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Investigation of the mechanical properties of magnesium chloride on magnesium oxide improved kaolin clay

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Abstract

In our study, samples were prepared by mixing 2%, 4%, and 6% MgO doses with the dry weight of kaolin-type low-plastic clay. In each MgO dose, 1% and 2% of the soil weight, respectively, $MgCl_2$ chemicals were added, and all samples were mixed at the optimum water content ratio (16.2%). All components were mixed with a planetary mixer for 10 minutes until homogeneous, and then the mixture was poured to have 25 blows for 5 layers. All samples were cured under room conditions for 3–10 days to be tested on the Unconfined Compression Test. From the results, it was observed that the undrained shear strength of the sample increased as the percentages of $MgCl_2$ and MgO rose. It can be said that the interaction between MgO and $MgCl_2$ contributes to the cementation of the clay, and sorel cement plays a role in the mechanical strengthening of kaolin clay based on its effect on strength development. Extending the curing time also developed the mechanical properties of kaolin clay and improved the hardness of the samples by increasing the elastic modulus. In this way, early failures were attained at early strains, and the ductility of the samples increased. We finally saw that the mixture of MgO and $MgCl_2$ worked well as a building material for kaolin clay. The study also tried to get rid of some of the problems that come up with filling materials used in geotechnical engineering and shoring projects, like swelling, shrinkage, and low mechanical properties.

***Keywords*:** magnesium oxide, magnesium chloride, kaolinite clay, Harvard compaction test.

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1. Introduction

As a result of the rapid development of urban life, people have had to build structures such as highways, bridges, tunnels, and high-rise buildings in order to live in better conditions. Problems such as bearing capacity, liquefaction, and settlement arise in the building grounds [1].

Clay tends to swell and shrink under long- and short-term conditions in various dam, road, bridge, tunnel, shoring, and housing projects in geotechnical engineering. Kaolin clay has low plasticity, a low shrinkage tendency, low activity, and low cracking intensity compared to other clays (smectite and montmorillonite). However, these clays can be subjected to high volumetric changes in a humid environment. As a result of the interaction of water penetrating into the voids of the soil with the grains, the particulate organization of kaolin clay is disrupted, as a result of which it is included in the loess-like collapsible soil class [2].

Ground improvement systems have been developing from the past to the present. Today, materials such as cement and lime are used in ground improvement systems. However, in order to reduce carbon emissions due to global warming, technology has developed alternative materials and energy sources in this direction. There are various traditional and modern methods for treating such problematic soils in the literature. Traditional methods include deep mixing, vibro-flotation, freeze-thaw, and dynamic compaction, while modern methods include colloidal silicate, microfine cement, and solidification with microbiological solutions [3]. Magnesium oxide (MgO), which has recently appeared in the literature as an alternative to traditional chemicals used in soil improvement, is used in many fields, from the construction industry to the medical field, from the recycling sector to food.

Magnesium oxysulfate, or sorel cement, is obtained when MgO (magnesium oxide), a white hygroscopic solid mineral naturally occurring in the form of periclase, and $MgCl_2$ (magnesium chloride), a colorless inorganic compound in the form of a crystalline anhydrous solid or hexahydrate from typical ionic halides that dissolve well in water, are mixed in various proportions [4]. In this study, MgO and $MgCl_2$ were used to improve kaolin clay.

Sorel cement is the result of a brine solution of magnesium chloride ($MgCl_2$) in a ratio of H_2O, $MgCl_2$, and MgO mixed with magnesium oxide (MgO), and the chemical reaction required for its production can take many forms, forming a 5-phase hydrated magnesium oxychloride product, as shown in (1) [5].

$$5\ MgO + MgCl_2 + 13\ H_2O \rightarrow 5\ Mg\ (OH)_2 \cdot MgCl_2 \cdot 8\ H_2O \tag{1}$$

However, the stability of magnesium chloride phases decreases after prolonged exposure to water. This instability of the binding or bonding phases leads to the leaching of magnesium chloride or magnesium hydroxide [6]. According to the proportion of reactants, four main phases can be identified in the $MgO\text{-}MgCl_2\text{-}H_2O$ system. $3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ (Phase 3, MOC 3-1-8) and $5Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ (Phase 5, MOC 5-1-8) are two hydrate phases that can be made at room temperature and stay stable until they react with CO_2 or H_2O. These two phases are the main products responsible for the hardness and strength of magnesium oxide cement (MOC) [7]. The desired mechanical properties are a result of the needle-like pointed structure of both Phase 3 and Phase 5 [8]. The needles in the structure can be described as coiled-pipe strands that interlock together in rapid growth, resulting in a very rigid structure that becomes denser due to the intergrowth of the spikes when there is no space for growth [9]. The remaining two phases, $2Mg(OH)_2{\cdot}MgCl_2{\cdot}4H_2O$ (Phase 2, MOC 2-1-4) and $9Mg(OH)_2{\cdot}MgCl_2{\cdot}5H_2O$ (Phase 9, MOC 9-1-5), can be prepared and are also stable at about 100^{o}C [8, 10, 11]. During the complex reactions in the production of sorel cement, there is a gradual decrease in the amount of MgO over time, while the amount of phase-5 crystals in sorel cement increases. Within 48 hours from the start, 89% of Phase 5 crystals are formed, while after 96 hours, MgO formation is less than 5% [12].

In the construction industry, especially in cladding works, nano-MgO additives are used with Sorel cement (magnesium chloride cement) as a binder. Sorel cement is preferred over Portland cement for its many superior properties, such as high fire resistance, low thermal conductivity, and strong bonding with inorganic and organic aggregates [6]. The physical, chemical, and mechanical properties of Portland and Sorel cement are compared in Table 1. Sorel cement has a minimum of 87% magnesium oxide, while Portland cement has a maximum of 5%. Physically, the setting start and end times for Portland cement are a minimum of 60 minutes and a maximum of 10 hours, respectively, while the start and end times for Sorel cement are 3-6 hours and 7–15 hours, respectively. While SO_3 and Cl are present in trace amounts in Portland cement, sorel cement is generally free of these substances. In terms of compressive strength, Portland Cement has 7 and 28-day compressive strengths of 21 MPa and 32.5 MPa, respectively, while Sorel Cement has only 7 and 28-day tensile strengths of 7 MPa and 10.5 MPa, respectively [13].

Additives play a significant role in the development of sorel cement. These additives can change the physical and mechanical properties of the cement and have a significant effect on its compressive strength and water resistance. For example, phosphoric acid (H_3PO_4), soluble phosphates, alkali metals, ferric, aluminum, or ammonium (NaH_2PO_4, $Mg_2(PO_4)_3$, Na_3PO_4, or NaH_2PO_4) have been used to increase the water resistance of concrete. According to the literature, a small amount of phosphorus should be added to increase the water resistance of sorel-based concrete. The effects of these additives are based on increasing the stability of Phase 5 crystals in water solutions. Granite chips are used to increase the compressive strength. Granite chips have high durability and resistance to scratches, moisture, cracks, spalling, and both high and low temperatures. Therefore, with the addition of granite chips, the concrete has greater plasticity and mechanical properties. The addition of granite fragments also affects the corrosion processes in this material.

Magnesium oxide, one of the main ingredients of sorel cement, significantly improves the physical and mechanical properties of soil when introduced to the soil under appropriate curing conditions and in the right way. According to related studies, when 6% nanomagnesium oxide is mixed with clay soils, there is a significant increase in engineering properties. In another study using 1.0% nanomagnesium oxide on sandy clay, it was concluded that at the end of a 1-day carbonization period (exposure of MgO hydration products to carbon dioxide), the compressive strength of the soil is close to the 28-day strength of cement-improved soil.

In addition, China accounts for 62.06% of the world’s annual magnesium oxide production (excluding US production), with an annual production of 18 million tons in 2021. Turkey produced 1.9 million tons of magnesium ore in 2021 [14]. Therefore, the mechanical and physical healing properties of sorel cement, which has high compressive strengths formed with magnesium oxide and magnesium chloride, on kaolin clay, which has the potential to pose a problem in geotechnical engineering, have been a matter of curiosity and have been investigated in this study.

2. Materials and method

In our study, a sorel cement-based chemical mixture, which is a combination of dead-burnt type magnesium oxide (MgO) with a purity of 98% and magnesium chloride ($MgCl_2$), a colorless inorganic compound that has binding properties and can be cemented, and kaolin-type low-plasticity clay, were used. General properties of the ground are presented in Table 1. Necessary data regarding the chemicals used (MgO-$MgCl_2$) are given in Tables 2 and 3.

As a result of the physical tests of soils, it was determined that kaolin clay has both low plasticity and activity. In this type of clay, problems such as low bearing capacity and excessive settlement due to its molecular structure may occur due to sudden increases in water content. Therefore, it is realized that such soils can be used in situ or as filling material in various construction projects if their engineering properties are improved. At this point, one of the main goals of this study is to find ways to stop these kinds of problems from happening and to make the soil harder to work with by using the highly binding crystals that are made when magnesium oxide, magnesium chloride, and water react.

Prior to sample preparation, preliminary studies were carried out to determine the optimum water content of kaolin clay. In this sense, a miniature Harvard compaction test was performed on kaolin clay without adding any additives, and it was compressed in 5 layers with 25 blows at various water contents; thus, the optimum water content was determined for each MgO dose level. As a result, the optimum water content for each MgO dose level was found to be 16.2%.

Soil Properties	Results
Maximum Dry Density (g/cm^3)	1.71
Specific Gravity (G_s)	2.63
Optimum Water Content (%)	16.2
Liquid Limit (%)	28
Plastic Limit	21
USCS Soil Classification	CL

Table 1. Pyshical properties of kaolin clay

Pyshical and Chemical Properties	Results
MgO (%)	88.19
SiO_2 (%)	5.28
CaO (%)	2.61
Fe_2O_3 (%)	0.68
Loss of Ignition (%)	3.04
Specific Surface Area (m^{2}/g)	18.33
Density (g/cm^3)	3.58
Colour	White
Average Particle Size (µ)	90/100
Melting Point (^{0}C)	2800
Boiling Point (^{0}C)	3600
Type	Dead-Burnt
Calcination Temperature Range (^{0}C)	1000-1500

Table 2. General properties of magnesium oxide

Chemical and Pyshical Properties	Results
Molar Mass (g/mol)	95.21
Colour and Appearance	White(colorless)
Boiling Point (^{0}C)	412
Melting Point (^{0}C)	714
Solubility (g/100ml)	54.3
Density (g/cm^3)	2.32
pH	>7

Table 3. General properties of magnesium chloride ($MgCl_2$)

Subsequently, samples were prepared by mixing 2%, 4%, and 6% MgO doses into the dry weight of kaolin-type low-plastic clay. For each MgO degree, $MgCl_2$ chemicals were added at 1% and 2% of the soil weight, respectively, and all samples were prepared at this optimum water percentage (16.2%). All components were mixed with a Thermomac mechanical mixer for 10 minutes until they became homogeneous. Then, the mixture was compressed into 5 layers, 25 blows per layer, in a mold with a diameter of 38 mm and a height of 76 mm, and subjected to the miniature Harvard test.

After waiting in the mold for a certain period of time (1-2 hours), the samples were removed from the mold and wrapped with stretch foil to prevent water loss. All samples were cured at 23°C and 41% humidity for periods of 3 to 10 days. After the necessary physical measurements and calibrations were made, all samples were subjected to an unconfined compression test, and load-deformation data were obtained with various corrections.

3. Results and discussion

The samples prepared under the methods and conditions specified in our study were subjected to unconfined compression tests at the end of 3 and 10 days of curing periods. Those experiments were carried out under strain-controlled conditions at a speed of 1.27 mm/min, and the obtained unconfined compressive strength results are shown in Figure 1. Abbreviations for the samples used in the graphics and the percentage distribution of the chemicals in these samples are presented in Table 4.

Abbreviations	**Percentages (%)**	**$q_{u,max}$ (kPA) (3 days)**	**$q_{u,max}$ (kPA) (10 days)**
N1O	%2 MgO	157	380
N1A	%2 MgO + %1 $MgCl_2$	138	410
N1B	%2 MgO + %2 $MgCl_2$	142	190
N2O	%4 MgO	160	380
N2A	%4 MgO + %1 $MgCl_2$	165	310
N2B	%4 MgO + %2 $MgCl_2$	271	285
N3O	%6 MgO	462	410
N3A	%6 MgO + %1 $MgCl_2$	300	395
N3B	%6 MgO + %2 $MgCl_2$	280	618

Table 4. Sample name and contents

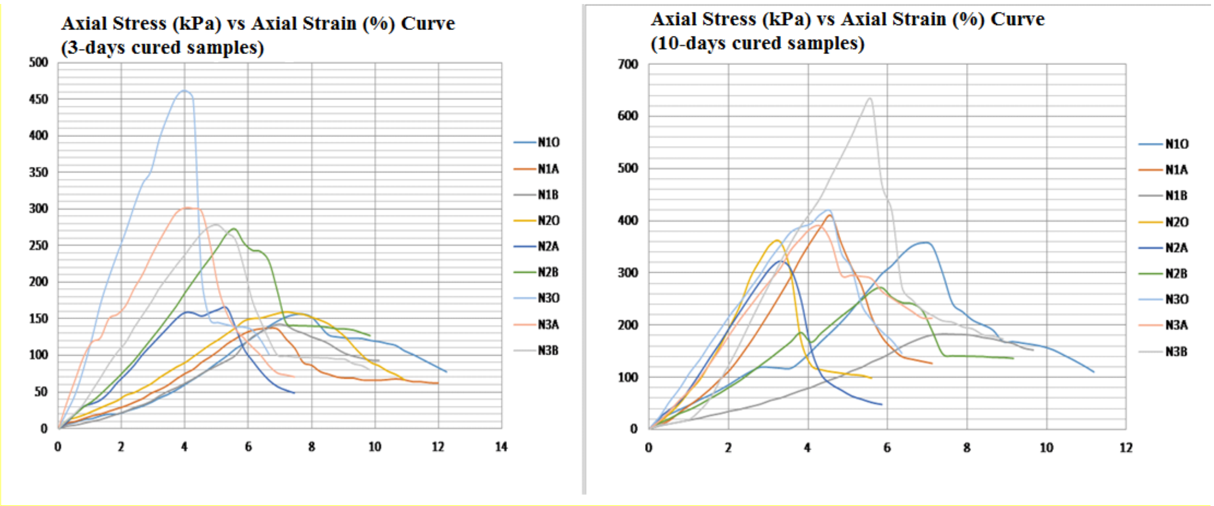

Figure 1. The stress-strain graphs for both 3 and 10 cured samples

Even though the amount of magnesium chloride has a limited effect on the mechanical strength of the samples under short-cure conditions (3 days), this effect increases under long-cure conditions (10 days). This is because the reaction between MgO and $MgCl_2$ makes a lot of Phase-3 and Phase-5 crystals from different hydrate phases in 3 days. But in 10 days, the needle-like structures of these crystals connect with each other and make room for growth, which leads to even more growth. Otherwise, it can be shown that bending these structures inward creates spiral-tube wires with a very rigid structure.

It is obtained that the strength increase of N3Bs up to 300% may be due to Phase-9 crystals formed after 3 days [8, 9]. In samples prepared with only MgO, the mechanical increase was highest in the sample with a low MgO dose under a short cure time, while the strength of samples containing low dose MgO decreased under a long cure time, and the strength of samples containing high dose MgO increased. The strengths of samples containing only MgO were found to be in the range of 300–400 kPa. Based on this, the fact that the curing time and MgO dose do not have much effect on the strength increase in samples containing only MgO may be due to the fact that the soil used is kaolin clay with low plasticity.

Since the magnesium hydroxide products obtained as a result of MgO hydration cannot interact sufficiently with the clay grains, it is possible that complex magnesium hydrate molecules will not be formed and will not increase their strength to a very high degree. In this sense, the highest strength was obtained in the N_3B sample (MgO 2% + $MgCl_2$ 2%) under 10-day curing conditions. As a result, the MgO-$MgCl_2$ complex, which can form sorel cement at appropriate rates, improved the physical and mechanical behavior of kaolin clay, and it was observed that the undrained shear strength of the clay increased as the dose rates increased.

4. Conclusion

The interaction between MgO and $MgCl_2$ contributed to the cementation of clay through the formation of Sorel Cement and played a role in the mechanical strengthening of the ground. Extending the curing time also accelerated the increase in the undrained shear strength of kaolin clay and contributed to the brittleness of the samples by increasing the Elastic Modulus. In this way, cracks were observed in the cemented samples at early strains, where high strengths were reached, and the sample brittleness increased. As a result, the positive effects of the mixture of MgO and $MgCl_2$ used as building materials on kaolin clay were observed, and the weaknesses such as swelling, shrinkage and low mechanical properties, which pose problems in filling materials and shoring projects used in geotechnical engineering, were tried to be eliminated with this study.

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