

Gel time of calcium acrylate grouting material*

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Received Sept. 28, 2003; revision accepted Feb. 17, 2004

Abstract: Calcium acrylate is a polymerized grout, and can polymerize in an aqueous solution. The polymerization reaction utilizes ammonium persulfate as a catalyst and sodium thiosulfate as the activator. Based on the theory of reaction kinetics, this study on the relation between gel time and concentration of activator and catalyst showed that gel time of calcium acrylate is inversely proportional to activator and catalyst concentration. A formula of gel time is proposed, and an example is provided to verify the proposed formula.

Key words: Chemical grouting, Gel time, Reaction kinetics, Calcium acrylate, Polymerization reaction

Document code: A

CLC number: TQ150.9; O646.5; X783

INTRODUCTION

One of the main advantages of chemical grouts is easy control of gel time (Mollamahmutoglu and Littlejohn, 1996; Šnupárek and Soucek, 2000). Calcium acrylate is a chemical grout usually used in geotechnical engineering (Zelanko and Karfakis, 1997), and is a water-soluble monomer that polymerizes in an aqueous solution. The rate of polymerization is controlled by the concentration of catalyst and activator. The polymerization of calcium acrylate is free radical chain polymerization (Yamada *et al.*, 2000). Free radical polymerization simply discussed in the context of this study on the gel time of calcium acrylate, the result of which can be applied for grouting practices.

PROCESS OF FREE RADICAL POLYMERIZATION

Radical chain polymerization is a chain reaction consisting of a sequence of three steps (Zhao, 1995; Zang, 1995): initiation, propagation, and termination.

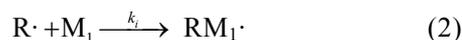
Chain initiation

The initiation step is considered to involve two reactions. The first is the production of free radicals by any one of a number of reactions. The usual case is the homolytic dissociation of an initiator species I to give a pair of radicals R·:



where k_d is the rate constant for the initiator dissociation.

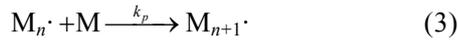
The second step of initiation involves the addition of the initiator radical to the first monomer molecule to produce the "real" chain initiating species $M_1\cdot$:



*Project supported by the Education Department of the Railway Ministry, China

Chain propagation

As propagation continues and each monomer unit is added, the radical has the same identity as the radical before except that it is larger by one unit. Therefore, Eq.(2) becomes:



Chain termination

Propagation with growth of the chain to higher molecular weight polymer takes place very rapidly. But at some point the propagating radical at the end of the polymer chain stops growing and terminates. Termination of the radical centers occurs by bimolecular reaction between two radicals. They react with each other by coupling or by disproportionation. The two different modes of termination can be expressed by:



where k_a and k_b are the rate constants for termination by coupling and disproportionation, respectively.

Polymerization rate

The overall rate of polymerization (R_p) can be considered as the rate of disappearance of monomer with respect to time, $-d[M]/dt$. This depletion is due to both the initiator-monomer reaction and the propagation reaction:

$$R_p = k_p \left(\frac{fk_d}{k_t} \right)^{1/2} [I]^{1/2} M \quad (6)$$

where f is the mole fraction of initiator radicals formed which actually add to monomer and initiate polymerization, and $k_t = k_a + k_b$.

In Eq.(6) R_p is the consumption rate of monomer M , so R_p may be expressed as:

$$R_p = -d[M]/dt \quad (7)$$

Suppose the starting concentration of mono-

mer M equals $[M]_0$. Integrating Eq.(7) and combining Eq.(6) yields the time t as:

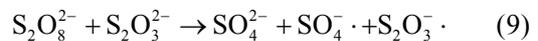
$$t = \frac{\ln \frac{[M]_0}{[M]}}{k_p \left(\frac{fk_d}{k_t} \right)^{1/2} [I]^{1/2}} = \frac{\ln \frac{[M]_0}{[M]}}{k [I]^{1/2}} \quad (8)$$

Eq.(8) shows the relation between gel time t and monomer concentration $[M]$, with reaction rate constant being k .

POLYMERIZATION OF ACRYLATE CALCIUM

Polymerization mechanism

The polymerization reaction utilizes ammonium persulfate as catalyst and sodium thiosulfate as activator. The molecular formula of ammonium persulfate is $(NH_4)_2S_2O_8$, that of sodium thiosulfate is $Na_2S_2O_3 \cdot 5H_2O$. Reaction leading to formation of free radicals is expressed by following equation:



Free radicals $SO_4^{\cdot -}$ and $S_2O_3^{\cdot -}$ that are produced by Eq.(9) may activate the two chains of calcium acrylate molecule. Thus the π electron of the two chains is activated to produce two unattached electrons. The state is not steady, and the two electrons easily combine with other molecules to transfer the activation to them. In this way molecules are chained one by one to accomplish the polymerization of calcium acrylate.

According to Eq.(6) the polymerization rate of calcium acrylate may be expressed as:

$$R_p = -\frac{d[M]}{dt} = k_p \left(\frac{fk_d}{k_t} \right)^{1/2} \cdot [(NH_4)_2S_2O_8]^{1/2} [Na_2S_2O_3 \cdot 5H_2O]^{1/2} [M] \quad (10)$$

where k_d , k_p , k_t respectively denotes the rate constant of chain initiation, chain propagation and chain termination, M denotes concentration of cal-

cium acrylate monomer.

According to kinetics theory, free radicals react with one another to terminate by coupling; the rate of polymerization is proportional to the square of initiator concentration; and when they react with one another to terminate by disproportionation; the rate of polymerization is proportional to the initiator concentration. One molecule of calcium acrylate has many free radicals. Therefore it is impossible for one molecule of calcium acrylate to terminate by coupling. So Eq.(10) is transformed into Eq.(11):

$$R_p = -\frac{d[M]}{dt} = k_p \left(\frac{fk_d}{k_t}\right)^{1/2} \cdot [(NH_4)_2S_2O_8][Na_2S_2O_3 \cdot 5H_2O][M] \quad (11)$$

Suppose the concentration of monomer M equals $[M]_0$ at the beginning of reaction ($t=0$). Integrating Eq.(11) yields Eq.(12):

$$t = \frac{\ln \frac{[M]_0}{[M]}}{k_p \left(\frac{fk_d}{k_t}\right)^{1/2} [(NH_4)_2S_2O_8][Na_2S_2O_3 \cdot 5H_2O]} \quad (12)$$

Eq.(12) shows the relation between time t and concentration of ammonium persulfate and of sodium thiosulfate. In the next section Eq.(12) is discussed to verify its correctness.

Impact of initiator concentration on gel time

Tables 1 and 2 data show $(NH_4)_2S_2O_8$ and $Na_2S_2O_3 \cdot 5H_2O$ concentration's effect on gel time (HIAEIM, 1984) (concentration is expressed in quality percent in original data), respectively.

By conclusion of grout gelling, some fixed proportion of monomers in the grout will have been converted. It was deduced that the rate $[M]_0/[M]$ is fixed when the grout gels, and thus Eq.(12) is transformed into the Eq.(13):

$$t = \frac{\ln \frac{[M]_0}{[M]}}{k_p \left(\frac{fk_d}{k_t}\right)^{1/2} [Na_2S_2O_3 \cdot 5H_2O]} \cdot \frac{1}{[(NH_4)_2S_2O_8]} \quad (13)$$

$$= c \cdot \frac{1}{[(NH_4)_2S_2O_8]} \quad (13)$$

$$c = t \cdot [(NH_4)_2S_2O_8] \quad (14)$$

Take Table 1 for example. Temperature is steady, and the concentration of calcium acrylate and sodium thiosulfate is also steady. Then for different concentration of ammonium peroxydisulfate the coefficient c should be constant. That is to say, by Eq.(14) the product of gel time and sodium thiosulfate concentration should be constant. Table 1 data were used to calculate different sodium thiosulfate concentration c to verify Eq.(13), and the results are listed in Table 3.

The same is true for sodium thiosulfate:

$$c = t \cdot [Na_2S_2O_3 \cdot 5H_2O] \quad (15)$$

Different sodium thiosulfate concentrations and corresponding c value are listed in Table 4.

Table 1 Effect of $(NH_4)_2S_2O_8$ on gelling time

Concentration (mol/L)	0.0579	0.0482	0.0386	0.0289	0.0193
Gel time (s)	410	490	610	820	1310

Note: Concentration of calcium acrylate equals 25%, concentration of ammonium peroxydisulfate equals 1.4%, temperature is 25 °C

Table 2 Effect of $Na_2S_2O_3 \cdot 5H_2O$ on gelling time

Concentration (mol/L)	0.0887	0.0665	0.0444	0.0222	0.0111
Gel time (s)	170	232	342	699	1429

Note: Concentration of calcium acrylate equals 25%, concentration of ammonium peroxydisulfate equals 1.4%, temperature is 25 °C

Table 3 Ammonium peroxydisulfate concentrations and c

Concentration (mol/L)	0.0579	0.0482	0.0386	0.0289	0.0193
c	23.7	23.6	23.5	23.7	25.3

Table 4 Thiosulfate concentration and c

Concentration (mol/L)	0.0887	0.0665	0.0444	0.0222	0.0111
c	15.1	15.4	15.2	15.5	15.9

In Tables 3 and 4, c basically is constant. The results showed that gel time of calcium acrylate is inversely proportional to concentration of catalyst ammonium peroxydisulfate and activator sodium thiosulfate. Eq.(13) shows the relation between gel time and initiator concentration.

CONCLUSION

Gel time of calcium acrylate grout is inversely proportional to ammonium peroxydisulfate and sodium thiosulfate. In practice gel time of calcium acrylate grout may be set by changing the concentration of ammonium peroxydisulfate and sodium thiosulfate.

ACKNOWLEDGMENTS

The author thanks Professors Han Huizheng, Luo Jian, and Gong Xiaonan for valuable assistance and discussions during this work.

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