Thixotropic cement slurry system types and evaluation methods

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Abstract: Thixotropy is one of the important contents of the rheology for dispersed systems. Thixotropy is widely used in engineering cement slurry, and the thixotropy of substances in actual engineering is often used as an auxiliary means and method of engineering technology. The concept and mechanism of thixotropy are briefly introduced. The thixotropic cement slurry system is divided into inorganic and organic types, and the shortcomings of various types of thixotropic cement slurry are pointed out. The evaluation methods of the thixotropic ring method, static shear force method, hysteresis ring total energy method, thixotropic index method, thin blade horizontal cutting method, step method, hysteresis loop method, and thixotropic coefficient method is introduced. Finally, future research on thixotropy has prospected.

Keywords: Thixotropy; Cement slurry; Thixotropic type; Evaluation method

1. Introduction

Thixotropic cement slurries are considered to be an effective treatment to prevent channeling and plug leakage layers in the oil industry. Thixotropic cement slurry is in the ordinary Portland cement slurry after adding thixotropic agent, in the action of the external force under the grout thin, in the stop of external force, and can quickly form a similar rigid gel structure of the grout. There is a big difference between the shear stress-shear strain curve of conventional cement slurry and thixotropic cement slurry, when the strain scale of thixotropic cement slurry is very small, the shear stress can decrease instantly, as shown in Figure 1. Therefore, thixotropic cement slurry system is widely used in cementing leakage, fluid channeling, repair broken casing, weak formation cementing and corroded casing, etc., and has good application prospects and far-reaching significance.

![Figure 1: Shear stress-strain relationship.](image)

Different kinds of thixotropic agents and test methods are used in the study of thixotropic cement slurries. Yao X et al. pointed out the research direction of thixotropic cement slurry, reviewed the design principle, chemical formula and field application of thixotropic cement slurry, and explored a set of methods to evaluate thixotropy. Liu C J et al. analyzed the measurement and evaluation methods of thixotropic cement slurry, introduced the conventional characteristics, application and formula of...
thixotropic cement slurry, and put forward the thixotropic related model of cement slurry[4].

In this paper, the thixotropic and mechanism of action, the types of thixotropic cement slurry systems, the evaluation methods of thixotropic cement slurry and the development direction of thixotropic cement slurry are reviewed.

2. Thixotropy and Its Mechanism

"Thixotropy" was originally used to describe the isothermal reversible gel-sol (solid-liquid) transition produced by mechanical agitation [5]. At first, Barnes H A et al. defined thixotropy as "gradual reduction of viscosity under shear stress and gradual recovery of structure after removal of stress"[6]. However, many scholars believe that the internal structure of thixotropic slurry is destroyed when it is subjected to external force, and when the external force stops, the internal structure of thixotropic slurry is restored to the initial state.

When no thixotropic agent is added to cement slurry, the internal particles are dispersed. When thixotropic agent is added to cement grout, its dispersed particles gradually form flocculent products and further form a network structure. The thixotropic cement slurry is in a state of motion when subjected to external force, the network structure inside the slurry is broken, and a flocculent structure is gradually formed, which further becomes dispersed particles, as shown in Figure 2. Therefore, the thixotropy of cement slurry is the thixotropy agent can form a network structure in cement slurry. When subjected to shear force, the network structure within the slurry is destroyed, the cement system recovers the flow, the shear force stops, and the system re-forms the network structure to prevent the slurry flow. When the slurry is stationary, it resolidifies, thus exhibiting the thixotropic properties of the grout.

![Figure 2: Thixotropic mechanism of cement slurry.](image)

3. Thixotropic Cement Slurry System Types

The selection of thixotropic agent is the key to the preparation of thixotropic cement slurry. At present, according to the type of thixotropic agent, thixotropic cement slurry is mainly divided into the following two categories.

3.1 Inorganic Type

3.1.1 Clay type

The thixotropic cement slurry of the clay system is formed by adding swelling clay into the cement slurry. Once the clay particles are injected into the cement slurry, a large number of anions are produced, which will adsorb the cations in the cement slurry, so that a certain network structure is formed inside the slurry. When subjected to external force, the internal network structure of the slurry will be destroyed, and the internal structure can be restored after eliminating the external force, so that the whole system presents a thixotropic phenomenon. The main disadvantage of thixotropic cement slurry system of the clay is that the viscosity of cement grout changes little before and after the action of external force, and the thixotropic degree of the modified slurry is limited[7].

3.1.2 Calcium sulfate hemihydrate type

The calcium sulfate hemihydrate is added to the cement slurry to form a thixotropic cement slurry system of the calcium sulfate hemihydrate. The calcium sulfate hemihydrate added to the cement slurry that undergo a chemical reaction to generate gypsum, and then react with C3A in the cement to form crystals "calcium-luminum- vanadium", vanadium-aluminum-calcium in the cement slurry has a
promoting hydration effect, which will promote the formation of a network structure in the large particles in the cement slurry. When the cement grout is subjected to external forces, the formation of the network structure will be destroyed, the grout system into a fluid again, so that cement slurry of the calcium sulfate hemihydrate has thixotropy. In addition, the thixotropic cement slurry of the calcium sulfate hemihydrate can also resist sulfate corrosion well, but is incompatible with many water loss agents [8].

3.1.3 Aluminum sulfate and ferrous sulfate type

The thixotropic cement slurry system of aluminum sulfate and ferrous sulfate was formed by adding aluminum sulfate and ferrous sulfate into the cement slurry. Adding aluminum sulfate to cement slurry plays a catalytic role, its role is irreversible. The ferrous sulfate is a relatively weak retarder, and play a role in blocking aluminum sulfate, so that the whole system thixotropy. The thixotropic cement slurry of aluminum sulfate and ferrous sulfate is relatively weak, and can not well meet the needs of anti-channeling, leakage and other aspects [9].

3.1.4 Carbonic acid and alkali metal carbonate type

The thixotropic cement slurry system of the carbonic acid and alkali metal carbonate is formed by adding carbonic acid and alkali metal carbonate into cement slurry. The hydration reaction of carbonic acid and alkali metal carbonate and cement produces Ca²⁺, which produces smaller gel particles that make the cement slurry system thixotropic. In particular, the slurry exhibits thixotropy only when hydration releases enough Ca²⁺ to participate in the reaction. The cement slurry system is conducive to maintaining good pumpability of early cement injection, but the thixotropic delay time is uncontrollable.

3.2 Organic Type

3.2.1 Emulsion swelling type

The thixotropic cement slurry system of the emulsion swelling is formed by adding emulsion swelling to the cement slurry. The addition of emulsion to the slurry will promote the hydration reaction, so that a large amount of water molecules in the cement slurry are consumed, resulting in the aggregate aggregation of the cement slurry, the system has a certain gel strength, and the formation process of this gel strength is reversible, resulting in thixotropic cement slurry system of the emulsion swelling [10]. The volume of thixotropic cement slurry system of the emulsion swelling will expand during the setting process, thus improving the thixotropic effect of slurry. The thixotropic cement slurry system of the emulsion swelling expands during the setting process, thus improving the thixotropic effect of slurry.

3.2.2 Transition metal elements such as zirconium and yttrium type

Transition metal elements such as zirconium and yttrium were added into the cement slurry to form a thixotropic cement slurry system. Under the combination of water-soluble cellulose ester and metal cations, this kind of thixotropic cement slurry system generates a network structure inside the slurry, and the network structure is destroyed under the action of external force. After eliminating the external force for a period of time, the network structure is formed again, so that the slurry shows a certain thixotropy. However, the transition metal elements such as zirconium and yttrium has limited thixotropy, especially in high-temperature and low-density slurries that are not easy to control [11].

3.2.3 Mixed layered metal hydroxides

The thixotropic cement slurry system of the mixed layer metal hydroxide was formed by adding mixed layer metal hydroxide to cement slurry. Mixed metal hydroxide will produce a large number of positively charged metal cations in the slurry, and a large number of anions present in the slurry will be connected around the metal cation, the positive and negative ions combine to form a network structure, which will be destroyed when the external force is eliminated, the network structure will be quickly restored after eliminating the external force, so that the mixed layer metal hydroxide cement slurry has good thixotropy [12].

4. Evaluation Method for Thixotropy of Cement Slurry

The commonly used methods to evaluate the thixotropy of cement slurry are as follows.

4.1 Thixotropic Ring Method

Start with the lowest speed with a rotational viscometer, gradually increase the rotor speed all the way to the maximum, then reduce the speed to the minimum and record the shear stress at the individual
rotor speeds. Shear stress and shear rate are plotted as a ring graph, whose graph area can represent the relative magnitude of thixotropy [13]. The larger the graph area, the stronger the thixotropy. The thixotropic effect can be directly reflected by the size of the thixotropic ring area, but so far, the method has not standardized the operation process, so the experimental results are greatly affected by human factors and experimental instruments, and the thixotropic ring method cannot reflect the influence of time on the thixotropic effect.

4.2 Static Shear Force Method

A shear rotor with a special shape (pulp type) was used to measure the sum of the static shear forces after 10 s and 10 min at rest when the shear rate of the slurry was approaching zero (about 1 s⁻¹), and the thixotropy of the slurry was represented by the difference value \( \Delta \tau = \tau_{10} - \tau_1 \). Since the static shear force of the slurry after 10 min of rest does not change much, but the static yield stress is much larger than, it is generally recognized that the static shear force of the slurry at rest for 10 min is determined as the maximum static shear force of the slurry. This method has two shortcomings [14]: the thixotropy at the initial temperature is different from the thixotropy tested during the temperature change. And the static shear force when standing for 10 minutes sometimes does not necessarily represent the maximum static shear force after the rest of its slurry.

4.3 Hysteresis Loop Total Energy Method

Using the different shear rates of each rotational viscometer, the corresponding peak shear stress and steady-state shear stress at the beginning of the shear of the cement slurry system were measured respectively. The hysteresis energy of each shear rate was obtained, and obtain the total hysteresis energy (thixotropic energy) of the hysteresis energy at each shear rate. Due to the difficulty of process operation and large amount of calculation, this method is only used when the quantitative calculation of thixotropy is high, but this method cannot reflect the change of coagulation strength with time.

4.4 Thixotropic Index Method

Using a viscometer, the thixotropic index of Newtonian fluid refers to the viscosity ratio of 6 r/min and 60 r/min; the thixotropic index of non-Newtonian fluids refers to the viscosity ratio of 5.6 r/min and 65 r/min. The internal structure of the slurry will be destroyed under the shear action of the viscometer, and the ability of the slurry to restore its original structure is expressed by the thixotropic index method. This method is simple and intuitive, and is usually suitable for the evaluation of thixotropy of building adhesives [15].

4.5 Thin Blade Horizontal Cutting Method

Using the blade inserted into the slurry to slowly cut the slurry structure from left to right, the resistance of the blade reflects the strength of the internal structure of the slurry, that is, the blade resistance is used to indicate the gelling strength of the slurry at the corresponding moment [16]. This method can reflect the change of slurry strength well, can overcome the superfluous damage of rotor shear to the internal structure of the slurry in the rotational viscometer method, and can continuously detect the gel strength of the slurry at different moments, but the test device used in this method is complex and the mechanical error is relatively large.

4.6 Step Method

The rotor of the rotary viscometer is used to stir the slurry from the lowest speed, and the initial and equilibrium shear stress of the rotor is measured at a certain shear rate. After the rotor speed changes, the measurement is repeated according to the above steps until there is no thixotropy under a certain shear rate [17]. The step method combines the characteristics of constant speed shear and cyclic shear of the rotor, and can systematically understand the changes of the internal structure of the slurry.

4.7 Hysteresis Loop Method

The rotor torque is set to linearly increase and then decrease with the angular velocity, so that the two torque curves generated by the thixotropic grout result in a hysteresis loop [18]. The hysteresis circulation
can be used as a preliminary index to measure the thixotropy of slurry, but it can not be used to quantify the thixotropy. The thixotropic behavior of this torque curve can be quantified by integration, or at a constant angular velocity, the decay of the torque measurement over time from the initial value to the equilibrium value can be calculated to reflect the thixotropy of the slurry.

4.8 Thixotropic Coefficient Method

The static yield stress of thixotropic cement slurry is about 200 Pa, and the fluidity of the slurry is initially lost, that making the slurry a semi-solid state. Therefore, the difference between the static yield stress of 10 min and 200 Pa is the ratio of the difference to the static yield stress at the initial moment, which reflects the thixotropy $^{[19]}$. This parameter takes into account the absolute value of the rheological parameters and the relative values of the rheological parameters before and after thixotropic.

5. Prospect

At present, the research on thixotropic cement slurry system is still in the initial stage, and there is a relative lack of in-depth and systematic scientific research on this phenomenon. The development trend and research direction of thixotropic cement slurry are summarized as follows.

(1) Analyze the scientific law of thixotropic cement slurry, combine chemical and physical characterization methods to study the internal mechanism of thixotropic formation, and guide the development of new materials.

(2) Research and development of good thixotropic cement slurry system under complex environmental conditions, in order to meet the requirements of various field conditions, and make the inorganic and organic thixotropic agents reasonable mix, play their respective advantages.

(3) Thixotropy has been studied in industry, daily life and medicine, etc. These principles can be applied to the study of thixotropy cement system.

(4) Based on the conventional evaluation method of thixotropic cement slurry, considering the shear history, artificial operation, the length of standing time and other factors, the thixotropic cement slurry evaluation method to form a standard system.

References


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