**The Impact of Accelerators on Compressive Strength and Setting Time of Agro-Industrial Ash Blended Cement for Achieving High Early Strength in 3D Concrete Printing**

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**Abstract**

The advancement of 3D concrete printing (3DCP) technology has revolutionized the construction of complex structures by enhancing efficiency and reducing costs. However, achieving rapid early setting and strength development in 3DCP remains a significant challenge. This study investigates the effects of various accelerators on the setting time of ordinary pozzolana cement and agro-industrial ash blended cement. Accelerators used in this study include Calcium Nitrite (CN), Calcium Chloride (CaCl₂), Sodium Hydroxide (NaOH), Triisopropanolamine (TIPA) and Triethanolamine (TEA). The results indicate that the use of these accelerators significantly decreases setting time and increases compressive strength. These findings can be utilized to optimize mix design parameters for 3DCP, facilitating the rapid curing of robust structures. Consequently, this research contributes to the practical application and broader acceptance of 3DCP technology within the construction industry.

**Introduction**

The development of 3DCP technology has completely changed the construction profession by opening up new opportunities for the cost-effective and efficient building of complex structures. [1]. Innovative technology has changed the construction of complex buildings by exchanging computer-guided concrete layering for traditional formwork. Even with recent advancements, achieving rapid strength gain in 3D-printed concrete remains a significant challenge, limiting its effectiveness for fast-track construction and timely project completion. [2,3]. With the objective to overcome this challenge and enhance the achievement of early strength in 3DPC, this study explores the impact of accelerators on the compressive strength and setting time of cement and agro-industrial ash blended cement (bagasse ash, fly ash), aiming to enhance early strength properties crucial for 3D printing applications. Accelerators are chemical admixtures that significantly reduce the setting time and increase the early strength of concrete. This study investigates how different accelerators, such as tri-isopropanolamine (TIPA), calcium nitrite (CN), sodium hydroxide (NaOH), triethanolamine (TEA), and calcium chloride (CaCl₂), along with their varying dosages, impact the core properties of 3D-printed concrete (3DPCExperimental tests were carried out on the 3DPC mix to assess the impact of these accelerators.

In this study, the concrete mix was mixed with several accelerators at varying doses. To determine the effect of accelerators on these properties, observations were taken of the setting time, which shows how long it takes for the concrete to reach a stable state, and the compressive strength, which shows how effectively it can withstand loads. The outcomes of this investigation show that adding accelerators to 3D-printed concrete increases its compressive strength and drastically shortens its setting time. These results suggest that accelerators may accelerate the early strength in rise of 3D-printed concrete, hence resolving an important challenge related to this construction technique. Accelerator type and dosage optimisation is one way to optimise mix design parameters and achieve fast curing of long-lasting 3D printing concrete structures. The findings of this study have a direct influence on the practical use and broader adoption of 3D concrete printing (3DCP) technology within the construction industry. Incorporating accelerators to improve early strength in 3D-printed concrete increases construction efficiency, shortens project durations, and reduces costs . [4]. The results of this study help in the optimisation of mixed design parameters and offer practitioners and engineers valuable information about how to apply 3D concrete printing technology.

**2. Experimental investigation**

*2.1. Materials*

To enhance early strength development for experimental purposes, various mix proportions of the binder, including OPC-43 (ASTM C150), bagasse ashash (BA) and fly ash (FA)were utilized for experimental purpose. The cement's specific surface area, measured by the Blaine air permeability method, is 2320 cm²/g. In the soundness test, its expansion was determined to be 7.5 mm. Bagasse ash obtained from industries was not fully burnt, so it was incinerated in an oven at 650ºC for 2 hours to achieve a finer particle size of up to 100 microns.” Chemical compositions of Bagasse Ash and Fly Ash cement shown in Table-1. “The Class-F fly ash (as per ASTM C 618).” were mixed with NaOH and Na.SiO3 alkali activator (molarity 8M–12M) The fine aggregate used was passed through a 2.36 mm sieve with a dry specific gravity of 2.62 and a fineness modulus of 2.4 (conforming to ASTM C128 and ASTM C136). The fine aggregate’s physical properties are presented in Table 2. In this study, the alkaline activator solution was prepared by dissolving sodium hydroxide (NaOH) pellets in distilled water and stirring until completely dissolved. The NaOH solutions, with molarities of 8M, 10 M, and 12M, were then left to stand for 24 hours before being used in subsequent procedures [11].

A polycarboxylate-based superplasticizer (SP) was utilized to reduce the water-binder ratio, enhancing both the workability and strength of the 3D-printed concrete. Carboxymethyl cellulose-based viscosity modifying agent (VMA) was added to enhance the properties of fresh concrete, preventing issues like excessive bleeding, honeycombing, segregation, and plastic cracking. Different types of accelerators were used for this study, including Calcium Chloride (CaCl₂), Calcium Nitrite (CN), Sodium Hydroxide (NaOH), Triisopropanolamine (TIPA) and Triethanolamine (TEA). The results indicate that the inclusion of accelerators substantially decreases the setting time and enhances compressive strength. Calcium chloride, as a chemical accelerator, accelerates the cement hydration process, leading to faster hardening and earlier strength development in the concrete. We compared the accelerator dose in a control mix (cement + sand) and an agro-industrial ash blended cement (cement + fly ash and bagasse ash). We observed that accelerators are more effective in the control mix and take some time to show effectiveness in the agro-industrial ash blended cement. The amount of CaCl₂ used as an accelerator varies based on the desired acceleration rate, temperature, and type of cement. Since excessive amounts can lead to issues such as increased shrinkage and potential corrosion of embedded metal reinforcements, it is generally used in controlled, limited quantities. [13]. Solutions of CaCl₂ with concentrations of 12 M and 10 M were prepared and allowed to stand for 24 hours before being used in the subsequent experiments. Nitrate molecules act as accelerators by fastening the hydration of cement particles, which causes the concrete to harden faster and gain strength more quickly. In cold weather, nitrate accelerators are especially useful because they help mitigate the slowing effect of low temperatures on the body’s natural hydration process [10,11]. The dosage of nitrate accelerators can vary based on the desired acceleration rate, temperature, and type of cement used [8]. Triethanolamine (TEA), a low tertiary alkanolamine, is used in cement production and as an additive in concrete formulations. Depending on the cement type and dosage, CaCl₂ can either accelerate or retard the setting process. Specifically, CaCl₂ acts as a set accelerator at 2 % for quick-hardening cement, a moderate set accelerator at 4 %. The quantity of CaCl₂ incorporated influences the strength development of cement pastes and agro industrial ash blended cement [7,8]. Triisopropanolamine (TIPA), a higher tertiary alkanolamine, was incorporated in small quantities into cement pastes, enhancing their strength in fascinating ways at different ages. [9,14]. An average improvement of 10% in compressive strength was observed in the control mix, while the agro-industrial ash blended cement paste showed a 7% average increase in compressive strength.

**Table 1. (Chemical composition) of Baggase Ash and Fly Ash**

|  |  |  |
| --- | --- | --- |
| Element | BA(%) | FA (%) |
|  |  |  |
| SiO2 | 56.69 | 58.24 |
| Al2O3 | 24.87 | 30.37 |
| Fe2O3 | 3.86 | 4.88 |
| CaO | 6.78 | 0.99 |
| Mgo | 0.96 | 0.62 |
| Na2O | 0.32 | 0.31 |
| K2O | 1.03 | 1.16 |
| TiO2 | 1.30 | 1.16 |
| P2O5 | 0.32 | 0.48 |
| Cr2O5 | 0.02 | 0.04 |
| MnO2 | 0.05 | 0.04 |
| SO3 | 0.53 | 0.2 |
| LOI | 4.9 | 4.6 |

**Table 2**

**Properties Fine aggregates.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Properties | Indian Standard sieve | Fine Aggregate Zone | Specific gravity | Fineness modulus |
| Value | 2.36 mm | Zone II of IS: 383 -1978 | 2.62 | 2.40 |

|  |  |  |  |
| --- | --- | --- | --- |
| **(a)** | **(b)** | **(c)** | **(d)** |
| **(e)** | **(f)** | **(g)** | **(h)** |

Fig. 1. Agro-industrial ash mix with additives (a) NaOH – 8 M, (b) NaOH:10 M; (c) NaOH :12 M, (d) CaCl₂ – 2%, (e) CaCl₂ 4%, (f) TEA – 2 %, (g) TEA – 4 %; (h) TIPA - 4 %.

*2.2 Mix proportion*

The study examined the physical properties and chemical compositions of bagasse ash, fly ash and Ordinary Portland Cement (OPC),. These additions were used to meet the hardening requirements of the blend admixture. For the various blends studied, the water-cement (w/c) ratio was 0.3 for the control mix and 0.45 for the agro-industrial ash blended cement, as illustrated in Fig. 1. The setting tests on the cement pastes were conducted using Vicat equipment and following the IS 12269 method. Compressive strength tests were performed on cubic specimens with dimensions of 50×50×50 mm to evaluate their hardening properties. The specimens were cast in metal molds and maintained at a temperature of 27°C for 24 hours. After demoulding, they were submerged in water at 27°C ± 2 until testing. Compressive strength was measured using a testing machine in accordance with IS:516 Part 1.

*2.3* Mixing and Molding Process

To guarantee the reactivity of the solution, NaOH was produced before the alkaline activator, cement and agro-industrial blended cementwere combined. An automatic mixer was used to blend the cement and the alkaline activator until a homogenous paste was created. First, sodium silicate and NaOH solution were combined and operated for five minutes. Five more minutes were added to the mixture after adding the cement. For unconfined compressive strength, a cement-based paste that quickly hardens was cast into 50×50×50 mm cubes in compliance with IS 4031 (Part 6). The samples were tested for unconfined compressive strength after 7 and 28 days using a compressive strength testing equipment.

*2.4* Specimen Evaluation

The setting times of OPC and agro-industrial ash blended cement-based paste were evaluated according to IS 12269 standards at an ambient temperature of 27°C. Using Vicat’s apparatus, the paste’s initial and final setting times were measured. A 2 mm needle, with a maximum penetration depth of 10 mm, was employed to measure the setting time of the quick-hardening cement when mixed with water and additive solution. The average results from three trials for each mix were recorded and analyzed in the results and discussion section. Additionally, unconfined compressive strength tests were conducted on days 1, 3, 7, and 28.

|  |  |
| --- | --- |
| **[a]** | **[b]**  **WhatsApp Image 2024-09-04 at 14.29.40.jpeg** |

Fig.2. Printability Test: (a) Printing was unsuccessful without an accelerator due to lateral flow under its own weight. (b) 3D printing was successful with the use of an accelerator.

**Table 4**

**Mixes investigated**.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Cement Type | OPC | C+BA+FA | C+BA+FA | C+BA+FA | C+BA+FA | C+BA+FA | C+BA+FA | C+BA+FA | C+BA+FA | C+BA+FA |
| Mix | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 |
| NaOH | - | 8M | 10M | 12M | - | - | - | - | - | - |
| CaCl₂ | - | - | - | - | 2% | 4% | - | - | - | - |
| Nitrate | - | - | - | - | - | - | 4% | - | - | - |
| % TEA | - | - | - | - | - | - | - | 2% | 4% | - |
| % TIPA | - | - | - | - | - | - | - | - | - | 4% |

# 3. Findings and discussion

*3.1 Influence of sodium hydroxide- NaOH*

The rate of solidification in the mixture was influenced by both the solid-to-liquid ratio and the molar concentration of sodium hydroxide (NaOH). Experimental data show that increasing the solid-to-liquid ratio reduces both the initial and final setting times. Additionally, higher concentrations of the alkaline activator result in shorter setting times. Tests with NaOH concentrations of 8 M, 10 M, and 12 M yielded varying unconfined compressive strengths: 15.44–16.51 MPa after 1 day; 28.2–27.82 MPa after 3 days; 37.8–38.5 MPa after 7 days; and 50.7–50.8 MPa after 28 days, as illustrated in Fig. 4.

After 1, 3, 7, and 28 days of testing, the unconfined compressive strength has grown in all three mixes with NaOH concentrations of 8 M, 10 M, and 12 M. Additionally, studies have shown that the mix's initial and ultimate setting times are significantly impacted by an increase in NaOH content. At a 12 M concentration of NaOH, the ultimate setting time was measured to be 43 minutes, although the starting setting time was recorded as 24 minutes.

In the 8 M, 10 M, and 12 M samples, however, testing at 1, 3, 7, and 28 days also revealed a decrease in compressive strength. Strength loss might result from two factors when NaOH concentration is raised.Initially, cement gains its strength via a reaction between calcium hydroxide (Ca(OH)2) and cementitious components such calcium silicate hydrate (C-S-H). NaOH is a strong alkali. The material may become weaker as a result of the additional chemicals produced by this reaction.An other explanation is that pores or voids may be created by NaOH and cementitious materials. These pores weaken the structure and decrease compressive strength by increasing porosity and decreasing density.

Fig.3. Initial/Final setting time of selected mixes

Fig.4.Compressive strength of selected mixes

*3.2 Influence of calcium chloride -CaCl₂*

The quick hardening Agro industrial ash blended cement addition of 2 and 4 % CaCl₂ had a major impact on the 3D printed concrete's (3DPC) curing time. The first setting time was significantly reduced from 25 to 18 minutes by adding 2 % and 4% CaCl₂. The final setting time was reduced by 37 minutes and 30 minutes, respectively, by adding 2 % and 4 percent CaCl₂. At the first three days, there was a 50% improvement in compressive strength, which is noteworthy at this early stage. After 28 days, the increase was 20%, which is appropriate for long-term durability. Additionally, by speeding up the hydration process, CaCl₂ can promote the development of early strength. This results in the synthesis of more hydration products and a denser microstructure, which in turn produces high early compressive strength with a shorter setting time. The results unequivocally show that, regardless of the kind of cement utilized, Calcium Chloride functioned as an effective hardening accelerator.

*3.3 Influence of triethanolamine- TEA*

The first setting time, which determines when cement paste changes from a plastic to a semi-solid state, was significantly shortened by using TEA. This speeding impact was compatible with the characteristics of TEA that have been proven as a catalyst for lowering setting time. The outcomes showed that TEA significantly accelerated the solidification process's beginning, which is necessary for 3D concrete printing technique. Furthermore, TEA continued to influence the ultimate setting time, but somewhat less so than CACL₂.The need of carefully controlling dosages when utilizing TEA is highlighted by this study, since high dosages might cause excessively quick solidification, which can compromise workability and building methods. A little reduction in compressive strength was seen in the 3DCP combination during preliminary testing when TEA was added at 2-4%

*3.4 Influence of calcium nitrate -CN*

In Agro industrial ash cement, calcium nitrate had a major impact on how early age compressive strengths developed. Comparing the compressive strength at the 1- and 3-day points to the control mix values revealed a roughly 50% increase, but the setting times only slightly improved. When calcium nitrate is included, the starting and finishing setting times are accelerated by 20% in comparison to the control mix. Nevertheless, because of its beginning setting time of 61 minutes and ultimate setting time of 242 minutes, with just a little reduction noted, CN cannot be utilized as an efficient quick setting accelerator. The ability of calcium nitrate to shorten the setting time appears to be influenced by the cement's composition.

*3.5 Influence of triisopropanolamine- TIPA*

The addition of 1% percent triisopropanolamine (TIPA) does not alter the initial and final setting times of Agro industrial ash blended cement; nevertheless, the mix's compressive strength increased significantly throughout all ages.

At 1,3,7, and 28 days, the strength increase was almost 50% more than that of the control mix. Through encouraging hydration responses and altering the microstructure, triisopropanolamine, or TIPA, improves both short- and long-term strength growth. Regardless of the type of cement used in the experiment, triiso-propanolamine performs better than triethanolamine in the creation of compressive strength.

# Conclusion

On Agro industrial ash blended cement samples, a range of admixtures, including as calcium chloride, sodium hydroxide, triisopropanolamine (TIPA), triethanolamine (TEA) and calcium nitrate (CN), have been examined to see how they impact the development of compressive strength and setting time. The CaCl₂ principally serves as a great setting accelerator with lowest setting time and appropriate compressive strength, based on the chemical composition of the Agro industrial ash blended cement Although there was less of a rise in compressive strength, NaOH likewise performs well in the early stage. Although a fairly noticeable strength enhancement was seen, further research must be done from the perspectives of printability and durability.

In this study, various admixtures—namely calcium chloride, sodium hydroxide, triisopropanolamine (TIPA), triethanolamine (TEA), and calcium nitrate (CN)—were tested on Agro-industrial ash blended cement to evaluate their effects on setting time and compressive strength. Calcium chloride (CaCl₂) proved to be an excellent setting accelerator, resulting in the shortest setting time and optimal compressive strength, given the chemical composition of the Agro-industrial ash blended cement. Sodium hydroxide (NaOH) also demonstrated promising performance in the early stages, though its impact on compressive strength was less pronounced. Despite observing a noticeable improvement in strength, further research is needed to explore aspects related to printability and durability.

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