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Influences of SiO_2/Na_2O Molar Ratio on Aging and Chemical Modification of Water Glass

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Abstract

In this paper, the content of water glass before and after adding modifying agent was measured by Trimethylsilyl-gas-chromatography. The experimental results showed that different modulus of water glass could generate different content of mono-silicate acid and oligomeric silicate acid in water glass. After a period of storage, different modulus of water glass led to decrease of silicate content at different levels. Because higher content of Na_2O in water glass tended to incur the alkaline polymerization, the occurrence of depolymerization of silicate species would lead to an increase of oligomeric silicate species, resulting in a drawback of silicate species content after a period of storage. And contrary to that, lower content of Na_2O in water glass tended to incur the acidic polymerization. When the modifying agent was added to the newly made water glass, the amount of mono-silicate acid and oligomeric silicate acid also decreased. In modified water glass, the change of each silicate acid species was less than that in unmodified water glass. These results showed that the modifying agent retarded the aging of water glass. It had remarkable significance on the theory and practical application of water glass chemistry.

Keywords

Water Glass, Modulus, Polymerization Mechanism, Chemical Modification, TMS-GC Method

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1. Introduction

Water glass is colorless, odorless and non-poisonous aqueous solutions, generally called aqueous solutions of all kinds of poly-silicates. Due to producing no poisonous or irritant gas in the process of mixed sand shell moulding, hardening and casting, the studies of water glass moulding are attracting more and more attention in recent years [1] [2]. Among them, sodium silicate ($Na_2O \cdot mSiO_2$) is commonly used in the moulding and casting, the second is the potassium sodium silicate ($K_2O \cdot mSiO_2$), besides, the lithium sodium silicate ($Li_2O \cdot mSiO_2$) is also widely used. On account of widespread application of sodium silicate, it is taken as an example to carry out deep studies.

There are several significant parameters on sodium silicate, which directly affects their chemical and physical properties, and also affects the technological performance of water glass sand with sodium silicate as binder. However, the structure, composition and properties of water glass will change with time during storage, which is called aging phenomenon of water glass. Due to reducing the bonding strength of water glass, the aging deteriorates its processing properties, and shortens its storage life, directly affecting the economic benefit of water glass application. In order to solve these problems, a series of methods are adopted to modify the water glass during the past decades. The experimental results show that [3]-[6] the aging can be temporarily eliminated, depending on providing energy to the water glass system by physical methods, such as heating reflux, autoclave, magnetization and ultrasonography, etc., but re-aging will happen after storage for a short time. Therefore, it also relies on chemical method, namely adding chemical reagents to the water glass (usually containing -COOH, $CO-NH_2$, $C=O$, $-NH_2$, -OH polar groups of organic reagent), to change its polymerization properties, thus retard the aging phenomenon, such kind of work has been reported [7] [8], but most of them are qualitative experiment, and it's not very clear how the various silicate species change and what role of the chemical mechanism is during the aging of water glass.

In this paper, with the polyacrylamide as modifier, the content of water glass before and after adding modifier is determined by Trimethylsilyl-gas-chromatography (TMS-GC method), and the changes of monomeric species and oligomeric silicate species after storage are also studied. Finally, the mechanism of chemical modification discussed.

2. Experimental

1) Preparation of water glass: 300 grams modified and unmodified water glass solutions were prepared according to the amount of reagents in **Table 1**.

2) The silanization of water glass solution: the above eight kinds of formulated water glass solution and the water glass samples were stored for a month, two months and three months respectively, and the samples were diluted to 0.85 $mol \cdot dm^{-3}$ by repeated screening. Then the diluted water glass samples were silanized immediately, with the silylation method [9] being described as follows.

9 mL $HCl:H_2O$ (V/V 2:l), 8.75 mL hexamethyl disiloxane and l.25 mL internal standard solution (2 g n-Tetradecane diluted to 50 mL by adding hexamethyl disiloxane) were added into 15 mL acetone and stirred vigorously for 30 minutes at room temperature by means of a magnetic stirrer, then 10 mL water glass samples were added into the mixture solution to maintain the total amount of various silicate species at 8.5 mmol. All of these mixtures were kept stirred for 90 minutes. Then the reacted solution was separated by tundish, and the organic solution was washed repeatedly (each time by about 30 mL of distilled water) until the solution is neutral. Finally, 2 g of Amberlyst-15 cation exchange resin was added into the above solution, which was subject to ultrasonic

Table 1. The dosage of reagent in water glass solution.

Concentration (SiO_2%)	25%				25%			
Molar ratio	1.6	2.4	3.3	3.8	1.6	2.4	3.3	3.8
Silica gel (g)	75.0	75.0	75.0	75.0	75.0	75.0	75.0	75.0
NaOH (g)	62.5	41.6	30.3	26.3	62.5	41.6	30.3	26.3
Distilled water (mL)	162.5	183.4	194.7	198.7	161.5	182.4	193.7	197.7
Modifier (g)					1	1	1	1

treatment for 1 h, then filtered, and the leaching solution as silylation derivative was analyzed by gas-chromatograph.

3) The silanization of olivine standard samples: 2.2544 g of grinded olivine (containing Si 8.41 mmol) was silanized by the above silylation method.

Note: all samples were dissolved by stirring for about 4 - 5 hours.

4) Gas chromatography analysis: These silylation derivatives were analyzed in SC-6 gas chromatograph performed in a stainless steel column (3 m × 3 mm) packed with 3% SE-30 stationary phase coated Chromosorb GAW (DMCS, 80 - 100 mesh), and detected by FID with N_2 carrier gas flow rate of 30 mL/min. The best resolution and peak shape was obtained with the temperature of (FID) up to 250°C, with the air flow rate at 70 mL/min, and the hydrogen flow rate at 40 mL/min. The GC column temperature was then programmed at 4°C /min from an initial temperature of 90°C to a final temperature of 280°C, the gasification room was held at 220°C to keep the silylation derivatives entering FID in the state of gas. The optimum injection amount was 4.5 μl in order to get the best peak shape and column separation efficiency on organic silicon derivatives.

Since the temperature index of gas chromatography was limited, only the contents of organo oligomer silylation derivatives can be measured, while the amount of high polymeric silylation derivatives cannot be estimated directly, due to the required temperature of column separation for the latter being higher than that of gasification room.

3. Results and Discussion

3.1. The Qualitative Identification and Quantitative Calculation of Various Silicate Species in Water Glass

Some species of silylation derivatives chromatograms were obtained by chromatographic analysis, and chromatogram of the (modulus of 1.6) silylation derivative sample (stored for a month) was taken as an example, which was shown in **Figure 1**.

According to qualitative identification using hyphenated technology of GC-MS [10], each chromatogram peak in **Figure 1** corresponds to the mono-silicic acid or one of various oligomer species respectively, among which peak 2 is assigned to standard sample of n-tetradecane, and Monomeric, Dimer, Cyclic-trimer, Cyclic-tetramer, Trimer, Cyclic-octamer, Cyclic-heptamer, Cyclic-decamer, Cyclic-hexamer(a), Cyclic-hexamer(b) and Tetramer are marked 1, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 respectively.

Each mono-silicic acid content and oligomer species contents in water glass with different modulus before and after modification are listed in **Table 2** and **Table 3**.

3.2. Effects of SiO₂/Na₂O Molar Ratio on the Total Content of Various Silicate Species That Changes with Aging Time

The content of silicate species was plotted against aging time according to **Table 3** and **Table 4**, giving the curve shown in **Figure 2**.

Table 2. The qualitative results of various silicate oligomer derivatives in water glass.

Peak number	0	1	2	3	4	5	6	7	8	9	10	11	12
Retention time (min)	2.5	8.75	13.75	21.25	23.75	33	33.75	35	38.75	41.17	43.67	44.92	46.17
corresponding temp. (°C)	100	125	145	175	185	222	225	230	245	255	265	270	275
Peak name	Solvent	Monomeric	Internal standard	Dimer	Cyclic trimer	Cyclic tetramer	Trimer	Cyclic octamer	Cyclic heptamer	Cyclic decamer	Cyclic hexamer (a)	Cyclic hexamer (b)	Tetramer
Structure abbreviation		QM_4	N_{14}	Q_2M_6	Q_3M_6	Q_4M_8	Q_3M_8	Q_6M_8	Q_7M_{10}	$Q_{10}M_{10}$	Q_6M_{10}	Q_6M_{10}	Q_4M_{10}
Molecular weight (Mj)		384	198.4	606	666	888	828	1128	1230	1410	1170	1170	1050

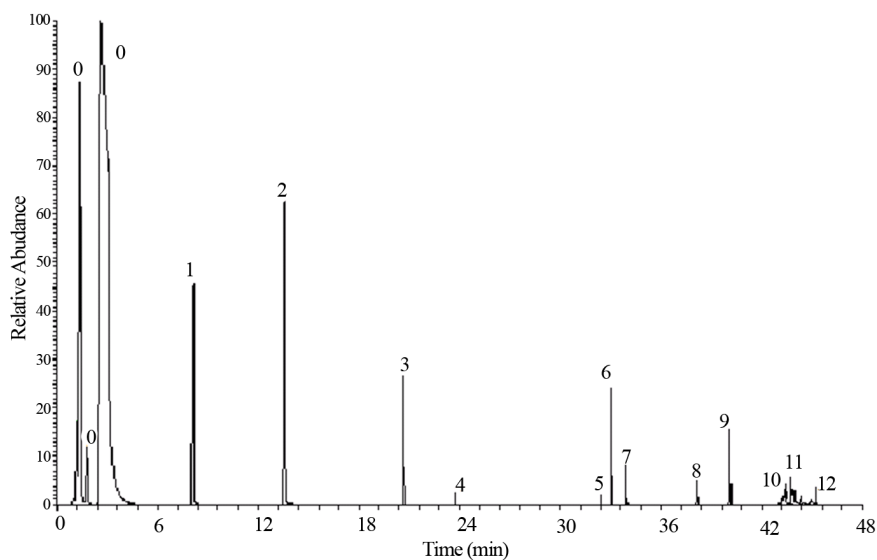Note: Q [SiO₄-], M [(CH₃)₃Si-], n-Tetradecane.

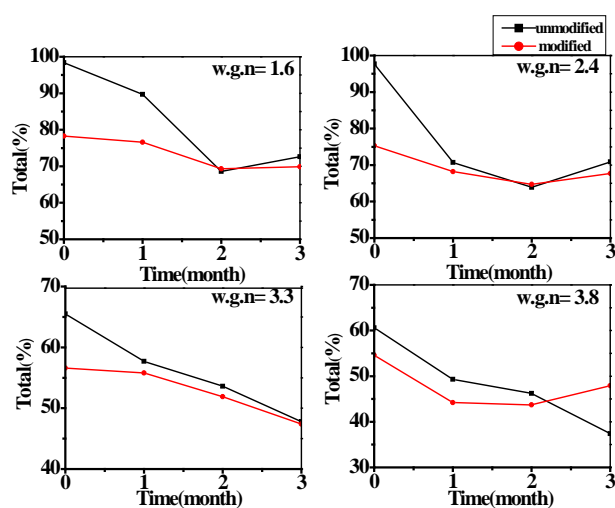**Figure 1.** Chromatogram of various silicate oligomer derivatives in the modulus of water-glass at 1.6 (just).

Figure 2. Relationship between the content of silicate species and storage time.

Table 3. The content of each component in the unmodified water glass.

Sample			Molar percent of component (%)											Total
Storage time	No.	Molar ratio	Monomeric	Dimer	Cyclic trimer	Cyclic tetramer	Trimer	Cyclic octamer	Cyclic heptamer	Cyclic decamer	Cyclic hexamer(a)	Cyclic hexamer(b)	Tetramer	$(\delta_{(uM)})$ (%)
Just	1	1.6	55.9	6.7	△	△	10.5	3.6	△	10.9	5.4	5.4	△	98.4
	2	2.4	52.5	6.7	△	△	14.1	2.7	△	10.9	5.4	5.4	△	97.7
	3	3.3	50.4	4.3	/	/	3.4	1.7	△	4.9	0.4	0.4	△	65.5
	4	3.8	38.6	4.5	/	/	3.6	1.7	△	5.4	4.0	2.8	△	60.6
A month	1	1.6	49.1	15.5	△	△	11.3	3.6	△	6.2	2.0	2.0	△	89.7
	2	2.4	47.9	8.0	△	△	8.6	0.4	△	4.4	0.7	0.7	/	70.7
	3	3.3	37.8	6.7	△	△	4.2	1.7	△	4.1	1.6	1.6	△	57.7
	4	3.8	34.0	3.3	/	△	6.3	0.2	△	1.5	0.5	0.5	△	49.3

Continued

Two months	1	1.6	39.1	12.3	▲	▲	7.6	1.5	▲	5.9	1.1	1.1	▲	68.6
	2	2.4	35.3	10.7	▲	▲	6.7	0.8	▲	7.8	1.3	1.3	▲	63.9
	3	3.3	34.9	6.7	▲	▲	3.6	0.8	▲	5.4	1.1	1.1	▲	53.6
	4	3.8	28.6	4.3	/	/	1.3	0.6	/	1.6	0.5	0.5	/	46.2
Three months	1	1.6	36.8	12.6	▲	▲	10.5	3.4	▲	6.2	1.0	2.1	▲	72.6
	2	2.4	30.7	12.6	▲	▲	10.5	3.5	▲	9.3	2.1	2.1	▲	70.9
	3	3.3	32.8	4.8	▲	▲	2.9	0.8	▲	4.7	0.7	1.1	▲	47.8
	4	3.8	31.5	4.8	▲	▲	9.2	1.3	▲	4.1	1.1	1.1	▲	37.4

Note: ▲ is said to content < 0.2%, the below is as the same as it. $\delta_{(uM)}$ represent the content of unmodified water glass. *added too much internal standard in the specimen, the result will decrease.

Table 4. The content of each component in the modified water glass.

Sample			Molar percent of component (%)											Total
Storage time	No.	Molar ratio	Monomeric	Dimer	Cyclic trimer	Cyclic tetramer	Trimer	Cyclic octamer	Cyclic heptamer	Cyclic decamer	Cyclic hexamer(a)	Cyclic hexamer(b)	Tetramer	$(\delta_{(M)})$ (%)
Just	1	1.6	50.8	9.6	▲	▲	9.0	1.5	▲	4.6	0.5	2.3	▲	78.3
	2	2.4	46.6	8.8	▲	▲	8.2	0.9	▲	6.9	2.9	1.0	/	75.3
	3	3.3	39.5	5.9	▲	▲	3.4	1.1	▲	4.1	1.3	1.3	▲	56.6
	4	3.8	36.1	6.1	▲	▲	3.8	1.0	▲	5.6	1.0	1.0	/	54.6
A month	1	1.6	43.7	10.7	▲	▲	9.2	2.5	▲	7.8	2.0	0.7	/	76.6
	2	2.4	38.2	8.6	▲	▲	8.6	0.9	▲	7.4	0.7	3.8	▲	68.2
	3	3.3	37.8	6.0	▲	▲	3.7	1.1	▲	4.4	1.3	1.3	/	55.8
	4	3.8	35.3	3.2	▲	▲	1.7	0.6	▲	2.0	0.7	0.7	/	44.2
Two months	1	1.6	39.5	14.4	▲	▲	8.0	1.3	▲	5.1	0.5	0.5	▲	69.3
	2	2.4	37.8	8.0	▲	▲	2.9	1.1	▲	7.7	1.6	1.6	▲	64.7
	3	3.3	37.4	5.1	/	/	3.2	0.8	/	3.6	0.7	1.1	▲	51.9
	4	3.8	33.2	3.7	/	/	2.3	0.8	/	2.3	0.7	0.7	▲	43.7
Three months	1	1.6	37.0	14.2	▲	▲	9.2	1.3	▲	6.4	0.8	1.0	▲	69.9
	2	2.4	36.5	8.8	▲	▲	8.4	2.1	▲	7.7	2.1	2.1	▲	67.7
	3	3.3	32.3	5.3	▲	▲	3.6	0.6	▲	3.8	0.8	1.0	▲	47.4
	4	3.8	30.2	5.9	▲	▲	3.2	1.3	▲	3.1	2.1	2.1	▲	47.9

Note: $\delta_{(M)}$ represent the content of modified water glass.

1) It can be observed that, with the modulus of water glass increasing, the contents of monomeric silicate species, Dimer, Cyclic-trimer, Cyclic-octamer, Cyclic-decamer, Cyclic-hexamer (a) and Cyclic-hexamer (b) all decreased accordingly, but the Trimer content reached a maximum value instead when the modulus of water glass was 2.4. The total amount of oligomeric silicate species decreases as the modulus of water glass increases, which is due to the higher SiO_2/Na_2O molar ratio of water glass leading to a lower content of Na_2O in water glass.

Because two different polymerization mechanisms occur in the water glass with different SiO_2/Na_2O molar ratios, the low SiO_2/Na_2O molar ratio probably causes the acidic polymerization mechanism; but the high SiO_2/Na_2O molar ratio probably causes the alkaline polymerization mechanism. The former leads to an increase of polymer species, and the latter leads to depolymerization of polymer species, consequently having relative high content of monomeric species and oligomeric silicate species.

After the water glass was aged without modification, the contents of monomeric species, Cyclic-decamer, Cyclic-hexamer (a) and Cyclic-hexamer (b) all decreased, but the content of Dimer silicate species increased with aging time, then gradually decreased after storage for a month, while after storage for two months, the content of Dimer silicate species changed little. Furthermore, the contents of Cyclic-trimer and Cyclic-octamer silicate species decreased after storage for a month, but after storage for two months, the contents of them drew back. When the modulus of water glass reached 3.3 and 3.8, the total amount of oligomeric silicate species underwent changes $65.5 \rightarrow 57.7 \rightarrow 53.6 \rightarrow 47.8$ and $60.6 \rightarrow 49.3 \rightarrow 46.2 \rightarrow 37.4$ respectively, which basically continued downward trend. However, when the modulus of water glass decreased to 1.6 and 2.4, the total amount of oligomeric silicate species underwent changes $98.4 \rightarrow 89.7 \rightarrow 68.6 \rightarrow 72.6$ and $97.7 \rightarrow 70.7 \rightarrow 63.9 \rightarrow 73.9$ respectively, indicating that the total amount of oligomeric silicate species began to decrease with aging time until it dropped to minimum point after storage for two months, and then it drew back to 72.6 and 73.9 respectively. What's more, the change Δ for each modulus of water glass (unmodified) was calculated as: $\Delta_{1.6(uM)} = 25.8$, $\Delta_{2.4(uM)} = 23.8$, $\Delta_{3.3(uM)} = 17.7$ and $\Delta_{3.8(uM)} = 23.2$ respectively.

The contents of monomeric species and oligomeric silicate species decrease in the water glass aging process (Σi contents of some specimens have drawn back after three months, refer to (4) below). Since water glass is a mixture of monomeric species, linear dimeric species, linear trimeric species and polymeric silicate species, silicate species would polymerize in the storage process, having many polymerization ways, such as monomeric species $\rightarrow$ monomeric species, monomeric species $\rightarrow$ oligomeric silicate species, oligomeric silicate species $\rightarrow$ polymeric silicate species, and so on. Therefore, the content of monomeric species and oligomeric silicate species will decrease after water glass aging.

Therefore, when the modulus is lower, the content of Na_2O in water glass becomes higher, the water glass tends to undergo alkaline polymerization, and the content of oligomeric silicate species increases with aging time because of occurring of depolymerization [11]. Whereas, when the modulus is larger, the content of Na_2O in water glass becomes smaller, the water glass tends to undergo acidic polymerization, and the content of oligomeric silicate species decreases with aging time because of further polymerization.

2) In the initial stage of water glass prepared with modifying agent, the total content of monomeric species and oligomeric silicate species was significantly lower than that of pure prepared water glass, as shown in **Figure 3**, while the total content of monomeric species and oligomeric silicate species of the modified glass with the modulus at 1.6 and 2.4 was significantly larger than that of the modified glass with the modulus at 3.3 and 3.8. It is because the modifying agent dispersed in water glass belongs to entropy model space stability type [12], two or more dispersed particles would be pulled together by polyacrylamide for "creating the bridge", which led to polymerization of monomeric species and oligomeric silicate species, thus the entropy of system Δ_{repel} decreased, and the free energy ΔG increased, it resulted in the system reaching a relatively stable state. The reason why aging rate of water glass decreased after adding the modifying agent could be found in above discussions. What's more, lower modulus of water glass would have higher Na_2O in water glass, which led to alkaline polymerization; while higher modulus of water glass would have lower Na_2O in water glass, which led to acidic polymerization. There probable existed the depolymerization of silicate species in water glass within high pH range in presence of higher Na_2O [11], which would lead to an increase of oligomeric silicate species, so lower modulus of water glass would cause the total content of monomeric species and oligomeric silicate species to
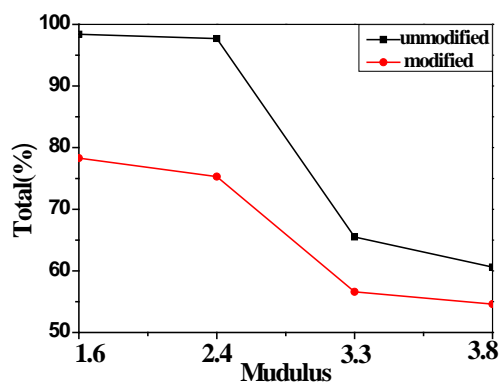

Figure 3. Relationship between Σi and different modulus of water glass.

increase. Another reason could be considered, namely, the lower modulus of water glass solution had higher pH value, and this might be more beneficial to the polyacrylamide "creating a bridge" mechanism.

3) When the modulus of water glass was 1.6, the total content of monomeric silicate species and oligomeric silicate species changed little after storage for a month; however when the modulus of water glass was 2.4, 3.3 and 3.8, the total content of monomeric and oligomeric silicate species changed significantly.

By comparing **Table 3** with **Table 2**, the total content of monomeric species and oligomeric silicate species in modified water glass was less than that in original water glass. When the modified water glass was aged for one month, two months and three months, the total amount of oligomeric silicate species underwent changes $78.3 \rightarrow 76.6 \rightarrow 69.3 \rightarrow 69.9$ for the modulus of water glass at 1.6, $75.3 \rightarrow 68.2 \rightarrow 64.7 \rightarrow 67.7$ for the modulus of water glass at 2.4, $56.6 \rightarrow 55.8 \rightarrow 51.9 \rightarrow 47.4$ for the modulus of water glass at 3.3 and $54.6 \rightarrow 44.2 \rightarrow 43.7 \rightarrow 47.9$ for the modulus of water glass at 3.8 respectively. This means that change Δ for each modulus of water glass (modified) was calculated as: $\Delta_{1.6(M)} = 8.4$, $\Delta_{2.4(M)} = 7.6$, $\Delta_{3.3(M)} = 9.2$ and $\Delta_{3.8(M)} = 6.7$.

In contrast to the changes $\Delta_{(uM)}$ for unmodified water glass shown as $\Delta_{1.6(uM)} = 25.8$, $\Delta_{2.4(uM)} = 23.8$, $\Delta_{3.3(uM)} = 17.7$ and $\Delta_{3.8(uM)} = 23.2$, the modified water glass had less change $\Delta_{(uM)}$ than those of unmodified water glass, indicating that the aging of water glass was retarded by adding modifier polyacrylamide. So above mentioned results can be both explained by thermodynamic stability of modified water glass, and by the DLVO theory [13] [14], which states that the dispersion stability of disperse system is the result of interaction dynamic forces between particles phases.

Because the modifier polyacrylamide is a nonionic polymer and the water glass is a dispersion system of monomeric species and oligomeric silicate species, when the modifier is adsorbed on the surface of silicate particles in water glass, the modifier forced the ions away from stern layer of silicate particles, leading to the diffuse double layers becoming thicker. So when two particles meet closely, the repulsion potential $V_{repulsion}$ increases with increase of superimposed parts of particles, so the Fan Dehua's attraction will be dominant when two particles meet. Therefore, the total potential energy barrier of the modified water glass system after being stored for a period is higher than that of unmodified water glass system, causing not easy polymerization reaction. So the total content of monomeric species and oligomeric silicate species in the modified water glass has smaller extent of decrease than those of the unmodified water glass after being stored for a period, that is to say, modifier polyacrylamide can delay the aging water glass.

4) As shown in the analysis of experimental data, it can be concluded that the change of temperature had effect on the composition of water glass. The experiment was carried out at room temperature, namely with no control of constant temperature, but after storage for three months, with the room temperature increased to 28˚C, 15˚C - 20˚C higher as compared with the original, the total content had a tendency to recover (the results could be seen from **Figure 2** (1) (2) (4)). When the modulus was 3.3 (SiO_2 concentration was 25%), the change of composition of water glass with time became minimum, and the influence of the temperature was not obvious (the results could be seen from **Figure 2** (3)). This issue is to be further explored.

3.3. Effects of SiO_2/Na_2O Molar Ratio on the Difference of Total Silicate Species Content between Unmodified and Modified Water Glass

Plotting $(\delta_{(uM)}-\delta_{(M)})$ versus modulus of water glass and plotting $(\delta_{(uM)}-\delta_{(M)})$ versus aging time give **Figure 4** and **Figure 5** respectively, where $\delta_{(uM)}$ and $\delta_{(M)}$ represent the total silicate species contents of unmodified water glass and modified water glass respectively at a certain modulus, from which we can draw the following conclusions:

1) As can be seen from **Figure 4**, when the modulus was 1.6 and 2.4, the water glass before and after modification had obvious differences, indicating maximum $(\delta_{(uM)}-\delta_{(M)})$ value. Because the water glass underwent alkaline polymerization at low modulus, the modifier polyacrylamide could play the role of bridging between oligomeric silicate species, inducing the significant decrease of total silicate species content.

There is intimate relationship between $(\delta_{(uM)}-\delta_{(M)})$ and modulus of water glass: with the increase of modulus, the $(\delta_{(uM)}-\delta_{(M)})$ value decreased, and when modulus of water glass reached 3.8, the $(\delta_{(uM)}-\delta_{(M)})$ value attained minimum value of -10.5.

When the water glass was stored for one month, though the $(\delta_{(uM)}-\delta_{(M)})$ value of water glass with modulus of 1.6 decreased to 13.1, it still had obvious differences. The $(\delta_{(uM)}-\delta_{(M)})$ values of water glass with modulus of 2.4, 3.3 and 3.8 all decreased to low value of 2.5, 1.9 and 5.1, respectively. When the water glass was stored for
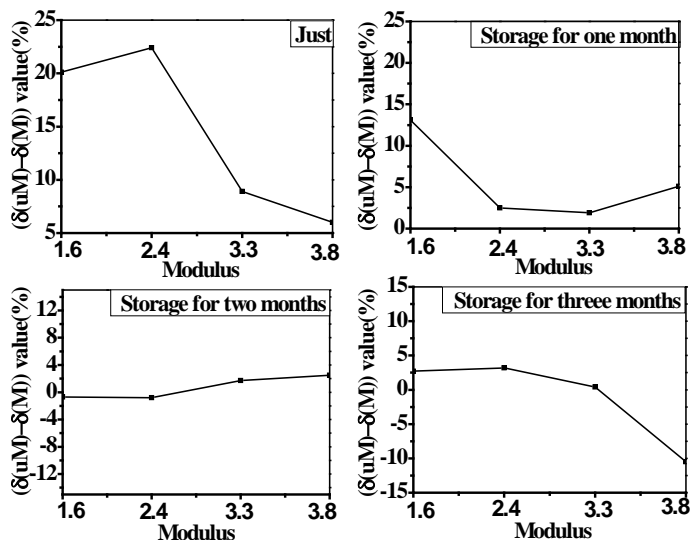
Figure 4. Relationship between the difference that unmodified water glass minus modified water glass and difference specimens.
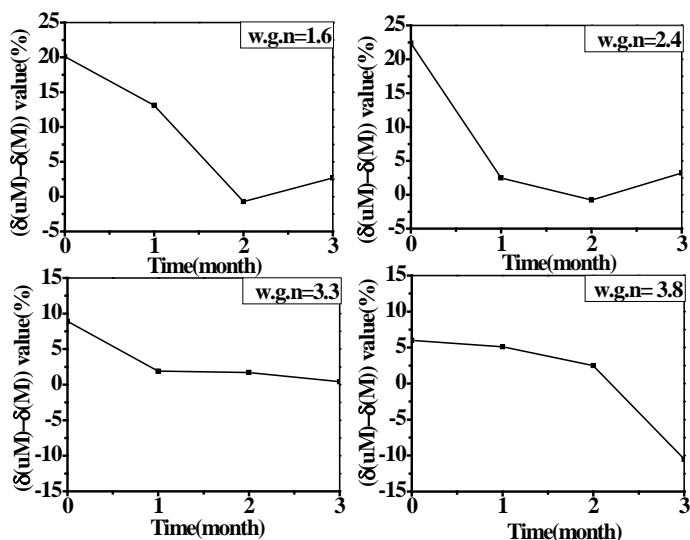

Figure 5. Relationship between the difference that unmodified water glass minus modified water glass and storage for time.

more than two months, water glass with modulus of 1.6 and 2.4 before and after modification had little difference. What's more, when the water glass was stored for more than three months, water glass with modulus of 3.3 and 3.8 before and after modification had little difference, which indicated all their $(\delta_{(uM)}-\delta_{(M)})$ kept at low value within range −10.5 - 0.4.

2) In contrast to Figure 4, the change tendency of $(\delta_{(uM)}-\delta_{(M)})$ value with aging time shown in Figure 5 displayed some differences. When the water glass was just made, the $(\delta_{(uM)}-\delta_{(M)})$ values of water glass with modulus of 1.6 and 2.4 had maximum value, higher than those of water glass with modulus of 3.3 and 3.8. With the storage time increasing, the $(\delta_{(uM)}-\delta_{(M)})$ value of water glass with modulus of 1.6 decreased steadily, until after two months, and the draw-back of the $(\delta_{(uM)}-\delta_{(M)})$ value from −0.7 to 2.7 occurred at three months of storage. The same observed phenomenon occurred on the $(\delta_{(uM)}-\delta_{(M)})$ values of water glass with modulus of 2.4. This further demonstrates that when modulus of water glass was 1.6 and 2.4 in absence of modifier, the alkaline mechanism of polymerization took major role on the water glass, and the depolymerization of silicate species would lead to an increase of oligomeric silicate species in presence of higher Na_2O [12].

But when modulus of water glass was 3.3 and 3.8, the ($\delta_{(uM)}$-$\delta_{(M)}$) values all decreased straightly with the aging time, and the draw-back of the ($\delta_{(uM)}$-$\delta_{(M)}$) value cannot be observed. This demonstrates that when modulus of water glass was 3.3 and 3.8 in absence of modifier, the acidic mechanism of polymerization took major role on the water glass, resulting in decrease of oligomeric silicate species.

4. Conclusions

1) The aging of water glass was that all sorts of silicate species in water glass formed high polysilicates with various polymerization methods.

2) After adding chemical modifier into water glass, modifier firstly decreased the content of monomeric species and oligomeric silicate species by the "creating a bridge" mechanism, which maintained the system in a relatively stable state of dynamic balance. Later, the change of content of various silicate species was smaller than that in unmodified water glass in the storage process.

3) Modifier polyacrylamide could delay aging by 1 - 2 months. As shown in the mechanism, physical modification could eliminate aging and chemical modification could retard aging, so we also carried out a chemical and physical modification test, namely using reflux and adding modifier of water glass. The result was that the content of oligomeric silicate species significantly increased than without the reflux, and the content of monomeric species also slightly increased, which indicated that the physical modification was equivalent to a reverse process of water glass aging, and that it could restore the water glass to the original state. Therefore, if the water glass was processed by chemical and physical modification, it would obtain delaying effect, which would open up a new field of water glass application.

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