Comparison of the Influence of Amino Trimethylene Phosphonic Acid and Sodium Gluconate on the Performance of Concrete

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Abstract: Comparison of the influence of amino trimethylene phosphonic acid (ATMP) and sodium gluconate (SG) on the performance of concrete are investigated in this paper. The comparison of the effects of ATMP and SG on concrete setting time at 20°C or 35°C, concrete slump loss, concrete compressive strength and cement pastes dry shrinkage are investigated. The results show that the retard effect of ATMP is much stronger than SG at 20°C and the dosage is higher the retard effect is obvious, the “temperature adaptability” of SG is much worse than ATMP; SG and ATMP both have the “auxiliary water reducing effect” and “slump loss resistant effect”, nevertheless the “slump loss resistant effect” of ATMP is better than SG; the development rate of concrete early age compressive strength within ATMP is slow than the concrete within SG, but the concrete later strength within ATMP will exceed the blank concrete and the concrete within SG at the dosage range from 0.06% to 0.15%; the relationship of cement paste dry shrinkage is ATMP＞SG.

Introduction

Retarders of concrete are required to delay the setting time of concrete and improved the workability duration of concrete without affecting it’s long-term mechanical properties. The concrete retarders are usually used in long-distance transportation of concrete[1], mass concrete construction[2], Roller Compacted Concrete (RCC) construction[3] and oil or gas well cementing operation[4,5].

SG is widely used in concrete engineering due to it’s effective retarding action for cement, reducing the loss of concrete slump, good adaptability with superplasticizer and economic price[6]. Some studies had shown that the retard effect of SG was strong, the concrete initial setting time and final setting time are 35.3h and 72.5h respectively in addition of 0.15% SG[7]. SG can reduce the loss of concrete slump effectively, the concrete slump can maintain unchangeable after 1h at the dosage range from 0.07% to 0.15%[8]. The compatibility between SG and polycarboxylate superplasticizer is better, SG can improve the superplasticizer dispersing ability and water-reducing rate, improve the compatibility between superplasticizer and cement effectively[9]. Amino trimethylene phosphonic acid belong to a kind of organic phosphonic acid, it is usual used for scale inhibitor for water treatment, meanwhile it is the base component of super retarder which is usual used for oil or gas well cementing operation at a higher tempetature[10,11]. Ramachandra, et al[12] firstly reported the organic phosphonic acid compounds had more intensive retard effect to Portland cement compared with other retarders. Li Beixing, et al[13] were investigated the retarding mechanism of ATMP to Portland cement, proposed that ATMP can chelate 3.5 moles Ca^{2+} in the Portland cement to form sparingly soluble calcium phosphonate ($Ca_{3.5}(C_3H_7O_{10}NP_3)$), and the sparingly soluble calcium phosphonate precipitates and forms a closed layer around the cement particles, which retards further hydration of C_3S minerals and formation of $Ca(OH)_2$.

Yet, the influence of ATMP on concrete performance is less be reported, the comparison of the influence of ATMP and SG on the performance of concrete are never be reported. The comparison of ATMP and SG on concrete setting time at 20°C or 35°C, concrete slump with time duration, concrete compressive strength and cement pastes dry shrinkage were investigated in this paper.

Experimental

Raw materials. The cement used was P·O 42.5 Portland cement, manufactured by Yadong Cement Company Ltd.(Wuhan,Hubei), the stair fly ash was produced by Wuhan Yangluo power plant, China Huaneng Group, the S95 slag powder was produced by Gezhouba Cement Plant.(Jingzhou,Hubei). The chemical compositions of the cementitious materials were shown in Table 1. The ATMP was obtained from the Shandong Taihe Water Treatment Co., Ltd. It was slightly yellow transparent liquid, the density was 1.37g/cm^3, the molecular formula of was $N(CH_2PO_3H_2)_3$. The parameters of ATMP was shown in Table 2. SG was from Sinopharm Chemical Reagent Co., Ltd, the purity was 99%. The polycarboxylate superplasticizer was obtained from the HuBei HengLi Construction Material Technology Co., LTD and it's solid content was 40%.

The fine aggregate used in this paper was natural river sand with a fineness modulus of 2.93, an apparent density of 2620 kg·m^{-3}. The coarse aggregate used was gravel with continous grading from 5 to 25mm, the density was 2630 kg·m^{-3}. The dosage of retarders were 0.06%, 0.10% and 0.15% of cementitious materials weight respectively, the composition of mix was shown in Table 3.

Table 1 Chemical composition of cementitious materials (w/%)

Cementitious materials	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Loss
Cement	21.02	62.38	4.80	3.68	1.03	2.02	0.60	3.78
Fly ash	52.7	4.01	29.15	6.20	0.72	1.32	1.61	2.45
Slag	32.93	33.64	14.72	1.40	8.72	3.46	1.28	1.82

Table 2 Parameters of ATMP (w/%)

Active Component	PO_4^{3-}	PO_3^{3-}	Cl^-	Fe^{3+}
50.84	0.77	2.47	1.61	8.38×10^{-3}

Table 3 Composition of mix (kg·m^{-3})

Cementitious materials			Coarse aggregate	Fine aggregate	Water	Superplasticizer
Cement	Fly ash	Slag				
258	86	86	1095.6	730.4	154.3	1.40

Experimental methods

（1）Concrete mixtures slump and setting time

The measurements of concrete mixtures slump and setting time were using slump cone according to Chinese Standards GB/T 50080-2002. It tested the initial concrete slump rapidly by using slump cone after the mixing of concrete. After finished the determination of initial concrete slump, the mixtures were placed under the condition of air temperature 20±2°Cand RH not less than 90% for 1 hour and tested the concrete slump immediately.

（2）Concrete compressive strength

The determination of concrete compressive strength added with retarders were conducted according Chinese Standards GB/T 50081-2002. Concrete specimen size was 100×100×100mm^3 and the specimens were prepared and cured under the condition of air temperature 20±2°Cand RH not less than 90% in molds for 24 hours, then demoulded and followed by curing water at 20±1°C. Concrete compressive strength at 3d, 7d and 28d curing ages were measured respectively.

（3）Cement pastes length change

The determination of cement pastes length change added with retarders were conducted according Chinese Standards JCT603-2004, under test condition of water to cement ratio 0.30. The measurements of the size of hardened paste by using gauge, the percentage of cement pastes dry shrinkage was characterized by the following formula 1:

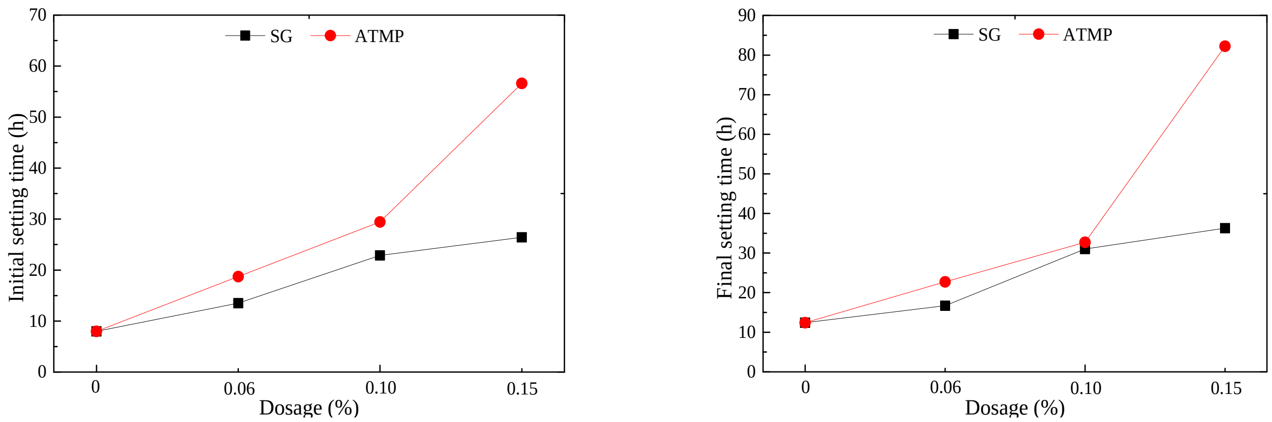
$$M_n(\%)=[(L_0-L_n)/L]\times 100\% \qquad 1)$$

L_0 were the initial gauge length of the specimens, Ln were the gauge length of the specimens at certain curing age, L was the effective length of the specimen.

Results and discussion

Concrete setting time at 20° C.

The comparison of concrete setting time in addition of ATMP and SG were discussed, the results were shown in Fig.1. SG and ATMP could delay the concrete setting time at different degrees, with the increasing of dosage of SG and ATMP addition the concrete setting time presented growth trend at the dosage range from 0.06% to 0.15%. The concrete setting time in addition of ATMP were always longer than the samples in addition of SG. At the dosage of 0.10%, the concrete initial setting time and final setting time addition ATMP were longer than the samples in addition of SG 6.6h and 1.7h respectively, at the dosage of 0.15%, the values were 30.2h and 46.0h respectively. It indicated that the retard effect of ATMP was stronger than SG, the dosage of ATMP was higher, the advantage of retard effect was obvious.



(a) Initial setting time (b) Final setting time

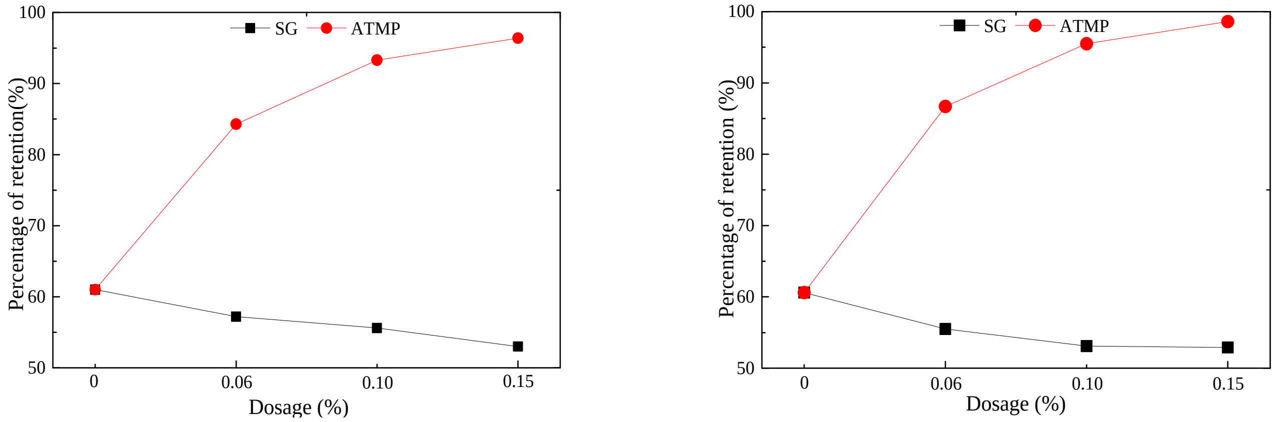
Fig.1 Effect of dosage of ATMP and SG on concrete setting time

Concrete setting time at 35° C

The "temperature adaptability" of retarders was particular important in hot summer concrete construction process[14]. It would lead to the retard effect invalid, it could not play the role of reducing the concrete slumps and delay the concrete setting time if the "temperature adaptability" of retarders was poor at the summer high temperature environment of concrete construction processing. It simulated the hot summer temperature in the laboratory, the "temperature adaptability" was characterized by percentage of retention of cement setting time in this paper:

percentage of retention of setting time=(Setting time at 35°C/Setting time at 20°C)×100% 2)

Percentage of retention of concrete setting time at 35°C was shown in Fig.2. It was obvious that the percentage of retention of concrete setting time in addition of SG showed to decrease with the dosage increasing, the value of in addition of 0.15% SG was only about 53%. In contrast, the percentage of retention of concrete setting time in addition of ATMP showed increasing trend with the dosage increasing, the value of in addition of 0.15% ATMP was about 96-98%. It demonstrated the "temperature adaptability" of ATMP was good, it could maintain intensive retard effect at higher temperatures, the higher the dosage was, the "temperature adaptability" of ATMP was better. However, the "temperature adaptability" of SG was poor and it couldn't maintain effective retard effect. The higher the dosage was, the disadvantage of SG became more obvious.



(a) Percentage of retention of initial setting time (b) Percentage of retention of final setting time

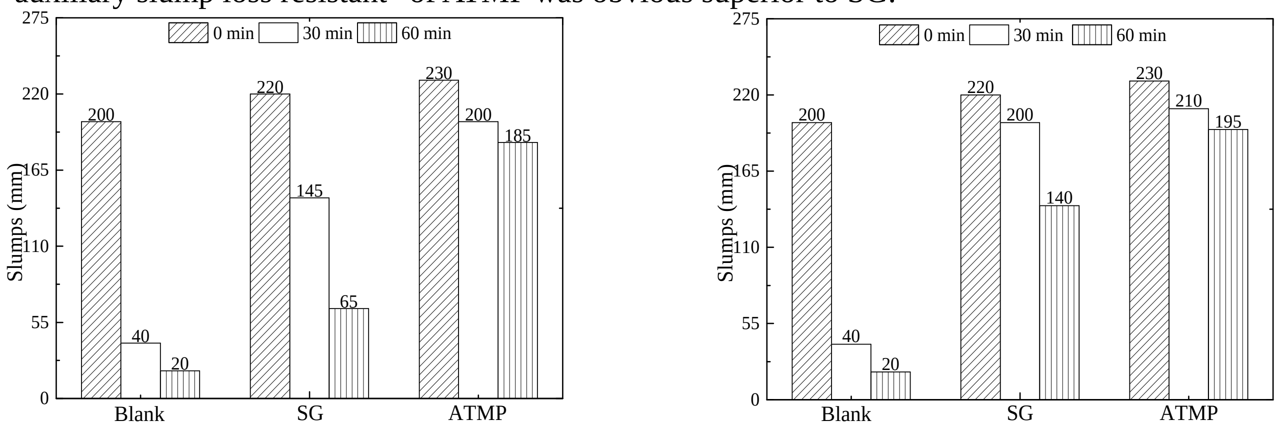
Fig.2 Percentage of retention of concrete setting time at 35° C

Concrete slumps

Retarders could reduce the concrete slumps loss at some degrees generally. The effect of ATMP and SG on concrete slumps time duration were discussed in this part, the results were showed in Fig.3. And the scene pictures of concrete mixing were showed in Fig.4-Fig.6.

ATMP and SG could improve the concrete initial slumps at different degrees. The initial slumps of concrete in addition of SG were greater than blank specimens 20mm, and the value of concrete in addition of ATMP was 30mm. It indicated that ATMP and SG both had the "auxiliary water reducing effect". It was due to SG could hydrolyze to form electric double layer functioned dispersion[15,16], it made electrostatic interaction of cement particle surface enhanced leading to intensify the cement particle dispersion. It showed that SG could improve the concrete initial slumps, water reducer dispersion and water reducing rate consequently[9,17]. The initial slumps of concrete in addition of ATMP were larger than in addition of SG, it suggested that the capacity form electric double layer and "auxiliary water reducing effect" of ATMP was greater than SG.

The scene pictures of concrete mixing showed that ATMP and SG could reduce the concrete slumps loss at different degrees clearly. With the increasing of dosage of ATMP and SG addition the concrete slumps loss presented decreasing. Meanwhile, the slumps loss of concrete in addition of ATMP were less than the concrete in addition of SG at the same dosage. Especially, the 1h concrete slumps in addition of 0.06% ATMP were 185mm, the value of concrete in addition of SG was only 65mm. It suggested that ATMP and SG had good adaptability with water reducing agent, ATMP and SG could play the role of "auxiliary slump loss resistant" commendably. The performance of "auxiliary slump loss resistant" of ATMP was obvious superior to SG.



(a) Content of 0.06% (b) Content of 0.10%

Fig.3 Effect of ATMP and SG on concrete slumps time duration

(a) 0 min (b) 30 min (c) 60 min

Fig.4 Scene pictures of slumps of blank concrete

(a) 0 min (b) 30 min (c) 60 min

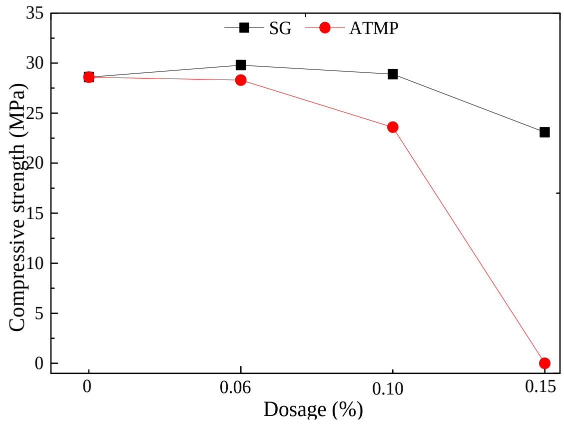
Fig.5 Scene pictures of slumps of concrete in addition of 0.06% SG

(a) 0 min (b) 30 min (c) 60 min

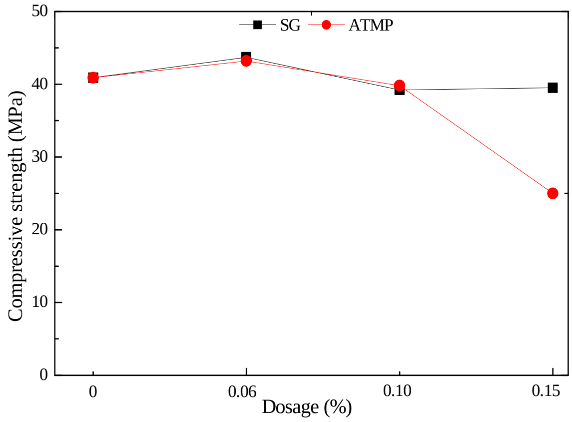
Fig.6 Scene pictures of slumps of concrete in addition of 0.06% ATMP

Compressive strength

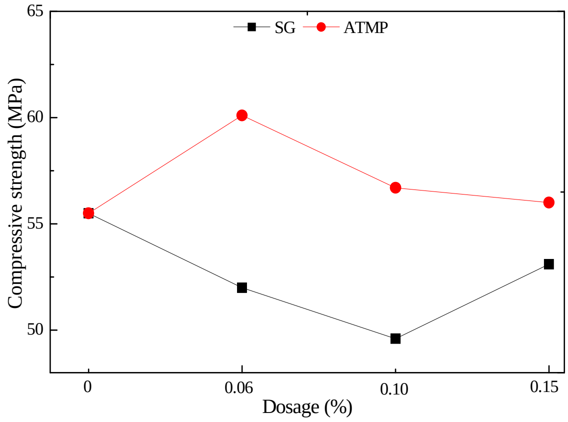
The effect of SG and ATMP on concrete compressive strength was showed in Fig.7. The setting time of concrete in addition of SG was shorter than the concrete in addition of ATMP at the same dosage resulting in the early age (3d and 7d) compressive strength of concrete in addition of ATMP was less than the concrete in addition of SG. The development rate of early age compressive strength of concrete in addition of ATMP was less than the concrete in addition of SG, however the development rate of later age compressive strength was higher, the concrete later compressive strength in addition of ATMP was higher than the blank specimens and the concrete in addition of SG at the same dosage. The 28d compressive strength of concrete in addition of 0.06% ATMP was higher 4.6 Mpa than blank specimens. It suggested that the development rate of concrete in addition of SG was fast and the 28d compressive strength was less than the concrete in addition of ATMP, Nevertheless, the development rate of concrete in addition of ATMP was slow but the development rate of later strength was fast, in the end the 28d compressive strength was less than the concrete in addition of ATMP. It indicated that the concrete within ATMP at the dosage range from 0.06% to 0.15% would not affect concrete long-term mechanical properties.



(a) 3d



(b) 7d



(c) 28d

Fig.7 Effect of ATMP and SG on concrete compressive strength

Dry shrinkage

The effect of SG and ATMP on cement pastes dry shrinkage was discussed, the results were showed in Fig.8. The dry shrinkage of cement pastes in addition of ATMP and SG were all greater than the blank specimens, the dry shrinkage of cement pastes in addition of ATMP was greater than the cement pastes in addition of SG at the same dosage. It exited some theories about interpretation of the dry shrinkage of concrete, there were mainly separating pressure theory, interlayer water transmission theory, capillary tube tension theory and variation of cement particle surface energy theory[18]. It summed up that the losses of absorbed water of C-S-H gel was the main reason leading to concrete dry shrinkage. The effect of different classes admixture on concrete dry shrinkage was also different. It was noticed that the relationship between dry shrinkage of cement in addition of retarder and the retard effect was consistent, it meant that the cement dry shrinkage relationship was ATMP＞SG at the same dosage. It was due to that the cement dry shrinkage was direct related to the moisture of the pore size between 3nm and 20nm. Retarders could transform the cement pore structure at different degrees and reduce the pore size of cement, it was beneficial to dispersion of cement particles leading to increasing of cement dry shrinkage . The retard effect of ATMP and SG on concrete was different, and the effect of improvement and reducing pore structure were also different[19]. The retard effect of retarders was effective, the impact of retarding the cement hydration process was intensive and the effect of improvement and reducing pore size was obvious. Therefore the cement dry shrinkage relationship in addition of retarders were ATMP＞SG at the same dosage.

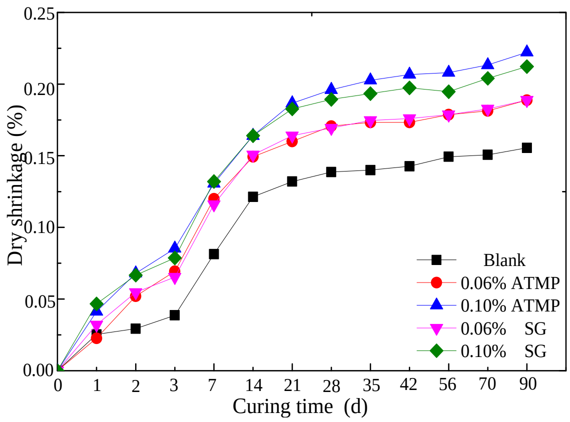


Fig.8 Effect of SG and ATMP on cement pastes dry shrinkage

Conclusions

(1) The setting time of concrete in addition of ATMP was longer than the concrete in addition of SG at the same dosage, the higher the dosage of ATMP was, the retard advantage was more obvious. The initial setting time and final setting time in addition of ATMP was longer than the concrete within SG 30.2h and 46.0h respectively at the dosage of 0.15% at temperature 20°C;

(2) The percentage of retention of concrete setting time in addition of 0.15% SG was only about 53%, but the value of concrete in addition of ATMP was about 96-98% at temperature 35°C,the "temperature adaptability" of ATMP was much better than SG;

(3) ATMP and SG could improve the concrete initial slumps at different degrees, they could reduce the slumps loss at the same time and the performance of "auxiliary slump loss resistant" of ATMP was obvious superior to SG. The development rate early age compressive strength of concrete within ATMP was slower than the concrete within SG, but the development rate of later strength was fast, in the end the 28d compressive strength was less than the concrete in addition of ATMP at dosage range from 0.06% to 0.15%;

(4) The cement dry shrinkage relationship in addition of retarders were ATMP＞SG at the same dosage range from 0.06% to 0.15%.

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