



EFFECT OF TiO₂ ON SETTING TIMES, WATER RESISTANCE AND COMPRESSIVE STRENGTH OF MAGNESIUM OXYSULFATE

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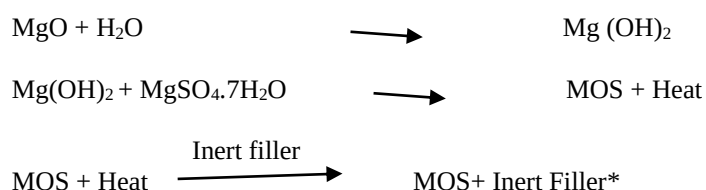
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Abstract : Magnesium oxysulfate cement (MOS) is a magnesia-based, air-dried material that is energy efficient and environmentally friendly. Non-hydraulic MOS has numerous advantages over conventional Portland cement. MOS is a very good binder, having excellent aesthetic value due to its white color, easy-to-prepare and cost-effective product. Despite its numerous advantages, its large-scale commercial application is not feasible due to its low early strength and poor moisture resistance. In this experiment, TiO₂ was used as an additive with MOS to overcome these drawbacks. The experimental results showed that titanium dioxide reduced setting times and significantly enhanced compressive strength and water resistance due to improved particle packing, reduced porosity, and enhanced hydration kinetics.

Keywords: Magnesium oxysulfate cement, Magnesia. Magnesium sulfate, Titanium dioxide, Compressive strength, Water resistance, etc.

I. INTRODUCTION

An inorganic binder called magnesium oxysulfate cement (MOS) was discovered in 1867 by French chemist S. T. Sorel [1]. This non-hydraulic cement is produced by mixing a concentrated solution of magnesium sulfate (MgSO₄·7H₂O) with powdered magnesium oxide (MgO) [2]. Heat is produced as a result of this exothermic process, resulting in weakening the cement and decreasing its ability to withstand moisture, making the finished product unsound. To overcome this problem, the matrix makes use of inert filler. Inert filler absorbs heat using a three-body collision mechanism rather than participating in the cementing reaction [3]. In this study, dolomite powder was utilized as an inert filler to lessen the cement's thermal shocks [4].



MOS has attracted attention for its rapid setting, high early strength, and environmental benefits, including lower CO₂ emissions during production [5, 6]. Nevertheless, moisture sensitivity and susceptibility of MOS towards sulfate leaching can undermine long-term performance [7,8]. Enhancing its durability without compromising mechanical properties is critical for broader adoption. Improving the performance of construction materials is crucial to meeting the growing demands for sustainable, durable, and high-performance infrastructure. MOS has drawn attention in recent years as an environmentally friendlier alternative to ordinary Portland cement, owing to its lower carbon footprint, rapid setting, and good bonding properties [9,10]. However, MOS still suffers from relatively high-water sensitivity and limited long-term strength development, which restrict its wider industrial adoption [11–13].

MOS offers many desirable mechanical and engineering characteristics, but its broader adoption is restricted by poor resistance to water, which causes a marked decline in strength when the hardened material is immersed or exposed to moisture over time [14,15]. High moisture uptake also leads to excessive dimensional changes, further undermining structural integrity. Compressive strength is primarily determined by the type, relative content, and microstructure of hydration products (xMg(OH)₂·yMgSO₄·zH₂O phases), which is significantly impacted by the molar ratio of MgO, MgSO₄, and H₂O, as well as temperature. The following magnesium oxysulfate phases are present in the magnesium oxide-magnesium sulfate-water (MgO-MgSO₄-H₂O) system at temperatures between 30°C to 120°C: 3Mg(OH)₂·MgSO₄·8H₂O (3·1·8 phase), 5Mg(OH)₂·MgSO₄·8H₂O (5·1·8 phase) 5Mg(OH)₂·MgSO₄·3H₂O (5·1·3 phase) or 5Mg(OH)₂·MgSO₄·2H₂O (5·1·2 phase), Mg(OH)₂·2MgSO₄·3H₂O (1·2·3 phase) and Mg(OH)₂·MgSO₄·5H₂O (1·1·5 phase) [16-18]. Wang et al. studied that quartz (Q) improves the early and later

mechanical strength of MOS cement by accelerating hydration and refining pore structure [19]. Optimal performance is achieved at 15 wt.% Q, beyond which the enhancement effect declines. Zhang et al. study shows that combining mineral admixtures like L-FA, G-BS, and SF enhances water resistance and compressive strength of magnesium oxysulfate cement by optimizing hydration products and pore structure, while H-FA and SF increase hydration rate but do not improve water resistance due to less pore refinement [20].

In addition, trace amounts of free lime (CaO) in the raw materials react vigorously with water to form calcium hydroxide, releasing heat that vaporizes moisture and induces internal stresses and microcracking; these defects exacerbate water ingress and reduce both durability and compressive strength [21]. Lee et al. studied that TiO₂ nanoparticles accelerate early hydration and improve compressive strength in cement composites, but may reduce surface microhardness depending on dosage and dispersibility [22]. A significant purpose for additives may be to alter the characteristics of oxysulfate cement. TiO₂ is being tested in this study as an additive to enhance the properties of magnesium oxysulfate cement.

II. EXPERIMENTAL

II.1. MATERIALS

The study's raw materials included dolomite powder as an inert filler, magnesium sulfate heptahydrate, lightly calcined magnesium oxide (MgO), and TiO₂.

- Magnesium oxide [23]: Commercial grade magnesia (lightly calcined) was used in the synthesis of MOS cement. The analysis of magnesite powder is SiO₂=4.51%, CaO=2.80%, MgO=89.70%, Fe₂O₃=0.12%, Al₂O₃=0.98%, LOI=3.42%.
- Magnesium sulfate [24]: Technical grade magnesium sulfate was used in the formation of MOS. The chemical composition of Epsom salt is MgSO₄ = 96.80%, Fe₂O₃=0.02%, Al₂O₃=0.07%, CaO=1.40%, Acid insoluble = 0.11%, moisture = 0.98%.
- Dolomite [25]: Commercial grade dolomite was used in the study. To prepare MOS, locally available dolomite powder was utilized as an inert filler. The chemical composition of Dolomite is SiO₂ =8.45%, CaO=36.68%, MgO=11.80%, Fe₂O₃=0.73%, Al₂O₃=0.13%, LOI=41.80%, CaCO₃=65.50%, MgCO₃ =24.78% Brightness=89.20%, Whiteness=92.60%.
- Titanium dioxide (TiO₂): It was collected from the store of the Chemistry Department of Rajasthan University.

II.2. Sample Preparation

The effect of TiO₂ was performed on the best composition of MOS [4]. Therefore, magnesium oxide and dolomite were mixed in a 1:1 ratio to produce a dry mix. 5%, 10%, 15%, and 20% of titanium dioxide was mixed with a dry mix in different samples. A proper amount of magnesium sulfate solution (25°Be) was added to the dry mix to prepare a workable consistency paste of MOS. To find out the effect of TiO₂ in the properties of MOS, the following experiments were carried out. All the experiments were repeated three times, and then the average is reported. The samples of the experiments were prepared according to Table 1.

Table- 1: Samples of the experiment

Sample No.	Composition of the dry-mix	
	MgO : Dolomite	% of TiO ₂
M1	1:1	0
T1	1:1	5
T2	1:1	10
T3	1:1	15
T4	1:1	20

III. METHODS

III.1. Setting time investigations: The effect of TiO₂ on the setting characteristics of magnesium oxysulfate cement was tested by admixing TiO₂ in various proportions (5%, 10%, 15% & 20%) in the dry mix. Initial and final setting times were calculated with the help of the Vicat needle instrument [26]. Figure 1 shows the results.



Fig. 1: Setting time blocks and moulds

III.2. Water resistance investigations: Water resistance is the inverse of the water absorption property [27]. The impact of TiO₂ on the soundness of the product was evaluated using a steam test. To conduct this assessment, all setting time blocks containing varying proportions of TiO₂ were cured under identical conditions for a period of 60 days. Following the curing period, the samples were placed in a closed steam chamber and exposed to boiling water for a minimum of 30 hours. The relative resistance to moisture absorption was monitored over time. Since moisture ingress negatively affects soundness, an inverse relationship was observed between the two. The outcomes of this study are summarized in Table 4.

III.3. Compressive strength investigations: To evaluate the effect of TiO_2 on the compressive strength of MOS, standard cubes measuring 70.6 mm on each side (equivalent to a surface area of 50 cm^2) were prepared using pastes with varying TiO_2 content. After curing for 30 days under consistent conditions, the samples were tested for compressive strength using a compressive strength testing machine. The results are represented in Table 5.

III.4. Linear changes: Standard blocks (200 mm $\times$ 25 mm $\times$ 25 mm) were prepared using wet mixes with varying amounts of TiO_2 to assess its effect on the linear changes in MOS. The initial lengths of the trial beams were measured after 24 hours using a micrometer. After 28 days of curing under the identical conditions, their final lengths were recorded. The difference between the two measurements indicated the linear dimensional change (either expansion or shrinkage). A smaller difference implies better dimensional stability and soundness of the material. The findings are presented in Table 6.

III.5. Spectral Analysis: FT-IR was performed on M1 and T1 (best modified cement sample with TiO_2). The results of FT-IR are shown in Fig. 4.

IV. RESULTS AND DISCUSSION

IV.1. Setting time analysis: The effect of TiO_2 on setting characteristics of MOS is represented in Fig. 2. M1 sample contains half amount of dolomite powder; hence, the heat amount of the exothermic reaction is absorbed by the inert filler dolomite powder via a three-body collision mechanism. It was observed that as the amount of TiO_2 increases, the initial as well as the final setting time of MOS also decreases. The early hydration process is accelerated by TiO_2 which shortens the setting time of cement-based materials. Despite partially replacing cement, the presence of TiO_2 provides additional nucleation sites, leading to faster formation of hydration products and thereby shortening both initial and final setting times.

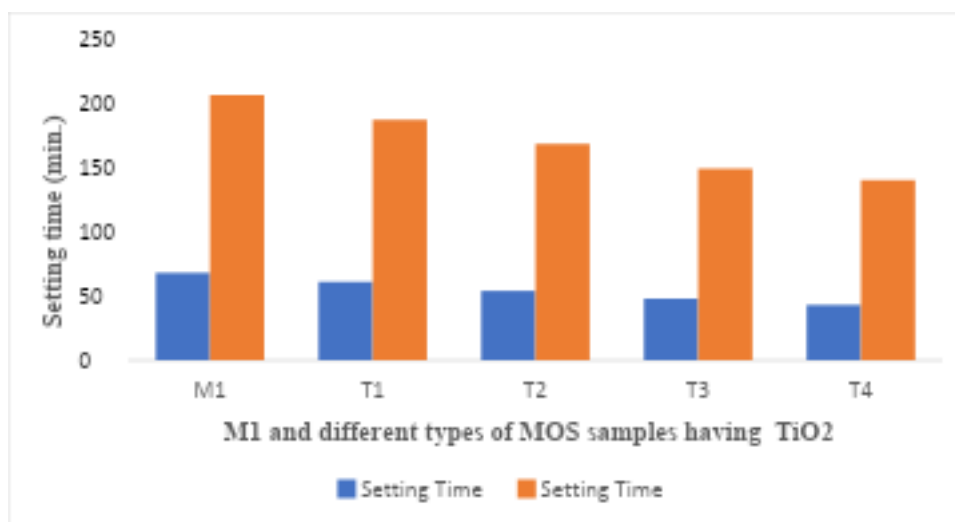


Fig. 2: Initial and Final setting times of different types of MOS samples.

IV.2. Water resistance investigations: The results of water resistance investigations after incorporation of TiO_2 in MOS are represented in Table 2. It was observed that TiO_2 significantly affects the water resistance of MOS. In the M1 sample, dolomite absorbs the excess heat, leaving a crack-free structure. It was observed that TiO_2 positively affects the water resistance of MOS. TiO_2 fills micro-voids, reduces capillary porosity, and promotes formation of a more compact and less permeable microstructure.

Table 2: Effect of TiO_2 on water resistance property of MOS

Sample	% of TiO_2 in dry-mix Composition	Cement blocks were kept in boiling water for					
		0-5 hrs.	5-10 hrs.	10-15 hrs.	15-20 hrs.	20-25 hrs.	25-30 hrs.
M1	0%		-	-	-	-	-
T1	5%	-	-	-	-	-	-
T2	10%	-	-	-	-	-	-
T3	15%	-	-	-	-	-	-
T4	20%	-	-	-	-	-	-

- = Not cracked

IV.3. Compressive strength analysis: Fig. 3 shows the effect of TiO_2 on the compressive strength of MOS. It is noticed that the compressive strength is enhanced by increasing the amount of additive. The highest compressive strength was observed for the T1 sample (5% TiO_2), which is 52.20% higher than the M1 sample. The strength of T2 to T4 samples was observed in continuously decreasing trends. TiO_2 increases compressive strength at lower contents (5%) because of its filler action, which enhances particle packing, decreases porosity, and encourages the formation of dense hydration products. However, strength starts to decrease at higher dosages (10–20%) because of poor dispersion and particle agglomeration, which produce weak zones and prevent adequate hydration.

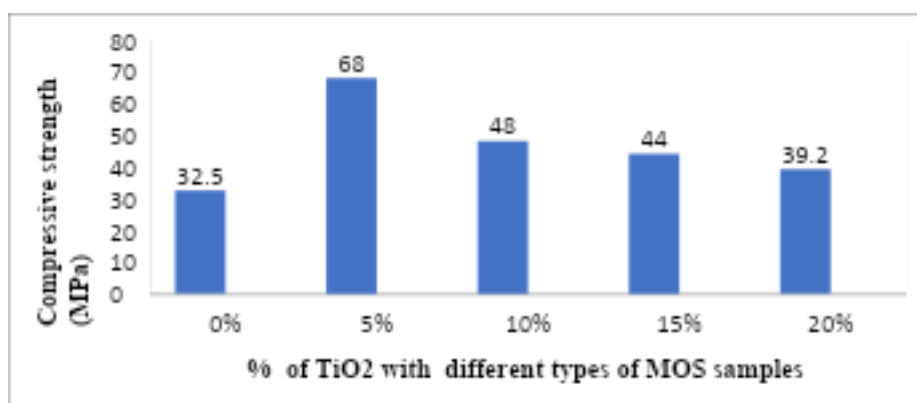


Fig. 3: Compressive strength of different type of MOS samples.

IV.4. Linear changes: The effect of TiO₂ on linear changes is shown in Table 3. The linear dimensional stability of MOS was influenced by the addition of TiO₂, particularly in terms of expansion and shrinkage behavior. In unmodified MOS, slight linear shrinkage occurs during the initial setting and drying stages due to loss of free water and crystallization of hydration products such as the 5-phase [5Mg(OH)₂·MgSO₄·7H₂O]. Upon incorporation of TiO₂ (in equal amounts up to 10% by binder weight), a noticeable reduction in shrinkage is observed. Overall, the combined use of TiO₂ enhances the dimensional stability of MOS by chemically reinforcing the matrix and reducing shrinkage-related deformations. At very high dosages (>10–15%), poor dispersion can lead to localized stress and slightly increased microcracking or irregular shrinkage.

Table 3: Effect of TiO₂ on linear changes of MOS

Samples	% of TiO ₂ in dry-mix Composition	Length of beam (mm)		Change in length (in mm)
		Initial	Final	
M1	0%	200.0	199.985	0.015
T1	5%	200.0	199.991	0.009
T2	10%	200.0	199.989	0.011
T3	15%	200.0	199.986	0.014
T4	20%	200.0	199.982	0.018

IV.5. FT-IR analysis: The spectra of M1 and T1 cement samples are shown in Fig. 4. It showed a sharp and more intense peak at the 3690-3700 cm⁻¹ range. With 5% TiO₂, this peak becomes sharper and more intense, suggesting improved hydration and greater formation of the 517 phases [5Mg(OH)₂·MgSO₄·7H₂O]. Similarly, the sulfate vibration peak at ~1070 cm⁻¹ shows increased intensity in the 5% TiO₂ sample, indicating denser sulfate phase formation. The carbonate peaks at 1410-1450 cm⁻¹ and ~870 cm⁻¹, visible in the M1 sample due to atmospheric carbonation, are significantly reduced in the T1 sample, suggesting a denser, less permeable matrix. No new peaks associated with Ti–O bonding are observed, confirming that TiO₂ primarily acts as a physical filler and hydration promoter rather than participating in chemical bonding.

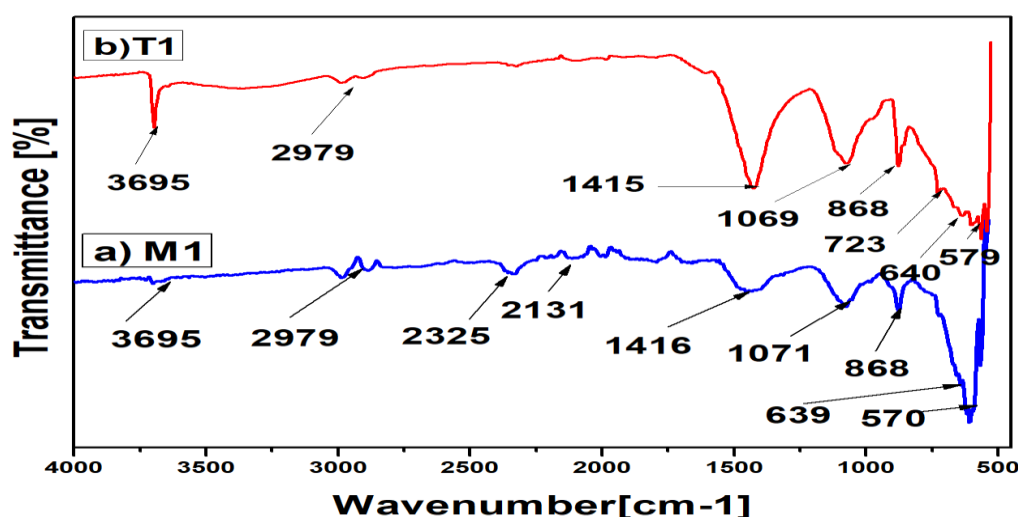


Fig. 4: Combine FT-IR spectra of M1 and T1

V. CONCLUSION

The incorporation of TiO₂ into magnesium oxysulfate cement enhances its physical and structural properties when used in optimal amounts. At 5% by weight, TiO₂ significantly improves compressive strength by refining the pore structure and promoting the formation of dense hydration phases, particularly the 517 phases. FT-IR analysis confirms enhanced hydration through sharper O–H and SO₄²⁻ peaks, while reduced carbonate signals indicate improved matrix densification and reduced porosity. Overall, TiO₂ is an effective additive to improve the strength, water resistance, and microstructure of MOS cement.

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COMPETING INTERESTS

The authors have no competing interests to disclose.

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