate Cement
MOXC	Magnesium Oxalate Cement
MOXC-HCP	Magnesium Oxalate Cement with Recycled Hydrated Portland Cement Paste Admixture
MOXC-DCP	Magnesium Oxalate Cement with Recycled Dehydrated Portland Cement Paste Admixture
MOXC-rCP	Magnesium Oxalate Cement with Recycled Portland Cement Paste Admixture
OPC	Ordinary Portland Cement
Ox	Oxalic Acid
Ox/MgO	Mass Ratio of Magnesia-to-Oxalic Acid Dihydrate Used to Produce CPO _x
PC	Portland Cement
RT	Room Temperature
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
TS	Turkish Standards
SF	Silica Fume
s/b	Sand-to-binder Ratio by Mass
W	Watt
w/c	Water-to-cement Ratio by Mass
w/b	Water-to-binder Ratio by Mass
wt. %	Percentage by Weight
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

CHAPTER 1

INTRODUCTION

1.1 Background

Although the binder in concrete has greatly varied throughout history, concrete can be considered one of the oldest materials used in civil structures. In modern construction, concrete is still one of the most common materials used in the world for both structural and decorative purposes. The most commonly preferred binder in modern concrete is portland cement. Modern portland cement was developed in the 19th century and continues to be improved since. Initially, attempts for improvement were focused on the mechanical properties, workability, and durability of portland cement. Recently, the focus has shifted towards reducing its environmental impact.

The production of portland cement accounts for 5 % of global anthropogenic carbon dioxide emissions, which causes the greenhouse effect, thus climate change and global warming (Habert, 2013). Along with studies on improvements to portland cement to reduce its carbon footprint, some alternative binder systems have also been suggested. Phair (2006) listed some of the promising alternatives as alkali-activated cements, sulfoaluminate cements, and magnesia cements.

The first known magnesia cement was developed by Stanislas Sorel in 1867. Although having many properties superior to portland cement, Sorel's cement was not widely adopted due to being non-hydraulic (Walling and Provis, 2016). Through the years, some other types of magnesia-based cements were developed in addition to Sorel's magnesium oxychloride cement, such as magnesium oxysulfate, magnesium silicate hydrate, magnesium carbonate, and magnesium phosphate cements. These cements utilize different compounds to react with magnesium oxide and rely on different reaction mechanisms. Thus far, they have not been able to replace portland cement as they have certain technical or economic drawbacks.

Recently, the pursuit of finding an environmental-friendly cementitious system has once again drawn attention to magnesia cements.

Magnesium oxalate cement (MOXC) is a previously unknown variation of magnesia cements that is based on acid-base reactions similar to magnesium phosphate cements. The proposed acid to accompany magnesia is oxalic acid in this type of cement. Oxalic acid is an organic acid that can be mass produced from water and carbon dioxide (Fischer, Lehmann, and Heitz 1981), among other methods. As such, the use of oxalic acid in making concrete can potentially trap higher amounts of carbon dioxide than the emitted in the production of magnesia, and carbon-neutral or even carbon-negative concretes can be possible. The reaction between magnesia and oxalic acid is rather quick and highly exothermic; therefore, directly mixing magnesia and oxalic acid results in flash setting of the mixture, causing workability problems. In order to control the reactions and stabilize the cement system, a premanufactured blend of oxalic acid with recycled portland cement paste was designed to be admixed to the final mix. The utilization of recycled portland cement paste is another environmentally friendly approach to developing a cementitious system. Since concrete recycling mainly focuses on utilizing coarse aggregates and recycled portland cement mortar has limited usage commercially and mostly remains as waste.

In summary, magnesium oxalate cements using recycled portland cement paste have the potential to be a low environmental impact alternative to portland cements. Since magnesium oxalate cements were designed to utilize a material, oxalic acid, that can be produced in the carbon capture and storage (CCS) process also they utilize industrial waste materials such as recycled portland cement paste or variations using pozzolans; they can have much lower carbon footprint compared to its alternatives.

1.2 Objectives and Scope

The main objective of this study is to investigate whether magnesium oxide and oxalic acid can form a stable and useful cementitious product. Additional objectives include the determination of their reaction mechanism, properties of the reaction product, and the effects of incorporating hydrated and dehydrated portland cement into the system, with other possible additives such as retarders and pozzolans.

This dissertation is composed of five chapters. Chapter 1 introduces the topic of this thesis, as well as its objectives and scope. Chapter 2 provides a brief background with a review of similar studies, as well as the usage and production of the raw materials used in this study. It also explains the idea behind magnesium oxalate cement. Chapter 3 introduces the raw materials used in the study, their relevant properties, and their preparation. The experimental methods followed and work performed, with their reasonings, are also summarized. Chapter 4 presents the results of the experiments performed and discussions of these results. Chapter 5 summarizes this study with concluding remarks and provides recommendations for further studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides background information about magnesia cements and the raw materials used in this study to produce magnesium oxalate cements with recycled portland cement paste as an admixture (MOXC-rCP). This summary can be helpful in interpreting the results obtained from the analysis of magnesium oxalate cements, which is not found in any published works. In regard to combining magnesium oxide with oxalic acid to produce a cementitious system, this can be considered a pioneering study.

2.2 Magnesium Oxide

Magnesium oxide (commonly referred to as magnesia or periclase) is the main ingredient in magnesia-based cements, considered to be a promising alternative to portland cement, of which the primary binders consist of calcium oxide (CaO), silicon dioxide (SiO₂), and aluminum oxide (Al₂O₃). Although their chemical compositions differ, magnesium oxide (magnesia), calcium oxide (lime), and calcium sulfate (gypsum) are classified as air-hardening binder materials (Zhang, 2011). Magnesium and calcium are similar at the atomic level as both are alkaline earth metals and have similar electron configurations. Thus, it may be expected of them to make similar chemical bonds with other elements. However, their chemistry and phase formation show significant differences, especially when forming compounds with silica and aluminum oxide, as explained by Walling and Provis (2016) by the ternary diagrams given in Figure 2.1.

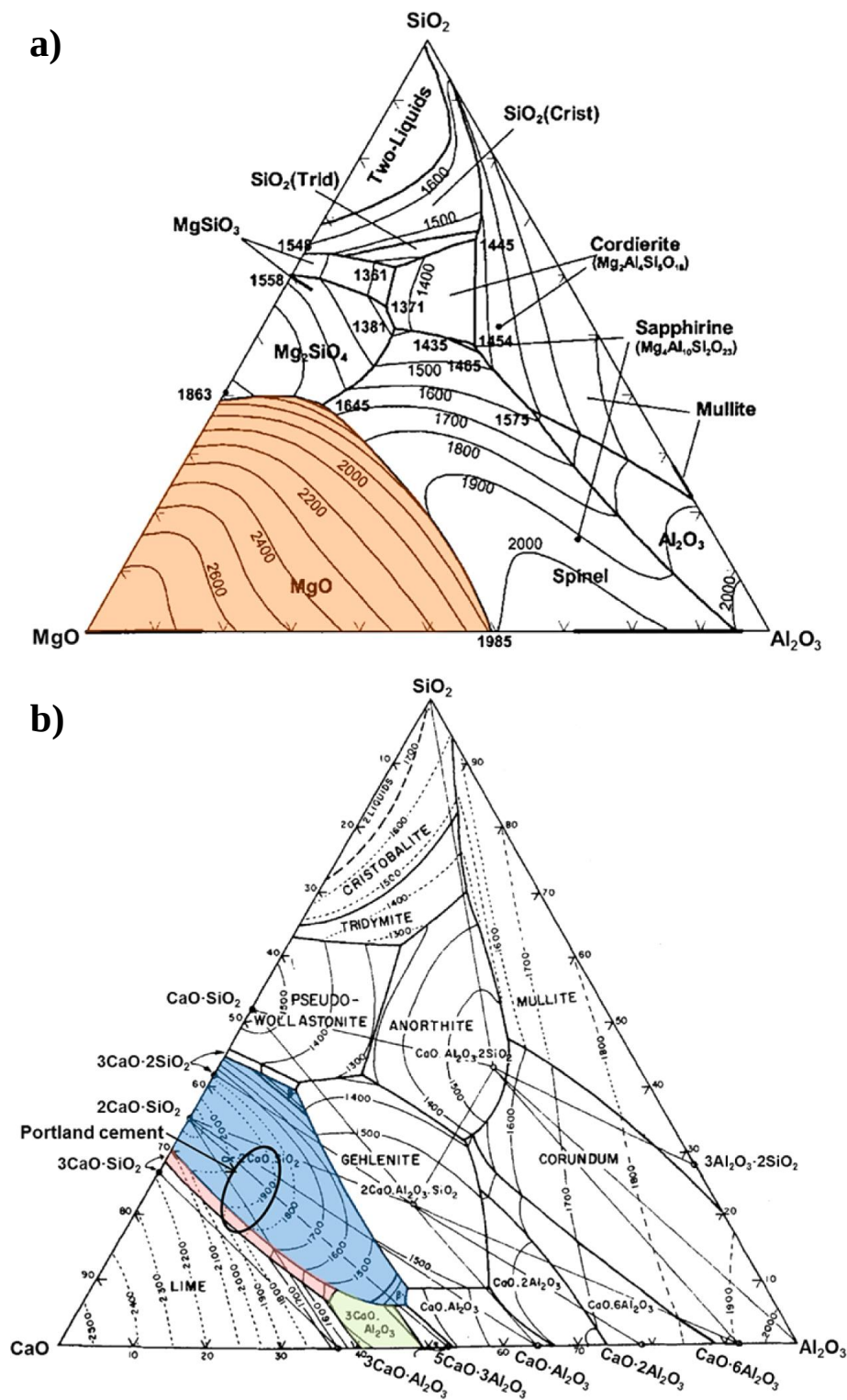


Figure 2.1. Ternary phase diagrams, in units of mass percent, for the systems: a) $\text{MgO-SiO}_2\text{-Al}_2\text{O}_3$, b) $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ (Walling and Provis, 2016)

The shaded area in Figure 2.1b marks phases with some cementitious properties, including portland cement. However, the counterparts of these calcium silicate phases do not form using magnesium oxide (Walling and Provis, 2016). Therefore, it is not possible simply to replace calcium oxide with magnesium oxide in portland cement. In order to produce a binder from magnesium oxide, different methods and cementitious reaction products need to be developed. In a similar vein, some discoveries and developments have already been made about the magnesia cements. The details for the proposed materials and mechanisms used in magnesia cements are briefly discussed in the following sections.

2.2.1 Production of Magnesium Oxide

The typical source of calcium oxide in portland cement is limestone (Mehta and Monteiro, 2006). Limestone is calcined at temperatures between 900 °C and 1200 °C releasing carbon dioxide by the following equation (Schorcht, Kourti, Scalet, Roudier, and Sancho, 2013):



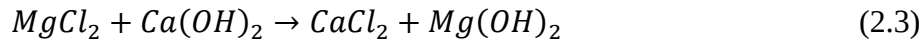
The calcium oxide formed continues to be heated in the rotary kiln to 1450-1550 °C and reacts with silicon dioxide (SiO₂) and aluminum oxide (Al₂O₃) to form the portland cement clinker. Similar to the calcination of limestone to produce calcium oxide, magnesium oxide can be produced by calcining mined magnesite (MgCO₃). While this process requires a lower temperature, around 600 °C, it also releases carbon dioxide:



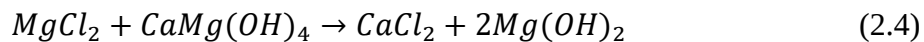
The calcination of magnesite, which is also called the dry route, is not the only way to produce magnesia. Additionally, there is a wet route that uses magnesium chloride (MgCl₂) to obtain magnesium hydroxide (Mg[OH]₂). The high-temperature

hydrolysis reaction is one of the methods used in the wet route (Schorcht et al., 2013). The source of magnesium chloride can be concentrated brines or seawaters. The wet route process is summarized as (Walling and Provis, 2016):

By reaction with slaked lime (Ca(OH)_2):



By reaction with dolime (CaMg(OH)_4):



The resultant magnesium hydroxide can then be filtered and calcined to produce magnesia (Green, 1983). Another wet method is the pyrohydrolysis of magnesium chloride in superheated steam up to 1000 °C (Shand, 2006):



However, in most cases of magnesia based cements, magnesium oxide is not used as obtained from these described processes as it can be very reactive. In order to reduce its reactivity, magnesium oxide can be typically calcined.

2.2.2 Calcination of Magnesium Oxide

Magnesium oxide is used in industrial processes mostly in its dead-burned form (Eubank, 1951). This is because exposing magnesium oxide to high temperatures reduces its surface area and increases its crystallite size by sintering effect (Walling and Provis, 2016). Thus, the reactivity of magnesia is reduced, allowing better workability when mixed with water. The European Commission describes magnesia grades depending on the chosen calcination temperature as follows (Schorcht et al., 2013):

- Caustic-calcined, 600-1300 °C;
- Dead-burned, 1600-2200 °C;
- Fused, >2800 °C.

The magnesia grading is based on calcination temperatures since properties of magnesia calcined at different temperatures show differences. Eubank (1951) concluded that gases escape between 300 °C and 500 °C, then when the temperature reaches 900 °C recrystallizations and sintering start to occur in magnesia. The release of the gases results in higher porosity with larger surface area, thus higher reactivity results by calcination at lower temperatures. Particle size increases; therefore, a decrease in surface area and reactivity results at temperatures higher than 1300 °C.

Eubank (1951) also compared x-ray diffractograms of the magnesia calcined at different temperatures. He concluded that magnesia calcined at 370 °C (Figure 2.2a) has smaller particle sizes due to the observed broad diffuse lines compared to the other temperatures. As the temperature increases, the interference lines became narrower and sharper, indicating an increase in particle and crystallite size.

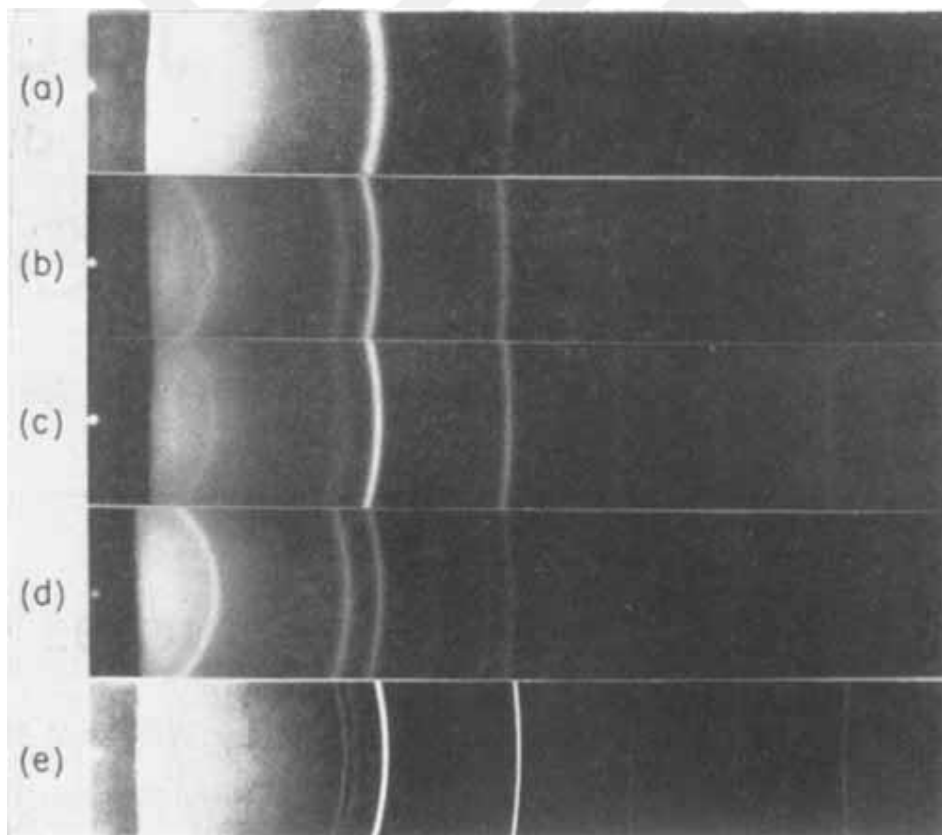


Figure 2.2. XRD patterns of magnesia calcined at various temperatures: a) 370 °C, b) 725 °C, c) 820 °C, d) 920 °C, and e) 1200 °C (Eubank, 1951)

Bilginer (2018) measured the specific surface area of magnesia calcined at different temperatures. He found that until the calcination temperature reaches around 1000 °C, the specific surface area does not change very much. After this point, the surface area decreases from ~11000 cm²/g to ~2000 cm²/g at 1400 °C (Figure 2.3).

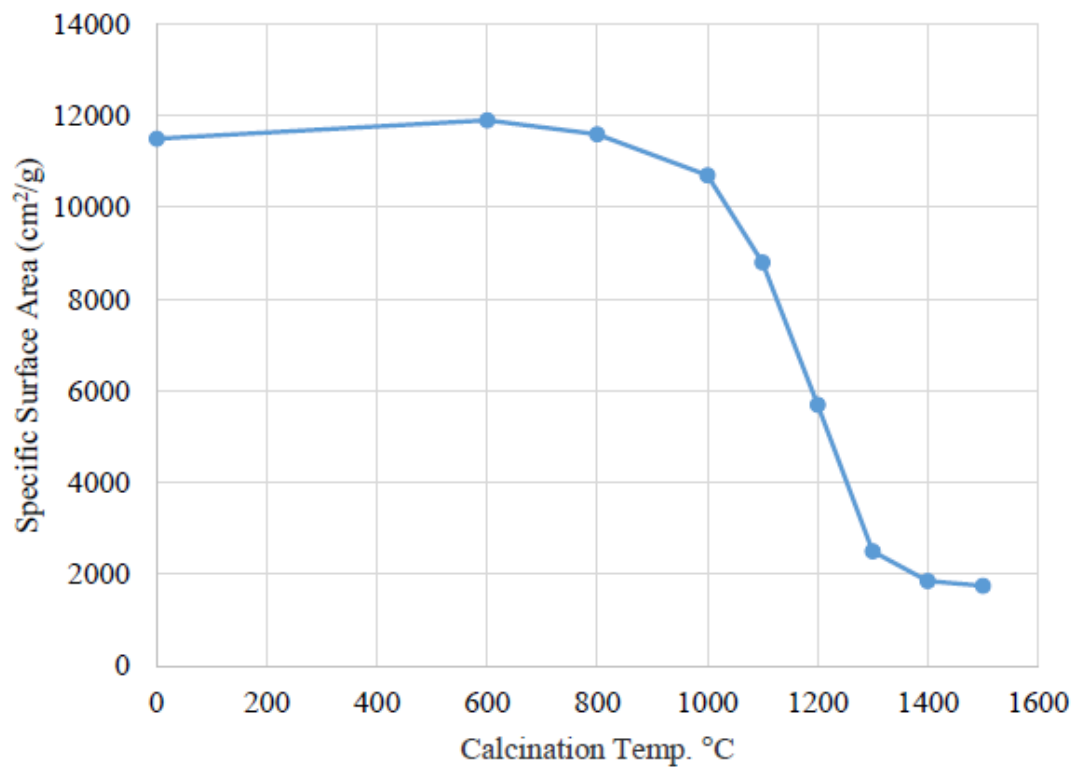


Figure 2.3. Blaine fineness (specific surface area) of magnesia calcined at various temperatures (Bilginer, 2018)

To observe the reactivity differences between calcined and uncalcined magnesia, Wagh and Jeong (2003) measured the rate of pH change of their solution with phosphoric acid (H₃PO₄) from the time of mixture (Figure 2.4). The solution prepared with uncalcined MgO reached a pH of 5 after 20 minutes. Beyond 20 minutes, the pH increase rate became significantly low, indicating the consumption of materials. On the other hand, the solution prepared with magnesium oxide calcined at 1300 °C showed a slower increase in pH to 3.5, in 75 minutes. The

difference in this acid-base reaction rate shows that calcined magnesium oxide is less reactive compared to the uncalcined magnesium oxide. Therefore, calcined magnesia is more suitable to avoid excessively rapid setting in binder systems.

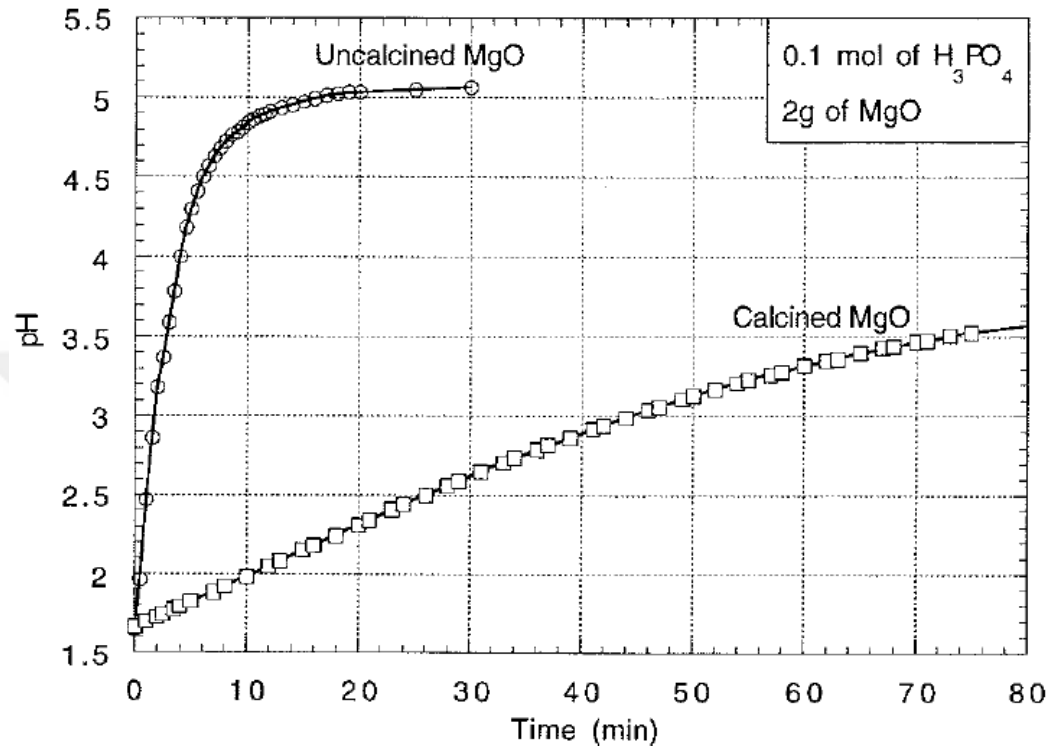


Figure 2.4. Rate of increase in pH with time during neutralization of calcined and uncalcined MgO (Wagh and Jeong, 2003)

2.3 Magnesia Cements

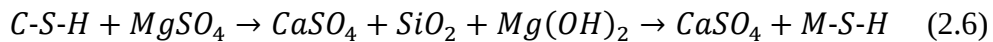
As mentioned in Section 2.2, magnesium oxide is not suitable to directly replace calcium oxide in portland cements. In order to use magnesium oxide as a binder, many types of magnesia cements were developed utilizing a variety of accompanying materials and different mechanisms. While the reaction mechanism of most types differs from magnesium oxalate cements, their general behavior and proposed remedies for workability and durability problems are similar among magnesia-based cement systems. Some of the methods and utilized materials researched to overcome practical problems and improve mechanical performance

were directly adopted from portland cement. Some were exclusive to magnesium oxide or the mechanism of the hydration. Since there are not any published studies on magnesium oxalate cements, it could be helpful to investigate similar magnesia-based cements to understand and predict their possible effects on magnesium oxalate cements.

2.3.1 Types of Magnesia Cements

2.3.1.1 Magnesium Silicate Hydrate Cements

Adopting a similar mechanism to replace calcium oxide in portland cement, the first idea for the magnesium silicate hydrate cements is documented back at the end of the 19th century with patents awarded to Cummings in 1889 and Steiger in 1899 (Walling and Provis, 2016). However, there was not any significant development about this type of cements until a crystalline hydrated magnesium silicate was found in a marine concrete by Cole (1953). Eventually, Mather (1967) explained the observed M-S-H formation as a result of sulfate attack to C-S-H gel:



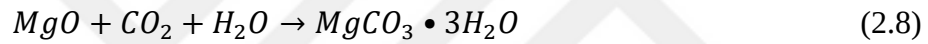
Since the formation of M-S-H was observed together with strength loss of the concrete, Cohen and Bentur (1988) concluded that M-S-H must be a non cementitious phase. However, a micro-silica producer, Elkem, was able to produce M-S-H cement paste utilizing jet-milled fine magnesia and micro-silica that was able to reach ~130 MPa of compressive strength in 28 days (Walling and Provis, 2016). A notable admixture to this system was the usage of the sodium hexametaphosphate ($[NaPO_3]_6$) to increase the fluidity of the fresh mixture (Wei, Chen, and Li, 2006).

The formation of magnesium silicate hydrate in the presence of portland cement hydrates requires magnesium sulfate ($MgSO_4$) rather than magnesium oxide (MgO).

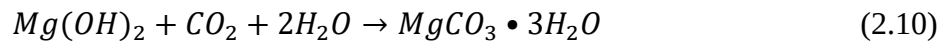
Therefore, it is unlikely to observe a direct interaction between the recycled portland cement paste with magnesium oxide in the studied system.

2.3.1.2 Magnesium Carbonate Cements and Reactive Magnesium Oxide Cements

Magnesium carbonate cements and reactive magnesia cements rely on the carbonation of magnesium oxide. In magnesium carbonate cements, the carbonation of magnesium oxide can occur directly to form magnesium carbonate ($MgCO_3$) or with the presence of water to form nesquehonite ($MgCO_3 \cdot 3H_2O$) as described by Walling and Provis (2016):



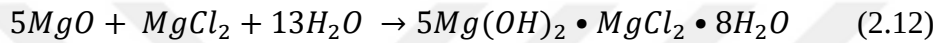
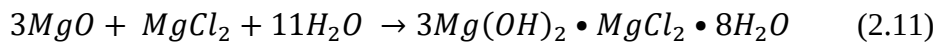
In reactive magnesia cements, magnesium oxide reacts with water first then the resultant magnesium hydroxide ($Mg(OH)_2$) carbonates to form nesquehonite in the presence of water:



Magnesium carbonate and reactive magnesia cements utilize caustic-calcined magnesia with the preferable presence of accelerating additives such as potassium nitrate (KNO_3), iron sulfate hydrates ($Fe_2SO_4 \cdot xH_2O$), and calcium chloride ($CaCl_2$) (Phair, 2006). It is unlikely that similar mechanisms would exist in magnesium oxalate cements.

2.3.1.3 Magnesium Oxychloride (Sorel) Cements

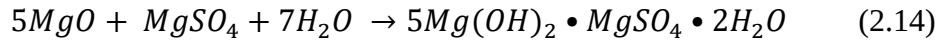
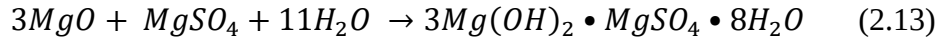
Magnesium oxychloride cements (also widely known as Sorel cements) were patented and produced by Stanislas Sorel in 1866 (Walling and Provis, 2016). They are based on the reaction between magnesium oxide (MgO) and magnesium chloride salt (MgCl₂) in the presence of water. Reactions with different molar ratios of reactants can be observed and may result in different reaction product phases. The reaction equations for two of the phases are:



Although having certain properties superior to portland cement, Sorel's cements have not been used as widely as portland cements; mainly because they suffer the decomposition of hydration products when exposed to water (Robinson and Waggaman, 1909). Among the many efforts to improve the water resistance and mechanical properties of Sorel cements some can be listed as: carbonation of hydration products (He, Poon, and Tsang, 2017), admixing of pozzolans such as amorphous silica (U.S. Patent No. 2466145A, 1945), admixing of fly ash (Chau, Chan, and Li, 2009), and admixing of other materials such as phosphates (U.S. Patent No. 1853522A, 1929), tartaric acid and phosphoric acid (Chen, Zhang, Wanli, and Cheeseman, 2019), and hydroxyacetic acid (Luo et al., 2020).

2.3.1.4 Magnesium Oxysulfate Cements

Magnesium oxysulfate cements are similar to Sorel's cement, also considered magnesia oxysalt cements. Their difference with magnesium oxychloride cements is the use of magnesium sulfate (MgSO₄) instead of magnesium chloride (MgCl₂). Similar to magnesium oxychloride cements, magnesium oxysulfate cements can also have many phases. Some of the several possible hydration reactions are:

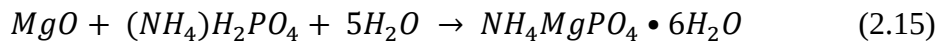


Compared to Sorel's cement, they are generally accepted to be more water-resistant. However, due to the lower solubility of magnesium sulfate at room temperature, they require high-temperature steam curing that limits their practical production (Walling and Provis, 2016).

Similar procedures and materials used in Sorel's cements have been used on magnesium oxysulfate cements to improve their mechanical properties. Some being: carbonation of hydration products (Ba, Xue, He, Wang, and Liu, 2019), admixing of fly ash (Zhang et al., 2019), admixing of sodium citrate and citric acid (Wang et al., 2018).

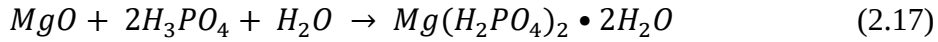
2.3.1.5 Magnesium Phosphate Cements

Magnesium phosphate cements are the closest type of magnesia cement to magnesium oxalate cements. Both cement types are based on acid-base reactions to form a cementitious product. Magnesium phosphate cements utilize a soluble phosphate acid salt such as ammonium phosphate ($[NH_4]_3PO_4$) or potassium phosphates (such as KH_2PO_4 , K_2HPO_4 , and K_3PO_4) to react with magnesium oxide (Walling and Provis, 2016). The reaction between magnesium oxide and ammonium dihydrogen phosphate ($[NH_4]H_2PO_4$) can be exemplified as follows:



Magnesium phosphate cement can also be produced using phosphate-containing acids. One such phosphate-containing acid is orthophosphoric acid, H_3PO_4 (Walling and Provis, 2016). Finch and Sharp (1989) observed two different crystalline products formed after the reaction of magnesium oxide with phosphoric acid. They

concluded the reaction might have occurred with different molar ratios and suggested the following reactions:



Acid-base reactions of magnesia phosphate cements are very rapid and highly exothermic, creating difficulties in their application. In order to control the rate of reactions, various methods, ingredients, and additives have been experimented with. The studies include the investigation of the curing temperature (Yang and Wu, 1999), the use of possible retarders such as sodium tripolyphosphate (Hall, Stevens, and El-Jazairi, 2001) and borates (U.S. Patent No. 3960580A, 1974), and the effect of adding materials such as fly ash (Li and Chen, 2013), ground granulated blast furnace slag (Gardner et al., 2015), and wollastonite (Singh, Ganga, Gaviria, and Yusufoglu, 2011).

2.3.2 Influence of Water Content on Magnesia Cements

Water content in magnesia cements affects the properties of the fresh mixture and final product, similar to its effects on other cementitious systems. In this section, the effects of water content on magnesium phosphate cements investigated in regard to flow, setting time, and compressive strength.

Lee et al. (2017) measured the initial flows and viscosities of magnesium potassium phosphate cement (MKPC) prepared using different water-to-binder ratios (W/B) and magnesium-to-phosphate ratios (M_{mp}). They found that both parameters influence the flow and viscosity. The flow of MKPC mortars increased as W/B increases, and the viscosity of mortars increased with an increase in M_{mp} and a decrease in W/B (Figures 2.5 and 2.6).

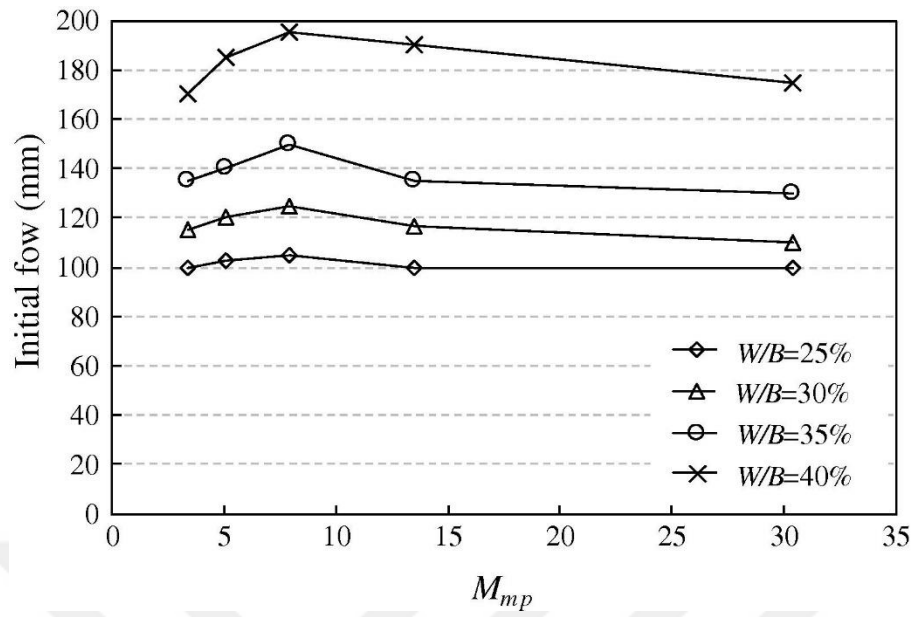


Figure 2.5. Initial flow of MKPC mortars with different water-to-binder and magnesium-to-phosphate ratios (Lee et al., 2017)

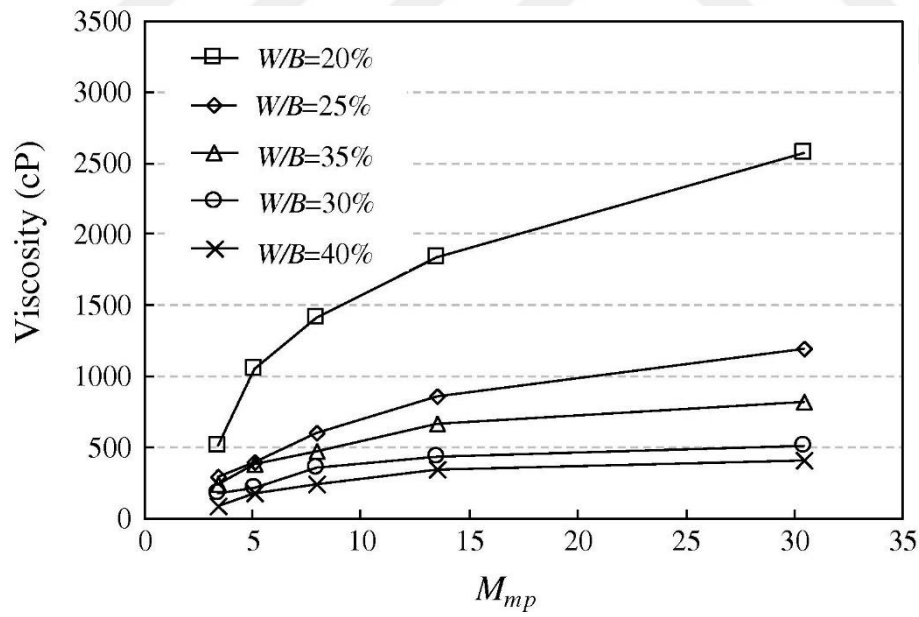


Figure 2.6. Viscosity of MKPC mortars with different water-to-binder and magnesium-to-phosphate ratios (Lee et al., 2017)

Li and Chen (2013) prepared magnesium phosphate cement (MPC) samples with different w/c at 20 °C ambient temperature to measure their setting times. They observed that as the water content increased, setting time also increased. While a mixture with w/c of 0.14 set after about 5 minutes, a mixture with 0.30 w/c set after about 35 minutes (Figure 2.7).

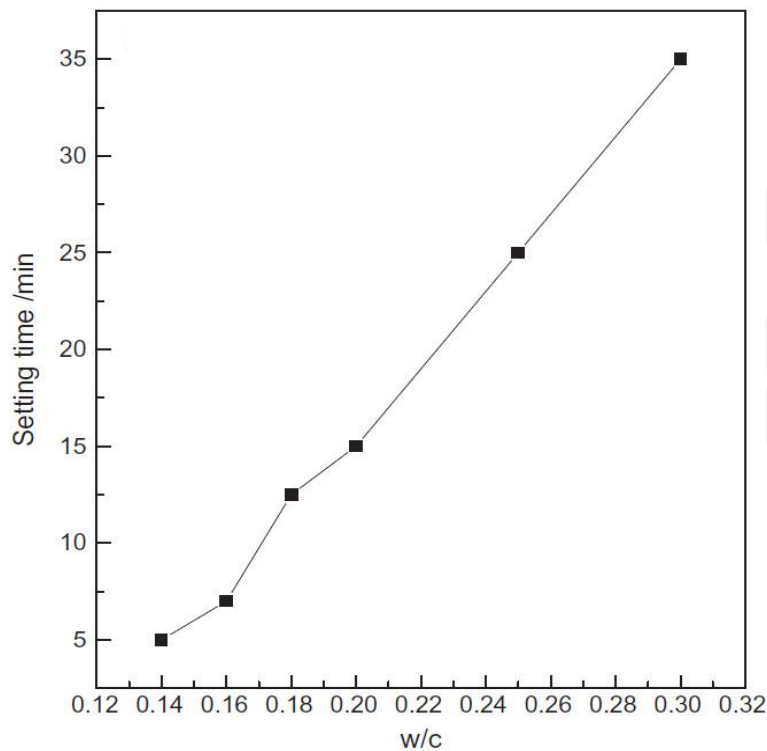


Figure 2.7. Effect of w/c on the setting time of MPC paste (Li and Chen, 2013)

In the same study, Li and Chen (2013) compared the compressive strength of the MPC pastes prepared with various w/c (Figure 2.8). Compressive strength decreases as w/c increases, for high w/c. However, the results showed optimum performance for a w/c of 0.16 and lower compressive strengths for the samples with a w/c of 0.14. Li and Chen (2013) commented that this behavior could be a result of poor workability and fast setting.

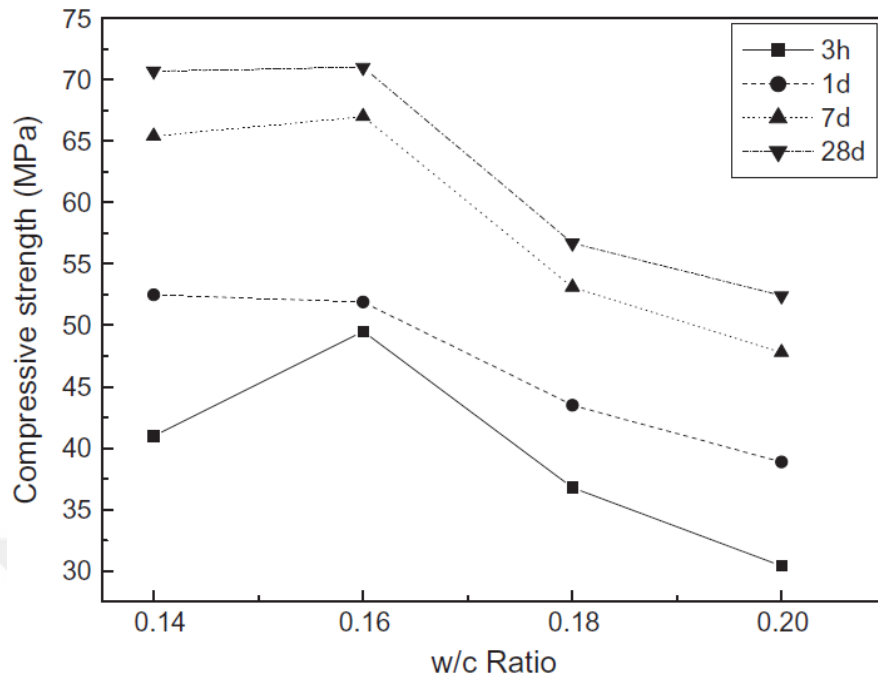


Figure 2.8. Effect of w/c on the compressive strength of MPC paste (Li and Chen, 2013)

Wang et al. (2013) performed a similar compression test, together with measurements of porosity, on a magnesium phosphate chemically bonded ceramic (MPCBC) system. They also reported that strength decreases as the liquid-to-solid ratio increases. They observed higher porosity as the liquid-to-solid (L/S) ratio increases and presented the inverse relation between compressive strength and porosity, given in Figure 2.9.

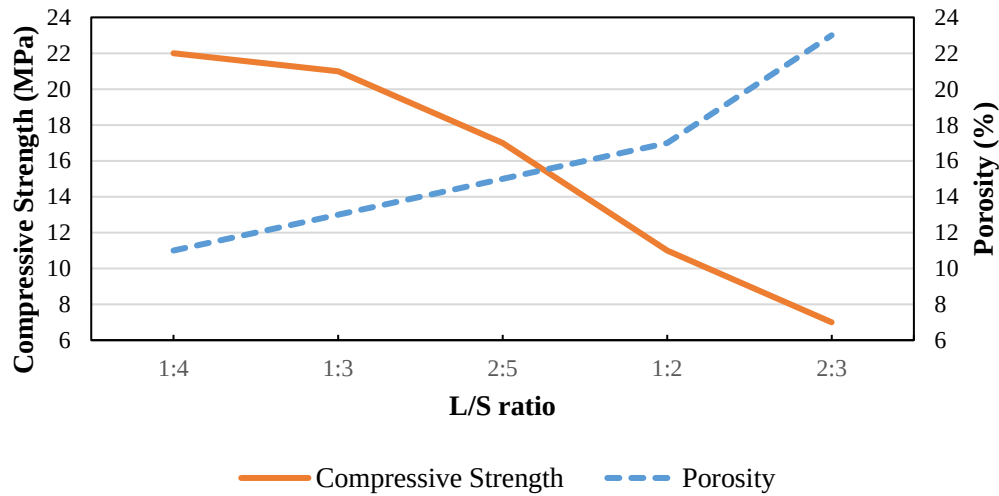


Figure 2.9. Porosity and compressive strength relation of MPCBC with different liquid-to-solid ratios (modified from Wang et al., 2013)

2.3.3 Influence of Retarders on Magnesia Cements

Magnesium phosphate cements, which rely on acid-base reactions, set rapidly releasing high amounts of heat, thus creates practical difficulties and performance problems (Walling and Provis, 2016). In order to decrease the rate of these exothermic reactions of magnesium oxide with phosphate-bearing acids, various studies were performed to find a retarder that is suitable for this cement system. Among such retarders, boron-based compounds are the most studied and most promising ones, as they are described as “the de facto standard for magnesium phosphate cements” by Walling and Provis (2016).

The retardation mechanism of borates in magnesia cements is controversial. Initially, Sugama and Kukacka (1983) claimed that $B_4O_7^{2-}$ ions form colloidal precipitation around magnesia (MgO) grains, this formation reduces the further dissolution of magnesium oxide, thus retards the sequent reactions. On the other hand, Hall et al. (2001) stated while it was possible to have such a system in an alkaline environment, it was unlikely to have a significant amount of $B_4O_7^{2-}$ ions available in a low pH system to retard the dissolution of magnesia. Their suggestion for the retardation

mechanism was still based on the slow dissolution of magnesia. Nevertheless, it was due to the adsorption of boric acid, $B(OH)_3$ or $B(OH)_4^-$, by magnesia. Another suggestion was offered by Wagh (2004) that boric acid (H_3BO_3) reacts with magnesium oxide in the acidic phosphate solution to form lüneburgite ($Mg_3[B_2(OH)_6][PO_4]_2 \cdot 6H_2O$) that acts like a solubility-limiting coating. This suggestion implies a requirement for phosphate ions in the system that may make the boric acid ineffective as a retarder in the solutions that do not contain phosphate.

Qiao (2010) investigated the effects of borax ($Na_2[B_4O_5(OH)_4] \cdot 8H_2O$) on the setting time and compressive strength of MKPC pastes. He found that as the borax content increases, the setting time increases; however, early strength of the samples with borax showed a decrease. Nevertheless, the observed decrease in strength during the early ages of the samples with higher borax content was compensated at later ages (Figure 2.10).

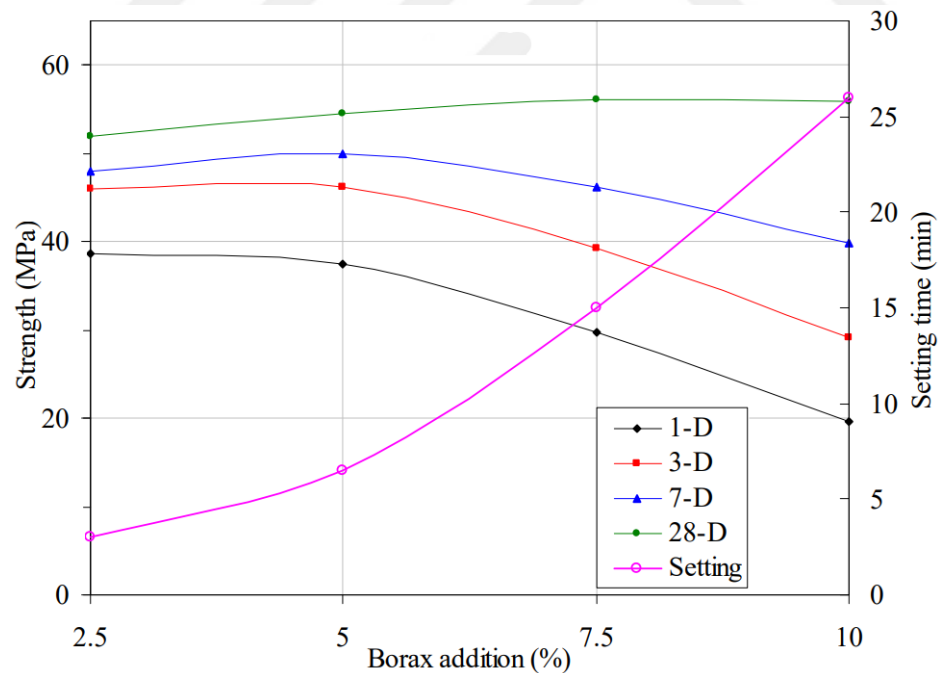


Figure 2.10. Influence of borax addition on the setting time and strength development of MKPC paste (Qiao, 2010)

$\text{Na}_2(\text{B}_4\text{O}_5[\text{OH}]_4) \cdot 8\text{H}_2\text{O}$ and H_3BO_3 affect magnesia phosphate cements similarly, and their effectiveness solely depends on the boron content in the mixture (Hall, Stevens, and El-Jazairi, 2001). Therefore, more borax needs to be added to the mixture to have the same retardation effect as boric acid. The addition of 10 g powder to a 1.5 kg batch of MPC mortar increases the setting time from 4 minutes to around 36 minutes, with boric acid, and to around 22 minutes, for borax (Hall et al., 2001). In order to increase the setting time to be around 36 minutes using borax, 20 g is needed (Figure 2.11).

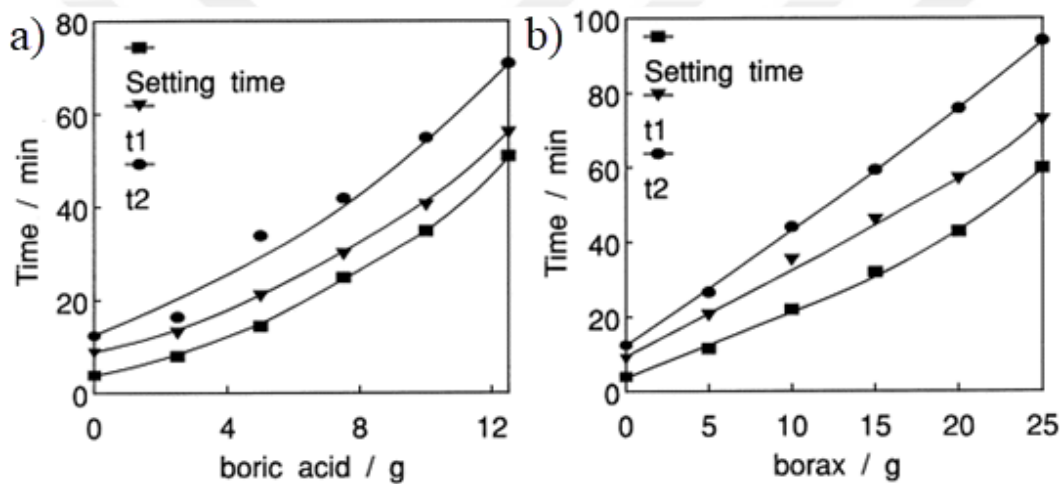


Figure 2.11. Setting times and calorimetry results for MPC mortar as a function of retarder contents: a) boric acid, b) borax (Hall et al., 2001)

Hall et al. (2001) measured and compared the flexural strength of MPC mortar prepared with boric acid and borax. They observed a similar range of results for double the content of borax compared to the boric acid content (Figure 2.12).

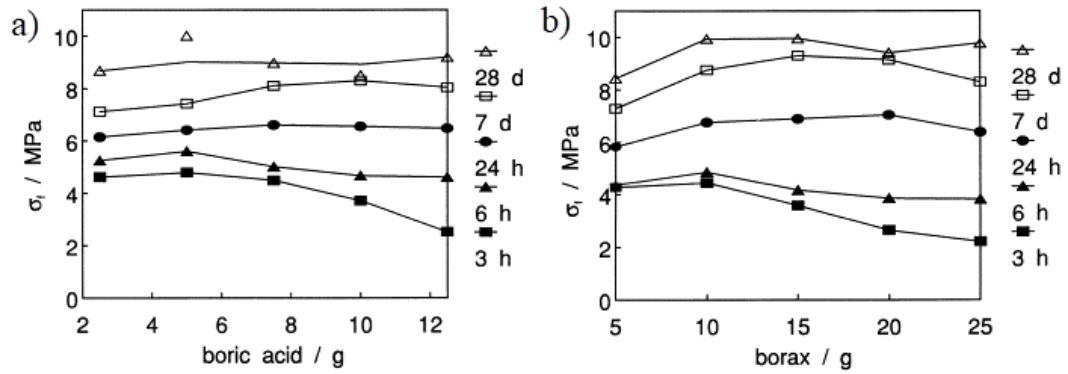


Figure 2.12. Flexural strength of MPC mortar as a function of retarder content, measured at various ages, using: a) boric acid, b) borax (Hall et al., 2001)

Besides boron-bearing compounds, citrate-bearing compounds, such as citric acid and sodium citrate, can be used as a retarder in magnesia cements. However, they are not widely adopted as boron-bearing compounds since they form insoluble magnesium citrate ($C_6H_6MgO_7$) when mixed with magnesium oxide (Salomão and Pandolfelli, 2011). Wang et al. (2018) investigated the effects of citric acid (CA) and sodium citrate (SC) on magnesium oxysulfate cements (MOS). By the addition of 0.5 wt. % of magnesia, they found that both CA and SC increase the setting time of MOS (Figure 2.13) by decreasing the rate of dissolution of magnesia. The hydrolysis of magnesia could be observed by the change of pH of the magnesia (MgO) and magnesium sulfate ($MgSO_4$) solution. Without the additives, the pH of MOS increases rapidly compared to mixtures prepared with CA and SC due to the release of OH^- ions. The pH of the control mixture later drops, since OH^- consumed by the reactions (Figure 2.14).

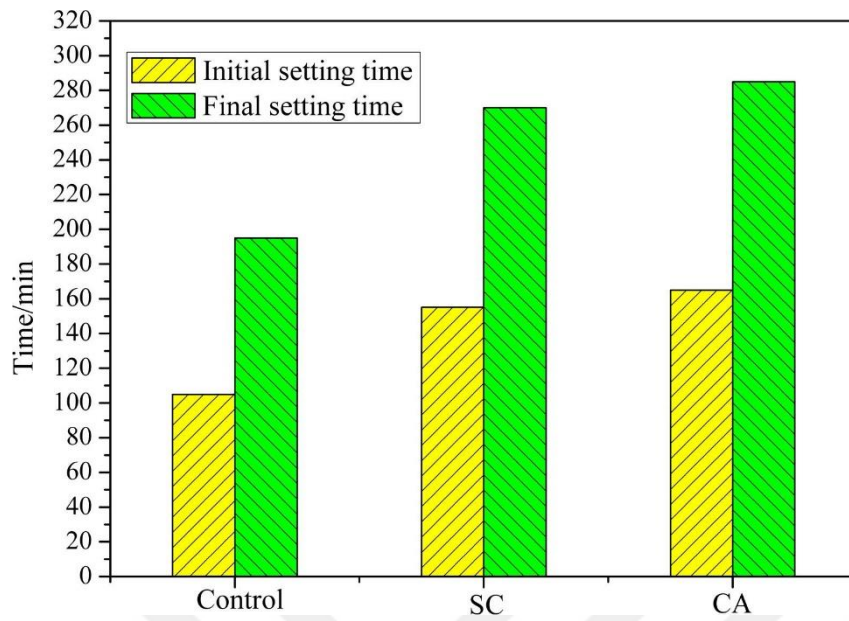


Figure 2.13. Setting time of MOS paste with and without additives (Wang et al., 2018)

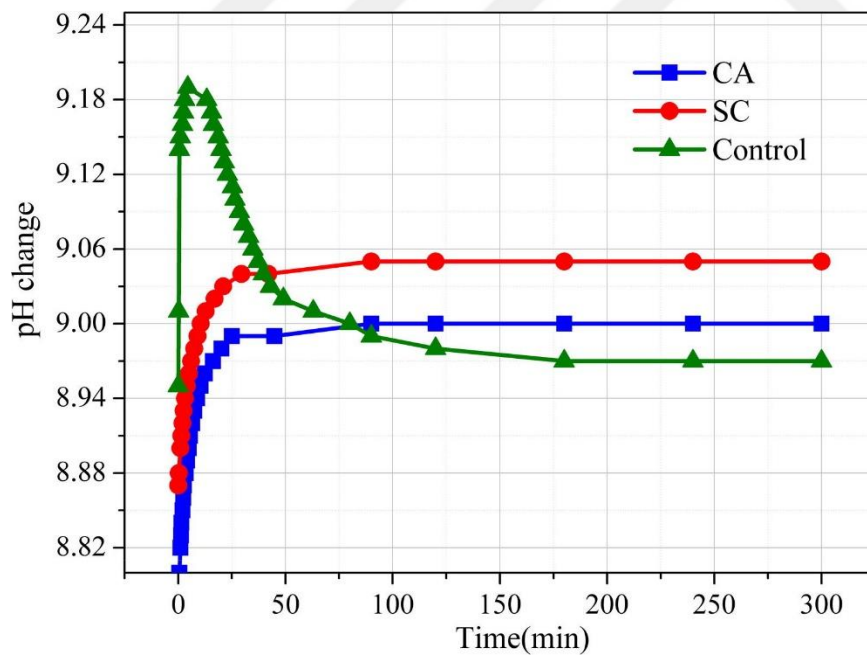


Figure 2.14. pH changes of MOS paste with and without additives (Wang et al., 2018)

The effects of citrate-based retarders on the strength of magnesium oxysulfate cements were observed to be favorable, as the mixtures with the addition of both CA and SC showed higher compressive strength (Figure 2.15). This significant increase in strength compared to control mixtures was mainly the result of the changed pore structure of the system (Wang et al., 2018). As shown in Figure 2.16, the total porosity and size distribution of pores were decreased by the admixture of CA and SC. Wang et al. (2018) concluded that this change resulted from increased needle-like hydration product phases on MOS cements.

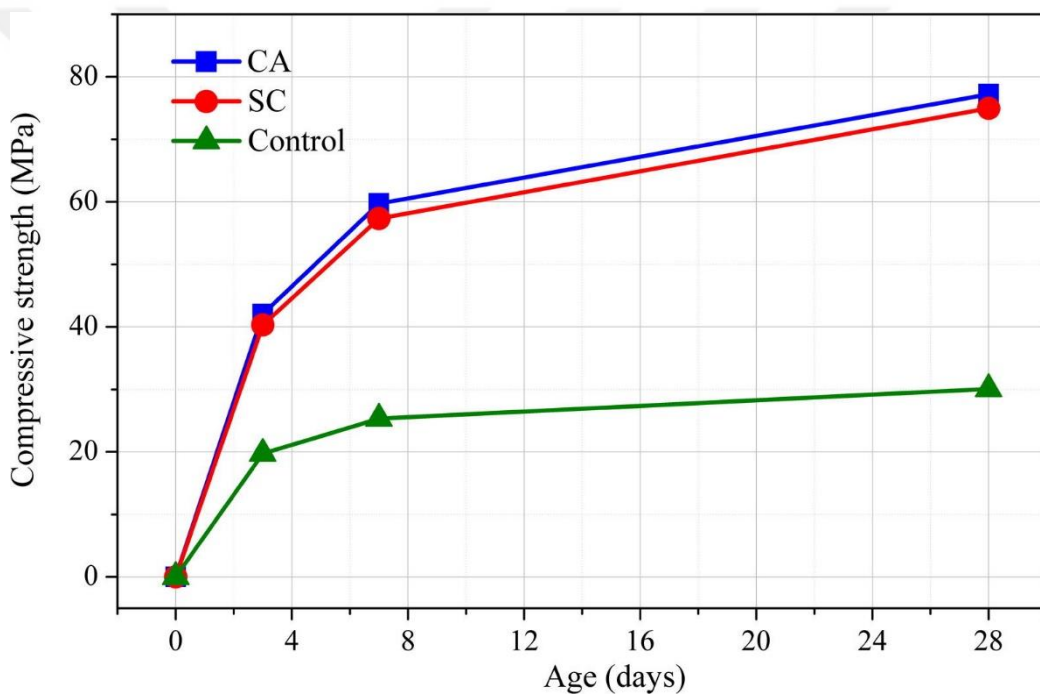


Figure 2.15. Compressive strength of MOS paste with and without additives at different curing ages (Wang et al., 2018)

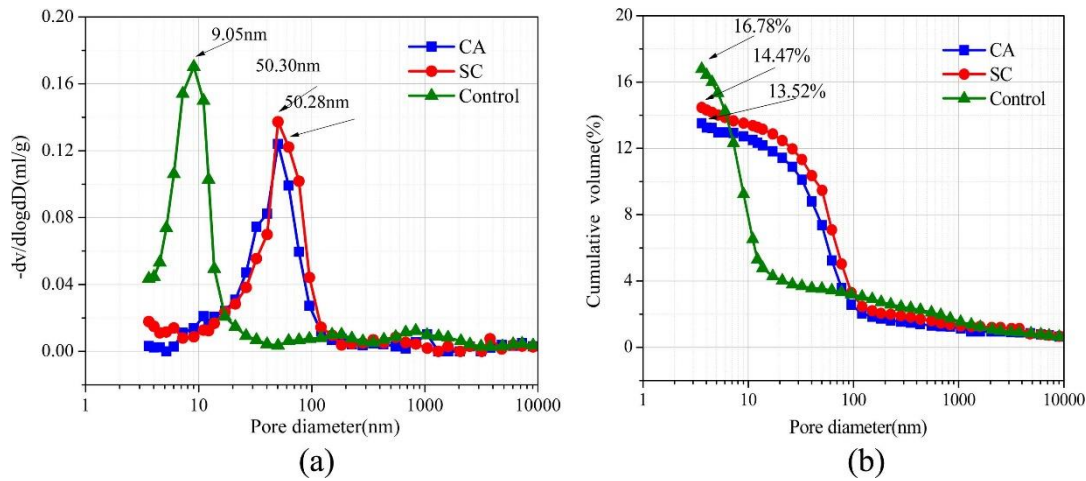


Figure 2.16. MOS pastes at 28 days: a) cumulative intruded pore volume vs. pore diameter, b) differential intruded volume vs. pore diameter (Wang et al., 2018)

2.3.4 Influence of Pozzolans on Magnesia Cements

Various kinds of pozzolans have been admixed into different types of magnesia cements to overcome problems related to workability, strength, durability, or to improve the properties of the system. Most of the pozzolan addition to magnesia cement aimed to reduce porosity and permeability, thus increase compressive strength or improve durability. On the other hand, the purpose of some admixtures was to improve the workability by increasing the flow of the fresh mixture or extending the setting time by dilution effect.

Chau et al. (2009) investigated the effects of fly ash on MOC; they measured the flow and setting time of mixes prepared with the addition of fly ash. They observed that the addition of fly ash to MOC increases the fluidity and setting times of the mortars (Figure 2.17).

Li and Chen (2013) conducted a similar study on MPC. They obtained results similar to the MOC case. Additionally, they experimented with higher fly ash replacement ratios, up to 60 %, and observed that above 40 % fly ash, the flow of the slurry was decreased; however, the setting time continued to increase (Figure 2.18).

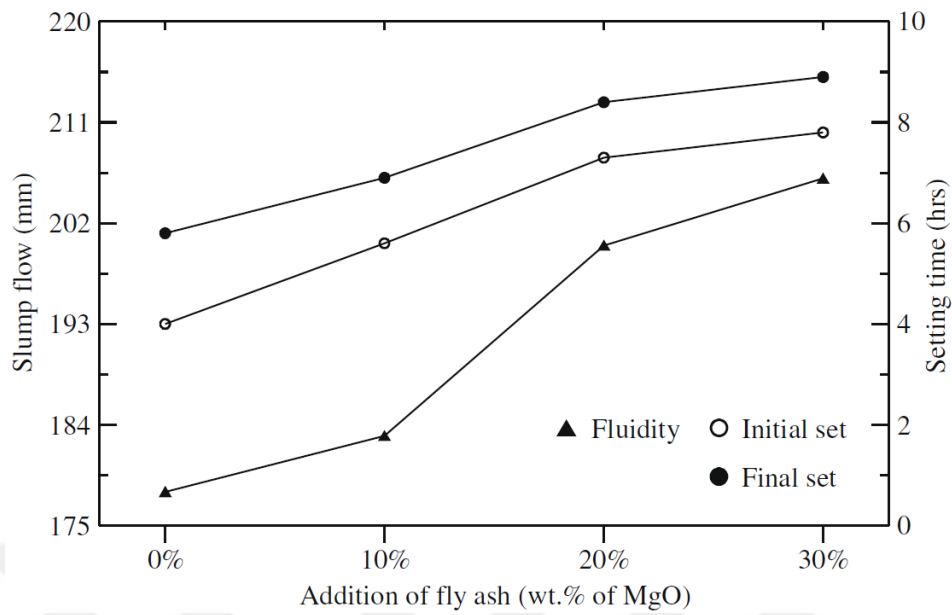


Figure 2.17. Fluidity and setting times of the MOC mortars blended with different ratios of fly ash (modified from Chau et al., 2009)

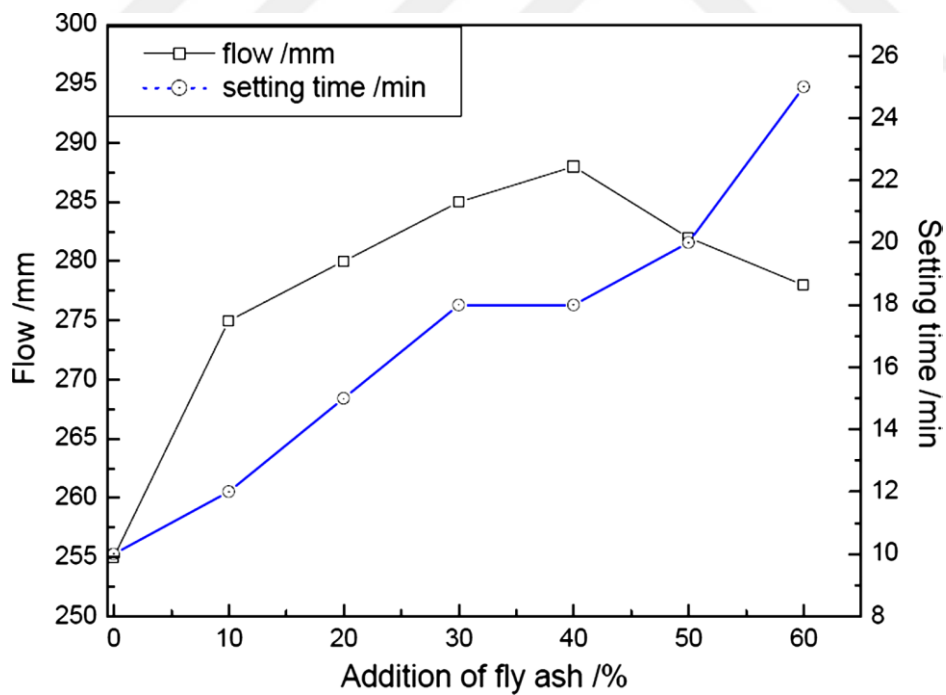


Figure 2.18. Fluidity and setting times of the MPC slurry blended with different ratios of fly ash (Li and Chen, 2013)

Xu et al. (2020) conducted a similar experiment using silica fume with a different type of magnesium phosphate cement, specifically magnesium silicon potassium phosphate cement (MSPPC). Their findings were also similar to the other studies mentioned. They also observed an increase in flow and setting times as the silica fume ratio increases. Beyond 15 % of silica fume addition, fluidity started to decrease but the setting time continued to increase (Figure 2.19).

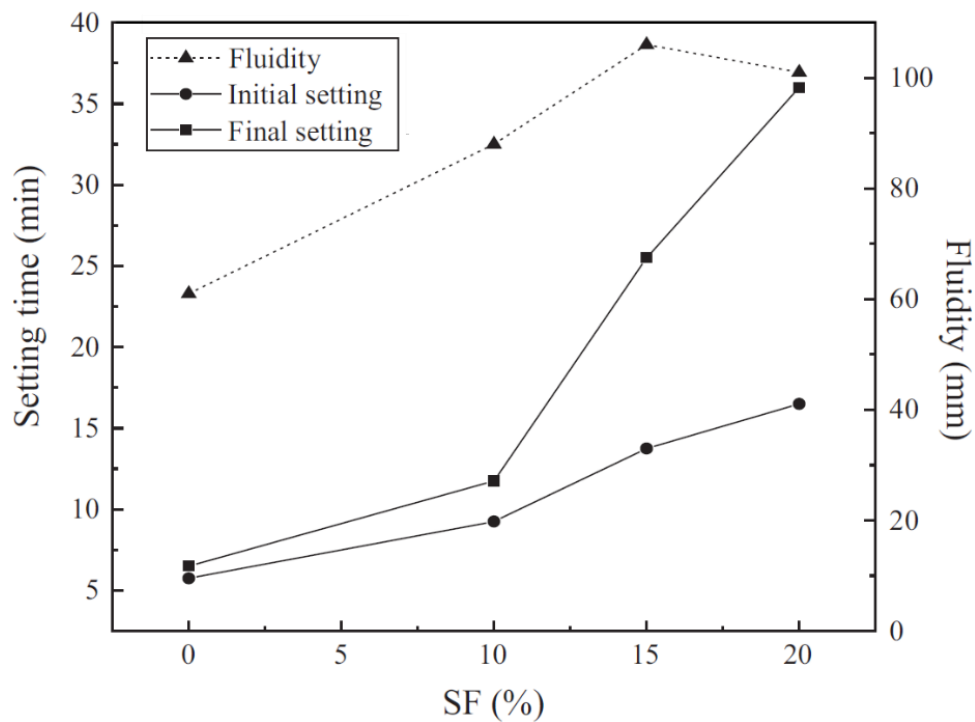


Figure 2.19. Fluidity and setting times of the MSPPC blended with different ratios of silica fume (Xu et al., 2020)

The studies on pozzolan admixture in several types of magnesia cements revealed the influence of pozzolans on flow and setting time. These effects are results of the physical interactions between the particles, such as dilution of binders to retard the setting times and modification of particle size distribution to allow better flow.

To observe the effects of pozzolans on mechanical properties, Chau et al. (2009) tested the strength development of MOC mortars prepared with various fly ash contents. They observed that as the fly ash ratio increased, the compressive strength of MOC mortars decreased (Figure 2.20).

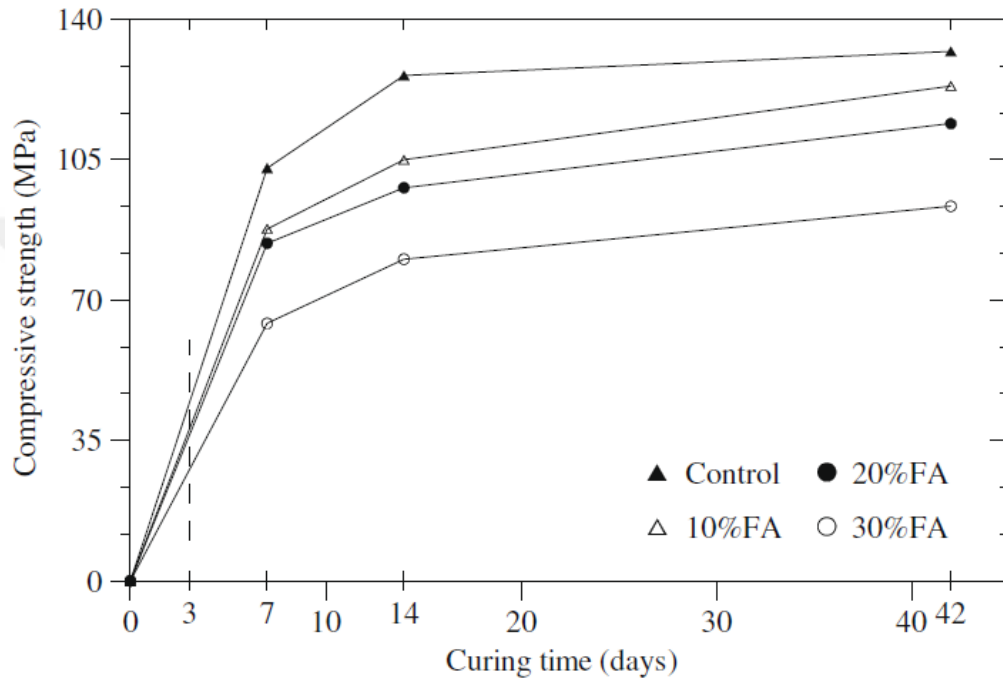


Figure 2.20. Effect of fly ash on the strength development of MOC mortars (Chau et al., 2009)

Li and Chen (2013) also measured the compressive strengths of MPC mortars with different fly ash addition ratios. They found that all the samples with fly ash addition performed poorly at early ages; however, by day 3, the samples with up to 50 % of fly ash addition showed similar compressive strength values with the samples not containing fly ash. On day 28, the mortars with fly ash additions showed higher compressive strength compared to the MPC mortars without the fly ash additions (Figure 2.21).

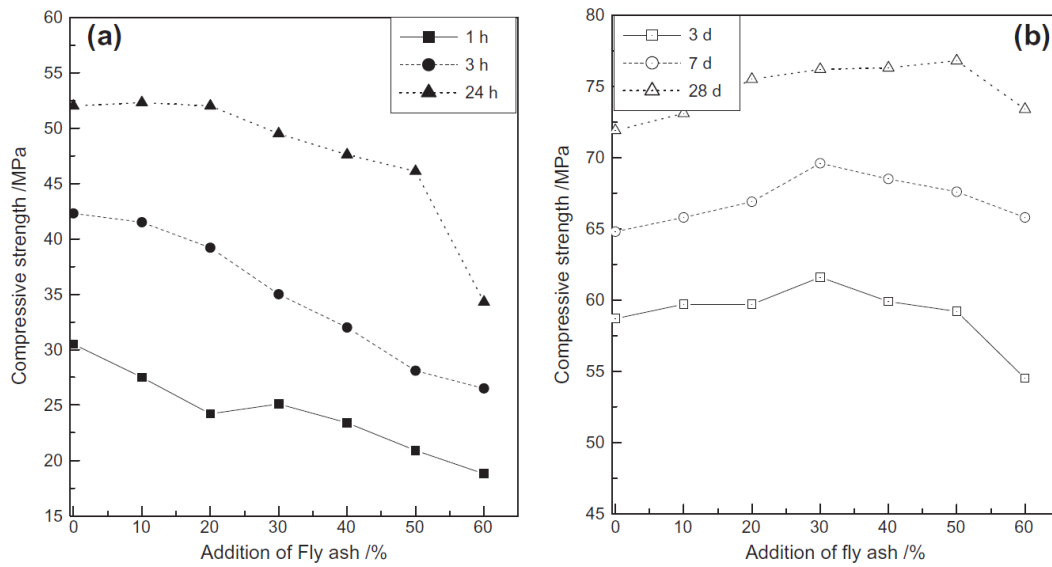


Figure 2.21. Effect of fly ash on strength development of MPC mortars: a) curing ages 1 h, 3 h, and 24 h; b) 3 d, 7 d, and 28 d (Li and Chen, 2013)

Xu et al. (2020) compared the effects of different levels of silica fume addition on MSPPC. They found that for MSPPC, it was crucial to have additional silica fume in the system for higher compressive strength values. They also observed that the compressive strength of the samples with 10 % silica fume decreased from 7 d to 28 d measurements. They suggested this may be a result of the moisture absorption of unreacted phosphate in the system. This reaction may generate expansion stress and microcracks that results in a decrease in the strength of the structure (Figure 2.22).

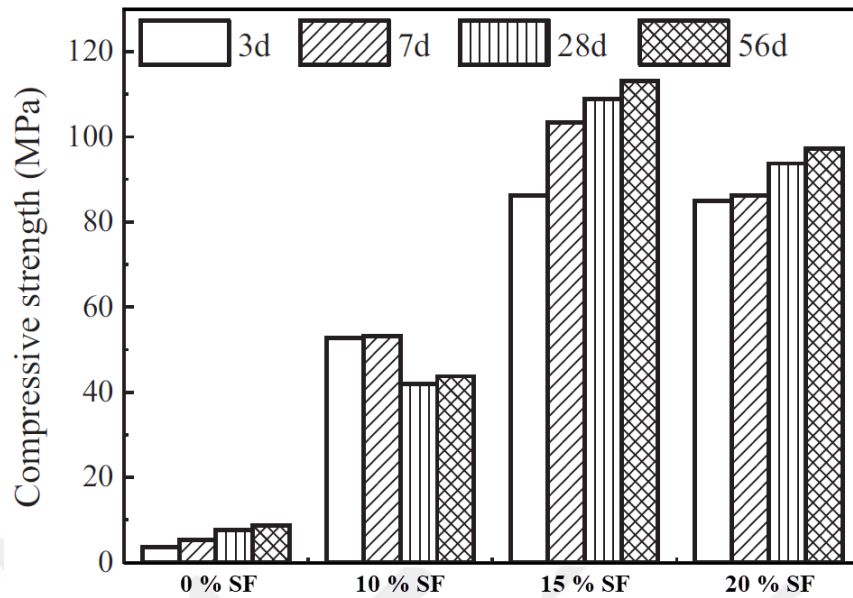


Figure 2.22. Effect of silica fume on strength development of the MSPPC mortars (modified from Xu et al., 2020)

Another generally observed effect of pozzolans on magnesia cements is to limit the volume change after setting. Depending on the type of cement and mix ratios, magnesia cements may show shrinkage or expansion. Chau et al. (2009) observed length changes of their MOC mortar prism samples. They found that all experimented mixtures showed an increase in their length at the early ages that stopped after 7 d, showing relatively small changes during the remainder of the test interval. The observed length change decreased as the fly ash content increased (Figure 2.23). On the other hand, mortars with greater length changes (with lower fly ash content) were observed to have higher compressive strength than the samples with lower length changes (with higher fly ash content), as discussed in Figure 2.20.

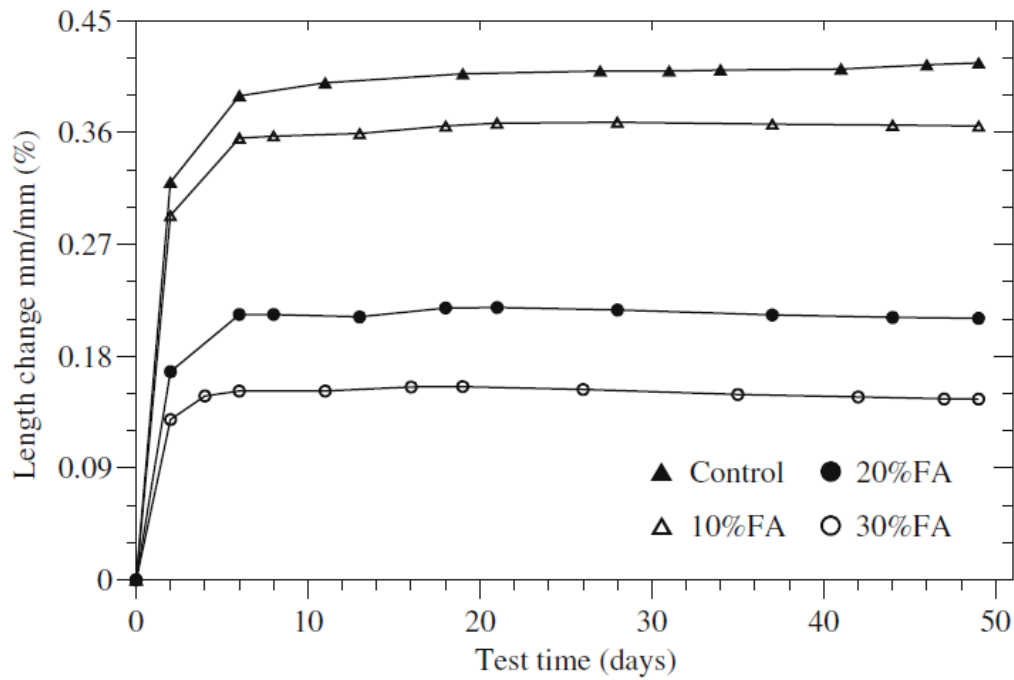


Figure 2.23. Effect of fly ash on length change of MOC mortars (Chau et al., 2009)

Li and Chen (2013) observed a similar volume change control with the addition of fly ash in MPC mortars. However, they observed slight shrinkage in MPC mortars rather than the expansion observed by Chau et al. (2009) in MOC mortars. Li and Chen (2013) compared the measured shrinkage of regular magnesium phosphate cement (MPC) mortar and that of ordinary portland cement (OPC) with average shrinkage of MPC mortars prepared with up to 60 % fly ash. They found that fly ash reduces the shrinkage of MPC mortars (Figure 2.24).

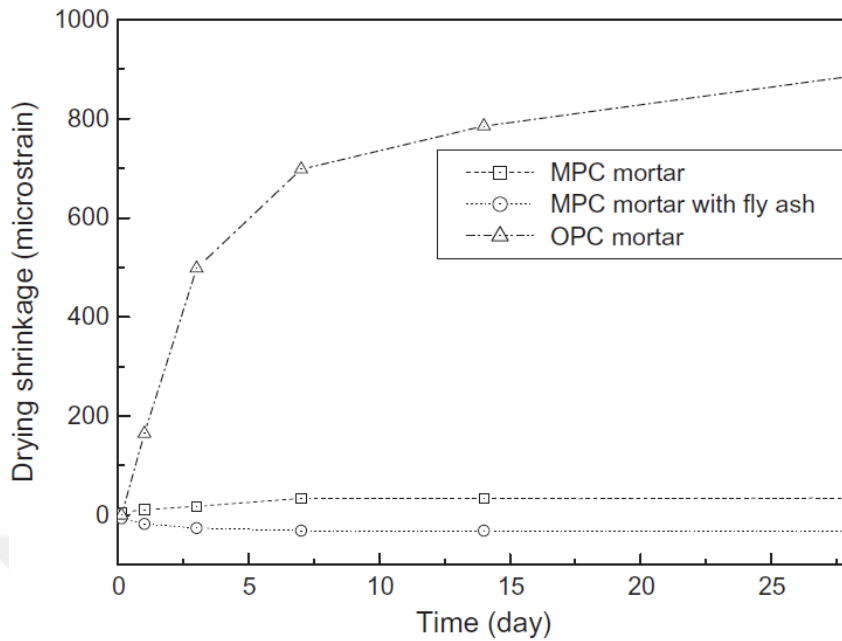


Figure 2.24. Effect of fly ash on the drying shrinkage of MPC mortars, compared with OPC mortar (Li and Chen, 2013)

2.4 Oxalic Acid

Oxalic acid (also referred to as ethanedioic acid) is the simplest dicarboxylic organic acid with the molecular formula $C_2H_2O_4$ (its condensed formula is $HOOC.COOH$) for its anhydrate form. Oxalic acid forms both neutral and acidic salts, mono-esters, or di-esters, a monoamide known as oxamic acid, and a diamide known as oxamide. Its salts with alkali metal ions (lithium, sodium, and potassium) are soluble; all other oxalates are very slightly soluble in water (Hodgkinson and Zarembski, 1968). Aqueous solubilities of some oxalates, which may be observed in magnesium oxalate cement with recycled portland cement paste, are given in Table 2.1. Some of the oxalates do not have quantitative data available. Instead of this, they are classified qualitatively, such as insoluble, slightly soluble, soluble, and very soluble (Lide, 2003). United States Pharmacopeia (2008) classifies a substance as insoluble when its solubility is less than 10 mg per 100 g of solvent and very soluble for more than

100 g per 100 g of solvent. Also, solubilities between 10 mg and 100 mg per 100 g solvent are classified as very slightly soluble.

Table 2.1 Solubilities of some oxalic acid salts (Lide, 2003)

Description	Solubility in water (mg/100 g)
Calcium oxalate (CaC_2O_4)	0.61 (20 °C)
Calcium oxalate monohydrate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$)	0.61 (20 °C)
Magnesium oxalate (MgC_2O_4)	38 (25 °C)
Magnesium oxalate dihydrate ($\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)	38 (25 °C)
Iron(II) oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)	78 (25 °C)
Iron(III) oxalate ($\text{Fe}_2[\text{C}_2\text{O}_4]_3$)	Very soluble
Aluminum oxalate monohydrate ($\text{Al}_2[\text{C}_2\text{O}_4]_3 \cdot \text{H}_2\text{O}$)	Insoluble

In neutral or alkaline pH, oxalate forms a calcium salt that has very low solubility, as this reaction may happen in the human body that may result in kidney stone problems. Williams (1976) reported that approximately two-thirds of kidney stones are calcium oxalate build-ups. Compared to calcium oxalate, magnesium oxalate is much more soluble in water. Even so, magnesium oxalate can be classified as very slightly soluble, according to United States Pharmacopeia (2008) classification. This solubility classification also includes struvite, one of the main hydration products of magnesium phosphate cements, with its solubility in water measured as 17 mg/100 g (Bhuiyan, Mavinic, and Beckie, 2007). The solubility of magnesium oxalate may indicate that water-resistance of magnesium oxalate cements could be similar to that of magnesium phosphate cements.

Oxalic acid can be found in nature and the human body. The source of oxalic acid in the human body is mainly the foods consumed. Green leafy vegetables such as rhubarb, spinach, and kale are the primary sources of oxalic acid in nature. Tea, cocoa, chocolate, and pepper are other common foods of high oxalate content. The

average diet contains variable amounts of oxalic acid estimated between 100 and 900 mg per day (Williams, 1976). Mass production of oxalic acid, however, is based on synthesis using other organic materials, acids, or in a better way from carbon dioxide. China is estimated to be the largest consumer and producer of oxalic acid; as of 2016, the total production of oxalic acid exceeded 200 kilotons (Valderrama, Putten, and Gruter, 2019). In the same review, Valderrama et al. (2019) summarize some commercially used production methods as oxidation of carbohydrates (such as glucose, sucrose, starch, dextrin, cellulose), ethylene glycol process, propylene process, dialkyl oxalate process, and sodium formate process. The use of carbon monoxide to prepare a diester of oxalic acid as a starting material has also been reported.

New technologies to produce oxalic acid from carbon dioxide by electrochemical reduction have been developed as a carbon capture and utilization (CCU) process. Fischer et al. (1981) reported one of the possible production methods that use an electrochemical cell to produce oxalic acid from carbon dioxide and water. The cell in their study contained zinc anodes, stainless steel cathodes, and acetonitrile with tetrabutylammonium perchlorate as the electrolyte. They were able to produce oxalic acid without any by-products. Another production method was developed by Lakkaraju et al. (2016), which converts CO₂ to formate, then the formate to oxalate. A summary of this process and other products formed is given in Figure 2.25. It starts with the electrocatalytic reduction of CO₂ in an electrochemical cell to formate, followed by passing the formate through a thermal reactor to produce oxalate in the presence of a base catalyst. Eventually, the oxalate can be converted into oxalic acid by a membrane-based electrochemical acidification process.

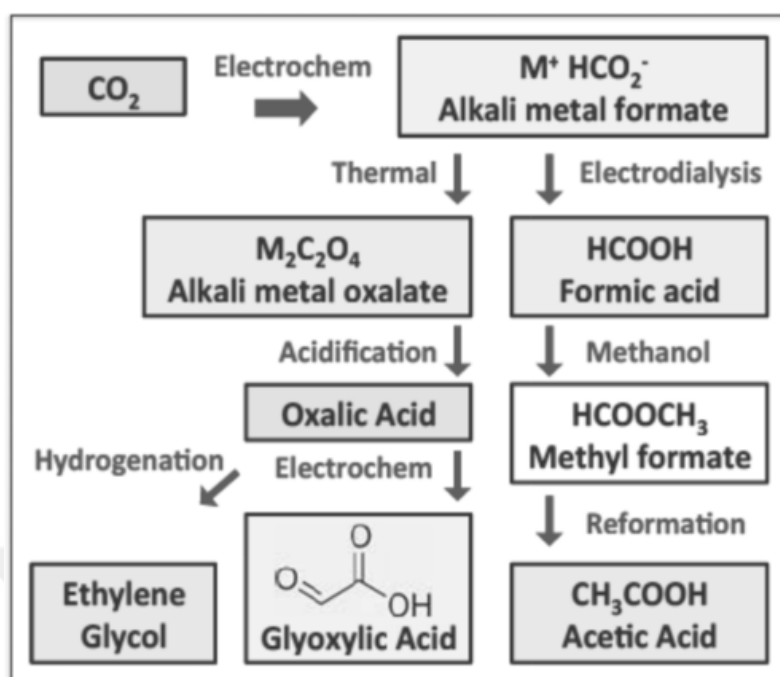
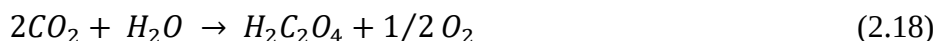


Figure 2.25. Conversion of CO₂ into value-added products (Lakkaraju et al., 2016)

The oxalic acid production method proposed by Fischer et al. (1981) can be summarized as:



According to this reaction equation, for the production of 1 kg oxalic acid, 977 g of carbon dioxide is consumed. This simple calculation does not consider the carbon footprint of the production process, yet may give an idea for the rate of carbon capture of oxalic acid.

The primary industrial usage of oxalic acid is as a reagent. It is an ingredient of cleaning solutions for removing paint, varnish, rust, and ink stains as well as being used extensively in laundries as a scouring agent to remove excess alkalinity remaining in washed fabrics. It is also used to clean bleaching wood and straw, as a chrome stripper and as a bleach in leather manufacture (Çalışkan, 2000). Oxalic acid can be used in limestone structures, such as statues and walls, for surface treatment

and to create a protective coating by form calcium oxalate (Cezar, 1998). It is widely used as a chelating agent to capture various metal ions, which can be utilized in removing toxic metals from the body and chemical treatment of water or soil (Oustan, Heidari, Neyshabouri, Reyhanitabar, and Bybordi, 2011). Another substantial usage of oxalic acid is for mite control in honey bee colonies (Rademacher and Harz, 2006).

However, there has not been any study or research found in the literature on the use of oxalic acid to produce a cementitious material or its mixture with magnesium oxide. In this regard, this thesis presents a pioneering study that aims to produce a magnesia cement with oxalic acid.

2.5 Recycled Portland Cement Paste

Among the wastes of the construction industry, concrete waste constitutes a considerable portion (Prošek et al., 2018). Traditionally, demolished concrete waste is used in landfills. However, this may lead to environmental pollution, since it takes several decades for the concrete to decay back to its originating earth materials (Wang, Mu, and Liu, 2018). When concrete waste is used as a filling material, its potential is not fully benefited from.

Recycling is another option for concrete to reduce its negative environmental impact and utilize more of the potential of waste. In the late 20th century, recycled concrete gained more interest, and concrete recycling became prevalent. Recycling of concrete is encouraged and even enforced by law in some countries. For example, Kwon et al. (2015) mention that Korea and Japan have laws that set a recycling target for construction waste and force large scale companies to recycle concrete waste. As a result of regulations, environmental concerns, and economic motivation, recycling of concrete is becoming a regular practice. Nowadays, Denmark, Netherlands, and Belgium recycle more than 80 % by mass of their construction and demolition waste (Corinaldesi and Moriconi, 2009).

Concrete recycling, however, is mainly focused on the recycling of larger aggregates, excluding fine aggregates and hydrated cement paste. Recycled aggregates often do not perform as well as natural aggregates due to adhered mortar and interfacial transition zone. The residual mortar on recycled aggregates affects the mechanical properties negatively due to having higher porosity and water absorption (Shi et al., 2016). Therefore, concrete mixtures prepared with recycled aggregates may face problems related to low workability, strength, and durability. Thus, the mix design should consider and take measures against the possible adverse effects of the recycled aggregate usage such as alkali-silica reaction, corrosion (due to chloride content), and freeze-thaw resistance (Gastaldi et al., 2015). The performance of the recycled aggregates can be enhanced by removing or strengthening the weak mortar covering the aggregates. Shi et al. (2016) review the researched methods for the removal of the mortar; the methods are grinding, which also can be done by heating the materials, pre-soaking in water, and pre-soaking in acid. While removing cement mortar from aggregates improve the performance of recycled aggregates, it creates more fine waste, which mostly remains unused. There have been several studies performed about recycling of this remained waste, which are mainly focused on rehydration of recycled mortar to utilize as a binder or using as fine aggregates (Neno, de Brito, and Veiga, 2014).

2.5.1 Rehydration of the Recycled Portland Cement Paste

It is possible to use hydrated cement paste (HCP) to form another cementitious structure by reintroducing it to water. One of the studied methods for reusing HCP is the carbonation of rehydrated HCP, similar to the attempts on some of the magnesia cements (Zhu, Fang, and Wei, 2018). However, this method includes pressurized carbon dioxide curing that is not practical to use in applications and would not perform well in larger sections that are difficult to carbonate from the surface. Another widely studied method is dehydrating the HCP by heating and then rehydrating without any required special curing regime. Since some of the researched

cement paste recycling methods heat the recycled concrete, heat-processed cement paste can be a typical product obtained from concrete recycling.

It has been reported that high-temperature exposure to concrete leads to physical and chemical changes to the HCP (Shui, Xuan, Chen, Yu, and Zhang, 2009). Alarcon-Ruiz et al. (2005) investigated the dehydration process of HCP to produce dehydrated cement paste (DCP) by heating it to 900 °C. They found that evaporable water and a part of the bound water escapes between 30 °C to 105 °C. Decompositions of gypsum and ettringite were observed by 170 °C. From 180 °C to 300 °C, the bound water escapes from C-S-H and carboaluminate hydrates, thus decomposing them. Between 450 °C to 550 °C, the dihydroxylation of the portlandite was observed. Lastly, between 700 °C to 900 °C, calcium carbonate decarbonates.

In an effort to utilize recycled portland cement paste, Farage et al. (2003) were able to rehydrate hydrated cement paste after heating it to 300 °C. Similarly, Alonso and Fernandez (2004) rehydrated DCP after heating HCP to 750 °C. Both studies observed the recovery of C-S-H gel after rehydration of the DCP. Moreover, HCP showed cementitious properties when it was introduced to water (Shui et al., 2009).

Hydration and dehydration processes change the chemical and mechanical properties of the cement. These changes affect the workability and performance of mixtures prepared with HCP and DCP. The most significant differences in workability are in setting time and water content to reach standard consistency, which may affect the ultimate strength of the rehydrated concrete. Shui et al. (2009) found that required water for standard consistency increases as the dehydration temperature increases for the hydrated cement pastes. While the unheated HCP requires 32 % water (by mass), DCP dehydrated at 300 °C requires 48 % water (by mass). The water requirement for standard consistency increases linearly as the dehydration temperature increases, DCP dehydrated at 900 °C requires 68 % water (by mass). A comparison for the water content to reach the standard consistency for DCP prepared at different dehydration temperatures with HCP (at room temperature [RT]) given in Figure 2.26. They suggested that the surface area of DCP particles increases as the

dehydration temperature increases due to the physical changes such as micro-cracking and decomposition of the previous hydrates.

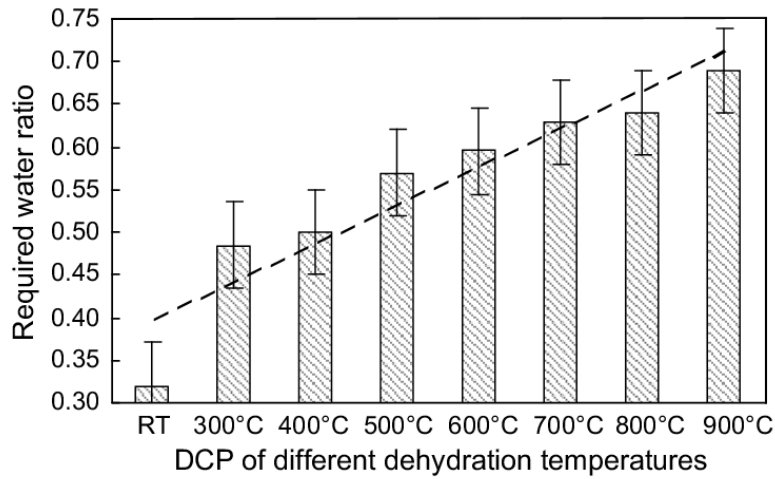


Figure 2.26. Required water of HCP (RT) and DCP burned at different temperatures for standard consistency (Shui et al., 2009)

Setting time of DCP pastes was observed to decrease parabolically as the dehydration temperature increases (Shui et al., 2009). The observed initial and final setting times are presented in Figure 2.27.

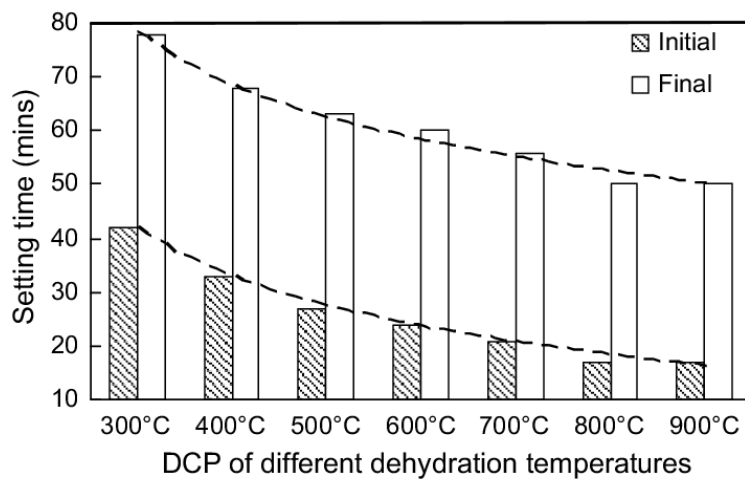


Figure 2.27. Setting time of DCP pastes with standard consistency (Shui et al., 2009)

The decreased setting time may indicate that DCP prepared at higher temperatures is more reactive than the dehydration lower temperatures. However, their degrees of rehydration rates did not show a significant difference among DCP prepared at different temperatures (Shui et al., 2009). The degree of hydration of rehydrated DCP, cured by fog-spraying, was observed to be between 65 to 70 % on the first day. The degree of hydration reached about 95 % on day 28 for all cases (Figure 2.28).

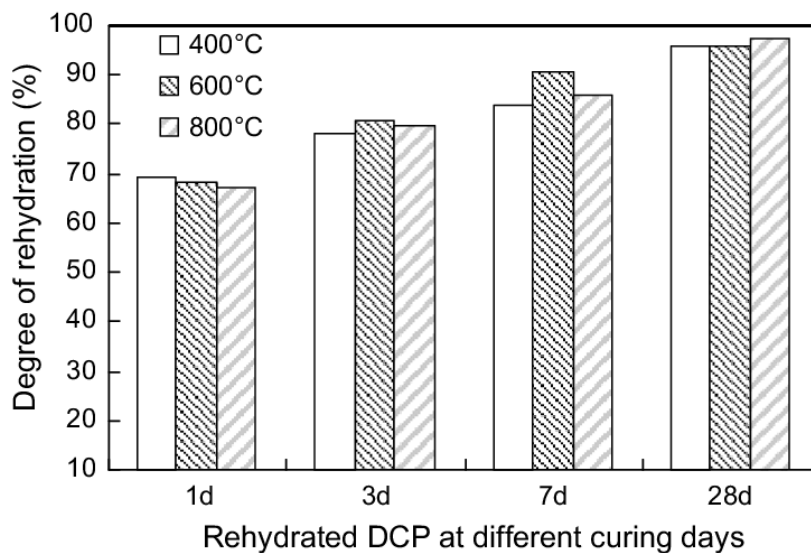


Figure 2.28. Degree of rehydration of DCP at different curing days (Shui et al., 2009)

The compressive strength gain rate of HCP was observed to be much lower compared to DCP (Shui et al., 2009). Shui et al. (2009) determined that the strength of HCP mainly resulted from the hydration of initially unhydrated cement grains. Dehydrated cement pastes showed better performance compared to untreated HCP. Their compressive strengths increase as the dehydration temperature increases at every measurement until 800 °C, except at 900 °C. The compressive strength of the DCP dehydrated at 800 °C was able to show similar results to the regular portland

cement 7 d. From day 7 to 28, the strength gain rate of DCP was observed to be lower than the regular portland cement. On the other hand, the strength of the untreated HCP doubles from 7 to 28 days (Figure 2.29).

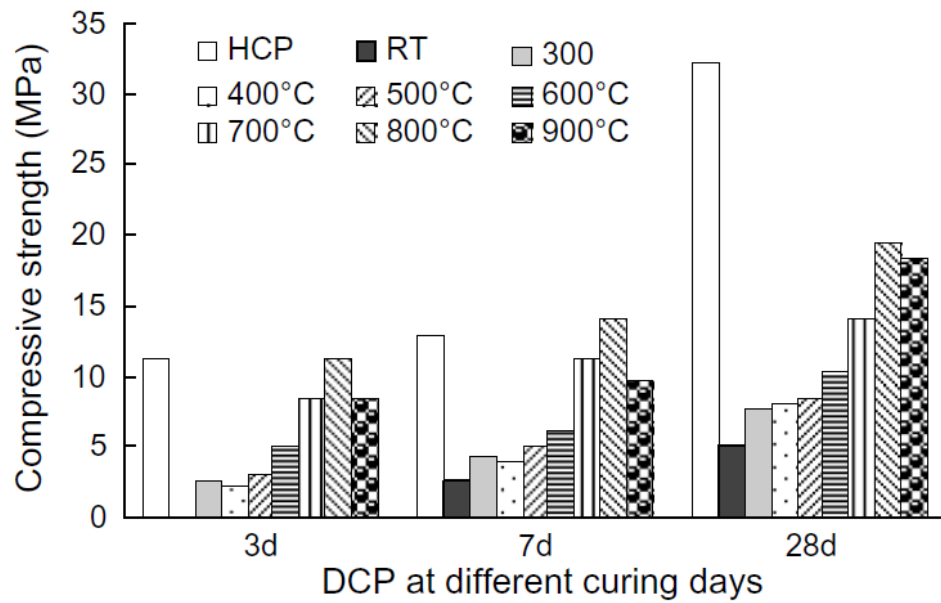


Figure 2.29. Compressive strengths of rehydrated DCP and HCP at different ages (Shui et al., 2009)

CHAPTER 3

MATERIALS AND EXPERIMENTAL PROCEDURE

In this chapter, the materials used and the experimental procedures followed in the study are presented. Related physicochemical properties of materials and their preparation processes (if they were processed after sourcing) are presented. The details of the experimental procedures followed are provided with the reasons for choosing them.

3.1 Materials

The main ingredients in magnesium oxalate cements are magnesium oxide (MgO) and oxalic acid (Ox). However, in this study, oxalic acid is first blended with hydrated portland cement paste (HCP) or dehydrated portland cement paste (DCP) in order to restrain the undesirably rapid reaction between magnesium oxide and oxalic acid. Ultimately HCP and DCP can be considered additional main ingredients of this study, included in almost all the samples tested.

In addition to the primary raw materials, the effects of some additives are studied too. Boric acid was experimented with as a retarder in order to make possible the preparation of some higher compressive strength mixtures, otherwise almost impossible to pour in large volumes, by using the control mixture that only includes the magnesium oxide and recycled portland cement paste-oxalic acid blends. In order to increase the compressive strength and improve the workability of fresh mixture, the effect of pozzolans was also examined. The influences of silica fume and a class F fly ash were investigated.

3.1.1 Magnesium Oxide

MgO (magnesia) can be found in nature as the mineral periclase. Also, it can be produced from magnesium-bearing compounds such as magnesium carbonate (MgCO_3), magnesium hydroxide ($\text{Mg}[\text{OH}]_2$), or magnesium chloride (MgCl_2).

Low-grade magnesia powder with an unknown calcination history was obtained from OSA Foreign Business in Ankara, Turkey. It can be physically described as a hygroscopic fine white powder. By calcination, it is observed that the color of the powder changes to orange. The molecular mass of magnesium oxide is 40.305 g/mol. The water solubility of magnesia is considered to be poor (PubChem Database, 2020a). Its density was measured as 3.10 g/cm³ before calcination, and after the calcination at 1500 °C, the density increased to 3.50 g/cm³. The Blaine fineness of magnesia decreased by calcination from ~11000 cm²/g to ~3100 cm²/g. The particle size distribution of magnesia calcined at 1500 °C, determined using low-angle light scattering, is presented in Figure 3.1. According to this measurement, the specific surface area of the powder is ~9980 cm²/g.

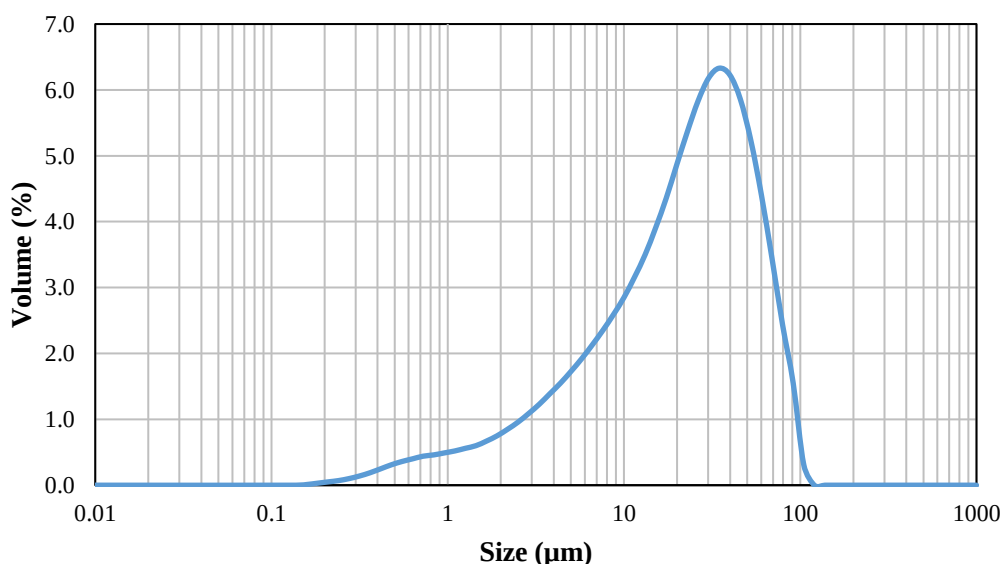


Figure 3.1. The particle size distribution of calcined magnesia at 1500 °C

The x-ray diffractograms of MgO before and after calcination are presented in Figure 3.2. Both the uncalcined and calcined powder show peaks of periclase clearly, indicating a high content (Downs and Hall-Wallace, 2003). Before the calcination, some peaks of quartz (SiO_2) were identifiable. However, after calcination, these peaks mostly disappeared. Instead, new peaks were observed, which indicate forsterite (Mg_2SiO_4) phases. These changes might mean that some of the periclase reacted with quartz to form forsterite during the calcination.

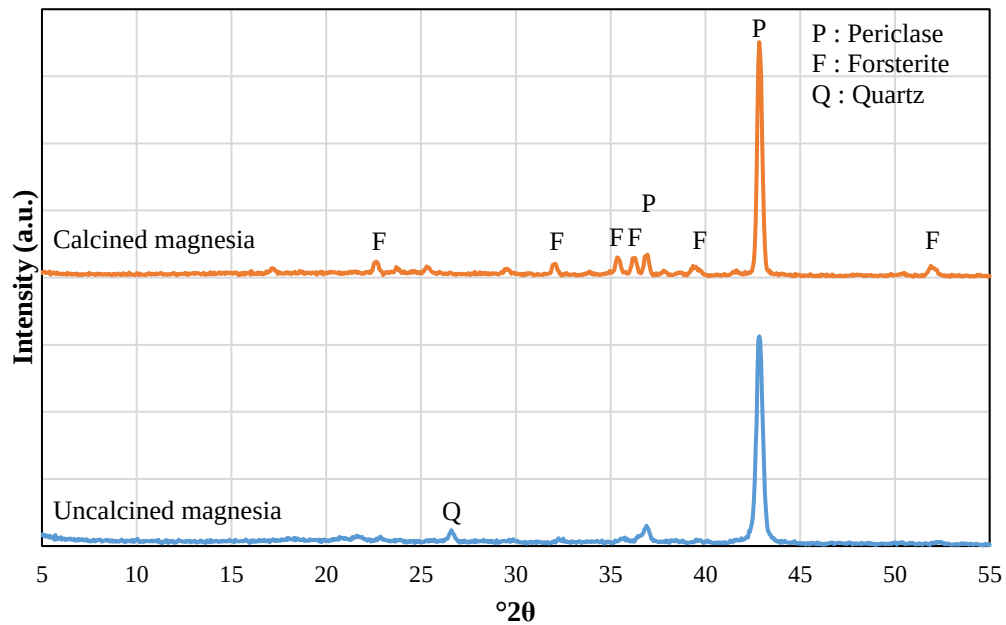


Figure 3.2. X-ray diffractograms of the magnesias before and after the calcination at 1500 °C

Chemical analysis of the powder by x-ray fluorescence can provide more detail about the composition. Bilginer (2018) analyzed magnesias powder obtained from the same source before and after calcination following the same process (Table 3.1). About 80 wt. % of the powder is MgO. SiO_2 is the second most abundant oxide in the powder with 10 wt. %. Also, the removal of some CO_2 from the powder by the calcination can be observed.

Table 3.1 Oxide composition of the magnesia powder before and after calcination at 1500 °C (Bilginer, 2018)

Oxides	As received	After calcination to 1500 °C
	wt. %	wt. %
MgO	81.3	82.8
SiO ₂	9.35	10.6
CO ₂	6.89	3.82
CaO	1.74	1.85
Fe ₂ O ₃	0.60	0.72
NiO	0.12	0.13
Al ₂ O ₃	0.06	0.08

3.1.1.1 Calcination of Magnesium Oxide

The as-received magnesium oxide powder was calcined in aluminum oxide crucibles to reduce its reactivity before its usage in the mixtures. The calcination temperature of the magnesia was chosen as 1500 °C based on Bilginer (2018). The high-temperature furnace was programmed to reach this temperature in 10 h, maintain 1500 °C temperature for 1 h, then gradually reduce the temperature at the same rate as heating. The volume reduction of magnesia powder upon calcination can be seen in Figure 3.3; the crucible was completely full prior to calcination.

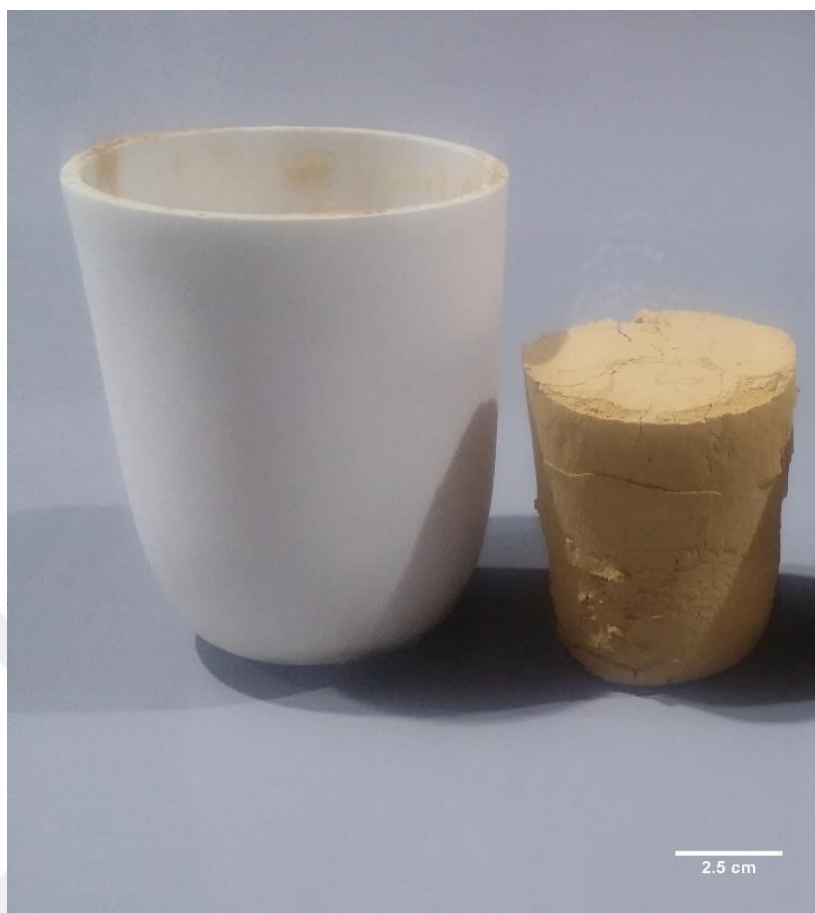


Figure 3.3. Magnesia powder after calcination at 1500 °C (Bilginer, 2018)

The magnesia powder solidified during calcination by sintering. The resulting mass was ground in a laboratory ball mill for about 30 minutes and then sieved through a 1 mm sieve.

3.1.2 Oxalic Acid

The oxalic acid used for this study was the most common form that is commercially available, oxalic acid dihydrate. The molecular formula for oxalic acid dihydrate is $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. It is a white and odorless fine crystalline powder. The powder tends to agglomerate during storage, yet this can be reversed by crushing.

The molecular mass of anhydrous oxalic acid is 90.03 g/mol, and for oxalic acid dihydrate, it is 126.07 g/mol. Water solubilities at 20°C are 9-10 g/100 ml for oxalic acid and 13-14 g/100 ml for oxalic acid dihydrate (PubChem Database, 2020b). Their densities are 1.90 g/cm³ for anhydrous oxalic acid and 1.65 g/cm³ for oxalic acid dihydrate (PubChem Database, 2020c). The x-ray diffractogram shows the crystalline phase of oxalic acid, which has its most significant peak at 28.9 °2θ, a smaller peak around 25.8 °2θ, and various smaller peaks (Figure 3.4). The XRD results and its quantitative analysis conclude there was no other significant compound other than the oxalic acid in the as-received powder.

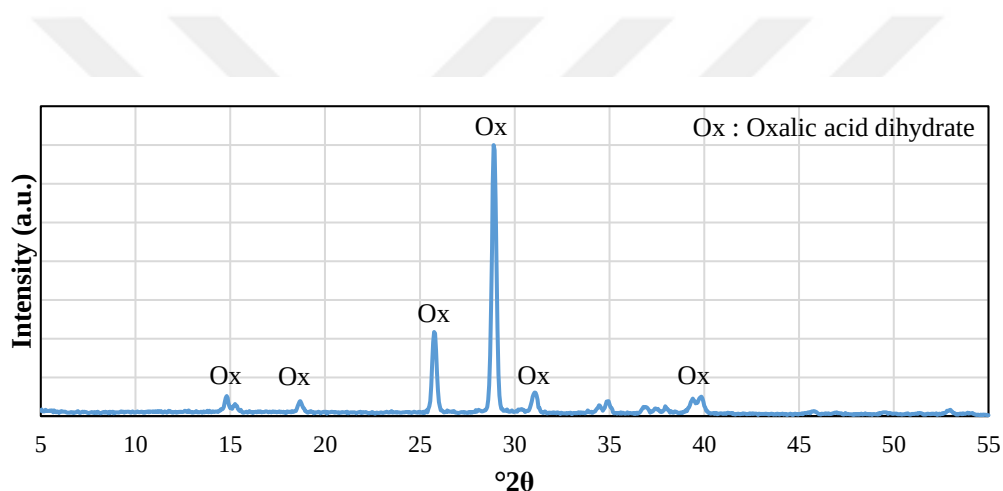


Figure 3.4. X-ray diffractogram of the as-received oxalic acid dihydrate

In this study, oxalic acid dihydrate was mostly used to blend with recycled portland cement paste to produce a cement paste oxalate (CPOx). During the preparation process, it is expected that the oxalic acid dihydrate became anhydrous. Anhydrous oxalic acid has two phases (α and β), which have XRD patterns different than oxalic acid dihydrate and each other. Since the XRD pattern information did not exist in the databases used, their XRD pattern for oxalic acid was obtained from Colmenero (2019). The XRD patterns of anhydrous oxalic acid polymorphs and oxalic acid dihydrate are presented in Figure 3.5.

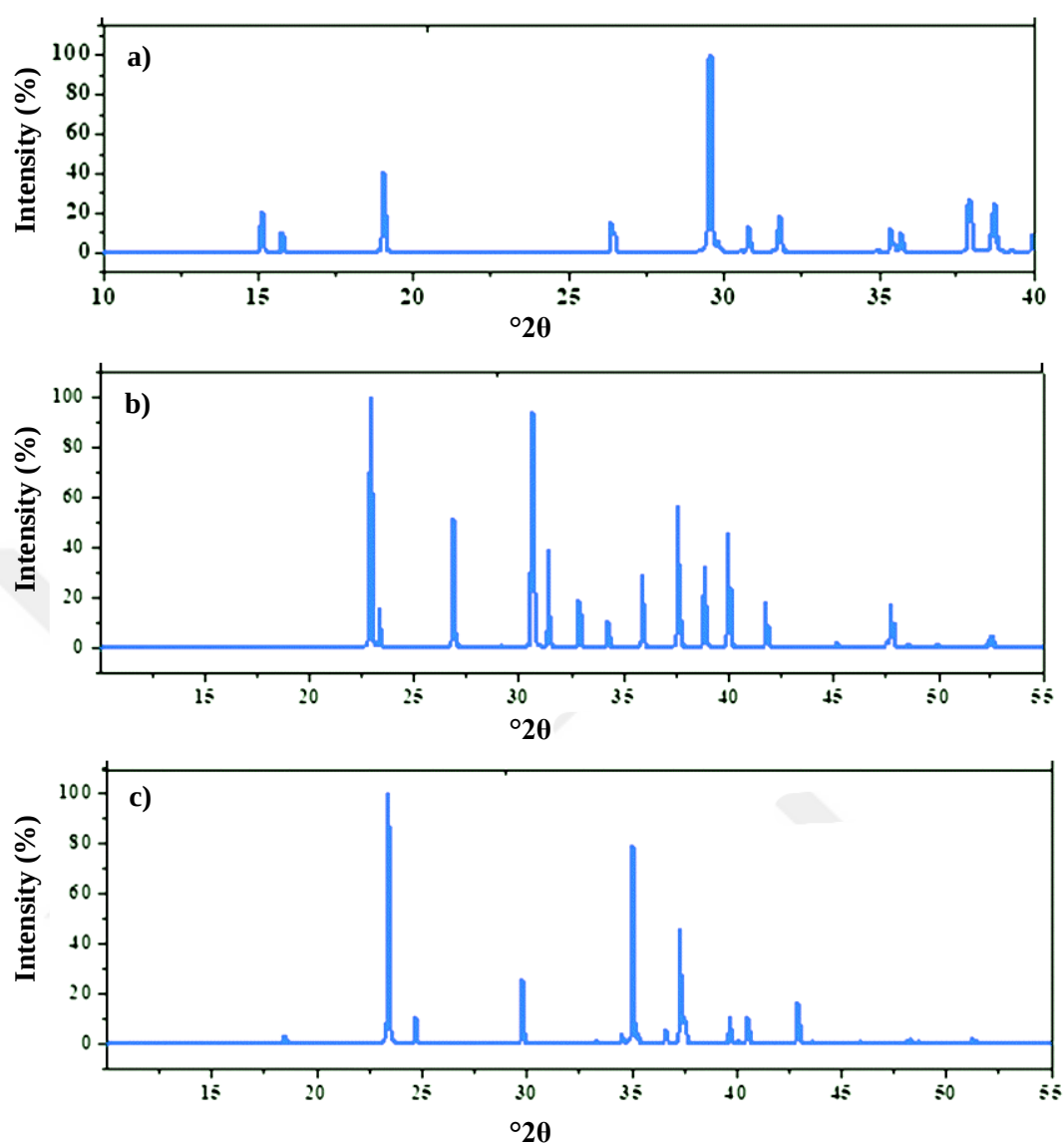


Figure 3.5. X-ray diffractograms of oxalic acid: a) oxalic acid dihydrate, b) α -oxalic acid, c) β -oxalic acid (modified from Colmenero, 2019)

3.1.3 Recycled Portland Cement Paste

The hydrated portland cement paste (HCP) used in the study was obtained from various portland cement mortar samples. The samples were 50 mm cubes and 25 mm x 25 mm x 250 mm prisms prepared for various purposes, such as to measure compressive strength, shrinkage, or expansion. The density of the HCP was measured as 2.50 g/cm³, and for DCP it was measured as 2.76 g/cm³. The Blaine fineness of recycled powders was measured as ~3500 cm²/g for HCP and ~2300 cm²/g for DCP.

Although this material is called paste, it was obtained by crushing portland cement mortar; therefore, it contains quartz and cement paste. X-ray diffractograms of the materials indicate a high amount of sand occurrence in the powder (Figure 3.6). This sand cannot easily be removed by the conventional methods used to obtain HCP; therefore, the powder was used as it is. Although the history and mix design of most samples are unknown, it is assumed that a standard test method such as ASTM C109 (2020) may have been followed for their mix design. The sand-to-binder ratio is 2.75 in ASTM C109 (2020). Assuming there was not any other admixture or replacement in the mix design, only ~27 % by mass of the mix is portland cement. Therefore, assuming w/c is 0.5, ~35 % by mass of the mortar samples must be hydrated portland cement paste.

The peaks of portland cement phases and changes in the XRD pattern due to decomposition during heating of hydrated portland cement is not easily recognizable since the content of the portland cement is rather low in the sample. The most significant change in the peaks due to dehydration is the newly occurred peak around 32.2 °2θ, which may correspond to alite. Alite formation is expected as a result of the decomposition of C-S-H. Similarly, some intensity increases around the biggest peaks of belite and lime were observed, yet they are not very clear.

Since the purpose of this study was to utilize recycled portland cement paste as it can practically be recycled (containing fine aggregates) and compare the effects of two possible types of recycled paste (hydrated and dehydrated); the composition of the recycled powder and changes to its structure during dehydration was not investigated in great detail. The effect of dehydration and rehydration on portland cement is expected to be similar to other studies, such as Alonso and Fernandez (2004). The sand content is not expected to show any chemical effect on the system due to being inert in water or at neutral or low pH but may affect the system physically.

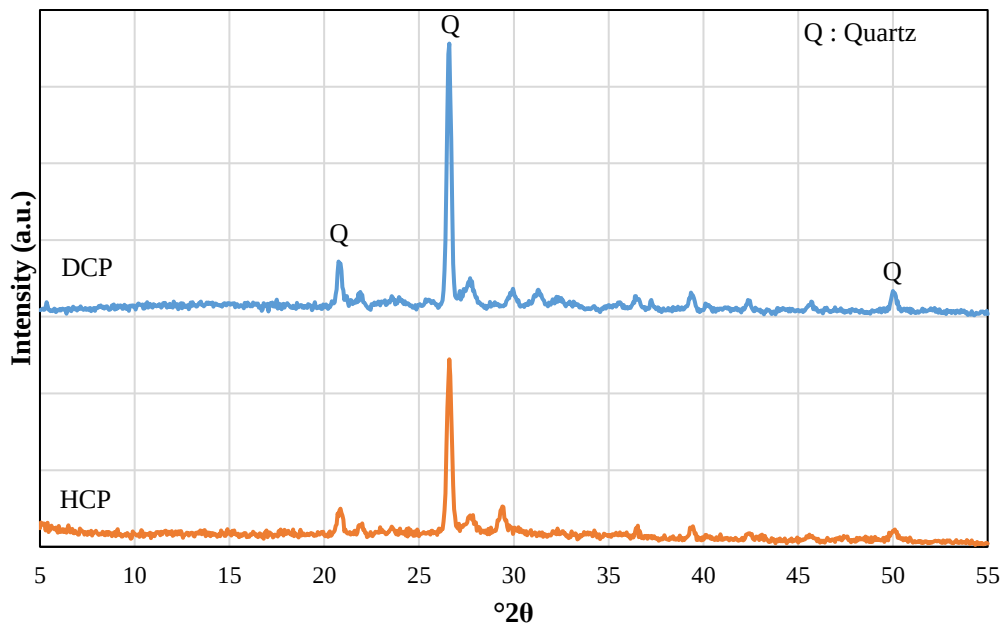


Figure 3.6. X-ray diffractograms of the HCP and DCP (dehydrated at 1200 °C)

The oxide compositions of the HCP and DCP show that high amounts of SiO_2 were contained in the powder. On the other hand, CaO , Al_2O_3 , and Fe_2O_3 contents are not low enough to verify the assumed PC content, which is ~ 25 wt. % of the powder. Therefore, more PC than assumed or other pozzolans may be contained in the powder. The loss on ignition of HCP was measured as 11.3 %.

Table 3.2 XRF analysis results of HCP and DCP

Oxide	Mass (%)	
	HCP	DCP
SiO ₂	48.3	47.7
CaO	30.6	30.9
Al ₂ O ₃	9.23	9.31
Fe ₂ O ₃	3.88	3.85
K ₂ O	1.96	1.81
Na ₂ O	1.94	1.59
SO ₃	1.52	2.04
MgO	1.50	1.58

3.1.3.1 Preparation of Hydrated Portland Cement Paste

Shi et al. (2016) reviewed some of the methods used to remove mortar from recycled concrete aggregates. Among these methods, the mechanical grinding of materials without heat treatment was adopted in this study to obtain HCP.

In order to obtain HCP, the recycled samples were crushed and ground in a laboratory ball mill for 10 minutes. The resulting powder was sieved through a 1 mm sieve to eliminate any large particles. However, it was expected to have a lot of fine aggregates in the so-called recycled portland cement paste.

3.1.3.2 Preparation of Dehydrated Portland Cement Paste

Dehydrated portland cement paste was obtained by heating the HCP powder. The temperature for dehydration of HCP was decided as 1200 °C since, by this temperature, HCP decomposes completely (Zhang and Ye, 2012). The furnace was

programmed to reach this temperature in 6 h. Figure 3.7 shows ground HCP before and after dehydration.



Figure 3.7. Recycled portland cement paste powder: a) before dehydration (HCP), b) after dehydration (DCP) (tray dimensions are 40 cm by 50 cm)

3.1.4 Portland Cement Paste and Oxalic Acid Blends

The reaction of magnesia and oxalic acid is rapid and highly exothermic. The short setting time due to fast reactions makes it impossible to work even with small mixtures. Lowering the dissolution rate of reactants can slow hydration reactions since concentrations of available ions of the reactants would be less compared to the regular reaction environment. The reaction, therefore, can be controlled as the primary reaction spreads over an extended duration. This is similar to the process of mixing salts, like potassium dihydrogen phosphate (KH_2PO_4), of phosphoric acid (H_3PO_4), rather than directly mixing it with magnesia, in preparing magnesium phosphate cements.

In this study, oxalic acid was blended with recycled portland cement to form an intermediate material (CPOx) that slowly releases oxalates during the final mixing with magnesium oxide. The material has a high solubility in water that allows releasing oxalate ions ($\text{C}_2\text{O}_4^{2-}$) to react with the magnesium oxide. It was produced by mixing oxalic acid with either HCP or DCP at various ratios in the presence of water in order to evaluate the influence of recycled cement paste type. The blends prepared with HCP and DCP are referred to as HCPOx and DCPOx, respectively. These blends were prepared as powders that can be added to the final mixture. That is to say, not all raw materials were added into the final mixture directly. The process followed, to produce magnesium oxalate cements with recycled portland cement paste, is summarized in Figure 3.8.

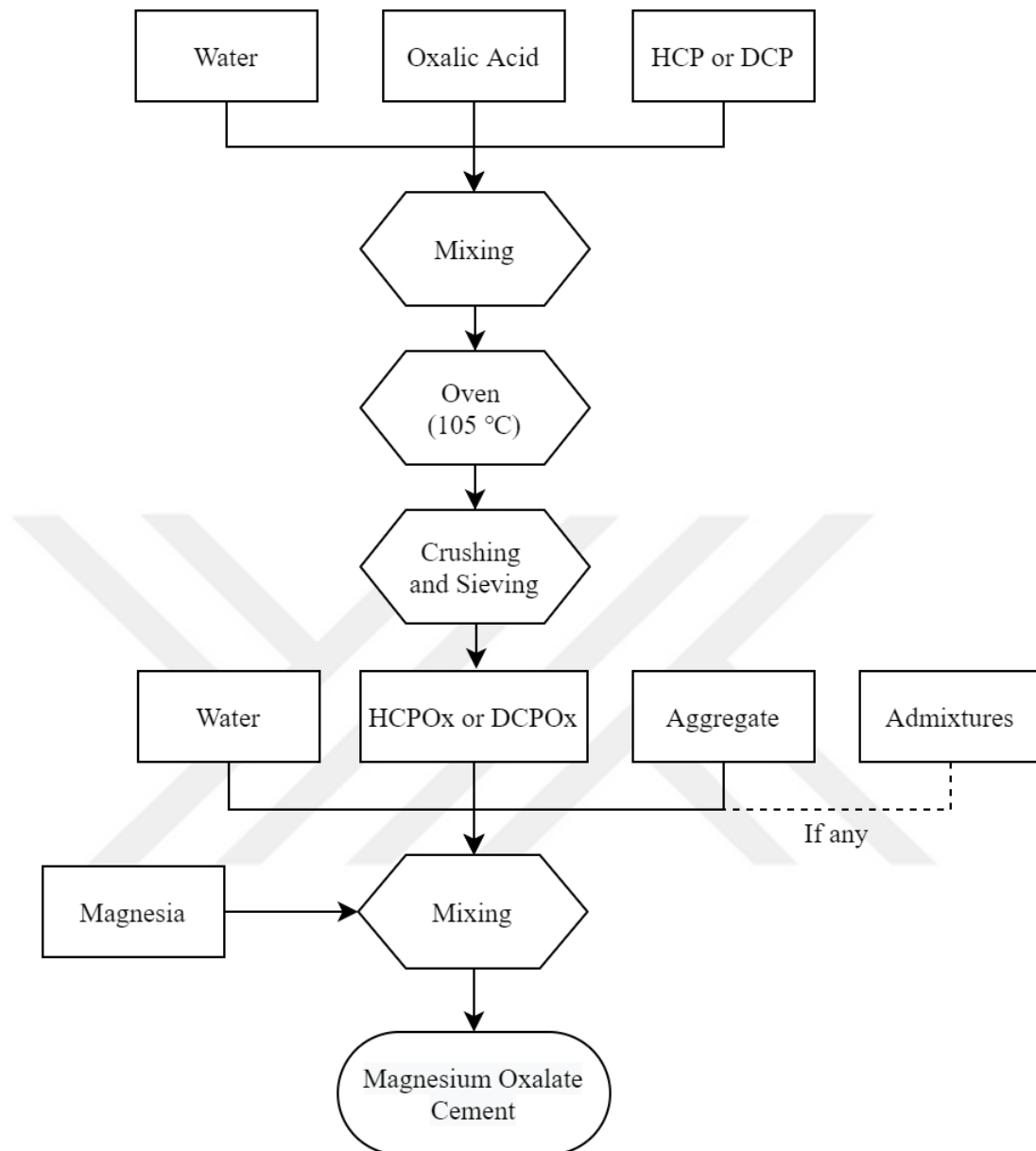


Figure 3.8. The production process of magnesium oxalate cements with recycled portland cement paste

The density of 1.0:1.0 HCPOx (obtained by mixing equal masses of HCP and Ox) was measured as 2.17 g/cm^3 , and for 1.0:1.0 DCPOx, it was measured as 2.15 g/cm^3 . The Blaine fineness of magnesia was measured as $\sim 3650 \text{ cm}^2/\text{g}$ for 1.0:1.0 HCPOx and $\sim 3500 \text{ cm}^2/\text{g}$ for 1.0:1.0 DCPOx. The particle size distribution of 1.0:1.0 HCPOx and 1.0:1.0 DCPOx, determined using low-angle light spectroscopy, are presented in Figures 3.9 and 3.10, respectively. According to this particle size distribution, the specific surface area of the 1.0:1.0 HCPOx is $\sim 10400 \text{ cm}^2/\text{g}$ and 1.0:1.0 DCPOx is $\sim 9390 \text{ cm}^2/\text{g}$, comparable to the fineness of magnesia powder calcined at 1500°C .

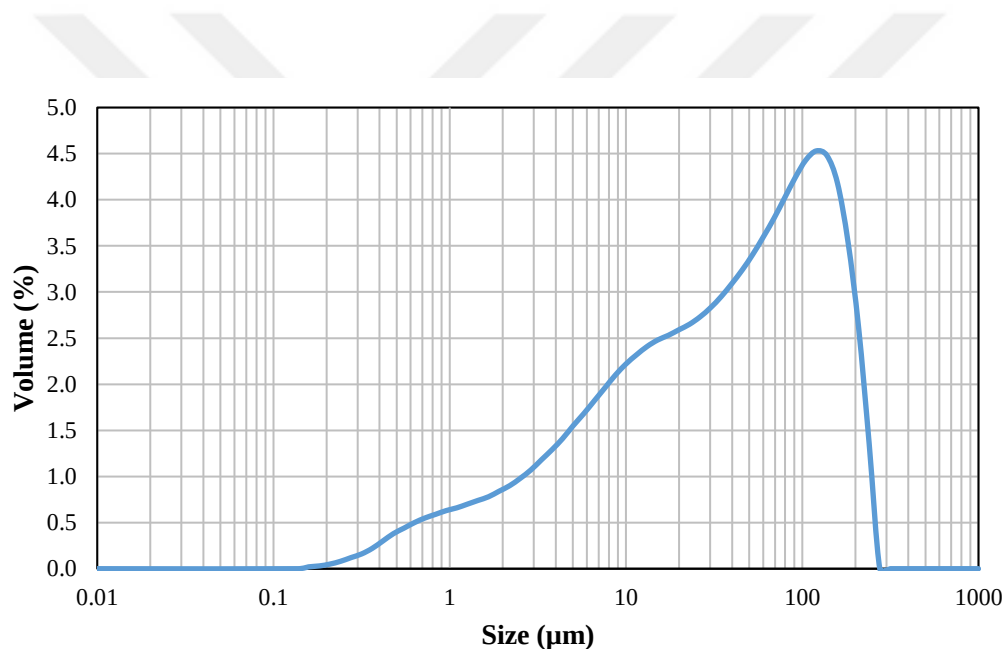


Figure 3.9. The particle size distribution of 1.0:1.0 HCPOx

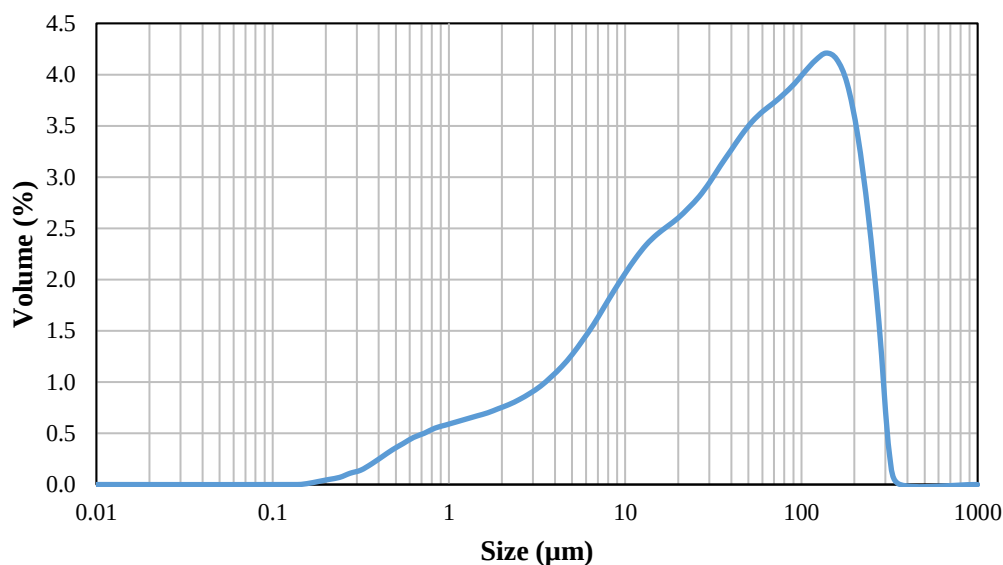


Figure 3.10. The particle size distribution of 1.0:1.0 DCPOx

XRD patterns of HCPOx and DCPOx are presented in Figure 3.11 and Figure 3.12, respectively, together with those of the HCP and DCP used to produce these blends. The portland cement paste and oxalic acid blends contain a significant amount of quartz originating from the recycled cement paste. This sand remained unchanged during the preparation of the blends. The peaks of oxalic acid dihydrate (the most prominent ones being at ~ 28.9 and ~ 25.8 $^{\circ}2\theta$) were not observed in the XRD of CPOx. On the other hand, peaks of anhydrous oxalic acid ($C_2H_2O_4$), which has a lower solubility compared to oxalic acid dihydrate ($C_2H_2O_4 \cdot 2H_2O$), could be observed in the blends. However, the dominant compound observed in the analysis was calcium oxalate monohydrate, whewellite, ($CaC_2O_4 \cdot H_2O$).

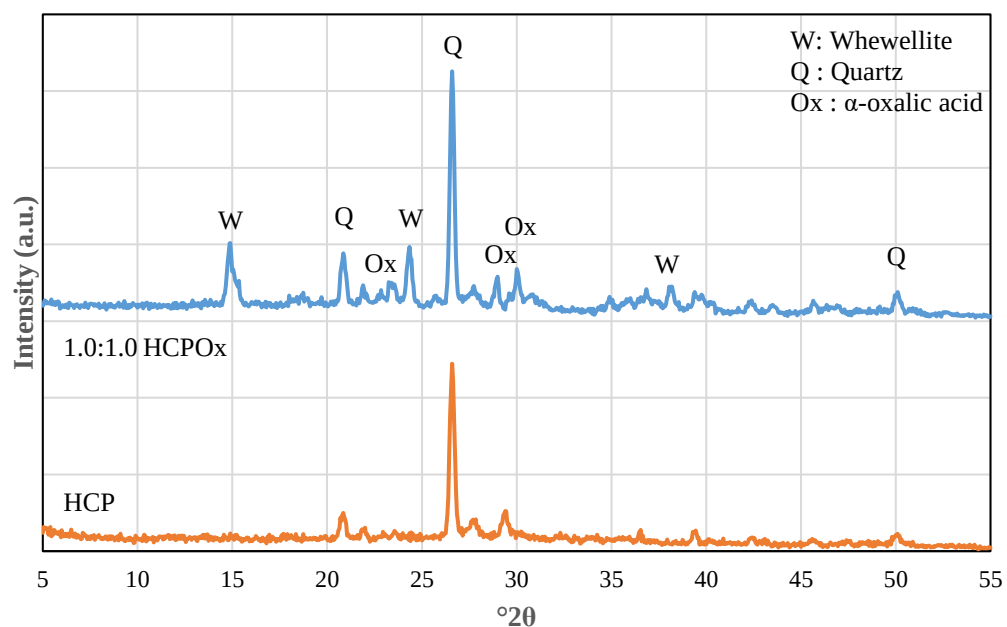


Figure 3.11. X-ray diffractograms of the 1.0:1.0 HCPOx and HCP

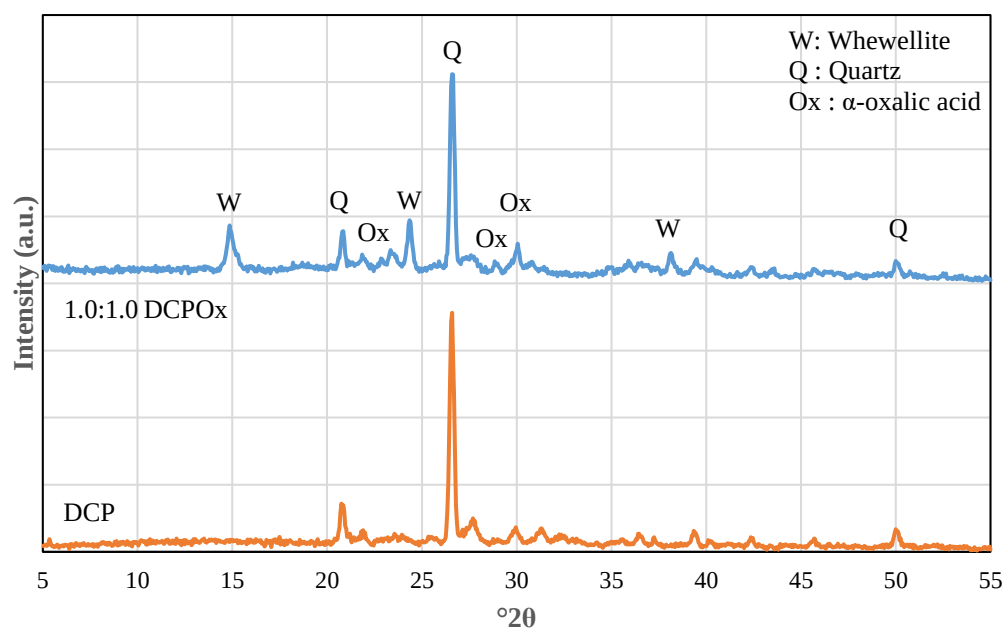


Figure 3.12. X-ray diffractograms of the 1.0:1.0 DCPOx and DCP

XRD patterns of CPOx prepared with different CP/Ox and different types of portland cement pastes (CP) do not show significant differences between each other in terms of mineralogy (Figure 3.13). Therefore, it can be concluded that similar reactions occur in each type of blend, which simply results in different amounts of reaction products.

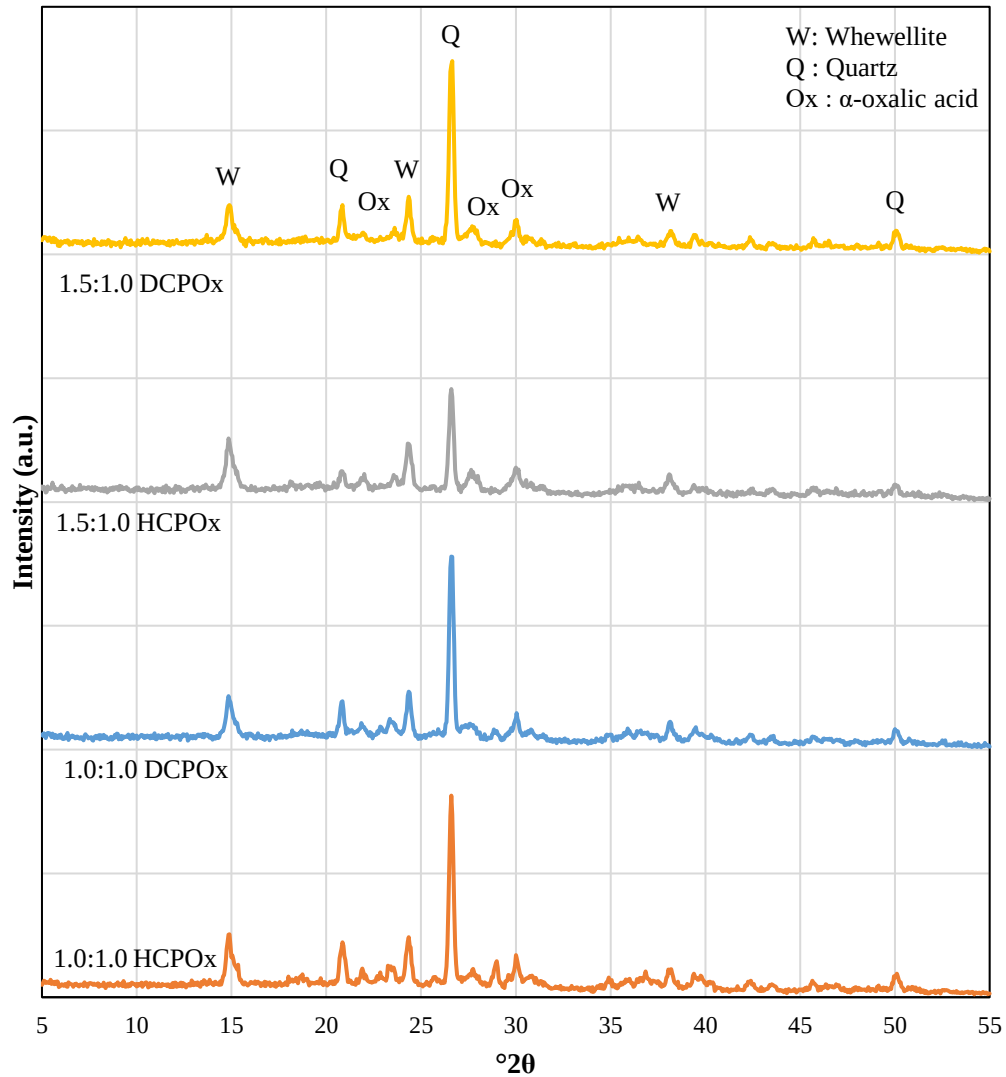


Figure 3.13. X-ray diffractograms of the various CPOx types

3.1.4.1 Preparation of CPOx

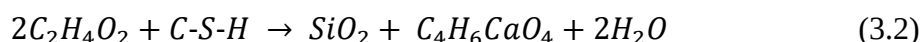
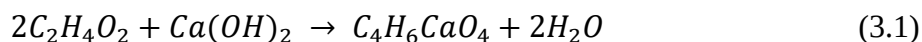
Preparation of CPOx starts with a mixture of the determined ratio of recycled portland cement paste and oxalic acid with the water. The water used in the mixtures is 50 wt. % of the solids. The mixture was observed to have an exothermic reaction that is more significant in the mixtures prepared with HCP, which releases more heat compared to DCP mixtures. Similar to heat release, more bubbling was observed in mixtures with HCP (Figure 3.14). This bubbling indicates a gas being released by a reaction, some kind of acid attack, between oxalic acid and the hydration product of portland cement paste since mixtures with DCP do not create as much bubbling as HCP mixtures.



Figure 3.14. Surface of the mixture of HCP, oxalic acid, and water

Oxalic acid attack on portland cement concrete has not been researched as much as other acid attacks. Nevertheless, attack by acetic acid might have some similarities with the reactions observed with oxalic acid. In portland cement concrete, acetic

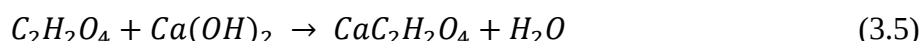
acid, $C_2H_4O_2$, reacts with calcium hydroxide, $Ca(OH)_2$, and calcium silicate hydrate (C-S-H) to form calcium acetate ($C_4H_6CaO_4$). The reactions can be exemplified as follows:



Similar reaction equations can be produced for oxalic acid to produce calcium acetate (Windt, Bertron, Larreur-Cayol, and Escadeillas, 2015); in these reactions by-product is oxygen gas (O_2) instead of water (H_2O):



Although these reactions may explain the bubbling in the mixtures with HCP, calcium acetate was not observed in XRD of HCPOx. This may indicate that calcium acetate was never produced by the proposed reactions (Eq. 3.3 and Eq. 3.4), or formed calcium acetate reacts even further to form other compounds. Calcium acetate is highly soluble in water (34.7 g/100 g [20 °C]); thus, further reactions are possible, such as the formation of calcium oxalate (Borchert, 1986). Also, calcium acetate can decompose into calcium carbonate ($CaCO_3$) and acetone (C_3H_6O). Calcium oxalate and calcium carbonate were observed in XRD analyses of the resulting powders. Acetone, on the other hand, would vaporize during the oven treatment process. The following reactions also might have occurred in mixtures with HCP, even though they do not explain the gas release:



The reactions proposed in Equations 3.3, 3.4, 3.5, and 3.6 might occur simultaneously. However, the resulting product contains a higher amount of calcium oxalate compared to calcium acetate (even if it exists in the final product) since calcium oxalate is more stable than calcium acetate.

The blend is mixed until the observed bubbling stops. Depending on the ratio of portland cement paste and oxalic acid, the blend may stiffen and show non-Newtonian viscoelastic properties, becoming shear-thinning, as the oxalic acid-to-portland cement ratio increases. After this point, the blend is placed in an oven at 120 °C and kept about 24 h (Figure 3.15).

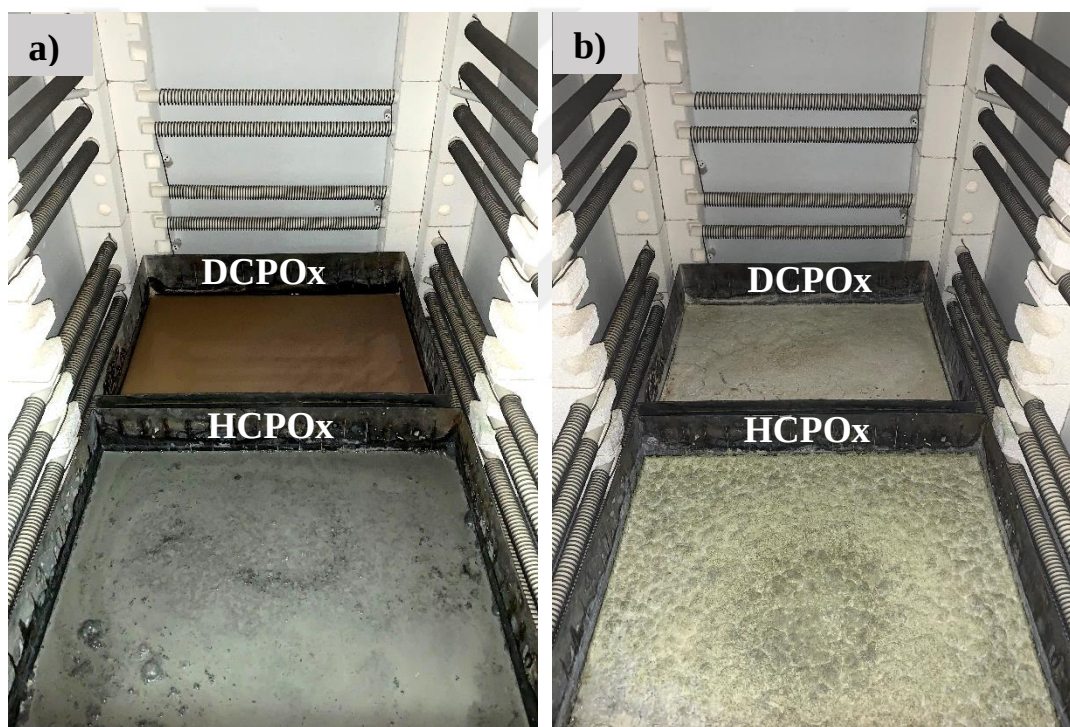


Figure 3.15. The oven-treatment process: a) DCPOx and HCPOx mixtures before the oven treatment, b) DCPOx and HCPOx after the oven treatment (tray dimensions are 40 cm by 50 cm)

The oven-dried mixtures are removed from the trays and briefly ground in a laboratory ball mill to finish the preparation of the powders. The dried mixtures

solidified but did not possess significant strength; however, as the oxalic acid ratio increased in the mixtures, the dried blends adhered more strongly to the metal trays. Blends with HCP generally created a more porous structure with larger pores after the oven treating process. In comparison, blends with DCP were mostly smooth on the surface and had smaller pores inside (Figure 3.16 and Figure 3.17).

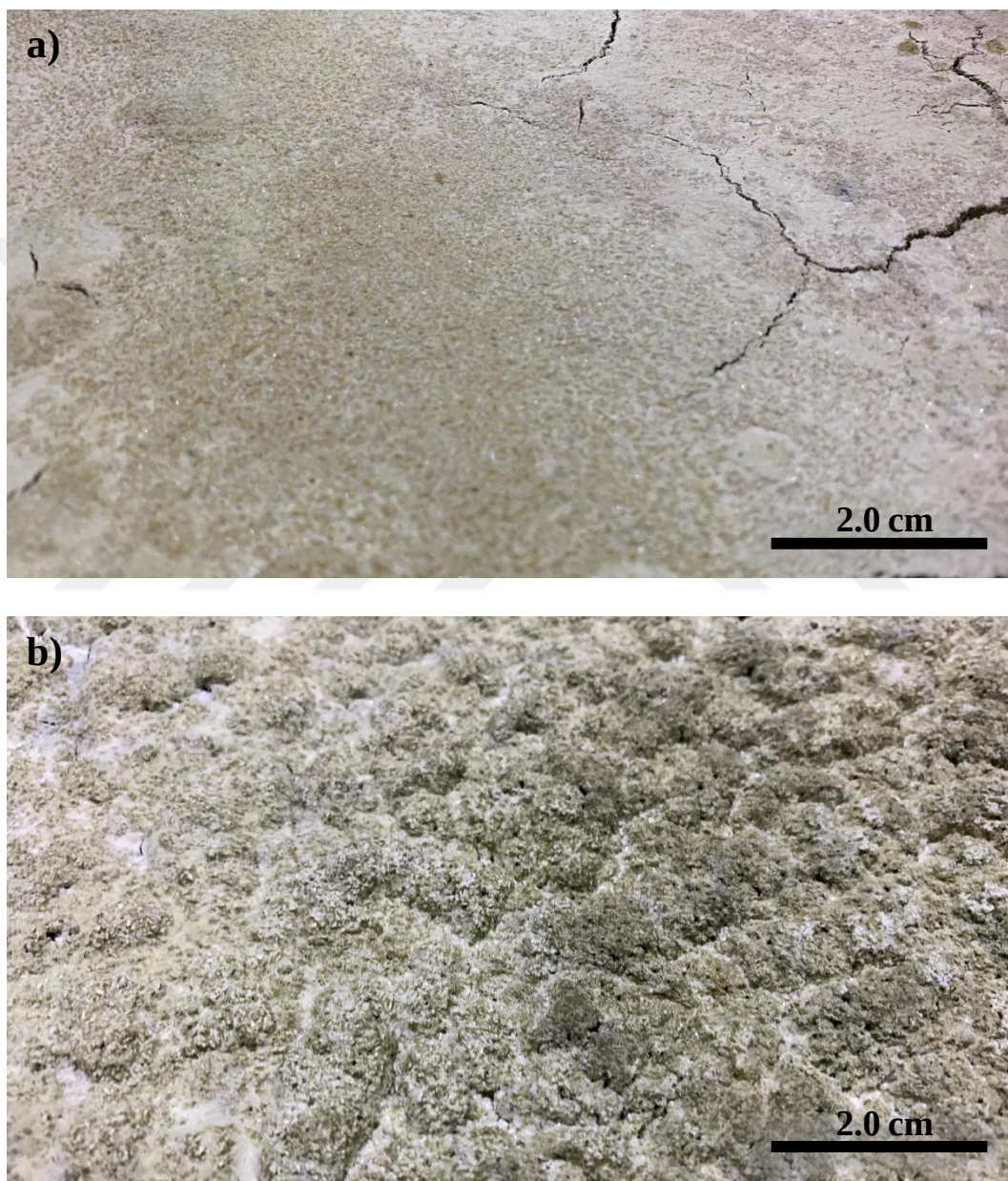


Figure 3.16. The surface of oven-treated: a) DCPOx, b) HCPOx



Figure 3.17. The inside of oven-treated: a) DCPOx, b) HCPOx

3.1.5 Boric Acid

Boric acid was utilized as a retarder in the studied cementitious system. Also, its influence on the compressive strength of magnesium oxalate cements was observed. Boric acid was obtained from Merck KGaA as a white colored powder. It is a kind of acid that shows physical similarities with oxalic acid. The molecular formula of boric acid can be expressed as H_3BO_3 , or BH_3O_3 , or $B(OH)_3$. The molecular mass of boric acid is 61.84 g/mol. Its density is 1.50 g/cm³, and water solubility at 20°C is 5.6 g/100ml (PubChem Database, 2020d). The x-ray diffractogram of boric acid is presented in Figure 3.18.

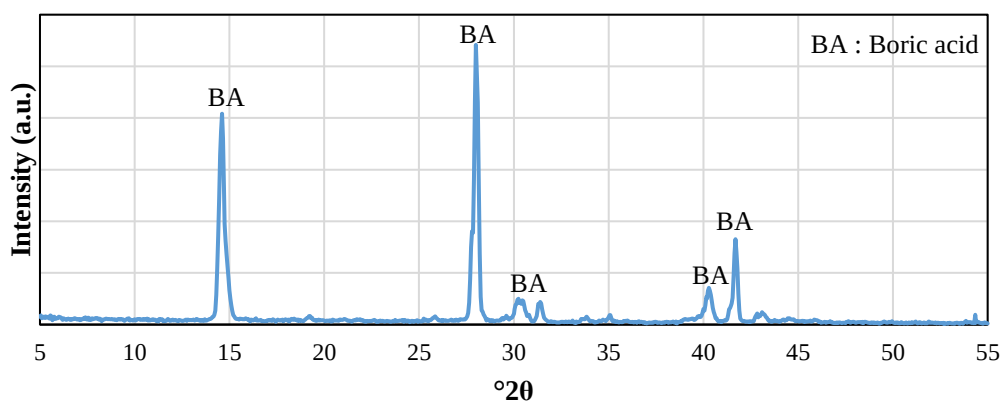


Figure 3.18. X-ray diffractogram of the boric acid

3.1.6 Citric Acid

Citric acid was also utilized as a retarder in some preliminary tests. It was obtained in monohydrate form from BDH Laboratory Supplies in Turkey, as a white colored powder. The molecular formula of citric acid monohydrate can be expressed as $C_6H_8O_7 \cdot H_2O$.

3.1.7 Silica Fume

Silica fume was experimented with as one of the pozzolans to be admixed to the final mixtures. It was expected to improve workability and increase the compressive strength of the system by creating a denser microstructure. The silica fume used was already available in the laboratory, grade 940 undensified micro silica from Elkem AS. The silica fume contains at least 90 wt. % of silicon dioxide (SiO_2), and its bulk density is between 200 to 350 kg/m^3 , according to the manufacturer. Loss on ignition is measured as 2.3 %. The particle size distribution of the silica fume is presented in Figure 3.19 (Shakouri, 2017). Its XRD analysis, provided in Figure 3.20, indicates an amorphous structure.

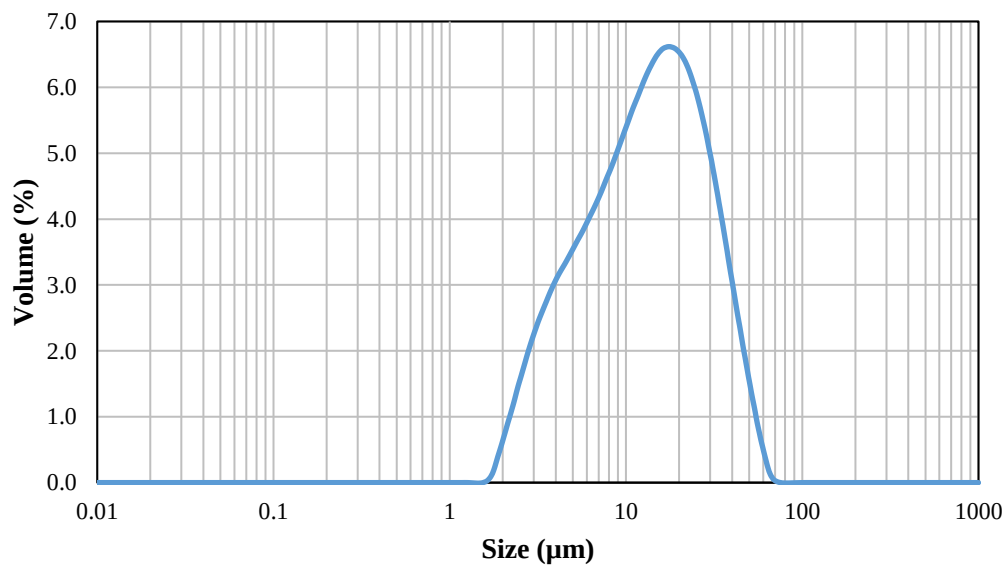


Figure 3.19. The particle size distribution of silica fume (Shakouri, 2017)

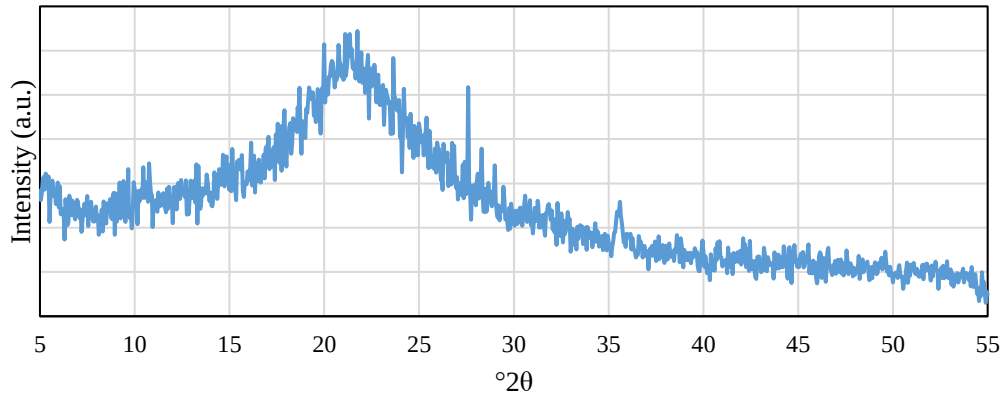


Figure 3.20. X-ray diffractogram of the silica fume

3.1.8 Fly Ash

Fly ash was used as another pozzolan to be admixed to the final mixture. It was obtained from Çatalağzı Coal Power Plant, previously classified as a class F fly ash (Tangüler, 2015). The density of the fly ash was measured as 2.00 g/cm³, and Blaine fineness as 2900 cm²/g. Data obtained from the x-ray diffraction analysis includes an identifiable peak around 26.6 °2θ of quartz (SiO₂) shared with mullite (3Al₂O₃•2SiO₂) with other smaller peaks of both phases, as presented in Figure 3.21.

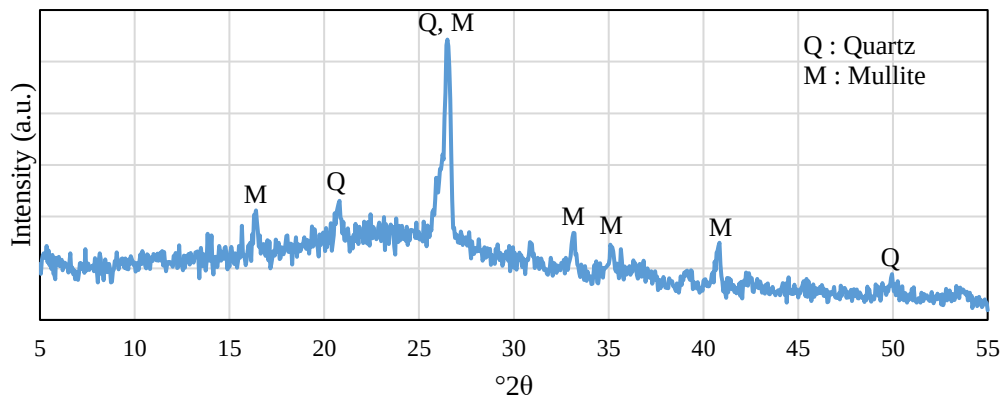


Figure 3.21. X-ray diffractogram of the fly ash

Oxide composition of the fly ash is given in Table 3.3. As can be seen from this data, silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) constitute most of the fly ash content. Calcium oxide (CaO) content is so low that it is not expected to have a substantial reaction between oxalic acid. Loss on ignition at 950 °C is measured as 3.3 %.

Table 3.3 Oxide composition of the fly ash used (Tangüler, 2015)

Oxides	Mass (%)
SiO_2	56.13
Al_2O_3	25.01
Fe_2O_3	5.89
CaO	1.70
MgO	2.18
SO_3	0.08
Na_2O	0.41
K_2O	3.88

3.1.9 Sand

CEN standard sand, in accordance with TS EN 196-1 (2016), was used in the mixtures as a filler material (aggregate). The grain sizes of standard sands are between 0.08 mm and 2.00 mm, and the related standard defines the particle size distribution. The average density of the standard sand was measured as 2.63 g/cm³. The x-ray diffractogram shows a significant peak of quartz at 26.7 °2 θ (Figure 3.22), indicating the sand is nearly pure quartz.

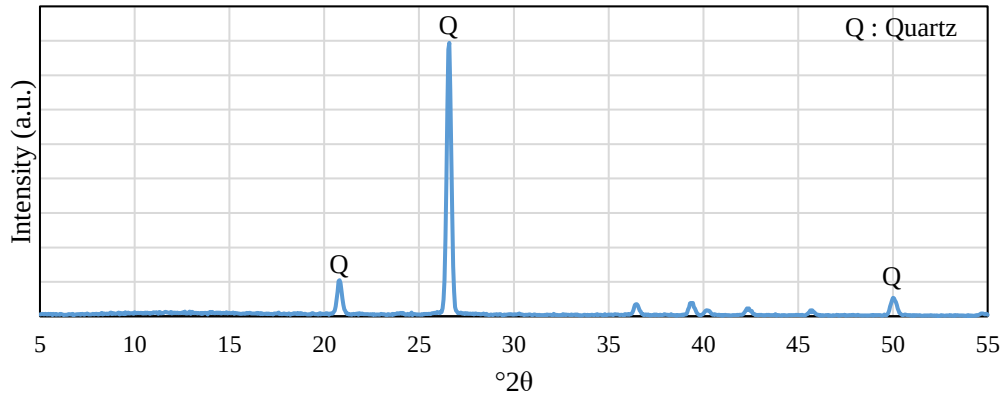
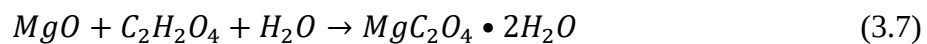


Figure 3.22. X-ray diffractogram of the standard sand

3.2 Experimental Procedures

Since there exist no published studies on magnesium oxalate cements (MOXC), the effects of raw materials and possible admixtures, hence a suitable mix design, are unknown. In order to evaluate the effects of ingredients, determination of a mix design to be used as a control case is necessary. Since there are three main ingredients (magnesium oxide, oxalic acid, and recycled portland cement paste) in the studied system, some assumptions were made to reduce variables, and preliminary tests were performed to determine a suitable mix design.

First of all, to observe the behavior of MOXC paste, the content of the binders was kept relatively high in the mortar samples. The aggregate-to-binder ratio was taken as 1.25 in the control mix. In order to eliminate another variable, the ratio of MgO-to-Ox was attempted to be fixed as an absolute value. It is assumed that magnesium oxide would react mainly with oxalate ions in the final mixture to form magnesium oxalate dihydrate ($MgC_2O_4 \cdot 2H_2O$). The expected reaction equation for the formation of magnesium oxalate hydrate is:



This acid-base reaction is not expected to be affected by the availability or molar ratios of reactants since there have not been reported any phases of magnesium oxalate salts either formed naturally or synthesized for different purposes with various reactants. Therefore, the resulting product is not expected to show variations, as is the case with magnesium oxychloride cements (MOC) and magnesium oxysulfate cements (MOSC). Hence the excess amount of reactants is expected to remain unreacted. Compressive strength tests were performed on mortar samples with varying magnesia-to-oxalic acid ratios to evaluate the effect of the ratio on strength. Additionally, XRD analyses were performed on pastes with varying magnesia-to-oxalic acid ratios to determine the presence of excess reactants and their amounts. After determining a fixed magnesia-to-oxalic acid ratio, some samples were prepared with varying recycled portland cement paste-to-oxalic acid ratios (CP/Ox) and tested for compressive strength. These samples are referred to as control samples. Some other samples were prepared using boric acid, citric acid, silica fume, fly ash, and reduced binder content (higher aggregate content) to evaluate their effects on strength. Also, some other analyses were performed to determine the properties of the raw materials and reaction products such as XRF, SEM, and TGA/DTA. Details of these analyses and samples used for the analyses are explained in the following sections.

3.2.1 Strength Development of MOXC Mortars

Compressive strength tests performed in the study are similar to the method specified in ASTM C109 (2020). The specimens were prepared by using a bench top lab mixer to blend the ingredients, then placing and compacting into the 50 mm cubic molds in two layers by tamping and by gently dropping the mold. Since the mixture sets rapidly, magnesium oxide was added to the mixture last, after reaching a homogeneous mixture with the other ingredients. Although several precautions were taken to reduce inconsistencies in sample preparation, human errors could still affect the results since fast setting and poor workability of some mixtures.

Due to the fast setting of the mixture, tests for standard consistency, flow, and setting time determination could not be performed. Also, the exact mixing procedure specified in ASTM C109 (2020) could not be followed. Minimum water content was determined by a preliminary test mixture to obtain adequate flow to place the mortar into the molds for each case. A special curing regime was not followed on the specimens; they were air-cured and stored in room conditions. Testing was performed according to ASTM C109 (2020).

Different mixtures were prepared and tested for compressive strength in order to evaluate the effects of ingredients on the strength of the magnesium oxalate cement system. There are several mixtures tested with a variety of ingredients and their ratios with each other. Table 3.4 presents an example of the mix proportions, which was also used in the control samples. The first three columns in the table define recycled cement paste (CP), oxalic acid (Ox), and magnesium oxide (MgO) content and their relative ratios. The values for CP and Ox are determined by the ratio of recycled cement paste and oxalic acid dihydrate used during the preparation of CPOx. The MgO content represents the ratio of magnesium oxide mass added in the final mixture to the mass of Ox, or CP used to prepare CPOx. The addition of CP, Ox, and MgO gives the total binder content in the mixture. The total binder content is used to calculate the ratios of other ingredients such as water, sand, retarders, and pozzolans.

Table 3.4 An example of mix proportions for MOXC-rCP

Sample	Binders			Sand/ Binder	Water/ Binder
	CP	Ox	MgO		
Mix #1	1.00	1.00	0.50	1.25	0.32
Mix #2	1.50	1.00	0.50	1.25	0.32

Hence, the mass ratio of CP-to-Ox used to prepare CPOx mix #1 is 1.0. For mix #2, this ratio is 1.5. The mass ratio of MgO-to-Ox is 0.5 in both mixtures. Concomitantly, the mass ratio of MgO-to-CP is 0.5 and 0.33 in mixtures #1 and #2, respectively. Total binder content is 2.5 ($= 1.0 + 1.0 + 0.5$) in mix #1 and 3.0 ($= 1.5 + 1.0 + 0.5$) in mix #2. Therefore, the sand content is 3.125 ($= 1.25 \times 2.5$) in mix #1 and 3.75 ($= 1.25 \times 3.0$) in mix #2.

The relative amounts of the solid ingredients are summed and divided by the total mass of the solids to be used in the mixture in order to find the required mass of each ingredient. The total mass of the solids used in the mixtures is taken as 250 g per 50 mm cube mold. According to this method, the total solid mass should be divided by 5.625 parts ($= 2.5 + 3.125$) for mix #1 and 6.75 parts ($= 3.0 + 3.75$) for mix #2. The required masses of each ingredient per 50 mm cubic mold is given in Table 3.5.

Table 3.5 Masses of each ingredient used to prepare a 50 mm cube sample according to mix proportions in Table 3.4

Sample	CP	Ox	MgO	Sand	Water
Mix #1	44.4 g	44.4 g	22.2 g	138.9 g	35.6 g
Mix #2	55.6 g	37.0 g	18.5 g	138.9 g	35.6 g

The name of each MOXC-rCP sample starts with a prefix that indicates the CP-to-Ox ratio. If the sample is prepared using HCPOx or DCPOx, then it is named MOXC-HCP or MOXC-DCP, respectively. In case of any variation in mix design, based on control samples, the sample name is followed by a suffix that specifies the change. The suffixes may refer to admixtures (such as BA for boric acid, FA for fly ash, and SF for silica fume) or compositional ratio changes (water-to-binder or sand-to-binder ratios). Apart from MOXC-rCP samples, some samples were prepared with no CP and MgO; these samples are named MOXC and HCPOx or DCPOx, respectively.

3.2.1.1 Contribution of Recycled Portland Cement Paste to MOXC-rCP Strength

In order to separately evaluate the contribution of the CP to the strength of MOXC-rCP, compressive strength tests for mortar specimens prepared with only recycled portland cement paste and water (no MgO) were planned. However, some preliminary tests on the specimens showed little to no cementitious properties and insignificant compressive strength.

On the other hand, compared to using only HCP or DCP as the binder, recycled portland cement paste and oxalic acid blends (CPOx) showed better cementitious properties and much higher strengths in preliminary tests. Therefore, instead of determining the compressive strength contribution of the recycled portland cement pastes, the compressive strength contribution of the CPOx was measured.

3.2.1.2 Contribution of CPOx to MOXC-rCP Strength

In order to evaluate the possible contribution of the hydration of recycled portland cement paste and oxalic acid blends (CPOx) to the whole system, a group of specimens was prepared using only CPOx and water (no MgO). For this case, only 1.0:1.0 CP/Ox was used. In order to keep the content of CPOx the same as in the control samples (Table 3.8), the content of sand was increased to balance the absence of MgO. Thus, there is an increase in s/b. The mixture was prepared with both HCP and DCP using as low water content as possible to have adequate flow. The mix proportions for the specimens are presented in Table 3.6.

Table 3.6 Mix proportions to evaluate the strength contribution of CPOx to MOXC-rCP

Sample	Binders			Sand/ Binder	Water/ Binder
	CP	Ox	MgO		
1.0:1.0 HCPOx	1.00	1.00	-	1.81	0.32
1.0:1.0 DCPOx	1.00	1.00	-	1.81	0.38

3.2.1.3 Effect of MgO/Ox on MOXC-rCP Strength

Many mix proportions can be used in the preparation of the samples. Reducing some of the possible variables in mix design is convenient for observing the effects of the rest of the raw materials. The MgO/Ox is one of the ratios that can be fixed since its effects are more predictable than the other variables, as explained in Section 3.2.

The reaction between magnesia and anhydrous oxalic acid can be formulated as presented in Equation 3.7. Thus, the theoretical optimum ratio for the complete reaction of reactants can be obtained. Considering that the molar mass of magnesium oxide is 40.304 g/mol, and oxalic acid is 90.034 g/mol, the mass ratio of magnesium oxide to anhydrous oxalic acid is 0.45 for full reaction.

The specimens were prepared using HCPOx with different CP/Ox and different MgO/Ox. They started with MgO/Ox = 0.5 and increasing MgO content to observe their compressive strength differences (Table 3.7). Increasing magnesium oxide content was selected since it was easier to observe excess magnesium oxide in the XRD analyses compared to oxalic acid. On the other hand, increasing oxalic acid content consequently increases the content of the recycled portland cement paste. Therefore, any additional contribution of CP to the strength might be misinterpreted as a result of the reaction between oxalic acid and magnesium oxide. Also, the effects of the addition of magnesium oxide could be observed during the preparation of samples, unlike increasing oxalic acid content. As the magnesium content was

increased, the setting time decreased and the rate of heat release increased significantly. The decrease in setting time made it impossible to produce samples with a MgO/Ox ratio higher than 1.5. The samples with 1.0:1.5 CP/Ox (samples 7, 8, and 9) could not be poured due to the rapid setting of the mixture. Therefore, citric acid, 2 wt. % of binders, was used as a retarder in these samples.

Table 3.7 Mix proportions to determine the optimum ratio of magnesium oxide to oxalic acid

Sample	Binders			Sand/ Binder	Water/ Binder
	CP	Ox	MgO		
1	1.50	1.00	1.50	1.25	0.33
2	1.50	1.00	1.00	1.25	0.33
3	1.50	1.00	0.50	1.25	0.33
4	1.00	1.00	1.50	1.25	0.33
5	1.00	1.00	1.00	1.25	0.33
6	1.00	1.00	0.50	1.25	0.33
7	1.00	1.50	2.25	1.25	0.33
8	1.00	1.50	1.50	1.25	0.33
9	1.00	1.50	0.75	1.25	0.33

3.2.1.4 Effect of CP/Ox and CP Type on MOXC-rCP Strength

In order to determine the performance and behavior of the MOXC-rCP, a group of samples was prepared and tested for compressive strength. The samples were prepared with both HCPOx and DCPOx with various CP/Ox. As the mix design of these samples was developed by some preliminary trials, they were expected to have relatively higher compressive strength and better volume stability compared to other mix design alternatives. For this reason, these samples are referred to as control mixtures. The mix proportions for the samples are provided in Table 3.8.

Table 3.8 Mix proportions to observe the effect of the recycled portland cement paste type (HCP and DCP) and CP/Ox

Sample	Binders			Sand/ Binder	Water/ Binder
	CP	Ox	MgO		
1.0:1.0 MOXC-HCP	1.00	1.00	0.50	1.25	0.32
1.5:1.0 MOXC-DCP	1.00	1.00	0.50	1.25	0.32
1.0:1.0 MOXC-HCP	1.50	1.00	0.50	1.25	0.32
1.5:1.0 MOXC-DCP	1.50	1.00	0.50	1.25	0.32

CP/Ox was used as 1.5:1.0 and 1.0:1.0 for these tests, since higher ratios would result in very low compressive strength and lower ratios could not be poured due to rapid setting. During the preparation of the samples presented in Table 3.8, it was observed that the samples with DCP require more water to have adequate flow to place into the molds easily. Some air pockets were observed in these samples as a result of poor compaction, which is mainly due to the inadequate flow. Consequently, a new set of samples was prepared with higher water content and a similar flow to the samples with HCP (Table 3.9). These samples were also useful to observe the effects of water content on compressive strength.

Table 3.9 Mix proportions to observe the effect of the water content

Sample	Binders			Sand/ Binder	Water/ Binder
	CP	Ox	MgO		
1.0:1.0 MOXC-DCP (w/b = 0.38)	1.00	1.00	0.50	1.25	0.36
1.5:1.0 MOXC-DCP (w/b = 0.36)	1.50	1.00	0.50	1.25	0.38

3.2.1.5 Effect of S/B on MOXC-rCP Strength

The control samples contain a relatively high binder content in order to better show the behavior of paste. However, standards for compressive strength determination of cementitious construction materials generally specify a higher aggregate content in mortar testing than the s/b used in the control samples. One such standard for portland cement mortars, ASTM C109 (2020), specifies the sand-to-cement ratio as 2.75 by mass. Therefore, a group of samples with a higher s/b than the control mixture was prepared. The volume of the binders is still more than the volume of portland cement in the PC mortar mixtures, as the density of magnesia and anhydrous oxalic acid blend is about 2.4 g/cm³ (with 0.5 of MgO/Ox), lower than that of portland cement, 3.15 g/cm³. These mixtures with reduced binder content were prepared using as low water content as possible for adequate flow (Table 3.10).

Table 3.10 Mix proportions to observe the effect of the reduced binder content

Sample	Binders			Sand/ Binder	Water/ Binder
	CP	Ox	MgO		
1.0:1.0 MOXC-HCP (s/b = 2.75)	1.00	1.00	0.50	2.75	0.34
1.0:1.0 MOXC-DCP (s/b = 2.75)	1.00	1.00	0.50	2.75	0.34
1.5:1.0 MOXC-HCP (s/b = 2.75)	1.50	1.00	0.50	2.75	0.38
1.5:1.0 MOXC-DCP (s/b = 2.75)	1.50	1.00	0.50	2.75	0.38

Although the total water content of the samples presented in Table 3.10 is lower than in the control mixture, their w/b is higher due to lower binder content in the mixture. The mixture with w/b = 0.38 has 25.3 g of water per 250 g of total solid material mass. The control sample has 35.6 g of water per 250 g of solid materials (calculated in Section 3.2.1).

The reduced binder content can cause a reduction in the rate of the reaction between magnesium oxide and oxalic acid. Therefore, some direct mixtures of Ox and MgO were attempted. Two cases were prepared with different water contents for the absence of the recycled portland cement and by directly mixing the oxalic acid into the mixture (Table 3.11). Similar to the situation with the mixtures presented in Table 3.10, in these samples, the total water content is lower than the control mixtures. Even the sample with higher water content has the water content 32.6 g per 250 g of solid material, compared to 35.6 g of water per 250 g of solids in the control mixture.

Table 3.11 Mix proportions to observe the effects of a direct mixture of magnesia and oxalic acid in reduced amounts

Sample	Binders			Sand/ Binder	Water/ Binder
	CP	Ox	MgO		
MOXC (w/b = 0.49)	-	1.00	0.50	2.75	0.49
MOXC (w/b = 0.39)	-	1.00	0.50	2.75	0.39

3.2.1.6 Effect of Retarders on the Strength Development of MOXC-rCP

Magnesium oxalate cement sets swiftly. The setting time decreases as CP/Ox is increased. However, as CP/Ox decreases, total oxalic acid and magnesia content decreases in the mixtures. Consequently, the system starts to become a recycled portland cement system with magnesia and oxalic acid addition. On the other hand, mixtures with low CP/Ox become uncontrollable due to fast reactions as if it was a direct mix of oxalic acid with magnesia. The preparation of mixtures with CP/Ox lower than 1.0 could not be completed due to the rapid setting. Even preparing mixtures with CP/Ox = 1.0 is challenging due to the short setting times.

In order to prepare mixtures with lower CP/Ox than 1.0, some additional measures should be taken to increase setting time and decrease the rate of reactions, such as

adding a retarding agent. Boron-based and citrate-based compounds were researched as retarding agents in magnesia-based cements. Boric acid was used as a retarder during the rest of the experiments since they are more commonly used in magnesia cements as they do not form a permanent structure with magnesium oxide. Also, it is not expected from boric acid to react with other ingredients.

Boric acid addition of 5 % by mass of the binders was selected according to some preliminary tests. This boric acid content was found to be the minimum admixing amount to prepare the mixtures with CP/Ox = 1.0:1.5 properly. Bilginer (2018) concluded that 5 % borax admixture doubles the setting time of the control mixture on MPPC while having a smaller impact on the early age compressive strength compared to higher retarder contents, even increases the later age compressive strength compared to the control mixture. Also, he found that while more borax addition increases the setting time, compressive strength decreases at the later curing times. On the other hand, Hall et al. (2001) observed that it requires half the mass of boric acid to show the same rate of effects with borax content. Therefore, 5 % of boric acid addition is expected to have the same level of effects of 10 % borax addition. Besides, MgO content in the binders is between 17 % to 23 % at the mixtures experimented with. Therefore, it is expected to observe a strength loss in the mixtures compared to control samples. So, to compare the effect of CP/Ox on the strength, samples with higher CP/Ox = 1.0:1.5 were also prepared and tested. Data gathered from these samples can be used to evaluate the effect of boric acid, by comparing with control samples, and the effect of CP/Ox on the strength to MOXC-rCP. Mix proportions with boric addition of 5 wt. % of binders are presented in Table 3.12.

Table 3.12 Mix proportions to observe the effects of low CP/Ox and boric acid (5 wt. % of binders) as a retarder

Sample	Binder			Sand/ Binder	Water/ Binder
	CP	Ox	MgO		
1.5:1.0 MOXC-HCP+BA	1.50	1.00	0.50	1.25	0.32
1.5:1.0 MOXC-DCP+BA	1.50	1.00	0.50	1.25	0.32
1.0:1.0 MOXC-HCP+BA	1.00	1.00	0.50	1.25	0.32
1.0:1.0 MOXC-DCP+BA	1.00	1.00	0.50	1.25	0.32
1.0:1.5 MOXC-HCP+BA	1.00	1.50	0.75	1.25	0.32
1.0:1.5 MOXC-DCP+BA	1.00	1.50	0.75	1.25	0.32

3.2.1.7 Effect of Pozzolans on MOXC-rCP Strength

The effects of some pozzolans on strength development were investigated for MOXC-rCP. The pozzolans used for these experiments were silica fume and a class F fly ash. They were used by replacing part of the sand in the mixture with 5 % for silica fume or 15 % fly ash by mass of the total binder (Table 3.13).

Table 3.13 Mix proportions to observe the effects of the pozzolanic admixture

Sample	Binders			Sand Binder	Pozzolan Binder	Water Binder
	CP	Ox	MgO			
1.0:1.0 MOXC-HCP + 15 % FA	1.00	1.00	0.50	1.10	0.15	0.41
1.0:1.0 MOXC-DCP + 15 % FA	1.00	1.00	0.50	1.10	0.15	0.41
1.0:1.0 MOXC-HCP + 5 % SF	1.00	1.00	0.50	1.20	0.05	0.41
1.0:1.0 MOXC-DCP + 5 % SF	1.00	1.00	0.50	1.20	0.05	0.41

3.2.2 X-Ray Diffraction Analyses (XRD)

In order to identify the crystalline phases, x-ray diffraction analyses were performed. The raw materials and various MOXC-rCP pastes were analyzed. Magnesium oxalate cement pastes were prepared to identify hydration products in an attempt to validate proposed reactions. Additionally, MOXC-rCP pastes with higher $\text{MgO/Ox} = 0.5$ were prepared to observe any unreacted MgO and effects of molar ratios of reactants on microstructure. The analyses were performed at the same age as the compressive test samples at the Material of Construction Laboratory in METU using an Olympus BTX-II XRD analyzer. The device has a measurable range between 5 to 55 $^{\circ}2\theta$ and uses Cu-K α wavelength. The samples need to be in powder form and pass through a 100-mesh sieve ($<150\text{ }\mu\text{m}$) to be analyzed. Thus, the paste samples were crushed and sieved immediately prior to analysis.

Acquired data were then compared with various databases for peak fitting with the help of various software, and quantitative analysis was performed when it could be beneficial to interpret the data. Apart from manually finding the peaks and fitting the possible phases, Match! software (from Crystal Impact GbR) was used. This software is also capable of performing quantitative analysis and calculate an agreement index according to the Rietveld refinement method (Rietveld, 1969). The peak patterns for phases were obtained from the Crystallography Open Database (COD) and the American Mineralogist Crystal Structure Database (AMCSD) (Downs and Hall-Wallace, 2003). The phases observed and their most prominent peaks, within the 5 to 55 $^{\circ}2\theta$ range, are provided in Table 3.14.

Table 3.14 Crystalline phases observed in XRD analyses and their AMCSD codes with associated peaks (Downs and Hall-Wallace, 2003)

Phase Name and AMCSD Code		Peaks and Intensity - °2θ (intensity %)
Alite (Ca ₃ SiO ₅)	0017753	29.4 (38 %), 32.2 (100 %), 32.5 (52 %), 34.4 (48 %), 51.8 (36 %)
Brownmillerite (Ca ₂ [Al,Fe] ₂ O ₅)	0003433	12.0 (22 %), 25.2 (12 %), 33.7 (100 %), 43.9 (20 %), 46.9 (41 %), 49.9 (18 %)
Brucite (Mg[OH] ₂)	0001637	18.8 (77 %), 38.3 (100 %), 51.3 (35 %)
Calcite (CaCO ₃)	0000098	29.4 (100 %), 36.0 (14 %), 39.4 (20 %), 43.2 (14 %), 47.5 (20 %), 48.5 (20 %)
Corundum (Al ₂ O ₃)	0009325	25.6 (62 %), 35.2 (97 %), 37.8 (45 %), 43.4 (100 %), 52.6 (50 %)
Forsterite (Mg ₂ SiO ₄)	0000885	17.3 (24 %), 22.9 (32 %), 32.3 (66 %), 36.5 (100 %), 39.7 (18 %), 52.2 (73 %)
Glushinskite (MgC ₂ O ₄ •2H ₂ O)	-	18.1 (100 %), 27.9 (50 %), 35.0 (8 %), 38.0 (20 %), 44.9 (24 %), 49.3 (25 %)
Gypsum (CaSO ₄ •2H ₂ O)	0004651	11.7 (78 %), 20.8 (100 %), 29.2 (72 %), 31.2 (48 %), 33.4 (36 %)
Boric acid (H ₃ BO ₃)	0018654	14.5 (63 %), 28.0 (100 %), 30.8 (25 %), 34.9 (17 %), 40.2 (15 %), 43.6 (11 %)
Larnite (Belite) (Ca ₂ SiO ₄)	0012179	32.6 (100 %), 34.2 (76 %), 41.2 (50 %), 45.8 (26 %)
Lime (CaO)	0008276	32.2 (38 %), 37.4 (100 %), 53.9 (53 %)
Magnesianoferrite (MgFe ₂ O ₄)	0001484	30.2 (37 %), 35.5 (100 %), 43.2 (18 %), 53.6 (13 %)
Magnesite (MgCO ₃)	0000099	32.7 (100 %), 35.9 (13 %), 43.0 (49 %), 46.7 (23 %), 53.9 (22 %)
Magnetite (Fe ₂ O ₃)	0000945	30.1 (28 %), 35.5 (100 %), 43.1 (20 %)

Table 3.14 Continued

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)	0001059	16.4 (75 %), 26.2 (100 %), 33.2 (47 %), 35.3 (52 %), 40.9 (63 %)
Oxalic acid dihydrate ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)	-	15.0 (20 %), 18.7 (40 %), 25.9 (20 %), 29.1 (100 %), 37.5 (28 %), 39.7 (27 %)
α -oxalic acid (anhydrous) ($\text{C}_2\text{H}_2\text{O}_4$)	-	22.8 (100 %), 27.2 (50 %), 30.9 (95 %), 37.3 (58%), 40.4 (44 %)
β -oxalic acid (anhydrous) ($\text{C}_2\text{H}_2\text{O}_4$)	-	23.2 (100 %), 29.3 (28 %), 34.6 (80 %), 37.3 (48 %)
Periclase (MgO)	0000501	37.0 (11 %), 43.0 (100 %)
Portlandite ($\text{Ca}[\text{OH}]_2$)	0000116	18.2 (64 %), 28.8 (17 %), 34.4 (100 %), 47.5 (24 %), 51.0 (28 %), 54.6 (15 %)
Spinel (MgAl_2O_4)	0001398	19.0 (28 %), 31.3 (34 %), 36.9 (100 %), 44.9 (55 %)
Quartz (SiO_2)	0000789	20.9 (20 %), 26.7 (100 %), 50.2 (13 %)
Sulfur trioxide (SO_3)	0009159	15.2 (93 %), 20.3 (100 %), 26.7 (64 %), 30.5 (75 %), 37.0 (22 %), 37.9 (37 %)
Tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$)	0017746	33.2 (100 %), 41.0 (24 %), 47.7 (46 %)
Whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$)	0000776	14.9 (100 %), 15.3 (30 %), 24.4 (53 %), 36.0 (30 %), 38.2 (31 %), 45.9 (14 %)

3.2.3 X-Ray Fluorescence Analyses (XRF)

In order to determine the composition of the raw materials, x-ray fluorescence analyses were performed at METU Central Laboratory using a Rigaku ZSX Primus II. Samples were provided to METU Central Laboratory in powder form, sieved

through 100 mesh sieve. They were tested over the boron-to-uranium elemental spectrum.

3.2.4 Scanning Electron Microscopy (SEM) Investigations

Scanning electron microscopy was performed at METU Central Laboratory using QUANTA 400F Field Emission SEM. The device has a resolution of 1.2 nm and capable of doing both SEM and EDX analyses. SEM was used to examine the microstructure of the paste visually and to determine the sizes of the particles. EDX was utilized to identify the composition of chosen regions within the sample. Four different samples investigated all prepared by HCP and DCP with CP/Ox is 1.0:1.0 and 1.5:1.0. The samples were air-cured for 4 months at room conditions.

3.2.5 Thermogravimetric / Differential Thermal Analyses (TGA/DTA)

Thermogravimetric / differential thermal analyses (TGA/DTA) were performed to observe the thermal decomposition of the hydrated products and investigate hydration reactions. The analyses were performed at METU Central Laboratory using TA Instruments Discovery SDT 650. The device can perform the analyses from ambient temperature to 1200 °C. The same samples investigated with SEM were analyzed in these analyses.

3.2.6 Laser Diffraction Analyses

Laser diffraction analyses were performed to determine the grain size of the raw materials. The tests were performed at METU Central Laboratory using Malvern Mastersizer 2000 with Scirocco 2000 dry powder feeder. The dry dispersion method was used to measure grain size from light reflection.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents results obtained from the tests performed and observations made during these tests. The tests are mainly focused on finding an optimum mix ratio and potential additives for a magnesium oxalate cement made using recycled portland cement paste with acceptable workability and high compressive strength. The effects of raw materials and their ratios are investigated in order to understand their contribution to workability, stability, and strength of the system.

4.2 Observations on Preparation and Structure of the MOXC-rCP

4.2.1 General Observations on the MOXC-rCP

Among different types of magnesia cement-based systems, magnesium phosphate cements (MPC) are the most similar to magnesium oxalate cements (MOXC) as they both rely on acid-base reactions. MPC are known for having problems related to their rapid reactions (Walling and Provis, 2016). Similar to MPC, MOXC suffers from the fast pace of reactions. The direct mixture of magnesia and oxalic acid reacts and hardens within seconds; this fast reaction creates practical problems in the mixtures even when they are prepared in small batches. The usage of portland cement paste and oxalic acid blends (CPOx) in the final mixture prolongs the setting time. CP/Ox affects the setting time by neutralizing the oxalic acid.

Usage of CPOx was not enough to eliminate the problems with quick setting time for all mix proportions. The extended setting times were not enough for most

experimented mix designs, as even some of the high oxalic acid containing mixtures started to set during mixing. For example, mixtures with CP/Ox of 1.0:1.5 or lower ratios could not be prepared properly for most of the samples and were excluded from the experiment plan. Similarly, due to the very rapid setting of the mixtures, it was not possible to perform setting time and flow tests. Also, during the preparation of the mixtures, the standard mixing procedure used for portland cements could not be used. These measures, however, were not able to prevent all problems related to workability. The samples with limited flow due to the particle size distribution, mix design, or low water content; were observed, during strength testing, not to have mixed properly. An example of such a sample is provided in Figure 4.1 (poorly mixed parts marked with arrows). Light-colored parts indicate the absence of magnesia due to poor mixing caused by inadequate flow. These parts are non-cementitious and behave as joints under loading.



Figure 4.1. A poorly mixed sample after compressive strength test

The prepared specimens could be removed from the molds for strength testing after 4 hours at room conditions. Compared to ordinary portland cement paste (OPC), they adhere more strongly to the mold, and sometimes it was observed that a part of the sample might stick to the mold.

It is expected to have a porous structure in the paste due to the formation of water during acid-base neutralization reactions. While the top surfaces of the samples were observed to be smooth, other surfaces that were in contact with the mold were porous (Figure 4.2). Also, the insides of the samples were observed to contain smaller pores up to 1 mm.



Figure 4.2. The surface of a MOXC-HCP specimen (50 mm cube)

The color of the samples is mostly affected by the type of recycled PC and magnesia. In general, samples with HCP can be considered beige, and samples with DCP are brown.

4.2.2 Hydration and Microstructure of the MOXC-rCP

XRD patterns for pastes with various CP/Ox at 28 d are presented in Figures 4.3 and 4.4. According to XRD, the reaction product of magnesia and oxalic acid is found to be magnesium oxalate dihydrate (glushinskite, $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). The peak intensities of glushinskite are observed to increase as CP/Ox decreases (thus Ox and MgO content in the mixture increases). Also, calcium oxalate hydrate (whewellite, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) is another identifiable product of oxalate in the MOXC-rCP paste. While some amount of whewellite can be observed in the CPOx, more whewellite seems to be formed with the presence of magnesia, which makes the solution more alkaline. Other products observed in MOXC paste were magnesioferrite (MgFe_2O_4) and spinel (MgAl_2O_4).

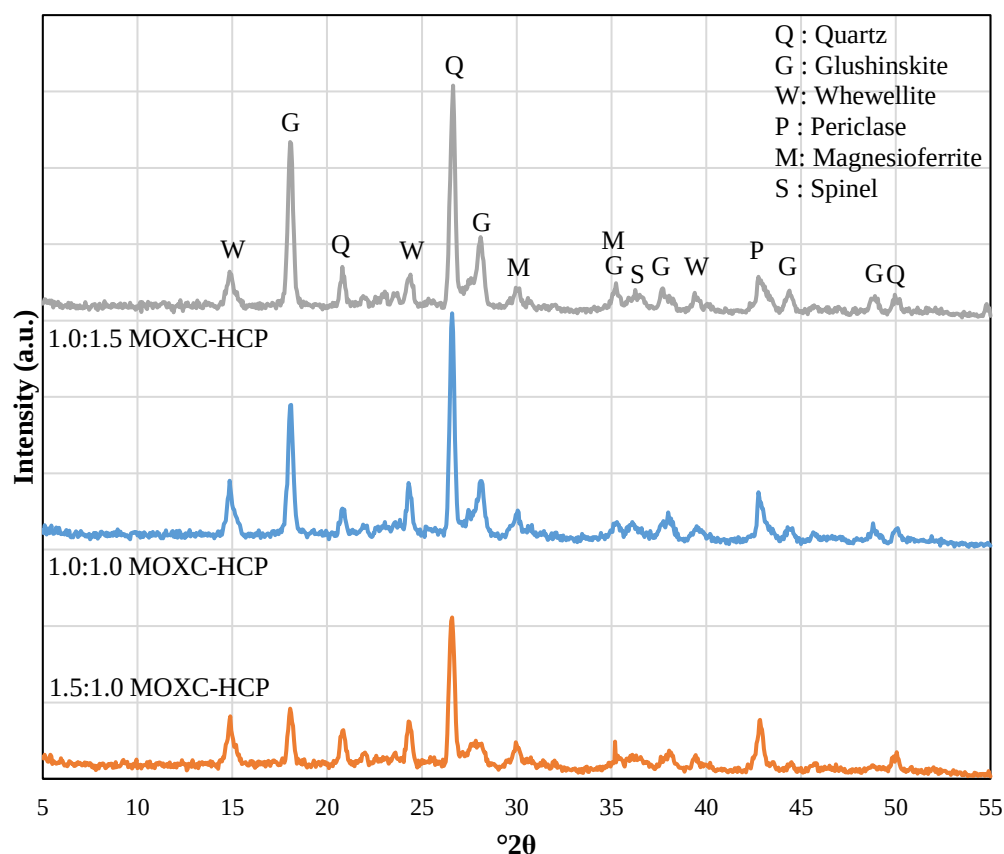


Figure 4.3. X-ray diffractograms of MOXC-HCP with various CP/Ox

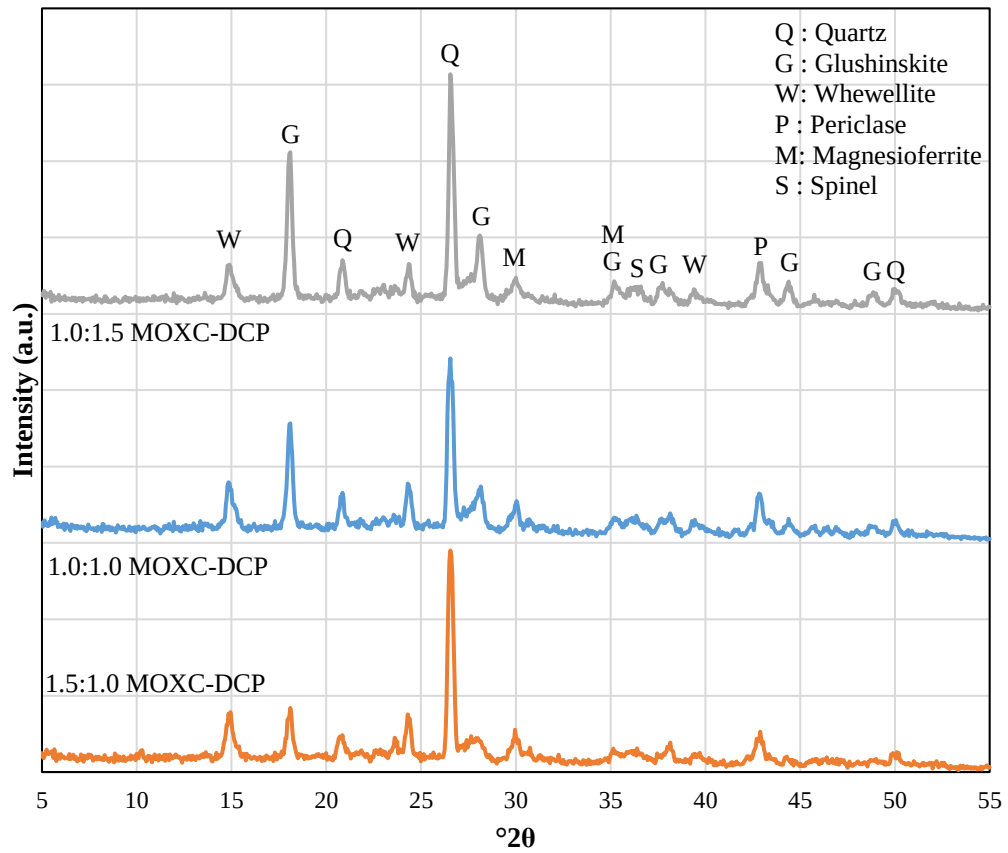


Figure 4.4. X-ray diffractograms of MOXC-DCP with various CP/Ox

The XRD patterns of the pastes prepared with different CP does not show a significant difference in their crystalline phases (Figure 4.5). Therefore, it can be concluded that the effects of the type of recycled portland cement paste on the system are mainly physical.

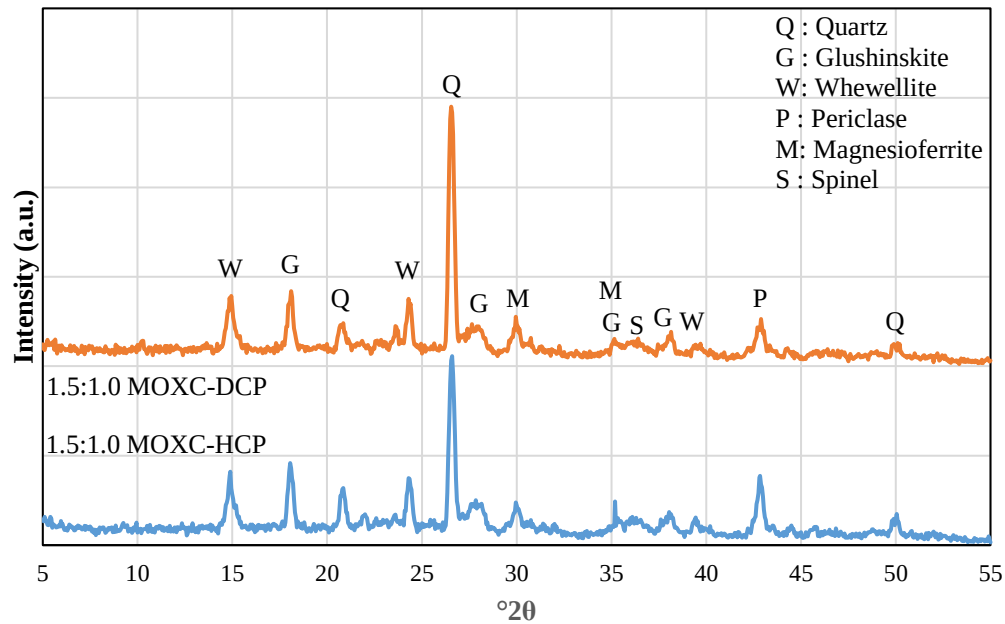


Figure 4.5. X-ray diffractograms of MOXC-rCP paste prepared with HCP and DCP

4.3 Strength Development of the HCPOx and DCPOx

The purpose of using CPOx in this system is to lower the reaction rate between magnesia and oxalic acid by slowing the dissolution of oxalate ions. The preparation and microstructure of these blends were discussed in Section 3.1.4. In summary, the blends contain oven-dried grains of rehydrated HCP and DCP, dehydrated oxalic acid, and newly formed calcium oxalate hydrates. While rehydration of only HCP or DCP results in a low strength paste (Section 3.2.1.1), hydration of the HCPOx or DCPOx forms a more robust cementitious system. Therefore, the strength development of these systems was observed and compared with the mixtures with magnesia addition.

Figure 4.6 presents the strength development of HCPOx and DCPOx mixtures, together with MOXC-HCP and MOXC-DCP. Compared to the MOXC-rCP, samples prepared only using CPOx showed lower strength. Also, MOXC-rCP gains strength at a higher rate than the mixtures prepared only using HCPOx or DCPOx.

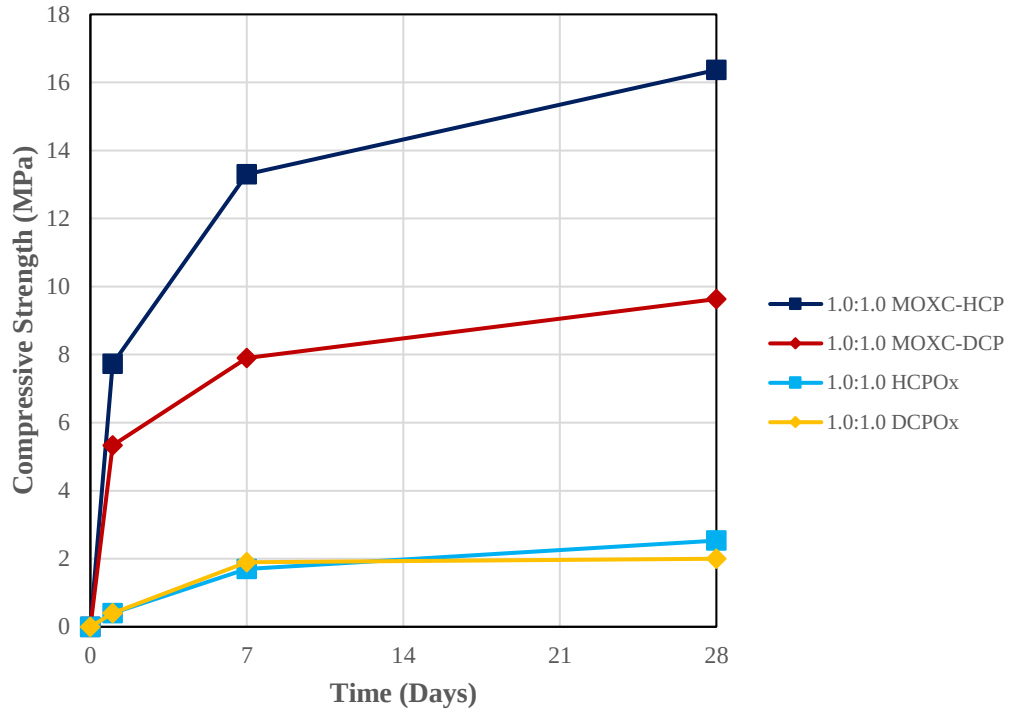


Figure 4.6. Compressive strength development of samples prepared using only HCPOx or DCPOx, and samples of MOXC-rCP

4.4 Strength Development of MOXC-rCP

As explained in Section 3.2, some mixtures were selected as the control mixtures. The compressive strength development of the mixtures shows that the samples with DCP have lower strengths than the samples with HCP (Figure 4.7). Considering that the contribution of the recycled portland cement pastes on the total strength of the system is relatively low compared to that of magnesium oxide (Figure 4.6), the difference in the ultimate strength mainly resulted from workability (thus water content) of the mixtures. Even though the w/b (thus total water content in the mixture) is the same in the mixtures prepared with HCP and DCP, the water requirement of the DCP is higher to achieve the same flow as HCP. Due to the poorer workability of DCP, mixtures showed difficulties during mixing and placing into the molds during the preparation. On the other hand, the water content used was suitable

for mixtures with HCP. Similar workability problems were not observed in mixtures with HCP. The poor workability of mixtures with DCP resulted in some poorly mixed parts and trapped pockets of air in the specimens. Ultimately these problems lead to having lower compressive strength compared to the mixtures which have better workability at the same water content. Increasing the water content of the mixture to reach the same flow for both cases leads to some other strength-related issues, discussed in Section 4.4.2.

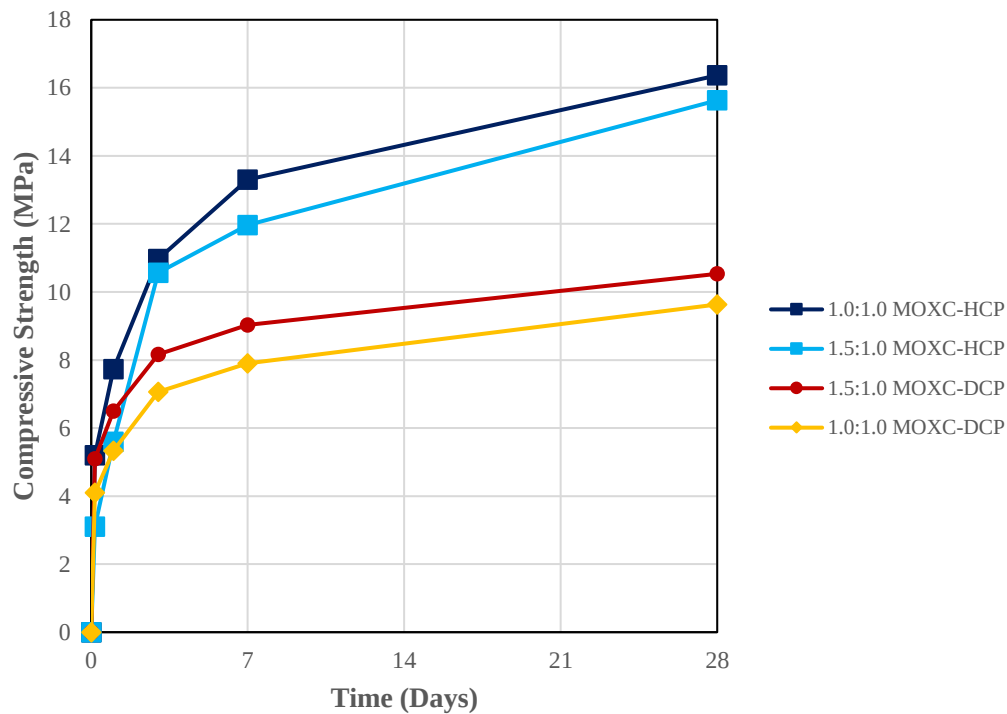


Figure 4.7. Compressive strength development of MOXC-rCP

The strength gain rate of MOXC-rCP is higher than a typical ordinary portland cement and similar to high-early-strength portland cement. In order to analyze and compare the strength gain rate with specified values, the ratios of compressive

strength measured at different ages to their 28-day compressive strength are provided in Table 4.1.

Table 4.1 Ratio of the compressive strength of the samples at various ages to their 28-day compressive strength

Age	1.0:1.0 MOXC-	1.0:1.0 MOXC-	1.5:1.0 MOXC-	1.5:1.0 MOXC-
	HCP	DCP	HCP	DCP
4 h	0.32	0.43	0.20	0.48
1 d	0.47	0.55	0.36	0.49
3 d	0.67	0.73	0.68	0.78
7 d	0.81	0.82	0.77	0.86
28 d	1.00	1.00	1.00	1.00

Some related standards indicate 28-day old strength requirements together with early age strength requirements for high-early strength portland cements. One of these standards is JIS R 5210 (2009) of the Japanese Standards Association (JSA), which specifies several intervals within the first 28 days. The minimum strength requirements for high-early strength portland cement and ultra-early strength portland cement specified in JIS R 5210 (2009) are listed in Table 4.2. Another standard is EN 197-1 (2011), which is used in Turkey. EN 197-1 (2011) specifies the minimum required strength of high early strength portland concrete on the 2nd day and 28th day of the curing (Table 4.3). The produced MOXC-rCP samples do not meet the specified requirements for ultimate strength; however, the strength gain rate is met.

Table 4.2 Minimum strength requirements and their ratios to 28-day old strength requirements for high-early strength portland cements according to JIS R 5210 (2009)

High-early strength portland cement			Ultra-early strength portland cement	
	Compressive strength (MPa)	Ratio to the 28-day strength	Compressive strength (MPa)	Ratio to the 28-day strength
1 d	10.00	0.24	20.00	0.40
3 d	20.00	0.42	30.00	0.60
7 d	32.50	0.68	40.00	0.80
28 d	47.50	1.00	50.00	1.00

Table 4.3 Minimum strength requirements and their ratios to 28-day old strength requirements for high-early strength portland cements according to EN 197-1 (2011)

32.5 R			42.5 R		52.5 R	
	Compressive strength (MPa)	Ratio to the 28-day strength	Compressive strength (MPa)	Ratio to the 28-day strength	Compressive strength (MPa)	Ratio to the 28-day strength
2 d	10.00	0.31	20.00	0.47	30.00	0.57
28 d	32.50	1.00	42.50	1.00	52.50	1.00

4.4.1 Effect of the MgO/Ox on Strength Development

As explained in Section 3.2.1.3, the magnesium oxide-to-oxalic acid ratio was attempted to be fixed to a single value for the rest of the experiments. Compressive strengths of the mixtures presented in Section 3.2.1.3 were measured 1 day after preparation to evaluate the effect of magnesia content on strength. The results of different CP/Ox with the same Ox/MgO were averaged to eliminate the effect of CP/Ox differences. For example, samples #3, #6, and #9 (presented in Table 3.7)

were averaged to obtain the values for $\text{Ox/MgO} = 1.0:0.5$. The strengths of different Ox/MgO does not show evident differences (Figure 4.8). The small difference in the strengths implies that the excess magnesium does not react, thus contribute to the strength of the mixture. On the one hand, as Ox/MgO is decreased, setting time decreases (by observation). Since rapid setting may cause workability issues throughout the other experiments, a magnesium oxide ratio as low as possible, $\text{Ox/MgO} = 1.0/0.5$, was selected for the following mixtures prepared to investigate the effects of the rest of the ingredients.

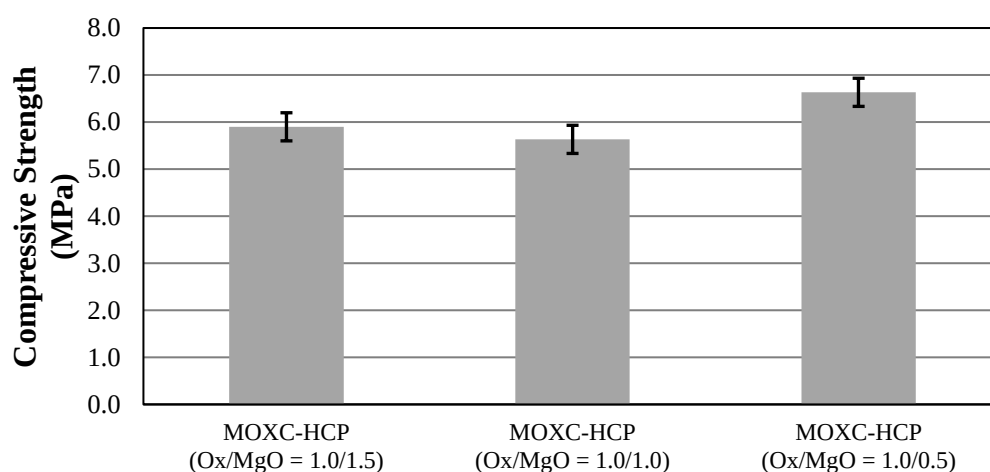


Figure 4.8. Comparison of 1-d compressive strengths of MOXC-HCP with various Ox/MgO

Also, XRD analyses of pastes were performed to determine if any different crystalline phases formed due to molar ratio differences and to observe free magnesia and its amount. The XRD data for these pastes are presented in Figures 4.9 and 4.10 for HCP and DCP, respectively. All the XRD analyses show that the reactions produced the same crystalline phase of magnesium oxalate. Therefore, it can be concluded that there is not a reaction mechanism in MOXC that may result in different reaction product phases such as in MOC and MOSC. The XRD patterns of

the 28-d pastes show the most significant differences at the intensity of the peaks around $42.8^\circ 2\theta$, representing periclase. While intensities of the other phases did not show significant changes, the intensity of periclase peaks in mixtures prepared with higher magnesia content increased. This indicates that more magnesia remained unreacted in these mixtures. In conclusion, MgO/Ox can be designed as 0.5 to use Ox and MgO more effectively without resulting in a significant strength loss or workability problems.

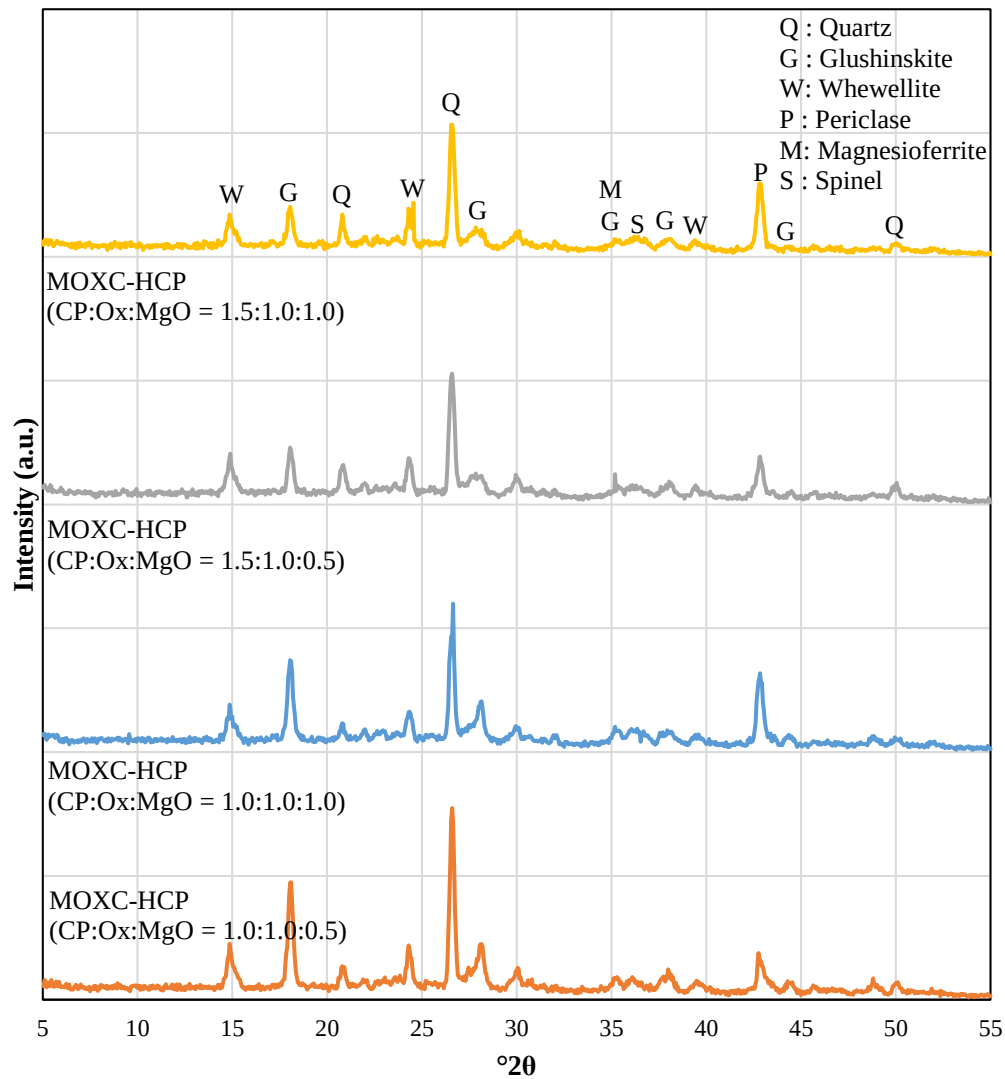


Figure 4.9. X-ray diffractograms of the MOXC-HCP paste prepared with different magnesia contents

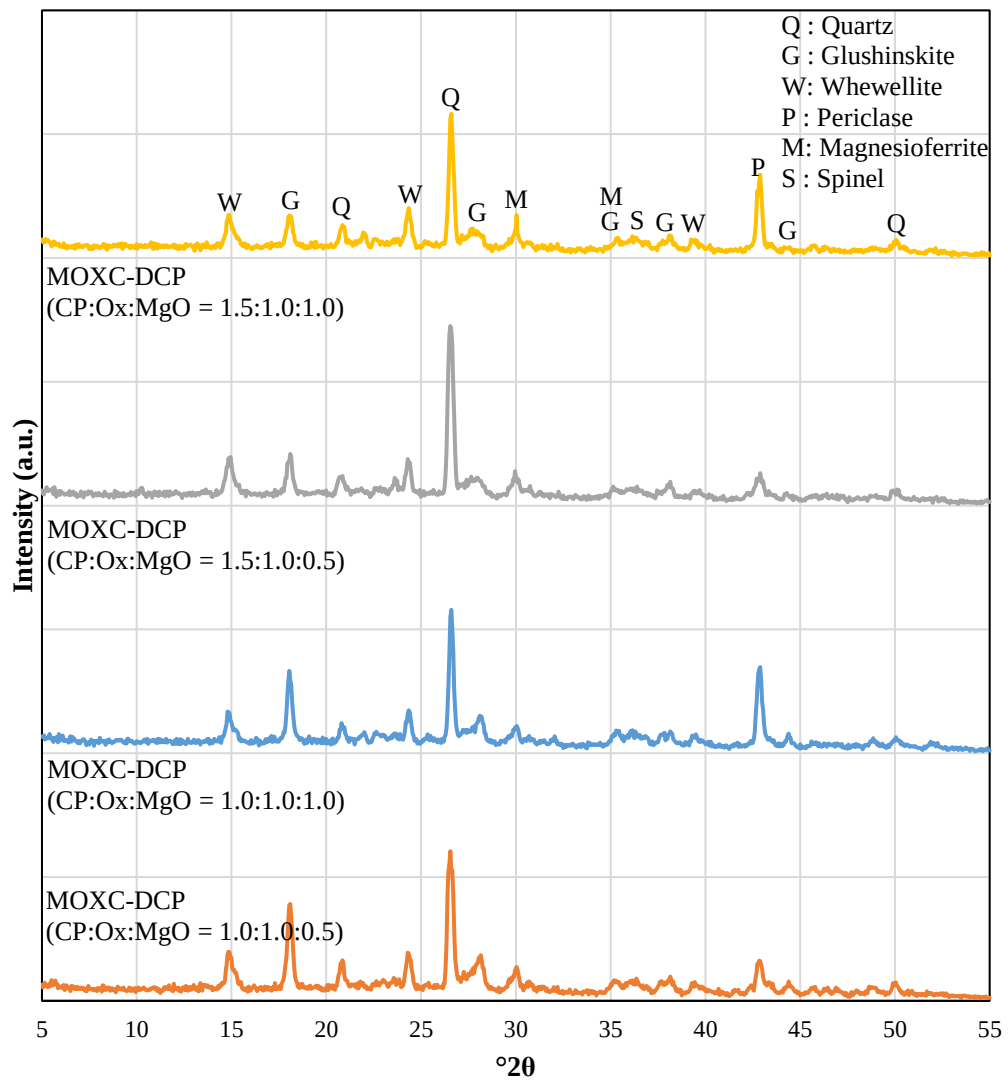


Figure 4.10. X-ray diffractograms of the MOXC-DCP paste prepared with different magnesia contents

4.4.2 Effect of Water Content on Strength Development

As discussed in Section 4.4, specimens with DCP require more water in order to have flow similar to their counterparts utilizing HCP. Using the same w/b for the control samples resulted in workability problems in the mixtures with DCP, while mixtures with HCP did not face similar problems. The MOXC-DCP samples were observed to have some trapped air pockets (due to poor workability, thus compaction) that may be the leading cause in the lower strength in MOXC-DCP compared to MOXC-HCP. In order to eliminate the effects of workability related problems, new mixtures with DCP were prepared to have a similar flow with the samples with HCP. Their compressive strength developments are compared with those of the control samples in Figure 4.11.

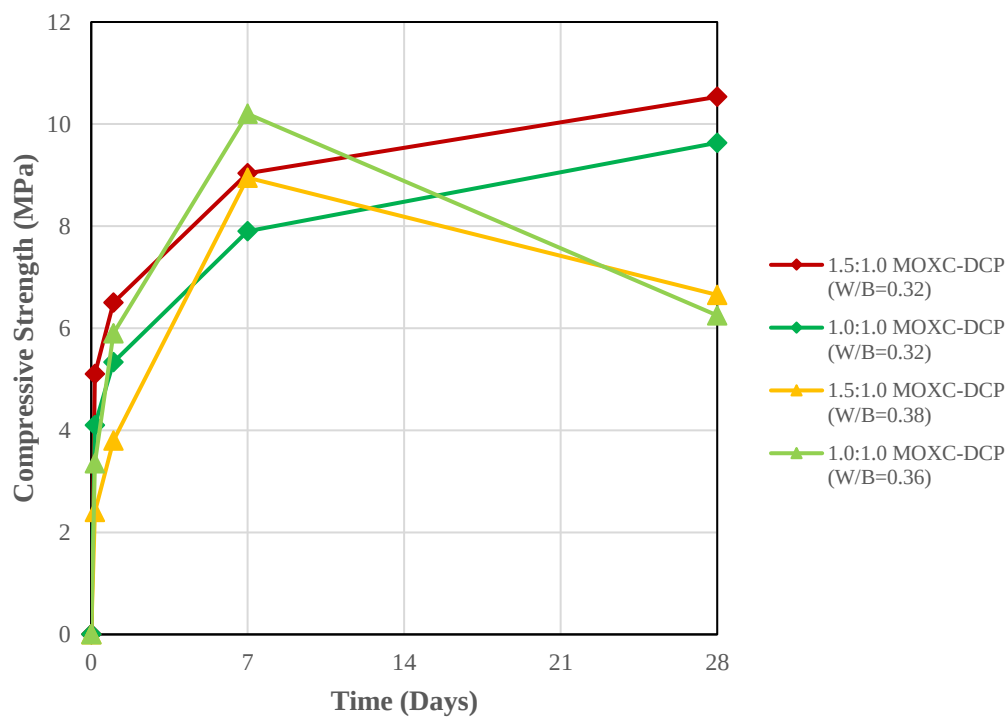


Figure 4.11. Compressive strength development of MOXC-DCP with different w/b

In order to achieve the same flow, the samples with higher DCP content (1.5:1.0 DCP/Ox) required even more water than the 1.0:1.0 DCP/Ox samples. When these two higher-water-content cases are compared, disregarding the difference in the ratio of cement paste to oxalic acid, the samples with lower water content showed higher compressive strength until 7d. However, the measurements at the 28d showed a decrease in compressive strength values for both cases.

4.5 Effects of Reduced Binder Content on Strength Development

A group of tests was performed to evaluate the performance of the MOXC-rCP system with less binder content than the control mixtures. The mix proportions are presented in Section 3.2.1.5. The compressive strength of the mixtures shows a decline after 7 d (Figures 4.12 and 4.13).

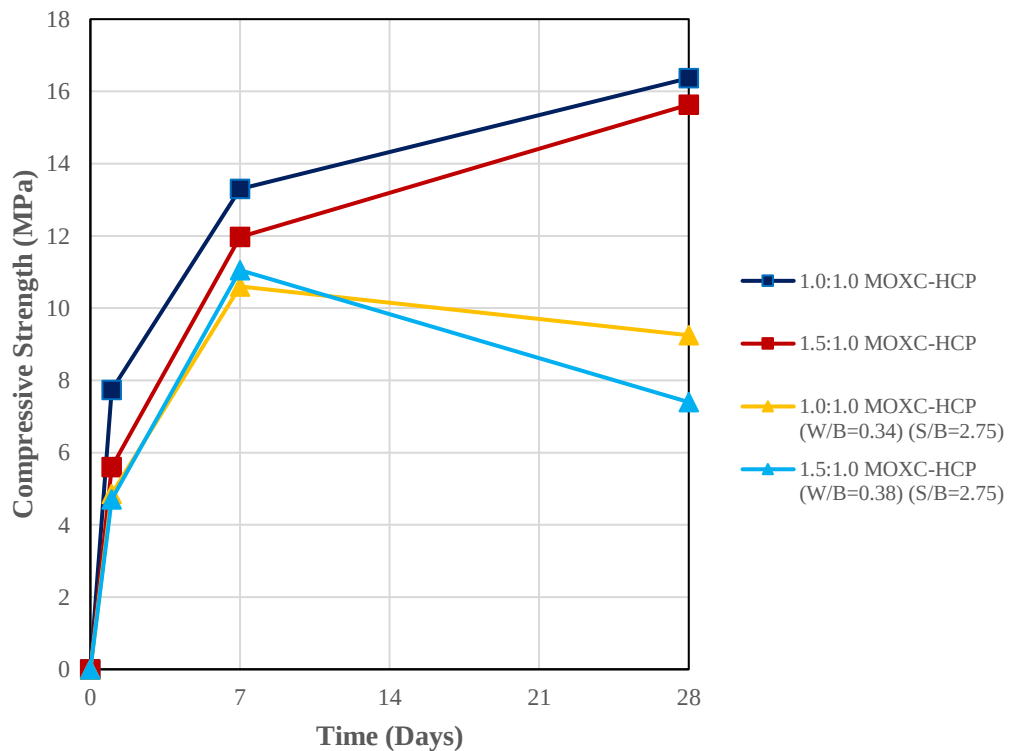


Figure 4.12. Compressive strength development comparison of MOXC-HCP with various s/b

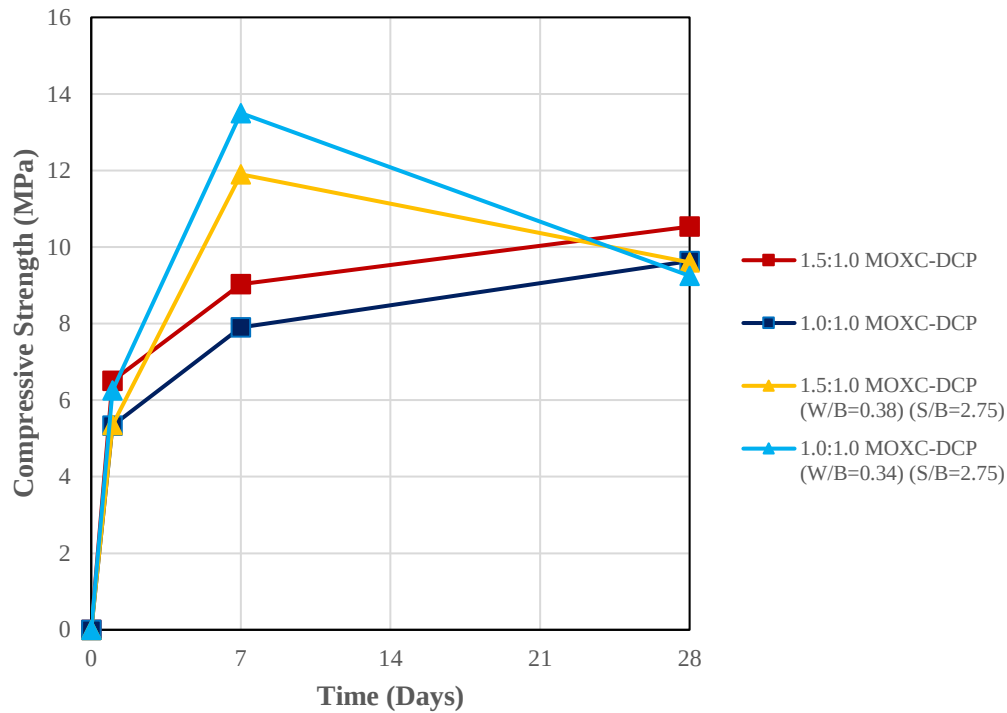


Figure 4.13. Compressive strength development comparison of MOXC-DCP with various s/b

By comparing the strength development of samples with reduced binder content with the control mixtures with similar water content, the similarities in their strength development can be observed (Figure 4.14). The samples with lower recycled portland cement paste (1.0:1.0 MOXC-DCP) showed a slightly higher rate of decrease in compressive strength after 7 d compared to higher portland cement paste containing samples (1.5:1.0 MOXC-DCP). This may indicate that the observed strength loss arises from the reactions between MgO and OX and its products.

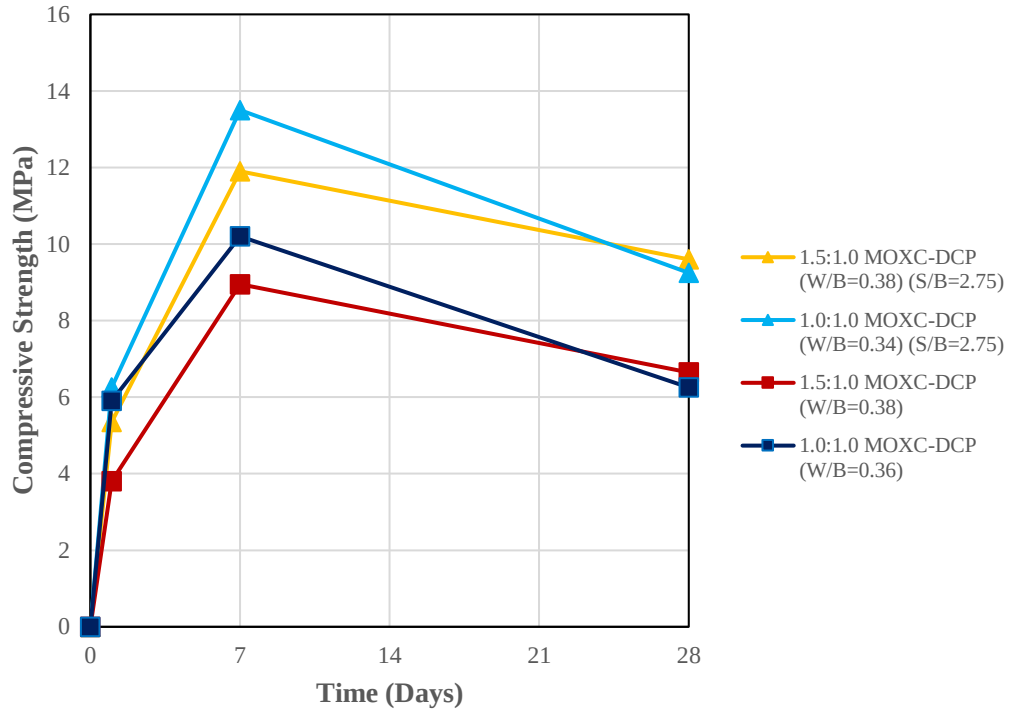


Figure 4.14. Compressive strength development comparison of MOXC-DCP with high water-to-binder ratios to the MOXC-DCP with high sand-to-binder ratios

4.5.1 Strength Development of the MOXC-rCP

As explained in Section 3.2.1.5, it can be possible to produce MOXC mixing MgO and Ox directly, without using recycled portland cement, since the rate of reactions is expected to be lower due to reduced binder content in the mixture. Figure 4.15 shows the strength curves of the samples prepared using MgO and Ox directly ($\text{MgO}/\text{Ox} = 0.5$). All the compared cases needed a relatively high w/b to have an adequate flow. Their strength developments are similar regarding the trends (a decline in strength after 7 d). The compressive strength of the samples prepared using CPOx are significantly higher than the direct mixture of the MgO and Ox (MOXC). The strength difference of these samples, with the same amount of MgO and Ox, shows CPOx has a positive effect on the cementitious reactions.

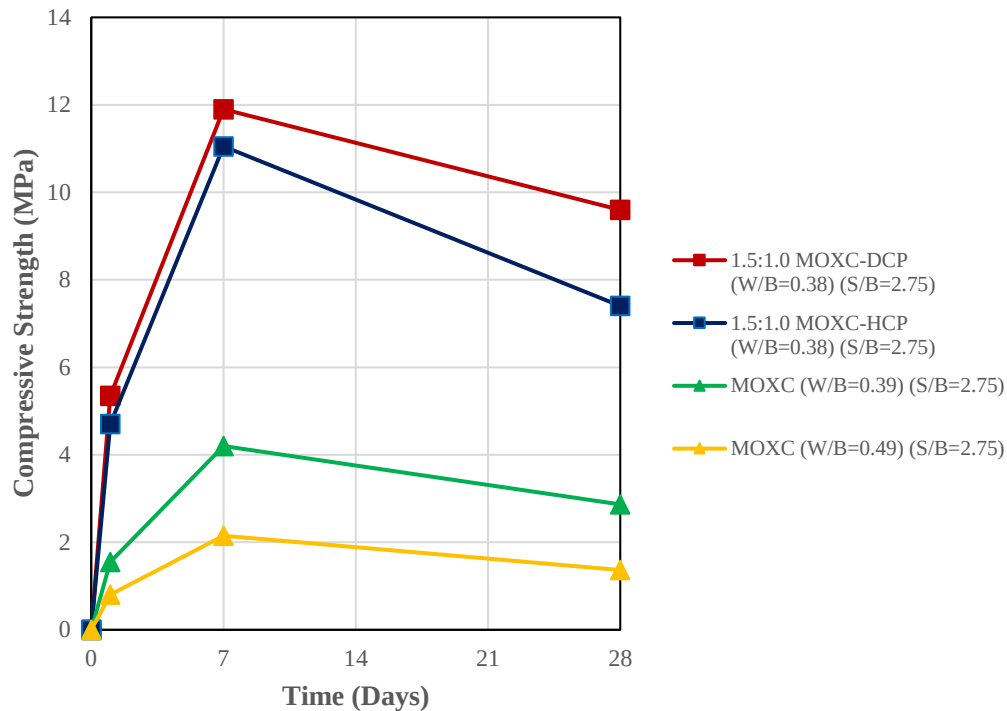


Figure 4.15. Compressive strength development of MOXC mixtures with the comparison of MOXC-rCP with the same s/b

4.6 Effects of Boric Acid

As CP/Ox is decreased in the mixture, setting time decreases notably. The rapid setting may lead to a poorly mixed mixture or difficulties in placing the mixture into the molds, consequently low compressive strength of the specimens. The mixtures that set quickly also have a high rate of exothermic reactions. The high-temperature that occurs in the specimens damages the samples in a similar mechanism with mass concrete in portland cement concrete. During the experiments, the mixtures with CP/Ox lower than 1.0 could not be appropriately prepared due to short setting time. In order to increase the setting time and reduce the high-temperatures that occurred in the specimens, retarders were used in the mixtures with lower CP/Ox than 1.0. Also, control mixtures were prepared by adding boric acid to compare the results and determine the effects of boric acid.

Although the setting times could not be measured, it was observed that boric acid increased the time for the initial setting for the samples. However, for CP/Ox of 1.0:1.5, the setting time was still critically short that the mixture started to set during the placement into the molds, yet the specimens could be prepared. Likewise, mixtures with lower CP/Ox still reached high temperatures in a short time. It was expected from the samples with a lower CP/Ox to have higher compressive strength since they have more magnesia and oxalic acid content in the mixture. However, the results showed otherwise, as presented in Figure 4.16. The decrease in strengths of lower CP/Ox than 1.0 may be a result of a partial set of the mixture during the placement into the molds, or much higher temperatures occurred after the set compared to the other mixtures with higher CP/Ox. The strength gain rate of the mixtures with CP/Ox lower than 1.0 decreased after 3 d. After 7 d, the rate of strength increase was observed to be similar to the rest of the mixtures compared in Figure 4.16.

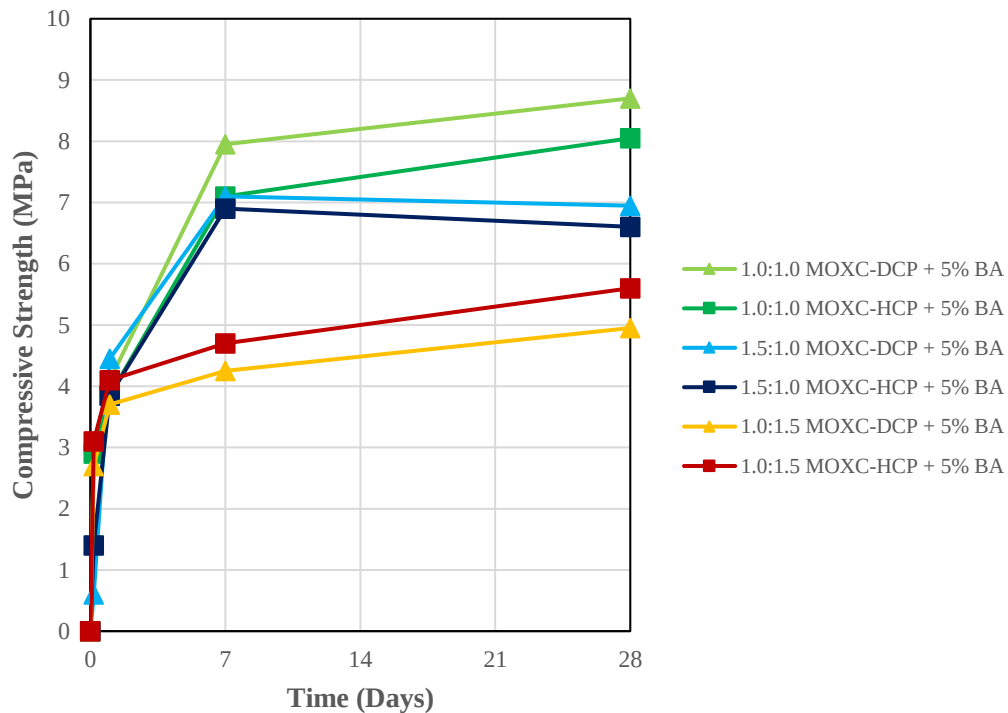


Figure 4.16. Compressive strength developments of MOXC-rCP with 5 % boric acid

In Figure 4.17, the comparison of the compressive strength development of the specimens with boric acid and the control specimens is presented. The mixtures with HCP showed a significant reduction in their compressive strength. On the other hand, the mixtures with DCP did not show a significant difference in their strength. However, the control samples with DCP suffered greatly from workability issues with the same water content. In contrast, the samples with boric acid did not show similar workability problems at the same water content.

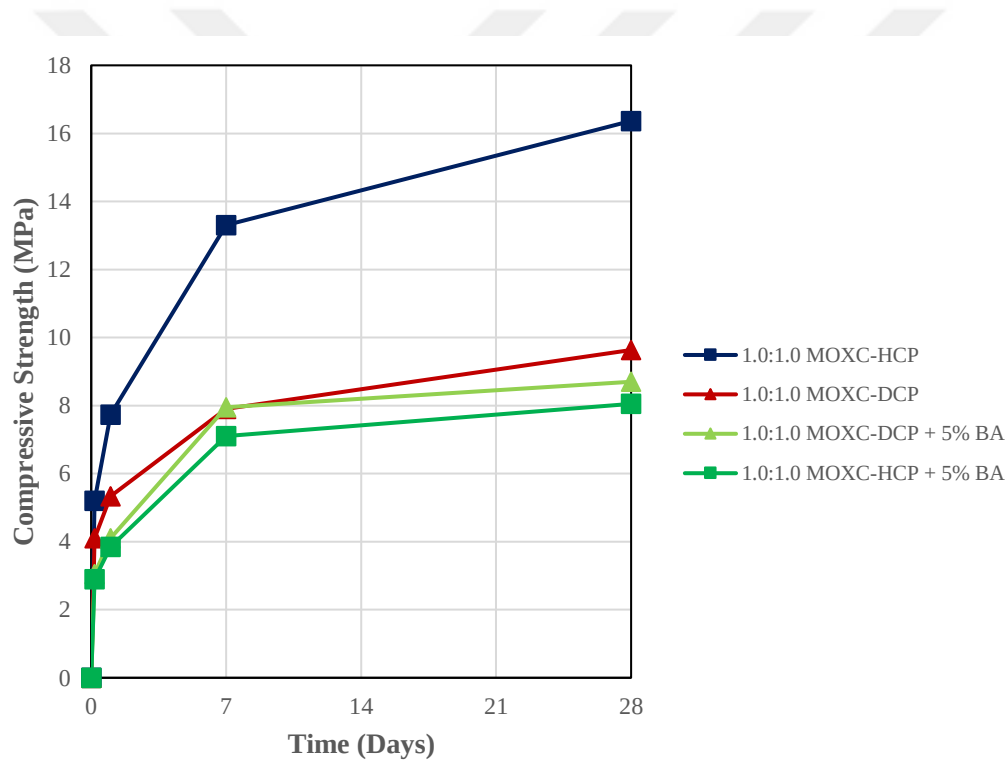


Figure 4.17. Compressive strength development comparison of boric acid added MOXC-rCP samples with control samples

XRD patterns of the pastes prepared with boric acid do not significantly differ from the regular pastes without boric acid (Figures 4.18 and 4.19). This observation complies with the findings of other research on the effect of boric acid in magnesia cements, which conclude a temporary effect of boric acid on magnesia grains that is not resulting in new reaction products.

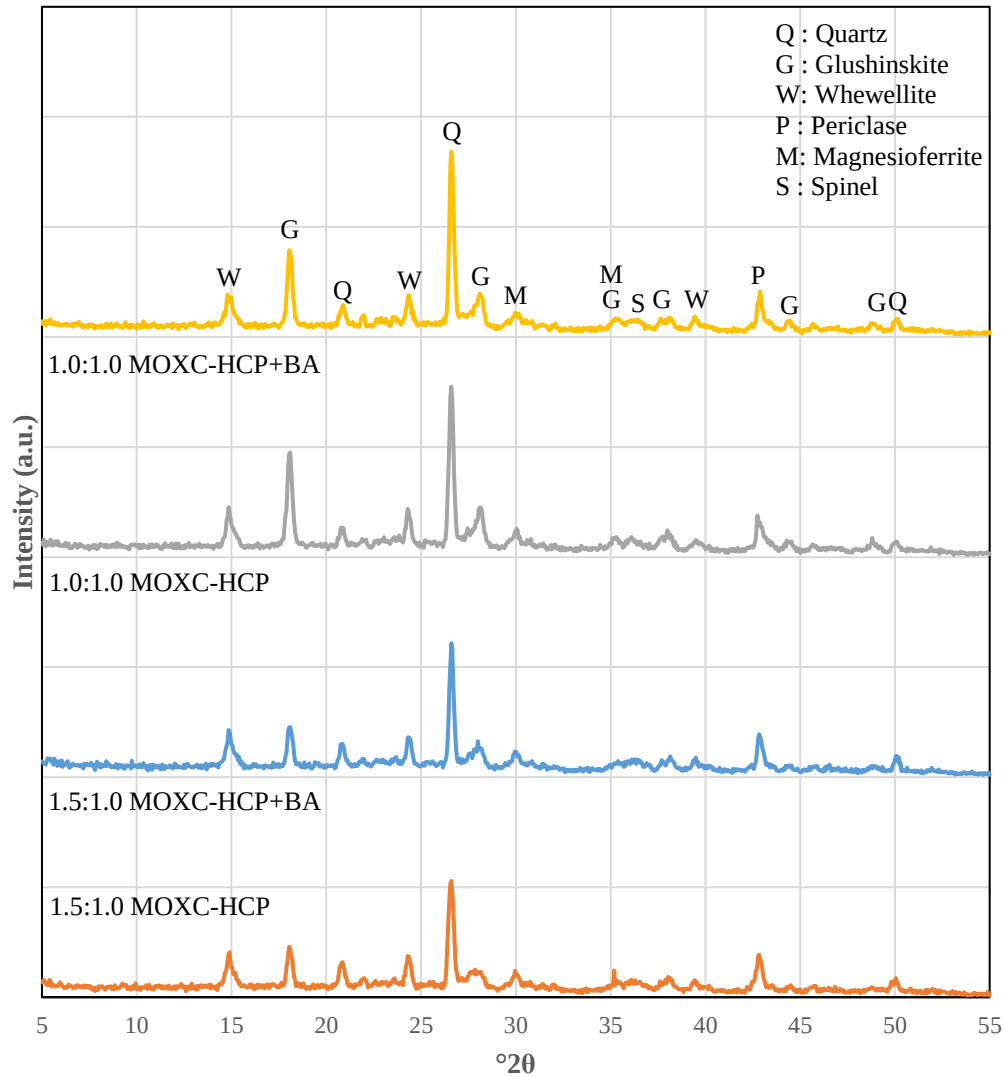


Figure 4.18. XRD pattern comparison of MOXC-HCP + 5 % BA pastes with MOXC-HCP

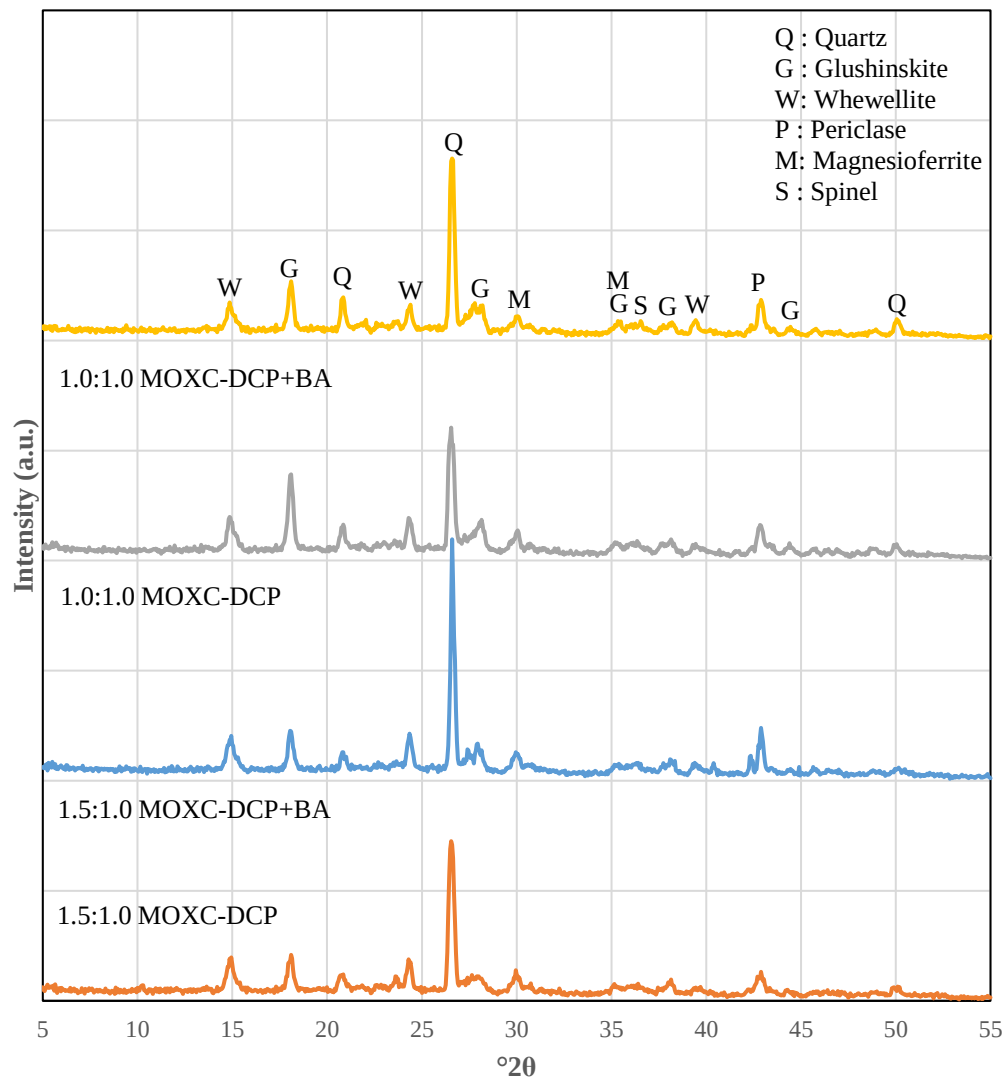


Figure 4.19. XRD pattern comparison of MOXC-DCP + 5 % BA pastes with MOXC-DCP

4.7 Effects of Pozzolan Addition on Strength Development

The effects of pozzolans on strength development were observed by replacing a certain amount of sand, similar to the procedure in ASTM C311 (2018). Consequently, this replacement increased the water need of the mixture due to the particle size distribution change of the ingredients. Compressive strength development shows a similar trend for admixtures of 15% class F fly ash and 5% silica fume (Figure 4.20).

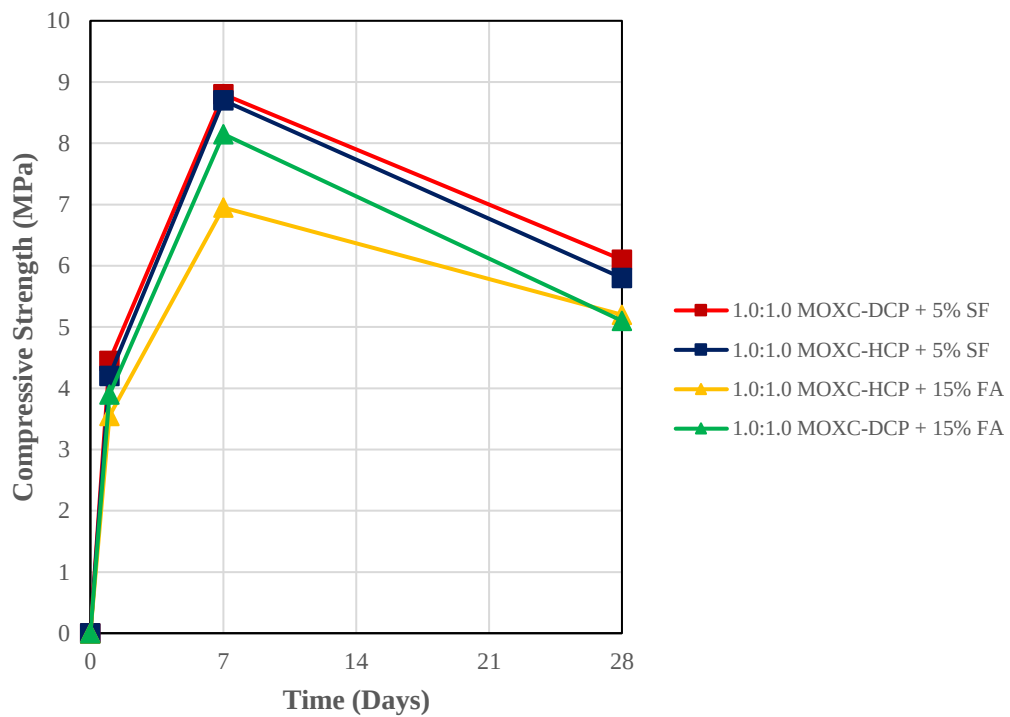


Figure 4.20. Compressive strength developments of MOXC-rCP with 15 % of fly ash and 5 % of silica fume

Increased water content in the mixtures caused a similar strength development to the other samples with high water content. Strength development comparisons with the control samples, together with high water content control samples, are presented in

Figures 4.21 and 4.22. Both pozzolans show the same effect of decreasing compressive strength after 7 d, mainly due to the increase in water content. Without the addition of the pozzolans, the specimens prepared with similar water content (w/b above 0.41) showed a much lower compressive strength in the preliminary tests. Therefore, it may be concluded the addition of pozzolans to the mixture prepared with such a high water content, increased the strength of the system. However, since the admixture of pozzolans is the reason for increased water need, the pozzolans do not provide a benefit to the system in this case.

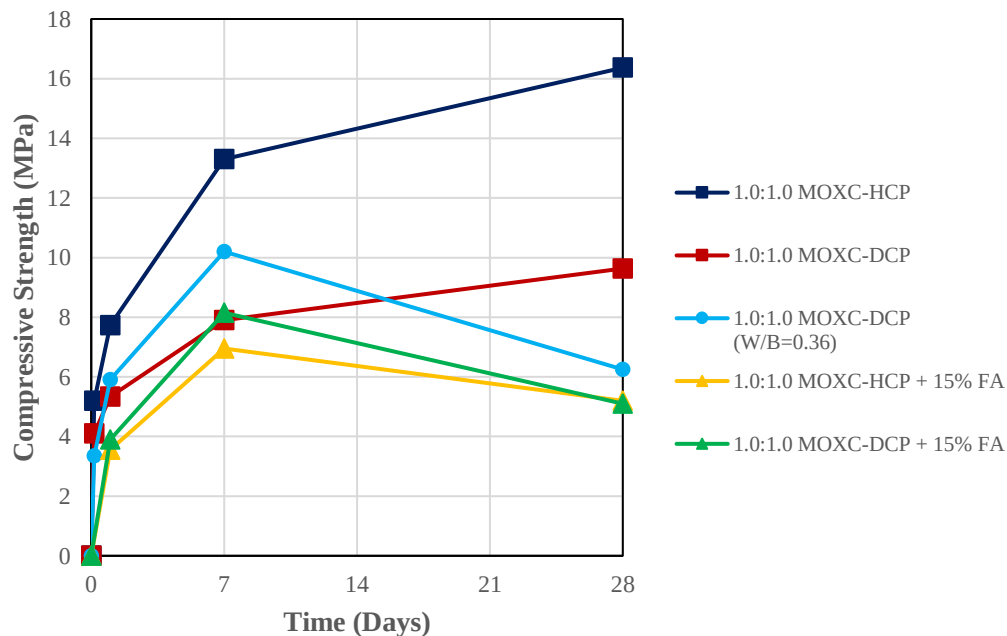


Figure 4.21. Compressive strength development comparison of MOXC-rCP with 15 % fly ash

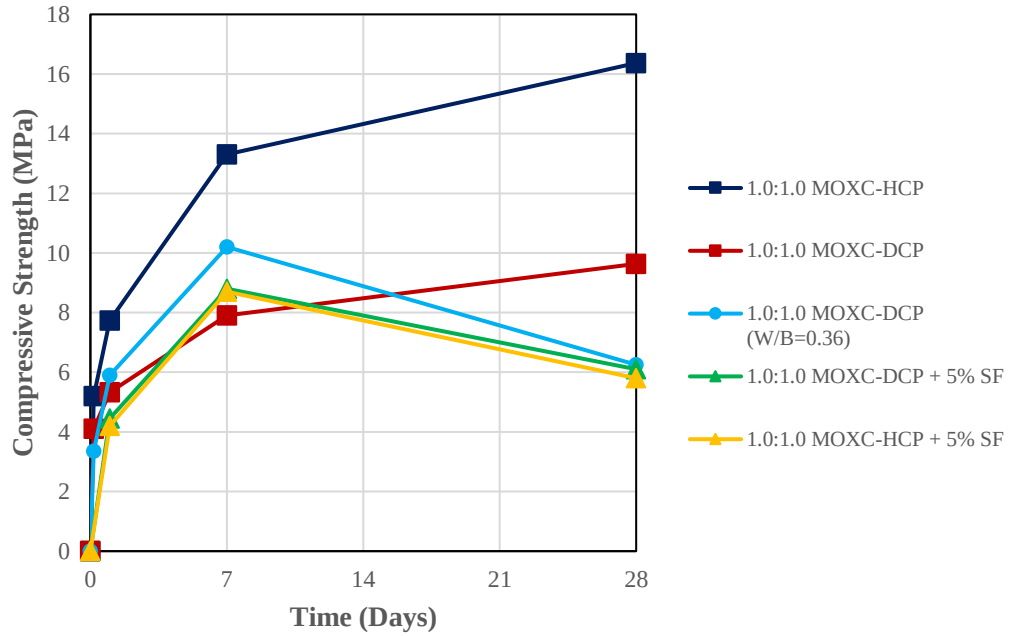
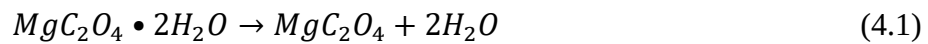


Figure 4.22. Compressive strength development comparison of MOXC-rCP with 5 % silica fume

4.8 Thermal Analysis of MOXC-rCP Pastes

Thermal decomposition of magnesium oxalate dihydrate occurs in two steps. In the first step, it turns into its anhydrous form by losing its water, between 160-240 °C:



Then the oxalate decomposes into carbon monoxide and carbon dioxide, leaving magnesium oxide at between 400-510 °C:



The mass losses were measured as 24.3 % in the first step and 47.9 % in the second step by Mastuli et al. (2014), while the calculated theoretical values are 24.3 % and 48.5 %.

Another oxalate expected to be found in the paste, calcium oxalate hydrate, decomposes in three steps (Frost and Weier, 2004). In the first step, it loses its water at around 180 °C:



Then it loses carbon monoxide and results in calcium carbonate at around 480 °C:



Finally, the calcium carbonate decomposes into calcium oxide and carbon dioxide at around 680 °C:



Hourlier (2019) measured the mass losses as 12.33 % in the first step, 19.32 % in the second step, and 30 % at the third step. The calculated theoretical values are 12.3 %, 19.2 %, and 30.1 %, respectively.

In addition to magnesium oxalate dihydrate and calcium oxalate hydrate, hydration products of CP existing in the paste can cause mass loss to some degree. In a typical hydrated portland cement paste C-S-H gel, ettringite, and gypsum are decomposed between 110-180 °C, and portlandite is decomposed at around 490 °C (Zhang and Ye, 2012). Also, hydrated and carbonated CP may contain calcium carbonate, which decomposes at around 680 °C.

The results for simultaneous TGA and DTA analyses results are presented in Figures 4.23 and 4.24. There are significant mass losses in the samples at around 140-240 °C, 430-550 °C, and 680-720 °C. The mass losses share similarities among the samples. Losses are higher when CP/Ox is 1.0:1.0 compared to when 1.5:1.0, and in samples with HCP compared to those with DCP. The difference between different CP/Ox can be explained by the decomposition of magnesium oxalate dihydrate since it is expected that samples with CP/Ox is 1.0:1.0 comprise more magnesium oxalate dihydrate.

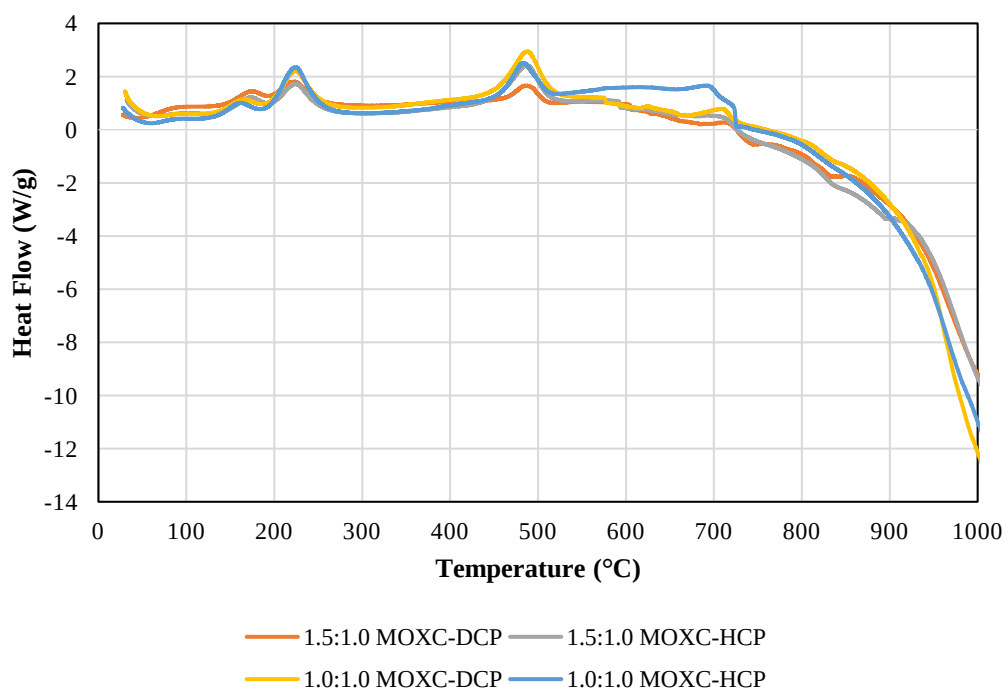


Figure 4.23. Heat flow of MOXC-rCP pastes upon heating

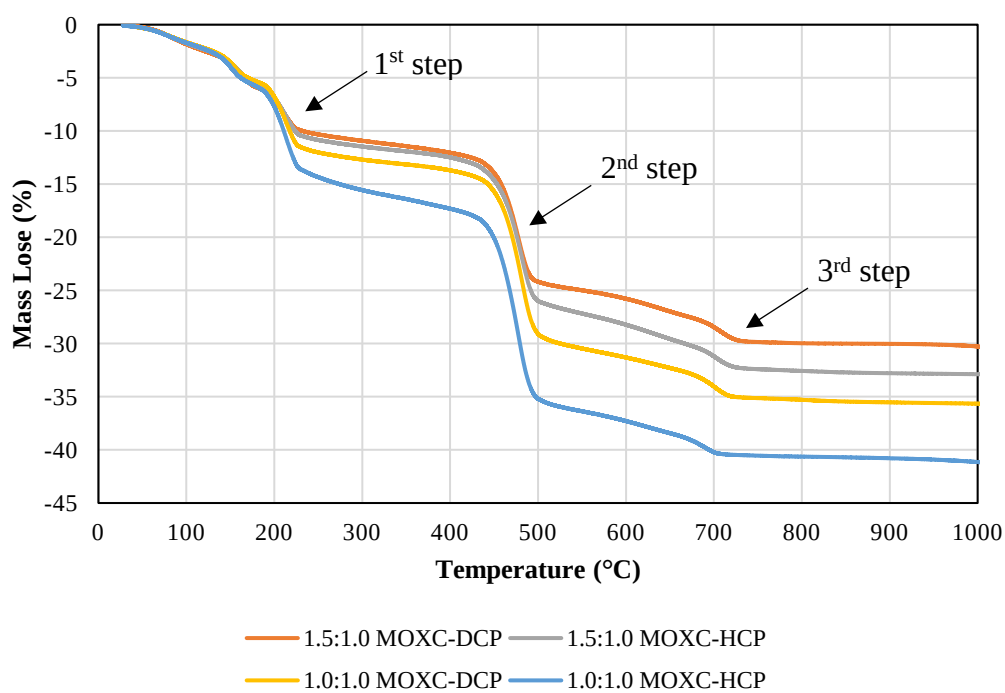


Figure 4.24. Mass loss of MOXC-rCP pastes upon heating

The mass losses between the steps are presented in Table 4.4. By the first step, the main cause of the mass loss is expected to be from released water from all the compounds. The mass loss up to the second step resulted from released carbon dioxide and carbon monoxide gases due to the decomposition of magnesium oxalate and calcium oxalates. Also, portlandite decomposes between steps 1 and 2, releasing water. Until step 3, mainly calcium carbonate decomposes into carbon dioxide and calcium oxide. This calcium carbonate could be a part of the decomposed hydration products of CP or calcium oxalate hydrate, either way; it originates from the calcium oxide in CP.

Table 4.4 Mass loss percentage of the MOXC-rCP pastes after each step

Sample	Mass Loss (%)		
	by 1 st Step	by 2 nd Step	by 3 rd Step
1.5:1.0 MOXC-DCP	-10.0	-24.1	-29.7
1.5:1.0 MOXC-HCP	-10.5	-26.1	-32.3
1.0:1.0 MOXC-DCP	-11.6	-29.9	-35.0
1.0:1.0 MOXC-HCP	-13.7	-35.3	-40.3

Assuming all calcium carbonate decomposed in step 3 comes from calcium oxalate hydrate, a calculation can be made to determine the mass percentage of magnesium oxalate dihydrate in the pastes. Since it is expected that calcium oxalate hydrate loses 30.1 % of its mass in step 3, the total mass percentage of calcium oxalate hydrate can be calculated. Also, making another assumption that in step 2, only calcium oxalate hydrate and magnesium oxalate dihydrate are decomposed, the total mass percentage of the magnesium oxalate dihydrate can be calculated. According to these assumptions and calculations, mass percentages of these oxalates in different reacted pastes are presented in Table 4.5. The mass percentage of magnesium oxalate dihydrate is higher in CP/Ox = 1.0:1.0 compared to other samples as expected from higher magnesium oxide and oxalic acid content in these samples.

Table 4.5 Mass percentage of the oxalates in MOXC-rCP pastes according to TGA

Sample	Mass (%)	
	$\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
1.5:1.0 MOXC-DCP	18.6	21.7
1.5:1.0 MOXC-HCP	20.6	24.0
1.0:1.0 MOXC-DCP	16.9	31.0
1.0:1.0 MOXC-HCP	16.6	38.0

4.9 SEM Investigations of MOXC-rCP Pastes

The 4-month-old samples investigated do not have significant differences in their microstructures (Figures 4.25, 4.26, 4.27, and 4.28). Surfaces of the samples are fairly homogeneous and mostly contain monoclinic crystal salts (Figure 4.29). The small size of the crystals ($<1 \mu\text{m}$) may indicate a fast reaction. In addition to the salt crystals, some of the sand and unreacted magnesia particles can be observed, which are in irregular shapes. Hydration products of CP, such as C-S-H and ettringite, could not be observed distinctly on sample surfaces. Investigated sample surfaces do not have a porous structure; however, there are spherical pores with diameters up to $200 \mu\text{m}$. These pores have salt crystals on their surface, indicating that the pores are a result of the reactions between oxalic acid and magnesium or calcium, which releases water. Although there are not many cracks present in the paste, one crack could be observed in 1.5:1.0 MOXC-DCP paste (Figure 4.30).

EDX analyses were performed to determine the elemental compositions of the paste samples in general (Table 4.6). The elemental compositions of the pastes were similar to each other except 1.5:1.0 MOXC-DCP, which composes more calcium and less magnesium compared to other samples. Although it is expected to contain more calcium and less magnesium from samples with higher CP/Ox, the results for 1.5:1.0 MOXC-DCP possibly were obtained from a region that is calcium-rich.

Table 4.6 Elemental composition of MOXC-rCP pastes

Element	Mass (%)			
	1.5:1.0	1.5:1.0	1.0:1.0	1.0:1.0
	MOXC-DCP	MOXC-HCP	MOXC-DCP	MOXC-HCP
Carbon	19.42	23.43	24.51	22.2
Oxygen	49.03	51.14	48.64	53.07
Magnesium	5.85	8.98	8.61	10.07
Calcium	18.44	5.93	4.04	5.08
Silicon	4.33	7.76	12.49	7.10
Aluminum	1.47	1.75	1.03	1.45
Iron	1.46	1.00	0.68	1.03

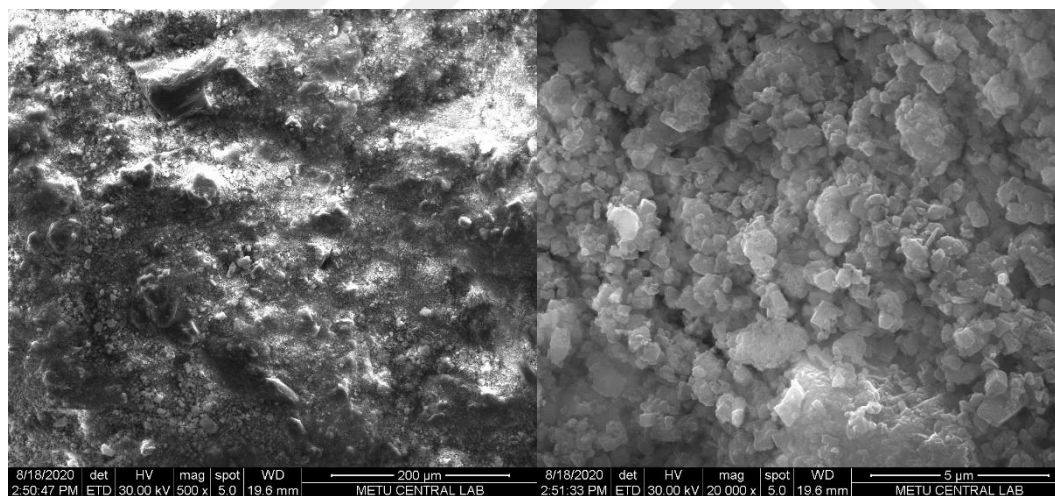


Figure 4.25. SEM images of 1.5:1.0 MOXC-DCP paste

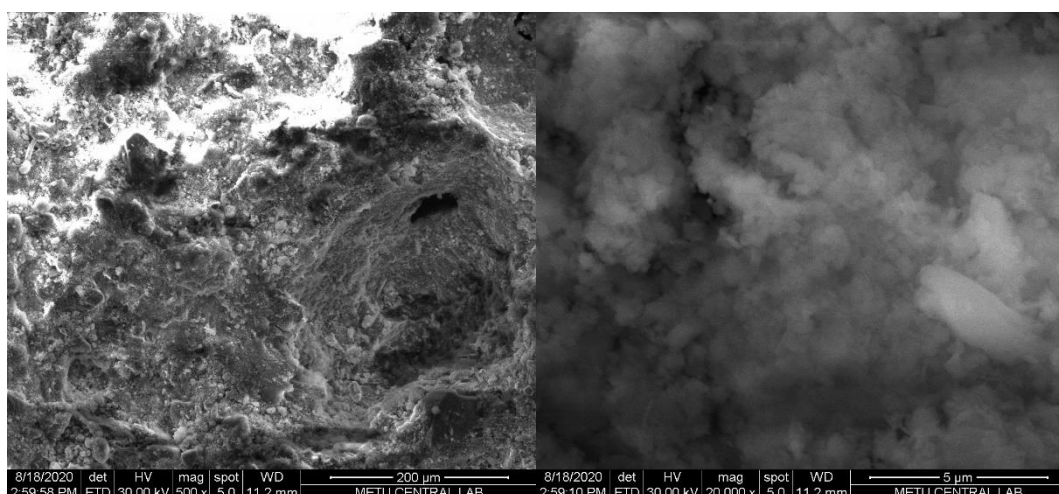


Figure 4.26. SEM images of 1.5:1.0 MOXC-HCP paste

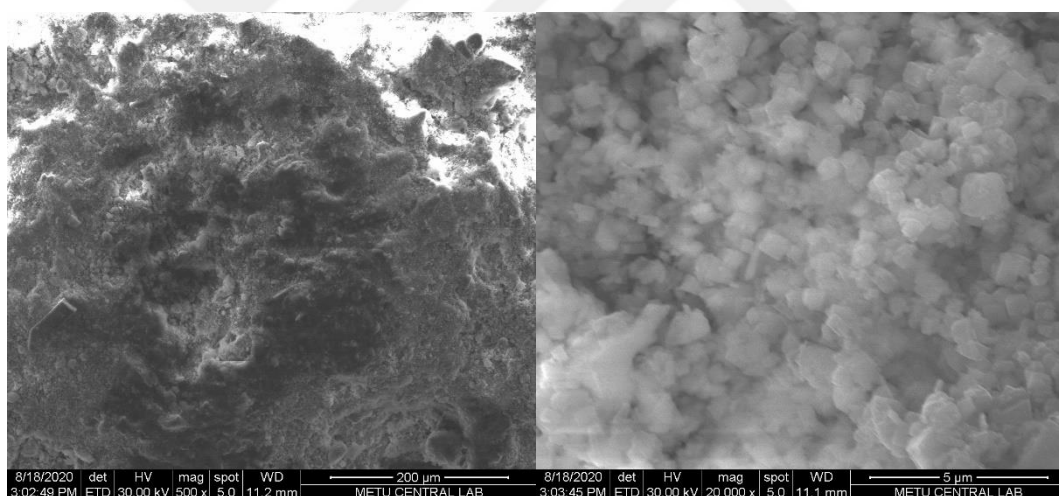


Figure 4.27. SEM images of 1.0:1.0 MOXC-DCP paste

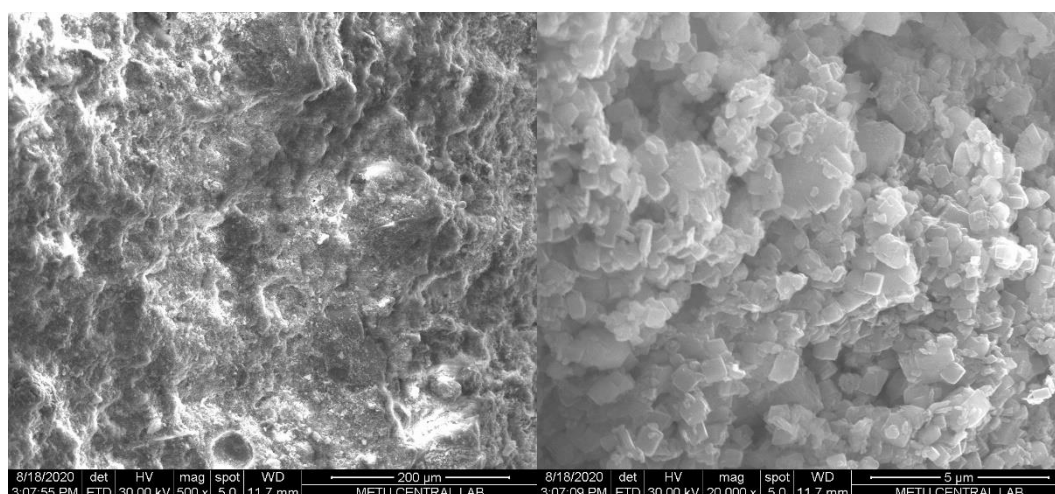


Figure 4.28. SEM images of 1.0:1.0 MOXC-HCP paste

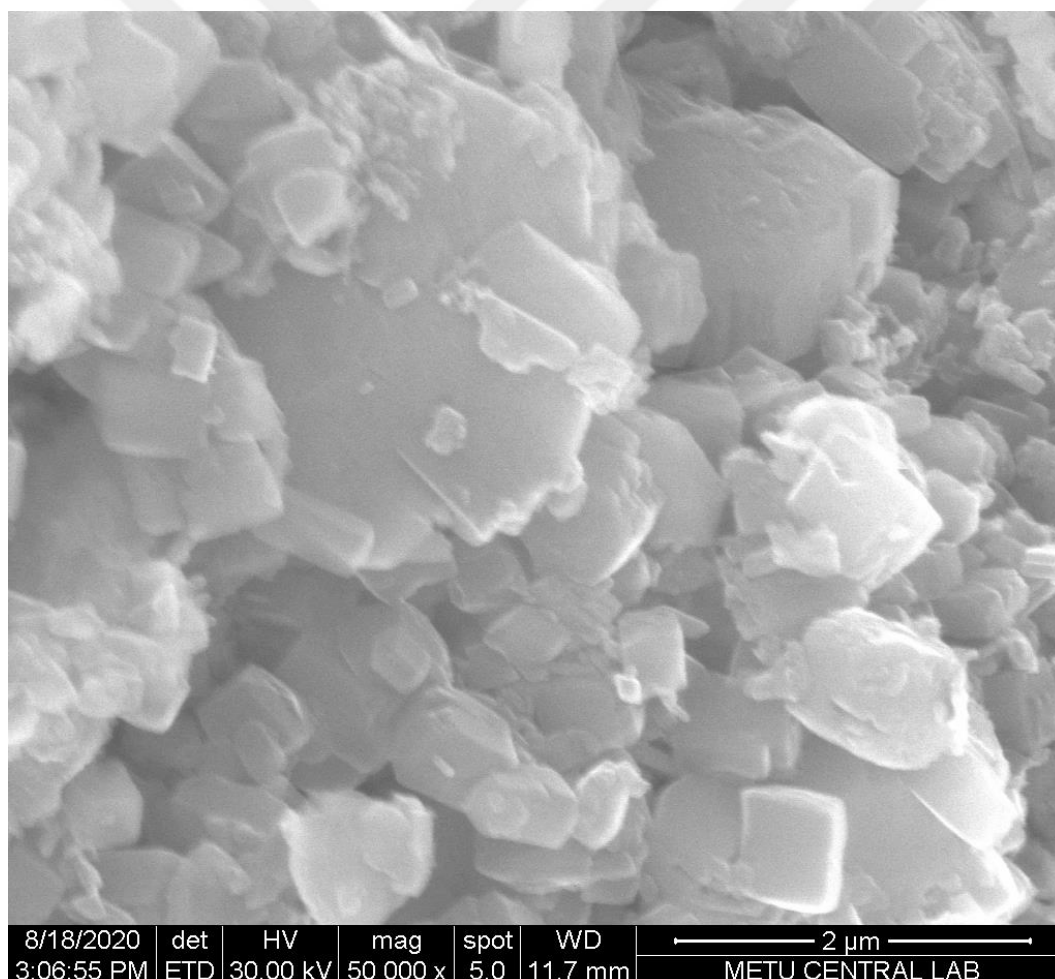


Figure 4.29. Surface of 1.0:1.0 MOXC-HCP paste

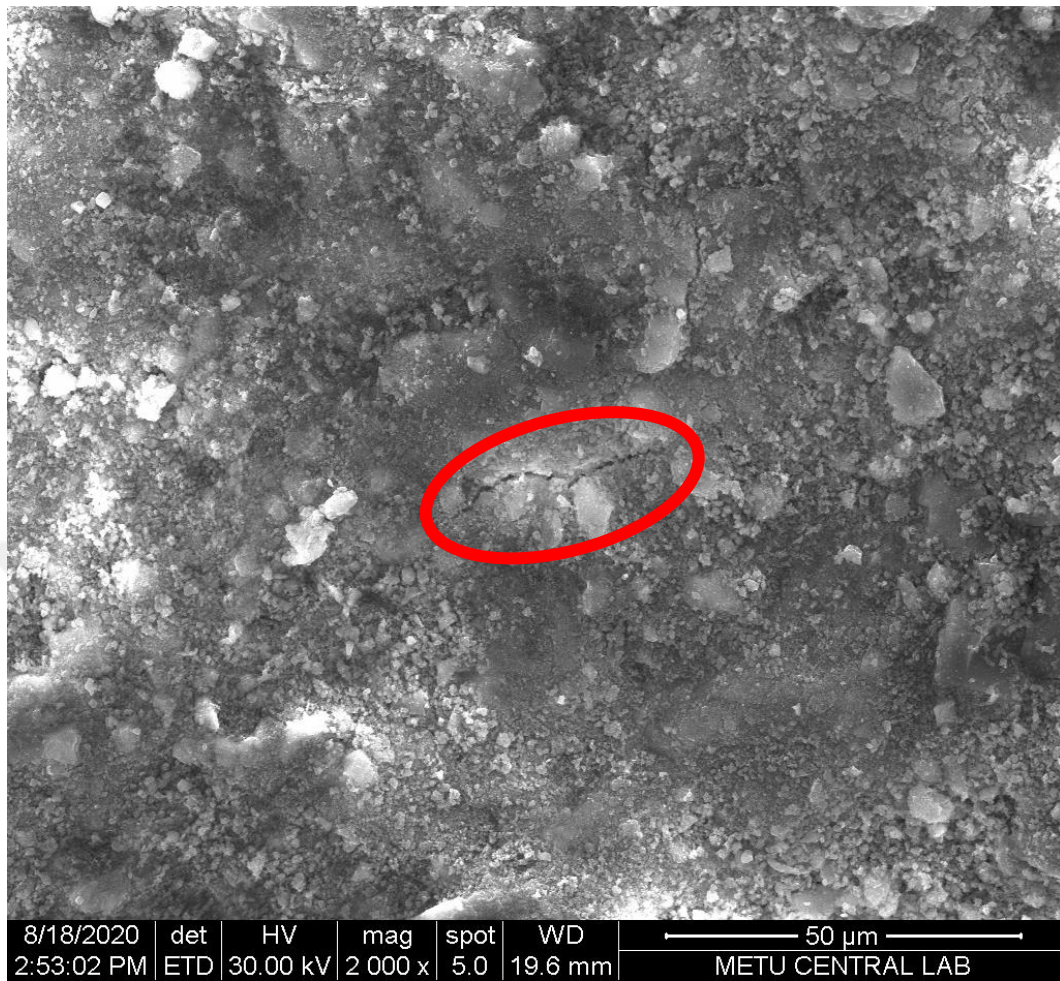


Figure 4.30. An observed crack in 1.5:1.0 MOXC-DCP paste

CHAPTER 5

SUMMARY AND CONCLUSIONS

5.1 Summary of the Works Performed and Conclusions

In this study, a new type of magnesia-based cement, named magnesium oxalate cement, was investigated. The methods of producing and the general characteristics of this cement can be summarized as follows:

- The reaction of magnesia and oxalic acid is capable of forming a cementitious binder. Mortar samples with compressive strength ~ 16 MPa at 28-d could be produced in this study.
- The main reaction products were found to be magnesium oxalate dihydrate and calcium oxalate hydrate (due to recycled cement paste presence).
- The rate of these acid-base reactions is very rapid and highly exothermic, especially when the mixture introduced with magnesia, consequently, creates problems in its practical usage.
- In order to reduce the rate of reactions, an intermediary produced by oxalic acid and recycled portland cement paste can be used. The theory behind producing this material is that the formed structure could temporarily bond the oxalate ions then slowly release the ion into the mixture to react with magnesia in a slower and more controlled manner.
- Production of such an intermediary (CPOx) was found to be possible by mixing oxalic acid and recycled portland paste in the presence of water, then oven-treating this blend to form a clinker-like material, which can be ground to a powder to add to the mixtures.
- CPOx can itself form a cementitious structure with water, and the strength of this structure is much higher than rehydrated recycled portland cement

pastes, yet not as strong as its mixtures with magnesia. Additionally, the hydrated product was observed to be highly soluble in water.

- The effectiveness of CPOx in slowing reactions is directly influenced by its composition. Higher oxalic acid contents in CPOx are unable to provide enough time for the preparation of the mixtures before setting. Therefore, mixtures with oxalic acid-to-recycled cement paste ratio higher than 1.0 require some other retardation methods.
- Comparing recycled cement paste as is, after grinding (HCP), and obtained after dehydration (DCP), HCP is more useful in producing mixtures with higher strength.
- Increasing water content improves workability by increasing flow and setting time of fresh mixtures. However, its effect on strength is much greater than the adverse effects of poor compaction. Therefore, it is beneficial to keep the water content as low as possible to have higher ultimate strength.
- Although boric acid increases the setting time of the mixture, its 5 % addition to binders was not enough to provide time for proper preparation of high oxalic acid containing mixtures. Overall, the use of boric acid was observed to affect compressive strength negatively.
- Pozzolan addition was observed to increase the water need of the mixtures. As a result, the compressive strength of the mixtures was observed to decrease.

5.2 Suggestions for Future Research

As magnesium oxalate cements are novel, there exist many characterization studies to be performed. The following are suggested:

- A suitable water-reducing chemical needs to be researched to improve the workability and strength of magnesium oxalate cements.
- Alternative industrial wastes can be researched to produce an intermediate material similar to recycled portland cement paste and oxalic acid blends used in this study.
- Lower dehydration temperatures to produce DCP may be experimented with since they are expected to require less water to have standard consistency. The temperatures used to heat the recycled aggregates to remove mortar are possible candidates.
- The mechanism behind the strength loss observed in some mixtures can be investigated.
- Different curing regimes can be investigated.
- Water resistance of magnesium oxalate cements can be investigated.
- The volume stability of magnesium oxalate cements can be investigated.
- Some other pozzolans or different replacement contents or mix designs with the same type of pozzolans can be investigated.

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APPENDICES

A. Results of Compressive Strength Tests

Table A.1 Compressive strength test results of 1.0:1.0 HCPOx

Age	Compressive Strength (MPa)		
	#1	#2	Average
1 d	0.4	0.4	0.4
7 d	1.4	2.0	1.7
28 d	2.7	2.3	2.5

Table A.2 Compressive strength test results of 1.0:1.0 DCPOx

Age	Compressive Strength (MPa)		
	#1	#2	Average
1 d	0.4	0.4	0.4
7 d	1.9	1.9	1.9
28 d	1.8	2.2	2.0

Table A.3 Compressive strength test results of 1.0:1.0 MOXC-HCP

Age	Compressive Strength (MPa)			
	#1	#2	#3	Average
4 h	5.4	5.2	5.0	5.2
1 d	8.1	7.3	7.8	7.7
3 d	11.3	10.5	11.1	11.0
7 d	14.1	12.9	12.9	13.3
28 d	16.2	16.9	16.0	16.4

Table A.4 Compressive strength test results of 1.0:1.0 MOXC-DCP

Age	Compressive Strength (MPa)			
	#1	#2	#3	Average
4 h	4.7	3.9	3.7	4.1
1 d	6.6	4.1	5.3	5.3
3 d	7.5	5.8	7.9	7.1
7 d	9.3	8.0	6.4	7.9
28 d	9.3	9.3	10.3	9.6

Table A.5 Compressive strength test results of 1.5:1.0 MOXC-HCP

Age	Compressive Strength (MPa)			
	#1	#2	#3	Average
4 h	3.0	3.2	3.1	3.1
1 d	5.6	5.7	5.5	5.6
3 d	10.8	10.6	10.3	10.6
7 d	12.1	12.3	11.5	12.0
28 d	13.9	15.6	17.4	15.6

Table A.6 Compressive strength test results of 1.5:1.0 MOXC-DCP

Age	Compressive Strength (MPa)			
	#1	#2	#3	Average
4 h	5.2	5.1	5.0	5.1
1 d	5.5	5.7	4.2	6.5
3 d	8.9	8.1	7.5	8.2
7 d	7.7	10.5	8.9	9.0
28 d	11.0	10.2	10.4	10.5

Table A.7 Compressive strength test results of MOXC-HCP with various Ox/MgO

Sample (CP:Ox:MgO)	Comp. Strength (MPa)
1 (1.50:1.00:1.50)	7.80
2 (1.50:1.00:1.00)	6.50
3 (1.50:1.00:0.50)	7.60
4 (1.00:1.00:1.50)	7.00
5 (1.00:1.00:1.00)	8.00
6 (1.00:1.00:0.50)	9.10
7 (1.00:1.50:2.25)	2.90
8 (1.00:1.50:1.50)	2.40
9 (1.00:1.50:0.75)	3.20

Table A.8 Compressive strength test results of 1.0:1.0 MOXC-DCP (w/b = 0.38)

Age	Compressive Strength (MPa)		
	#1	#2	Average
4 h	3.4	3.3	3.4
1 d	5.5	6.3	5.9
7 d	11.2	9.2	10.2
28 d	5.1	7.4	6.3

Table A.9 Compressive strength test results of 1.5:1.0 MOXC-DCP (w/b = 0.36)

Age	Compressive Strength (MPa)		
	#1	#2	Average
4 h	2.4	2.4	2.4
1 d	3.6	4.0	3.8
7 d	8.9	9.0	9.0
28 d	7.1	6.2	6.7

Table A.10 Compressive strength test results of 1.0:1.0 MOXC-HCP (W/B=0.34)
(S/B=2.75)

Age	Compressive Strength (MPa)		
	#1	#2	Average
1 d	4.6	5.1	4.9
7 d	10.3	10.9	10.6
28 d	9.9	8.6	9.3

Table A.11 Compressive strength test results of 1.0:1.0 MOXC-DCP (W/B=0.34)
(S/B=2.75)

Age	Compressive Strength (MPa)		
	#1	#2	Average
1 d	6.1	6.4	6.3
7 d	13.8	13.2	13.5
28 d	9.7	8.8	9.3

Table A.12 Compressive strength test results of 1.5:1.0 MOXC-HCP (W/B=0.38)
(S/B=2.75)

Age	Compressive Strength (MPa)		
	#1	#2	Average
1 d	4.8	4.6	4.7
7 d	10.8	11.3	11.1
28 d	8.0	6.8	7.4

Table A.13 Compressive strength test results of 1.5:1.0 MOXC-DCP (W/B=0.38) (S/B=2.75)

Age	Compressive Strength (MPa)		
	#1	#2	Average
1 d	5.3	5.4	5.4
7 d	12.0	11.8	11.9
28 d	9.0	10.2	9.6

Table A.14 Compressive strength test results of MOXC (W/B=0.49) (S/B=2.75)

Age	Compressive Strength (MPa)		
	#1	#2	Average
1 d	0.8	0.8	0.8
7 d	2.0	2.3	2.2
28 d	1.4	1.4	1.4

Table A.15 Compressive strength test results of MOXC (W/B=0.39) (S/B=2.75)

Age	Compressive Strength (MPa)		
	#1	#2	Average
1 d	1.6	1.5	1.6
7 d	4.2	4.2	4.2
28 d	2.8	3.1	2.9

Table A.16 Compressive strength test results of 1.0:1.5 MOXC-HCP + 5% BA

Age	Compressive Strength (MPa)		
	#1	#2	Average
4 h	2.7	3.5	3.1
1 d	3.8	4.3	4.1
7 d	4.4	5.1	4.7
28 d	5.0	6.2	5.6

Table A.17 Compressive strength test results of 1.0:1.5 MOXC-DCP + 5 % BA

Age	Compressive Strength (MPa)		
	#1	#2	Average
4 h	2.8	2.6	2.7
1 d	3.6	3.8	3.7
7 d	3.8	4.7	4.3
28 d	4.3	5.6	5.0

Table A.18 Compressive strength test results of 1.0:1.0 MOXC-HCP + 5 % BA

Age	Compressive Strength (MPa)		
	#1	#2	Average
4 h	3.0	2.8	2.9
1 d	3.3	4.4	3.9
7 d	7.0	7.2	7.1
28 d	7.7	8.4	8.1

Table A.19 Compressive strength test results of 1.0:1.0 MOXC-DCP + 5 % BA

Age	Compressive Strength (MPa)		
	#1	#2	Average
4 h	2.8	3.3	3.1
1 d	3.6	4.6	4.1
7 d	9.0	6.9	8.0
28 d	8.8	8.6	8.7

Table A.20 Compressive strength test results of 1.5:1.0 MOXC-HCP + 5 % BA

Age	Compressive Strength (MPa)		
	#1	#2	Average
4 h	1.4	1.4	1.4
1 d	3.9	3.8	3.9
7 d	6.7	7.1	6.9
28 d	6.7	6.5	6.6

Table A.21 Compressive strength test results of 1.5:1.0 MOXC-DCP + 5 % BA

Age	Compressive Strength (MPa)		
	#1	#2	Average
4 h	1.0	0.2	0.6
1 d	4.6	4.3	4.5
7 d	7.0	7.2	7.1
28 d	6.1	7.8	7.0

Table A.22 Compressive strength test results of 1.0:1.0 MOXC-HCP + 5 % SF

Age	Compressive Strength (MPa)		
	#1	#2	Average
1 d	4.1	4.3	4.2
7 d	8.8	8.6	8.7
28 d	5.4	6.2	5.8

Table A.23 Compressive strength test results of 1.0:1.0 MOXC-DCP + 5 % SF

Age	Compressive Strength (MPa)		
	#1	#2	Average
1 d	4.7	4.2	4.5
7 d	8.6	9.0	8.8
28 d	6.3	5.9	6.1

Table A.24 Compressive strength test results of 1.0:1.0 MOXC-HCP + 15 % FA

Age	Compressive Strength (MPa)		
	#1	#2	Average
1 d	3.5	3.6	3.6
7 d	6.6	7.3	7.0
28 d	5.5	4.9	5.2

Table A.25 Compressive strength test results of 1.0:1.0 MOXC-DCP + 15 % FA

Age	Compressive Strength (MPa)		
	#1	#2	Average
1 d	4.1	3.7	3.9
7 d	7.7	8.6	8.2
28 d	5.4	4.8	5.1