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# Hydration Mechanism of Fly Ash Cement and Grouting Simulation Experiment

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Fly ash cement grouts overcome the disadvantages of chemical grouts, which is poisonous, too expensive, and the gel strength is lower. It is a kind of grouts commonly used materials in grouting engineering. This paper reveals the hydration mechanism of fly ash cement according to the analyses of enthalpy and free energy. High temperature is the main reason to form fly ash activity, and fly ash with activity and cement to form stable cementation hardening body. The laboratory experiment is made on permeation grouting of small particle size sand by a self-developed testing device. The results shown that the strength and mechanical parameters of the grouted media are improved remarkably. Although the effect of grouting with thick grout-density is good, the grout-density has an influence to the spread of grouts. The penetration ability of thin grouts is strong than thick grouts. By the orthogonal design direct analysis, it is found that the influence of various factors to grouting quantity and diffusion radius of grout are decreasing in the following order: water cement ratio, grouting pressure and water segregation rate. And the regression model of grouting amount and diffusion radius with various impact factors have been put forward by test data.

## 1. Introduction

The materials and equipment of grouting play a very important role in grouting engineering. The characteristic of grouting agent directly relates to the success or failure of grouting engineering, quality and cost, thus science researchers always pay attention to the research of grouting agent (Li et al., 2010). The grouting agent could be divided into cement grouts and chemical grouts. The particle size of ordinary Portland cement is large, and the grouts is difficult to be injected into tiny cracks and pores of rock and soil mass. The development of superfine cement although overcome these shortcomings, but the price is higher. The disadvantage of chemical grouts is poisonous and too expensive, and the gel strength is lower. Meanwhile, many countries have prohibited to use most of chemical grout with the environmental protection being heater and heater. As a new adding material, the fly ash cement not only overcome the above problems, but also conducive to environmental protection (Zhang et al., 2015).

Research of fly ash cement performance, as well as the development of high performance fly ash cement is a hotspot of research in recent years. The roundness and specific surface area of fly ash can affect yield stress, plastic viscosity and thixotropy (Guan et al., 2001). The cement of low hydration heat and expansion is developed which over 50% fly ash as mixing material has been mixed, as well as small amount of slag powder and other additives (Chen et al., 2006). Fly ash cement would have better properties when the value of grey connection degree between the practical particle size distribution of fly ash cement and particle size distribution with the theory densest packing is higher (Zhang and Zhang 2007). The cement containing of 40%~50% volume fly ash is fabricated by the active reactions in accordance to the GB1344-1999 R32.5~R42.5 fly ash cement standard (Yang et al., 2008). The effect of the proportion and fineness of steel slag (SS), fly ash (FA) and types of gypsum on the properties of SSFAS composite cement are studied with orthogonal design experiment by Guan et al., (2011). The result shows that the finesse of FA is the key factor affected the strength. The math of SS and FA and the type of gypsum make the smaller effect on the strength compared with the fineness of FA. Ma et al., (2013) indicate that the yield stress, plastic viscosity and thixotropy increase with the increase of limestone powder content and the decrease of particle size of limestone powder in the compound pastes. Meanwhile, the cement-fly ash-limestone compound pastes appeared became stable when the shear rate further shear rate increased. The addition of 20%~40% (in mass) limestone powder could improve the rheological properties and stability of the cement-fly ash grouts.

Although most scholars make a lot of research on the characteristics of fly ash cement, and devote themselves to develop high performance fly ash cement, few research on hydration mechanism of fly ash cement and grouting mechanism. Therefore, this essay focuses on the hydration mechanism of fly ash cement and grouting diffusion regularity, and these research results can provide theoretical support for actual engineering.

## 2. Hydration mechanism of fly ash cement

### 2.1 Enthalpimetric analysis

The phase composition of fly ash contains glass, mullite, hematite and quartz, and so on. Glass and mullite have active, accounting for 85% of the total. The raw materials of fly ash are clay mineral, illite, kaolinite, montmorillonite, quartz and pyrite in coal. Their chemical formula and enthalpy are shown in Table 1.

*Table 1: Clay mineral composition and enthalpy of coal*

| designation | molecular formula | Enthalpy(KJ/mol) | percentage composition |
|---|---|---|---|
| Kaolinite / Montmorillonite | $Al_2O_3.2SiO_2.nH_2O$ | -4140.7 | 40% |
| illite | $2Al_2O_3.6SiO_2.nH_2O$ | / | 20% |
| quartz | $SiO_2$ | -911.1 | 15% |
| carbonate | $Ca(Mg)CO_3$ | -2328 | 15% |
| pyrite | FeS | -922.6 | 10% |

Their chemical reaction can be represented as:

$$S_i + Al + Ca(Mg) + Fe + S + H + O + C \rightarrow 3AL_2O_3 \cdot 6Sio_2 + 2Al_2O_3 \cdot 6SiO_2 + Ca(Mg)\mathrm{O}$$
$$+ Fe_2O_3 + SO_3 + H_2 + CO_2 + 3Al_2O_3 \cdot 6SiO_2 \cdot nH_2O + SiO_2 + Ca(Mg)CO_2 + FeS \tag{1}$$

The enthalpy of reaction between them could be obtained by Hess's Law. Hess's Law can be expressed for:

$$\Delta H = \sum \Delta H(\mathrm{product}) - \sum \Delta H(\mathrm{reagent}) \tag{2}$$

The change of the internal energy of fly ash could can be calculated as follow:

$$\Delta H(\mathrm{glass}) = \Delta H(\mathrm{fly\ ash}) = -901.6\mathrm{KJ/mol} \tag{3}$$

The results of table 1 and formula 3 are brought into formula 2, and we can obtain the enthalpy of fly ash cement reaction, as follow:

$$\Delta \mathrm{H} = -901.1 - (0.6 \times 4140.7 + 0.15 \times (-911.1) + 0.15 \times (-2328) + 0.1 \times (-922.6) = 2161\mathrm{KJ/mol} \tag{4}$$

The value of reaction result is positive. The result is shown that the reaction with the minerals in the raw coal turn into coal fly ash is not spontaneous, and it needs the energy from the outside. Thus the major cause why fly ash has active is high temperature.

### 2.2 Free energy analysis

When fly ash, cement (lime) and water to form a system, first cement clinker produces hydration reaction, and then the active substance $SiO_2$ and $Al_3O_2$ in fly ash and $Ca(OH)_2$ from cement clinker hydration reaction. The system is actually composed of $Ca(OH)_2$, $SiO_2(Al_2O_3)$, $H_2O$, and we can analyze to its occur course by thermodynamics. The hydration between Pozzolanic materials and cement clinker can be expressed by following formula:

$$x\mathrm{Ca(OH)_2} + \mathrm{SiO_2} + (n-1)\mathrm{H_2O} \rightarrow x\mathrm{Ca} \cdot \mathrm{SiO_2} \cdot n\mathrm{H_2O} \tag{5}$$

$$(1.5\text{-}2.0)\mathrm{Ca} \cdot \mathrm{SiO_2} \cdot \mathrm{aq} + \mathrm{SiO_2} \rightarrow (0.8-1.5)\mathrm{CaO} \cdot \mathrm{SiO_2} \cdot \mathrm{aq} \tag{6}$$

$$3\mathrm{CaO} \cdot \mathrm{Al_2O_3} \cdot 6\mathrm{H_2O} + \mathrm{SiO_2} + m\mathrm{H_2O} \rightarrow \mathrm{CaO} \cdot \mathrm{SiO_2} \cdot m\mathrm{H_2O} + y\mathrm{CaO} \cdot \mathrm{Al_2O_3} \cdot n\mathrm{H_2O} \tag{7}$$

If when $x \leq 2$ and $y \leq 2$, the hydration formula can be expressed for:

$$x\mathrm{Ca(OH)_2} + \mathrm{Al_2O_3} + m\mathrm{H_2O} \rightarrow x\mathrm{Ca} \cdot \mathrm{Al_2O_3} \cdot n\mathrm{H_2O} \tag{8}$$

If when $y \leq 3$, the hydration formula can be expressed for:

$$3\mathrm{Ca(OH)_2} + 2\mathrm{SiO_2} + \mathrm{Al_2O_3} + m\mathrm{H_2O} \rightarrow 3\mathrm{CaO} \cdot \mathrm{Al_2O_3} \cdot 2\mathrm{SiO_2} \cdot n\mathrm{H_2O} \tag{9}$$

Reaction equation shows that the final products are hydrated calcium silicate gel and solid solution from hydrated calcium aluminate. Analysis of the free energy of the reactants and products are as follows: ΔG($Ca(OH)_2$)=900.2KJ/mol; ΔG($Al_2O_3$)=1582.6KJ/mol; ΔG($SiO_2$)=848.6KJ/mol; ΔG($SiO_2$)=848.6KJ/mol; ΔG(H2O)=237.2 KJ/mol; ΔG(C-S-H)=6167.4 KJ/mol.
The Gibbs free energy calculation is as follows:

$$\Delta G = \Delta G(C-S-H) - \Delta G(Ca(OH)_2, Al_2O_3, SiO_2, H_2O) = -2598.8KJ/mol \tag{10}$$

The calculation result is a negative number. The result is shown that the hydration reaction can produce along the equation spontaneously, and system gradually becomes stable along with the internal energy flow from high to low. This is a fundamental reason that fly ash has activity and it can form stable cementation hardening body after reaction.

## 3. Fly ash cement grouting simulation test

### 3.1 Test apparatus and test materials

The testing apparatus developed for conducting grouting test are shown in Figure 1 and Figure 2 respectively. The testing apparatus comprises a pressure supply nitrogen bottle, a storage container and a test chamber. The high-pressure nitrogen gas cylinder is about 15Mpa; after depressurization through the decompression valve, 0-4Mpa air pressure is output to slurry storage container for test. The slurry storage container comprises of a steel cylinder, which is 10cm in diameter and 15cm in height, and upper and lower steel plates. The test chamber comprises a steel frame and Perspex sheets; the external dimension of the chamber is 600x600x600 mm.

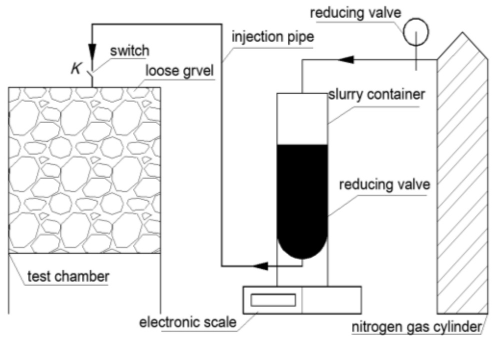



*Figure 1: Working principle of grouting test apparatus*

*Figure 2: Grouting test apparatus*

Building sand is selected as the noted medium. Particles gradations shall be with 1~2mm and 2~3mm. Fly ash cement shall be selected as the grouting material, in which the incorporation of fly ash shall be 30%. Water cement ratio (W/C) in the grouting test are 0.8, 1.0 and 1.25 separately, the grouting pressure can be selected as 0.1Mpa, 0.2Mpa or 0.3Mpa.Test water is tap water and the water temperature shall be controlled at 20 ± 2 ° C.

### 3.2 Test method

1L of cement grout shall be prepared each time, and stirred at 600rpm speed in a grout mixer for 5 minutes. After being prepared, the cement grout shall be immediately poured into the storage container, and open the pressure reducing valve in the nitrogen cylinder for the grouting test. Gradually increase the grouting pressure from low to high and reach the designed pressure value (0.1Mpa, 0.2Mpa, 0.3Mpa). Nitrogen gas flows into the storage container on the top of the storage container through the pipe, and then pressure is applied to the cement slurry and the fluid goes into the test chamber through the injection pipe at the bottom of the container. The grouting amount used in the test is accurately measured with an electronic balance at the bottom of the storage container; the diffusion radius of slurry shall be measured with the actual permeating distance of the slurry. After the grouting test, the grouting sand sample shall be kept in the test chamber for undisturbed maintenance for 24 hours; and then open the chamber, and put the grouting consolidation into the water to maintain for a period of predetermined number of days for the mechanical property test and microstructure analysis.

## 4. The test results analysis and discussion

### 4.1 Mechanical property of grouting stone body analysis

Cement grouts of water-cement ration (W/C) 1:1 are injected into sand, and grouting stone body is vertically put in water after grouting test. And then stone bodies are maintained 14 days, 28days and 90 days respectively. Stone bodies are cut into specimens size of 5x5cm, and their compressive strength are obtained by compression test, the results are shown in Table 2.

*Table 2: Compressive strength of cement grouting concretion body (unit: MPa)*

| Grout type | Curing time t/*d* | | |
|---|---|---|---|
| | 14d | 28d | 90d |
| cement grouting concretion body | 1.98 | 2.38 | 2.5 |
| pure cement slurry | / | 10.25 | / |

Table 2 is shown that the strength of grouting concretion body was lower than the strength of pure cement grout gels.

Shear strength contains cohesive force c and angle of internal friction $\varphi$. The values of c and $\varphi$ of specimen with maintaining 28 days respectively are 0.09Mpa and 31°. The values of c and φ of sand without grouting respectively are 0.015Mpa and 29°. Compared shear strength values of sand before and after grouting, the strength of the stone body has obvious improvement through grouting.

The difference of strength between pure cement grout gels and grouting concretion body is obvious, and the phenomenon is formed from different material interface and pore structure characteristics.

In the process of pure cement grout gels formation, the adhesion between crystal and non crystal, or between different crystal could be formed by chemical reaction, Van der Waals force and mechanical action. Therefore, the micropores of pure cement grout gels are little and small.

However, the aggregate of grouting concretion body is sand, which is inert substance and exists clay in particle surface. The results lead to insufficient contact between grout gels and particles. The mechanical action is a major action force between material interface, such as mutual build-in and occlusion. And because grouts drainage performance, the porosity is larger between stone bodies, and consolidating strength is lower.

### 4.2 Analysis of holes structure of the grouting concretion body

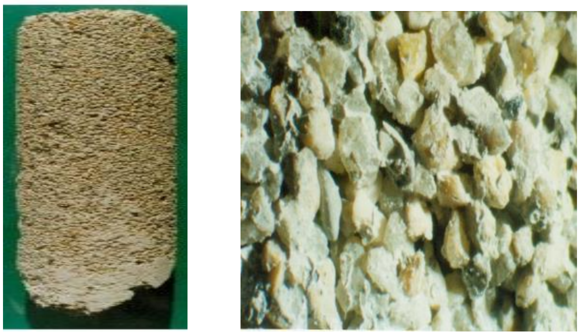
The grouting effects of slurry with water cement ratios of 0.8 and 1.25 on the sand with particle diameter 2~3mm are analyzed; the macroscopic and microscopic shapes of the consolidation are shown in Figure 3 and Figure 4.

It can be seen from Figure3 that the open space filling among sands with large particles by cement grout, whose water cement ratio is 0.8, is compact; there only exist some small cavities in parts; the gel of cement grout can total wrap the sand particles and there are only some isolated and disconnected micro-pores appeared in the grout cemented body.

As analyzed in Figure 4, the grout with a water cement ratio of 1.25 has a cohesive action on the porosities of sands; however, the exterior structure of consolidation is rough and the consolidation strength is low. Although, from a macro point of view, the grouting consolidation is compact; however, at the micro level, there exist a large quantity of porosities and cracks, which is caused by precipitation and drainage of the grout after the grouting and other factors. For dilute grout, therefore, larger porosities appear in the grout loaded body due to the precipitation and drainage of the grout particles, which reduces the effect of reinforcing and peaking stoppage, and causes a poor grouting effect if no supplemental grouting is provided.


(a) macroscopic features (b) microscopic features

*Figure 3: Macroscopic and microscopic features of concretion body( W/C 0.8, particle diameter 2~3mm)*



(a) macroscopic features (b) microscopic features

*Figure 4: macroscopic and microscopic features of concretion body( W/C 1.25, particle diameter 2~3mm)*

**4.3 Analysis the effect factors of primary and secondary for Permeation grouting**

The test results of grouting amount and grout diffusion radius are obtained by different grouting conditions, as shown in Table 3.

*Table 3: Grouting parameters and test results*

| water segregation rate $V$ (L/min.m.m) | Water-cement ratio (W/C) | Grouting pressure $P$(MPa) | Grouting amount $Q$(mL) | Diffusion radius $R$(mm) |
|---|---|---|---|---|
| 0.365 | 0.8:1 | 0.1 | 52 | 65 |
| 0.365 | 1:1 | 0.2 | 78 | 98 |
| 0.365 | 1.25:1 | 0.3 | 110 | 132 |
| 0.478 | 0.8:1 | 0.2 | 68 | 78 |
| 0.478 | 1:1 | 0.3 | 96 | 110.5 |
| 0.478 | 1.25:1 | 0.1 | 78 | 92.6 |
| 0.625 | 0.8:1 | 0.3 | 95 | 103 |
| 0.625 | 1:1 | 0.1 | 89 | 94 |
| 0.625 | 1.25:1 | 0.2 | 114 | 142 |

Combining orthogonal analysis, we calculate the size and range on the impact of various factors on test results, and determine test factors of primary and secondary relations, as shown in Table 4.

*Table 4: The orthogonal analysis results of grouting amount and diffusion radius*

| Calculation index | Grouting amount Q /mL | Range | Diffusion radius R /mm | Range |
|---|---|---|---|---|
| $K_1^V$ | 80.0 | | 98.3 | |
| $K_2^V$ | 80.0 | 19.3 | 93.7 | 14.7 |
| $K_3^V$ | 99.3 | | 113.0 | |
| $K_1^H$ | 71.6 | | 82.0 | |
| $K_2^H$ | 87.7 | 29.0 | 100.8 | 40.2 |
| $K_3^H$ | 100.7 | | 122.2 | |
| $K_1^P$ | 73.0 | | 83.9 | |
| $K_1^P$ | 86.7 | 27.3 | 106.0 | 31.3 |
| $K_1^P$ | 100.3 | | 115.0 | |

Analysis of Table 4, these factors, from the primary to the secondary, influencing the grouting amount and the diffusion radius of the grout is as follows: water cement ratio, grouting pressure, and media drainage rate.

**4.4 Mathematical model of grouts diffusion**

According to permeation law of grouts, the diffusion of chemical grouts and suspension slurry under pressure could be described by nonlinear equations. So we adopt multivariate nonlinear regression function to show test results.

$$\left.\begin{matrix} Q_i \\ R_i \end{matrix}\right\} = c_1 x_i^V \cdot x_i^H \cdot x_i^P$$
$$i = 1,2,3,...9 \tag{11}$$

Where Qi is grouting amount; Ri is diffusion radius of grouts; xiV is the value of water segregation rate; xiH is water-cement ratio; xiP is grouting pressure.

The equation 11 is take logarithm on both sides and changed into a linear equation, and undetermined coefficient of regression is calculated by least squares estimate. Combining with the test results of Table 4, regression equation is obtained as follows:

$$Q = 198.4V^{0.44}H^{0.79}P^{0.31} \qquad r^2 = 90\% \tag{12}$$

$$R = 218.6V^{0.35}H^{0.95}P^{0.32} \qquad r^2 = 93\% \tag{13}$$

Through F and T test, these equation and various factors are significant. So the credibility of the regression equation is higher.

## 5. Conclusions

(1)Hydration mechanism of cement fly ash is obtained by the thermal culvert analysis and free energy analysis: the main reason for the formation of the activity of fly ash is high temperatures; active fly ash and cement form a stable cement hardened body.
(2)If a self-made indoor grouting unit is adopted to grout the building sands, the mechanical properties of the material after the grouting will be significantly changed; the cohesion force will t increase by nearly 6 times and the angle of internal friction and the compressive strength will also be improved. The concentration of grouts has a significant influence on the grouting and the effect of thick grout is better than that of the thin grout.
(3) The sorting of factors, from the primary to the secondary, influencing the grouting amount and the diffusion radius of the grout is as follows: water cement ratio, grouting pressure, and media drainage rate. Combined with the test results, grouting amount diffusion radius estimating empirical equation is established; and the equation is applicable for grouting clay and gravel with small particles, but not for coarse grained soil infiltration grouting.

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