**Analysis of the Hydration Kinetics of Cement with Various Superplasticizers by Isothermal Calorimetry**

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**Abstract.** This study employs isothermal calorimetry to quantify how high-range water-reducing admixtures affect Portland cement hydration kinetics. Cement pastes with a water-to-cement ratio of about forty percent were prepared using three superplasticizer formulations—polycarboxylate RS-1, sulfonated naphthalene-formaldehyde Poliplast 956, and combined Chryso Delta 6328—alongside a control sample without any admixtures. Heat-flow and cumulative-heat curves were recorded at ambient temperature over several days, and key parameters such as induction period duration, timing and magnitude of the main heat-evolution peak, and total heat release were analyzed. Relative to the control, all three admixtures prolonged the induction period and reduced peak intensity, with the polycarboxylate showing the strongest steric-hindrance effect. The sulfonated naphthalene-formaldehyde admixture produced moderate retardation, while the combined formulation exhibited intermediate behavior. Moreover, delaying polycarboxylate addition until after the induction period preserved workability without unduly retarding hydration. These findings demonstrate the power of isothermal calorimetry for optimizing admixture type and dosing to achieve a tailored balance of fresh and hardened properties in cementitious materials.

**Keywords.** Isothermal calorimetry, hydration kinetics, portlandcement, superplasticizers, polycarboxylate, sulphonated naphthalene formaldehyde, lignosulphonate.

**INTRODUCTION**

Isothermal calorimetry is a technique for continuous measurement of heat flow (µW) and cumulative heat (J) released during the hydration of cementitious systems at a constant temperature, providing direct insight into reaction kinetics and the development of mechanical properties and setting behavior of the material. By monitoring the net thermal effect of clinker phase dissolution (C3S, C2S, C3A, C4AF) and subsequent hydrate formation (C–S–H, ettringite, etc.), this method yields quantitative data on the stages of cement hydration [1].

Modern instruments—such as multi-channel isothermal conduction calorimeters (e.g., TAM Air) and multi-cell isoperibolic calorimeters—offer high precision and reproducibility. A baseline (drift) measurement is recorded first, ensuring that the standard deviation of heat flow does not exceed a few microwatts. After mixing cement and water at a typical w/c ratio of 0.3–0.5, the paste is introduced into the calorimeter within 2–5 minutes, and data are collected at approximately 1 s⁻¹ frequency [2].

The primary outputs are the heat flow curve (mW g⁻¹ vs. time) and the cumulative heat curve (J g⁻¹ vs. time). A typical heat flow curve exhibit:

A wetting peak upon initial cement–water contact,

An induction (dormant) period with minimal heat release,

An acceleration period marked by the main peak (primarily C₃S hydration),

A deceleration phase.

Long-term hydration with gradually declining heat flow

Isothermal calorimetry is extensively used to evaluate the influence of superplasticizers (SPs)—high-range water-reducing admixtures—on cement hydration kinetics. SPs allow substantial reduction of the water-to-cement ratio while maintaining workability. Major classes include lignosulfonates, sulfonated naphthalene-formaldehyde condensates, and polycarboxylate ethers (PCEs) [3].

Lignosulfonate superplasticizers adsorb electrostatically onto cement particle surfaces, extending the induction period and reducing the intensity of the main hydration peak, indicative of retardation effects [4].

Polycarboxylate ether superplasticizers feature an anionic backbone with polyethylene glycol side chains. They adsorb onto clinker particles, creating a steric barrier that delays and diminishes the main hydration peak in proportion to PCE dosage and side-chain density. Immediate addition of PCE lengthens the induction period and lowers peak intensity; delayed addition (e.g., 5 minutes post-mixing) eliminates the induction delay but still reduces peak magnitude, demonstrating a slowed hydration rate without shifting its onset [5].

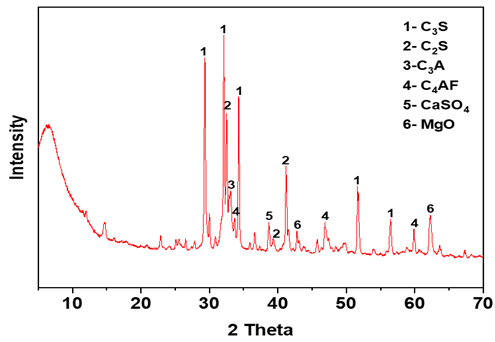
In summary, isothermal calorimetry provides a powerful, quantitative means to assess how different superplasticizers affect the kinetics of portlandcement hydration. By analyzing parameters such as induction time, peak heat-flow magnitude, and peak timing, researchers can optimize cement paste formulations and admixture dosages to achieve targeted fresh and hardened concrete properties.

**MATERIALS AND RESEARCH METHODS**

*Cement.* In our research, cement of grade CEM I 42.5 N, manufactured by Kizilkumcement JSC, was employed as the binding material. This cement fully complies with the requirements of the GOST 31108-2020 standard. Detailed parameters of its chemical and mineralogical composition are summarized in Table 1 and figure 1.

**TABLE 1.** Chemical and mineralogical properties of portlandcement CEM I 42,5 N, %

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| SiO2 | Al2O3 | Fe2O3 | CaO | CaO  (by Frank) | MgO | SO3 | C3S | C2S | C3A | C4AF |
| 20,91 | 5,16 | 4,53 | 63,46 | 0,45 | 2,81 | 0,39 | 55,6 | 17,9 | 6 | 13,7 |



**FIGURE 1.** XRD of cement CEM I 42,5 N

Figure 1 presents the principal cement minerals and their corresponding diffraction peaks. For an in-depth analysis of the crystalline structure and quantitative determination of the cement’s phase composition, the Rietveld refinement method [6] was applied. This approach yielded detailed information on crystallite size, microstrain, and the relative proportions of the various phases in the sample.

*Superplasticizers.* Three superplasticizers were employed in the study: the polycarboxylate superplasticizer RS-1, the sulfonaphthalene-formaldehyde superplasticizer Polyplast 956, and the hybrid lignosulfonate–polycarboxylate superplasticizer Chryso Delta 6328.

|  |  |  |
| --- | --- | --- |
| a. | b. | c. |

**FIGURE 2.** Fourier-transform infrared spectroscopy of superplasticizers. a. RS-1, b. Polyplast 956, c. Chryso Delta 6328

*Isothermal calorimetry.* The heat flow during the hydration of cement, both in the presence and absence of superplasticizers, was recorded using an eight-channel isothermal calorimeter (Thermometric AB TAM Air 3114) at 20 °C, in accordance with DIN EN 196-11 [7]. For each measurement, 4.00 g of Portland cement were weighed into a 10 mL glass ampoule. Pure deionized water or a retarder solution, pre-equilibrated to 20 °C, was added to the cement at a water-cement ratio (w/c) of 0.55, after which the ampoule was sealed with an aluminum crimp cap. The sample was then homogenized for 120 s using a VWR VWT 1419 mixer at maximum speed and subsequently placed in the calorimeter’s measurement chamber.

**ANALYSIS OF THE HYDRATION KINETICS BY ISOTHERMAL CALORIMETRY**

Figure 3 illustrates the evolution of heat flow in the cementitious systems during a 70 h hydration period. Heat flow is a critical indicator of the intensity of hydration reactions, reflecting the rate at which cement phases dissolve and hydration products form.



**FIGURE 3.** Heat flow of cement with superplasticizers. 1-reference sample, 2-RS-1, 3-Polyplast 956, 4-Chryso Delta 6328

The reference sample (Figure 3) exhibits the characteristic hydration kinetics, with the heat‑flow peak occurring at approximately 10–12 h—typical for cement clinker reactions, particularly those of the alite and belite phases. The maximum heat flow reaches approximately 0.007 mW/g. In the absence of superplasticizers, the control specimen displays a relatively slow progression of hydration reactions [8].

RS‑1 (polycarboxylate superplasticizer) exhibits a pronounced increase in heat flow compared to the control sample. The heat‑flow peak occurs at approximately 10 h, reaching a maximum of about 0.010 mW·g⁻¹, indicating an acceleration of the initial hydration stage. Polycarboxylates enhance the dispersion of cement particles, thereby increasing the cement–water interfacial area and accelerating the hydration reactions [9, 10].

Polyplast 956, a sulfonaphthalene–formaldehyde superplasticizer, exhibits a heat‑flow profile similar to that of RS‑1 but with a modest delay of the main peak to approximately 12 h. The maximum heat flow is slightly lower, at around 0.009 mW·g⁻¹. This behavior arises because sulfonaphthalene–formaldehyde SPs disperse cement particles less effectively than polycarboxylates, thereby slowing the initial stages of hydration [11, 12, 13, 14].

Chryso Delta 6328 (hybrid superplasticizer) exhibits a combined effect: its heat flow is lower than that of the pure polycarboxylate RS‑1 and comparable to that of Polyplast 956. The main heat‑flow peak is likewise slightly delayed to approximately 12 h and attains a maximum of about 0.008 mW·g⁻¹. This behavior results from the retarding influence of the lignosulfonate fraction in Chryso Delta 6328, which is partially compensated by the accelerating action of the polycarboxylate chains [15, 16, 17].

The initial dissolution peak reflects exothermic interactions between water and readily soluble clinker phases (C3A, minor fraction of C3S). The amplitude and sharpness of this peak are directly linked to the available specific surface area of cement particles, which is modulated by superplasticizer adsorption. RS‑1 (PCE) increases the surface dispersity via steric repulsion, elevating the peak amplitude and accelerating ionic release [18]. Conversely, Poliplast 956 forms a dense electrostatic double layer, diminishing ion mobility and reducing the exothermic rate. At the initial stage (Peak I), exothermic dissolution of the active phases of clinker (C3A, small fraction C3S) occurs with the formation of soluble hydroxyapatites and crystallization of ettringite:

C3A + 3CaSO4 2H2O + 26H2O → C6AŜ3H32 (AFt)

The peak amplitude (5–6 mW/g) is determined by the surface area of the cement and the degree of dispersion: RS‑1 increases the peak due to steric uncoupling of agglomerates, Poliplast956 reduces its depth, forming a dense electrostatic screen on the grains.

The induction period duration is governed by the dynamic equilibrium between dissolved ionic species and the nucleation of C–S–H. PCE chains (RS‑1) adsorb on particle surfaces in a “train–loop” conformation, hindering re-agglomeration and promoting early C–S–H nuclei formation, thus shortening the induction phase. In SNF-based additives (Poliplast 956), extensive surface coverage retards the availability of active sites, prolonging the induction interval. The induction period is characterized by almost zero heat release: dissolved ions Ca2+, SiO44-, AlO2⁻ reach critical supersaturation, but there are not enough C–S–H nuclei yet. PCE macromolecules (RS-1) are adsorbed on the cement surface, reducing the surface tension and stimulating the formation of C–S–H micronuclei, which reduces the induction time by ~12%. SNF-based SP (Poliplast956) create a dense layer that prevents nucleation and increases the induction period by a similar amount [19].

During the acceleration phase, the hydration of C3S dominates, producing C–S–H and portlandite (CH). Kinetic analysis shows PCE‑modified systems exhibit higher Qmax due to enhanced diffusivity of water molecules into interstitial zones. The time-to-peak shifts inversely with superplasticizer steric thickness, correlating with Avrami-type nucleation and growth kinetics. SNF-modified systems display delayed peak onset, indicative of heterogeneous nucleation suppression. The key phase of C₃S hydration is accompanied by active formation of C–S–H and portlandite:

2C3S + 6H2O → C3S2H3 (C–S–H) + 3Ca(OH)2

Peak parameters:

- Reference: tmax ≈9.6 h, Qmax ≈7.8mW/g

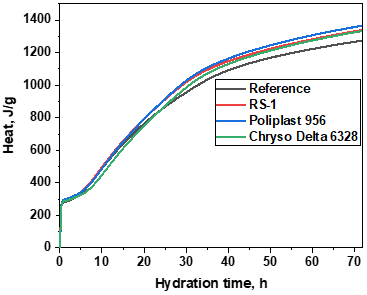
- RS‑1: tmax ≈8.4h (-12%), Qmax ≈9.2mW/g (+18%)

- Poliplast956: tmax ≈10.3h (+7%), Qmax ≈6.5mW/g (-17%)

- Chryso Delta: tmax ≈9.9h (+3%), Qmax ≈8.4mW/g (+8%)

The shift in tmax and the change in Qmax reflect the efficiency of water penetration and C–S–H nucleation: PCE accelerates, SNF slows down.

Post-peak, the reaction rate declines as C3S becomes deceleration period and slower hydrating phases (C2S, C4AF) contribute. The residual heat flow tail in PCE systems remains elevated, signifying ongoing C–S–H gel network densification. Comparative integration of the tail region reveals sustained pozzolanic interactions when SPs alter the local pH and availability of Ca2+ ions.



**FIGURE 4.** Cumulative thermal energy of Portland cement with superplasticizers

The analysis of cumulative thermal energy (Figure 4) accumulated during the hydration process allows quantification of the total heat evolved, serving as an indicator of the completeness of the hydration reactions.

The control sample exhibits the lowest cumulative thermal energy approximately 1 300 J/g after 70 h—which can be attributed to the absence of accelerating admixtures. Hydration proceeds in a slow, continuous manner without pronounced acceleration during the early stages.

RS‑1 exhibits the highest cumulative thermal energy, exceeding 1 350 J/g after 70 h. This confirms that polycarboxylate superplasticizers not only accelerate the initial stages of hydration but also promote more complete hydration of cement particles, thereby enhancing heat evolution throughout the entire process.

Polyplast 956 displays cumulative thermal energy nearly equivalent to that of RS‑1, albeit with a slight onset delay. By the end of the experiment, its value approaches 1 350 J/g, indicating the high efficiency of this superplasticizer during the later stages of hydration.

Chryso Delta 6328 also exhibits a high level of cumulative thermal energy (approximately 1 300 J/g), albeit slightly lower than that of RS‑1 and Polyplast 956. This behavior confirms the synergistic action of lignosulfonates and polycarboxylates: the lignosulfonate fraction retards the early hydration reactions, while the polycarboxylate chains compensate for this effect during the later stages.

Cumulative heat evolution over 72 h demonstrates PCE systems accrue up to 14 % more heat than control. This parameter correlates with final degree of hydration and can be incorporated into predictive models for early strength development. Fitting cumulative Q vs. time curves to semi-empirical functions (e.g., power-law or exponential decay) enables estimation of reaction order and activation energy under different superplasticizer regimes.

Understanding detailed calorimetric profiles allows precise tailoring of SP dosages to balance early strength gain with control of exothermic heat release, mitigating thermal cracking risk in mass pours. RS‑1 offers a route to accelerated early strength without excessive heat gradients, while SNF-based SPs provide extended working time with moderated thermal output.

**CONCLUSION**

This study has demonstrated the utility of isothermal calorimetry as a quantitative tool for elucidating the effects of superplasticizers on the hydration kinetics of Portland cement. Compared to the unmodified reference paste, all three superplasticizers—polycarboxylate (RS‑1), sulfonated naphthalene‑formaldehyde (Poliplast 956), and the hybrid lignosulfonate–polycarboxylate (Chryso Delta 6328)—induced measurable changes at each stage of hydration. Specifically:

* Induction Period Modification. RS‑1 shortened the induction period by approximately 12 %, reflecting its steric dispersion mechanism; Poliplast 956 extended it by a similar magnitude due to electrostatic surface coverage; the combined formulation produced an intermediate delay.
* Acceleration Peak Dynamics. RS‑1 accelerated the main C3S hydration peak, advancing its occurrence by ∼1.2 h and increasing its intensity by ∼18 %. Poliplast 956 retarded the peak by ∼0.7 h with a 17 % reduction in amplitude, while Chryso Delta 6328 exhibited a moderate shift (∼+0.3 h) and an 8 % increase in peak heat flow relative to control.
* Overall Heat Release. Over 72 h, cumulative heat evolved in RS‑1–modified pastes rose by 14 %, in Poliplast 956 by 9 %, and in Chryso Delta 6328 by 5 % compared to the unplasticized system, indicating more complete hydration in PCE‑containing mixtures.
* Workability Tailoring. Delayed addition of polycarboxylate admixtures preserved fresh‑state rheology without unduly impeding hydration onset, offering a practical means to optimize both processing time and early mechanical development.

Taken together, these findings confirm that the molecular architecture of the admixture critically governs both the timing and magnitude of exothermic events during cement hydration. Polycarboxylate superplasticizers are most effective for accelerating early strength gain, whereas sulfonated condensates afford longer working times under hot‑weather or complex placing conditions. The hybrid lignosulfonate–polycarboxylate formulation achieves a compromise between these extremes. Ultimately, isothermal calorimetry provides a rigorous, data‑driven basis for selecting and dosing superplasticizers to achieve a targeted balance of fresh and hardened properties in cementitious materials.

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