Setting Behavior of Cement Mixtures Containing Phosphate Retarders

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Setting Quality of Cement Mixtures: Investigation of the Setting Behavior of Cement Mixtures Using the Ultrasonic Method with Various Phosphate-based Retarder Additives

Introduction and Scope

A method was introduced for monitoring the setting process of various gypsum mixtures using ultrasonic technology. We have also worked with this method and can confirm the results described there for gypsum plasters and flowing screeds.

The ultrasonic device used consists of a central unit with a controller and two ultrasonic heads (1 transmitter + 1 receiver). About 200 ml of the test substance is placed between the two heads in a sample mold. The device measures the sound travel time with a resolution of 0.1 microseconds at selectable intervals starting from 0.1 seconds. The built-in controller calculates the sound velocity from the measured travel time and the entered measurement path. As the hardness of the sample changes, so does the ultrasonic velocity.

By validating the ultrasonic method with standard measurement techniques (Vicat test, consistency test), the method offers several advantages in daily lab and operational practice:

- Up to 250 test groups with over 5000 data points can be stored.
- Averaging measurements are possible, increasing accuracy.
- Non-destructive testing: the sample remains unchanged.
- The setting process of mineral binders can be tracked across a wide consistency range (from fluid to solid).
- The measurement cycle runs automatically.
- The sample can be stored either exposed (e.g., on absorbent surfaces) or completely sealed from external influences.
- Results can be processed and documented via computer, with post-processing for presentations.

Based on previous work with gypsum-based products, this method was further developed for cement-based mixtures.

The goal of our study was to compare the effects of two different setting retarders. Based on industry experience, we suspected differences in the viscous consistency range of cement products.

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- **Retarder 1**: Potassium diphosphate (DKP) – an established additive in the construction industry.
- **Retarder 2**: Sodium fluorophosphate (SMFP) – with a different mechanism of action.

Significant differences between the two products had previously only been identified using spread measurements in combination with the Vicat method. The Vicat instrument (or Vicat apparatus) is primarily used to determine the setting time and consistency of cement and other hydraulic binders. It's a standard tool in construction material testing, especially in quality control and research labs. The key standards for Vicat Testing include:

1. ASTM C191
    - Title: Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle.
    - Region: United States.
    - Scope: Defines procedures for determining the initial and final setting times of hydraulic cement using the Vicat needle.
2. EN 196-3
    - Title: Methods of testing cement – Part 3: Determination of setting times and soundness.
    - Region: Europe.
    - Scope: Covers both setting time and soundness of cement using the Vicat apparatus.
3. EN ISO 9597
    - Title: Cement – Test methods – Determination of setting time and soundness.
    - Region: International (ISO/EN harmonized).
    - Scope: Similar to EN 196-3 but harmonized for broader international use.
4. AASHTO T131
    - Title: Time of Setting of Hydraulic Cement by Vicat Needle.
    - Region: United States (used in transportation and infrastructure projects).
    - Scope: Mirrors ASTM C191 but tailored for highway and transportation applications.
5. EN 480-2
    - Title: Admixtures for concrete, mortar and grout – Test methods – Part 2: Determination of setting time.
    - Scope: Focuses on how admixtures affect setting time, using Vicat testing.

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6. EN 459-2
    - Title: Building lime – Part 2: Test methods.
    - Scope: Includes Vicat testing for lime-based binders.

These standards above ensure consistency and reliability in cement testing across different regions and applications. This study aimed to monitor the entire hydration process using a single measurement method.

Experimental Procedure

Cement Paste Used:

- Portland cement CEM I 32.5 R. This is a standardized type of cement defined under the European Norm EN 197-1, which classifies common cements based on their composition and strength development. Here's a breakdown of what each part of the designation means: CEM I refer to pure Portland cement. It contains 95–100% clinker, with minor additions like gypsum (to control setting time). It does not include other constituents like fly ash, slag, or pozzolana. 32.5 This number indicates the minimum compressive strength of the cement after 28 days, measured in megapascals (MPa). The "R" stands for Rapid hardening.
- 1000 g cement + 340 g tap water (≈26°dH) → water/cement ratio = 0.34 (26°dH indicates a water hardness level of 26 German degrees, which translates to roughly 150 ppm (parts per million) of calcium carbonate.
- 3.0 g retarder per kg cement (0.3%) – higher than typical (0.1%) to highlight differences.
- Mixed using a mortar mixer.

Spread Measurement:

- Conducted hourly to track consistency changes before setting began (for comparison with ultrasonic method).

Vicat Method:

- Used as a comparison. Automatic Vicat device with 30-minute intervals.
- Penetration depths recorded and graphically processed.

Ultrasonic Method:

- Non-destructive tracking of the full hydration process over 2 days. Averaging measurement every 10 minutes.
- Data transferred to a PC and graphically processed.

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Results

Spread Measurement:

- Without retarder: consistency changed significantly after 1 hour; setting began at 3 hours.
- With Retarder 1: slower decrease in spread, but still noticeable.
- With Retarder 2: consistency remained nearly constant until setting began.

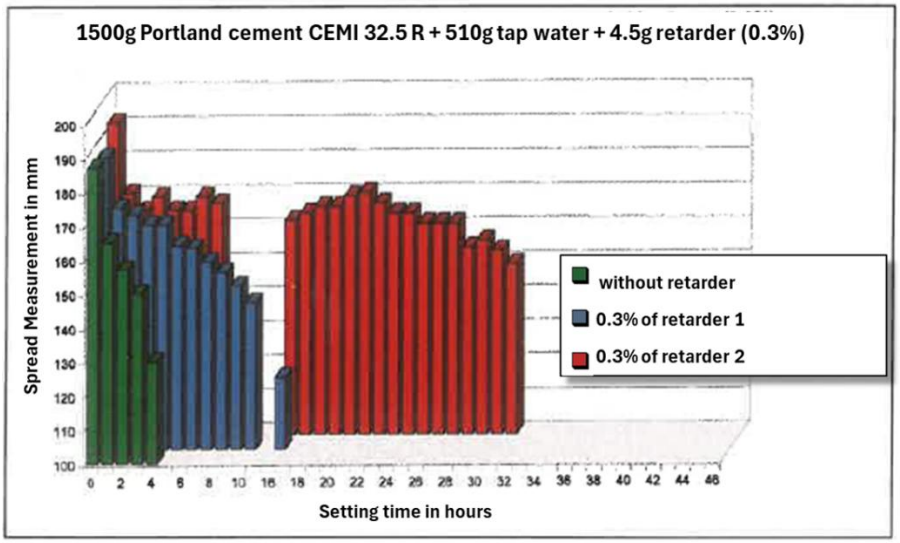

Figure 1: Spread Measurement.

Vicat Method:

- Needle penetrated 40 mm until just before setting began.
- Could not detect consistency changes before setting.
- Retarder 1: setting began at ~10.5 hours, ended at ~18.0 hours (7.5-hour span).
- Retarder 2: setting began at ~27.5 hours, ended at ~30.5 hours (3-hour span).
- Accuracy limited by 30-minute intervals.

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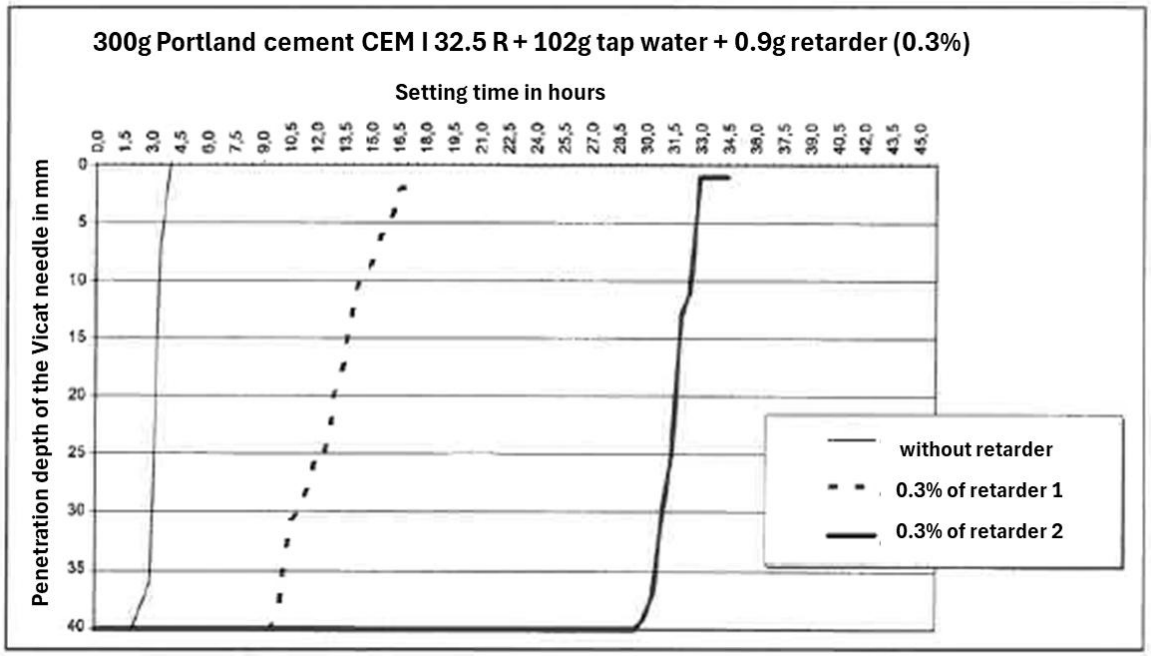

Figure 2: Setting quality using the Vicat method.

Ultrasonic Method:

- Retarder 1: curve began rising before actual setting, indicating early consistency change.
- Retarder 2: curve remained flat until setting began, indicating no early consistency change.
- Setting began at ~1200 m/s ultrasonic speed, ended at ~1480 m/s.
- Combines insights from both spread and Vicat methods.
- Post-setting curve also provides insights into strength development.

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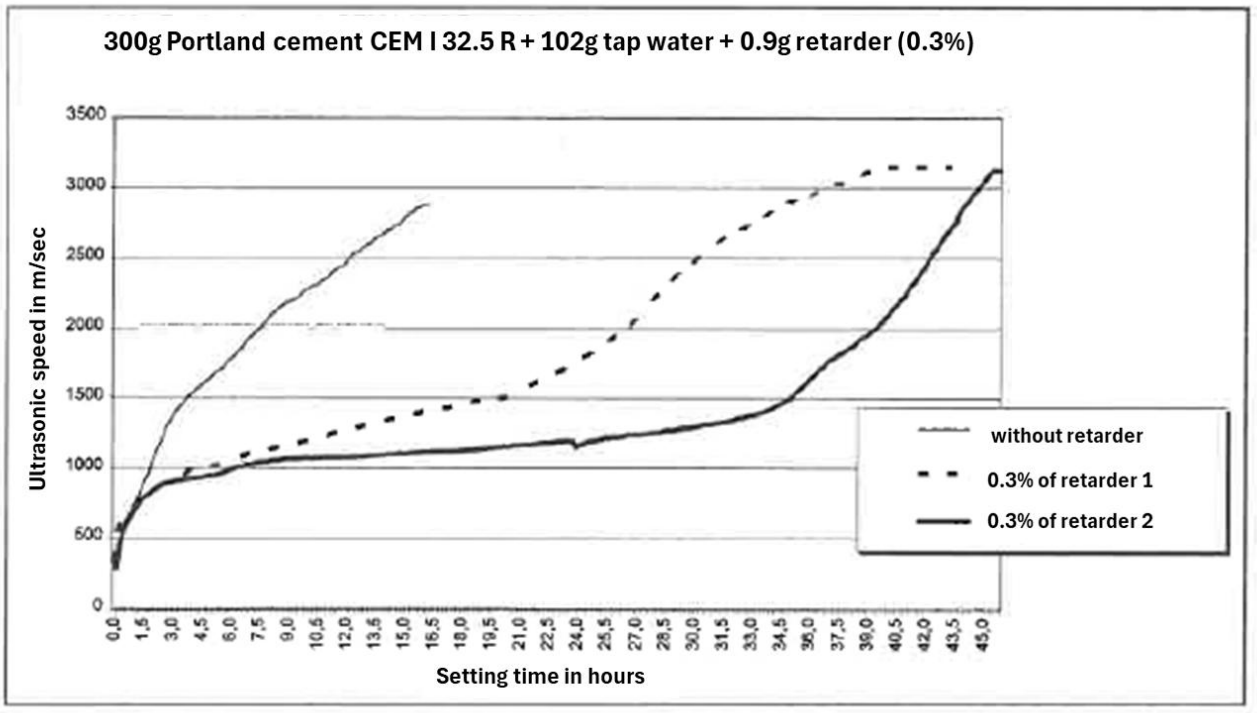

Figure 3: Setting quality using the Ultrasonic method.

Conclusion

- The ultrasonic method allows precise tracking of the setting process in cement-based products.
- Results are reproducible and non-destructive.
- Measurement covers a large sample area and is consistent in position, minimizing errors from air pockets or coarse particles.
- The different effects of the retarders are clearly visible:
    - **Potassium diphosphate, DKP (Retarder 1)** delays setting by several hours but still allows early stiffening.
    - **Sodium fluorophosphate, SMFP (Retarder 2)** causes a stronger delay with nearly constant consistency, which may be advantageous for cements prone to early stiffening.

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