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CONTRIBUTIONS TO THE MECHANISM OF WATER GLASS HARDENING BY USING THERMAL ANALYSIS METHODS AND X-RAY DIFFRACTOMETRY

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Thermal analysis methods and X-ray diffractometry provided data on and permitted practical use of the eutectic mixture between $Na_2O \cdot 2SiO_2$ and SiO_2, which melts at 790°C. Based on this, water glass was used as a binder to obtain artificial cluster granules, ceramically hardened by heating at 800°C. The process of water glass hardening in the presence of hardening reagents such as Na_2SiF_6, NH_4Cl, silica gel and ultra-fine silica was studied by thermal analysis. In the first stage, gelification of the SiO_2 sol takes place by neutralization of the NaOH deflocculant, while the second stage involves tridimensional cross-linking by polycondensation, promoted by powders rich in SiO_2.

The alkaline silicates Na_2SiO_3 and K_2SiO_3, technically called water glass, are obtained by melting a mixture of quartz sand, Na_2CO_3 (K_2CO_3) or Na_2SO_4 (K_2SO_4) and low quantities of coal in a furnace at 1300-1400°. The melt obtained is granulated in water and the granules are converted by autoclaving to a colloidal solution of various concentrations, called water glass [1].

Besides Na_2SiO_3, compounds such as Na_4SiO_4 and $Na_2Si_2O_5$, containing anions of orthosilicic acid and macromolecular anions formed by the polycondensation of SiO_4^{4-} tetrahedra, have also been identified in the melt [2]. The crystalline compound $Na_2Si_2O_5 \cdot 9H_2O$ has been obtained in the solid state [3].

Technical water glass contains Na (K) silicate and silicon dioxide, with a silica modulus of 2.5-3 for sodium glass and 3.5-4 for potassium glass and a density of 1.71-1.36 g/cm^3 [1].

In order for water glass solution to be used as a binder, its density should be 1.38-1.40 g/cm^3 when it contains 27% SiO_2 and 8% NaOH [3].

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Water glass is a colloidal solution of silicic acid deflocculated by NaOH resulting from the hydrolysis of sodium (potassium) silicates.

Depending on the pH, the silicic acid forms sols with negative particles at $pH \geq 7$, and sols with positive particles at $pH \leq 4.5$. The alkaline sols are more stable than the acid ones, and therefore the gelification time may be increased indefinitely by increasing the pH [4].

The hardening chemism of the water glass binder has not been fully clarified [1], and we should therefore like to make a contribution to this subject.

Experimentally, we found that the hardening of water glass at normal temperature occurs in stages: the first is the setting stage, consisting of the gelification of SiO_2 sol, and the second is the hardening stage, accelerated by hardening promoters such as Na_2SiF_6 [1], NH_4Cl, silica gel and ultrafine silica (UFS). Ceramic hardening at 800° is due to the formation of the eutectic mixture melt between $Na_2O \cdot 2SiO_2$ and SiO_2 with $p_t = 790°$ [3].

Our purpose was to use mainly thermal analysis to study the phenomena accompanying the hardening of the water glass binder at room temperature and at 800°.

Experimental

A Paulik-Paulik-Erdey 2895 derivatograph and an HZG-3 X-ray diffractometer attached to a TUR-M 62 source were used. The most representative DTG curves were recorded on the water glass solution, on each hardening reagent and on the hardened products. The water glass solution used in the experiments had a concentration of 40%, with a density of 1.4 g/cm^3.

Results and discussion

The thermal analysis carried out on the water glass solution (Fig. 1) shows a total mass loss of 60% up to 500°, consisting of the water bound in different ways, while the solid mass consists mainly of a mixture of polysilicates such as SiO_2 and $Na_2O \cdot 2SiO_2$. The existence of $Na_2O \cdot 2SiO_2$ crystals in the whole amorphous mass was obvious from the results of thermal analysis and X-ray diffraction as well (Fig. 2).

The derivatogram of the water glass sol (Fig. 1) led to the following findings:

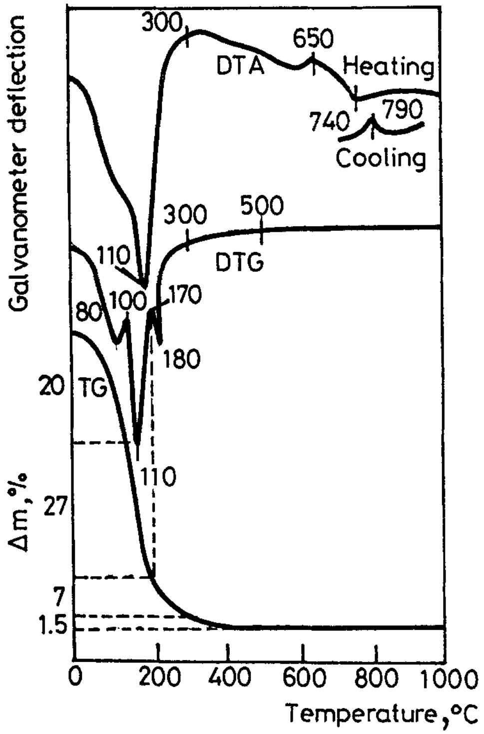

Fig. 1 Thermal curves of colloidal water glass solution ($\rho = 1.4$ g/cm^3)

– In the temperature range from 20° to 100° the free water is lost from the colloidal solution, with maximum rate at 80°.

– Between 100° and 170°, the water contained in the intermicellar space is lost, with maximum rate at 120°, a fact which is shown in Fig. 4, curve *d*. Intermicellar water is lost at a higher temperature than free water, because it is bound to the micelles in the silica gel, which are strongly hydrophilic, by hydrogen-bonds [2].

Generally, adsorbed and intermicellar water is lost continuously, based on a physical equilibrium dependent on concentration and temperature, which is confirmed in this case, too.

– From 170° to 250°, the crystallization water corresponding to the crystalline compound $Na_2O \cdot 2SiO_2 \cdot 9H_2O$ is lost, with maximum rate at 180°. The presence of this crystalline compound is revealed in the DTA curve (Fig. 1); a more evident crystalline arrangement is probably produced at 650°, followed by crystal melting at 740°. For additional checking, the cooling curve was also recorded, with compound recrystallization at 790°.

In the solid water glass mass, X-ray diffraction demonstrated no crystals; being present in low quantity, they were probably masked by the large amount of amorphous solid mass (Fig. 2*a*). After the solid water glass mass was heated at 650°, these crystalline structures clearly appeared in the diffractogram (Fig. 2*b*). It is likely that at 650° only a structural reorganization of the crystals takes place. Therefore, this third stage of mass loss was assigned to the dehydration of $Na_2O \cdot 2SiO_2 \cdot 9H_2O$, in accordance with the water loss calculated from the TG curve in this temperature range and the Na_2O content of the technical water glass used (considered as the crystallohydrate).

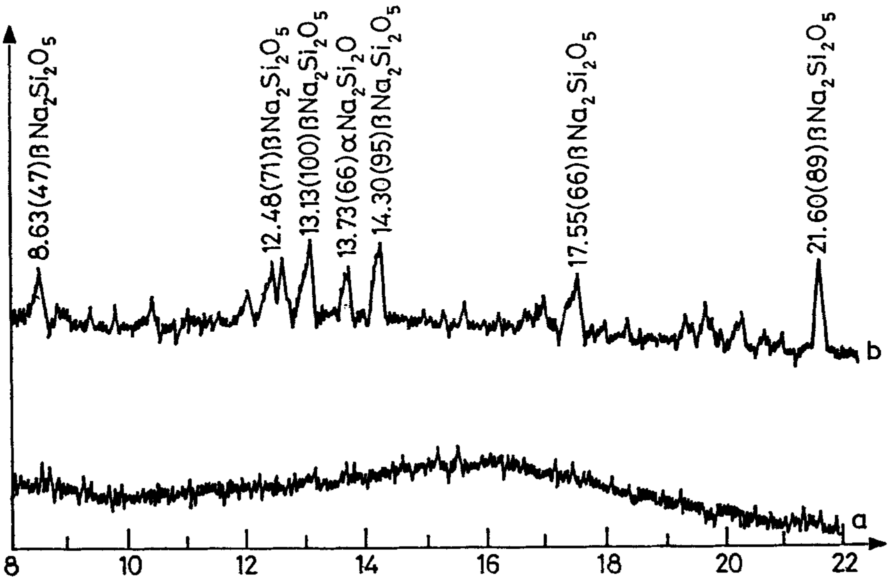

Fig. 2 X-ray diffractogram on hardened water glass, by keeping it under a film form for 2 days at room temperature (a) and by heating at 650°C (b)

The compound $Na_2O \cdot 2SiO_2$ is of interest because it melts at low temperature (874°) and together with SiO_2 forms a eutectic compound with p_t = 790° [3]. The formation of this eutectic compound was used to obtain ceramically hardened granules by heating at 800°.

– In the temperature range from 250° to 500°, the constitution water is gradually lost, with resulting crosslinking of the system (formation of oxygen bridges by the condensation of OH groups between micelles) [5].

Generally, the crystallization water and the constitution water are lost in limited temperature ranges, marked in the thermal analysis curves by well-outlined effects. For the water glass solution, the loss of the crystallization water observed this rule, while the loss of the constitution water did not, because the water removal took place in the inner structure of the gel. this latter effect is observed in a wide temperature range (300-500°) and at a low rate.

As concerns the process of hardening of the water glass binder at room temperature, we considered its mechanism and kinetics.

In the first stage, gelification of the silica sol probably occurs due to the neutralization of the deflocculant NaOH by the added "hardening promoters"; in the second stage, polycondensation occurs with accelerated tridimensional cross-linking, mainly of fine powders containing SiO_2.

The classical hardening promoter is Na_2SiF_6 in the presence of CO_2; the influence of this was studied by means of derived thermal gravimetry, illustrated in Fig. 3.

The deflocculant NaOH resulted from hydrolysis of the silicates and sodium fluorosilicate. The hydrofluoric acid resulting from hydrolysis of Na_2SiF_6 neutralizes most of the deflocculant, this phenomenon being accompanied by SiO_2 gelification. In the presence of CO_2, the remainder of the deflocculant is most probably converted to Na_2CO_3; as this is 5 times less soluble than NaOH, it crystallizes, promoting the hardening by SiO_2 gel cross-linking.

The DTG curves in Fig. 3 were obtained on technical colloidal water glass solution (curve *a*), Na_2SiF_6 hardening reagent (curve *b*), mixtures of water glass and Na_2SiF_6 (5%) at zero time (curve *c*), after a 2-day hardening, and with and without the 10 % addition of finely ground siliceous sand (0-0.125 mm) (curves *d* and *e*, respectively).

The percentages are considered *vs.* the $Na_2O{\cdot}nSiO_2$ content of the water glass.

Figure 3, curve *b*, reveals that Na_2SiF_6 exhibits thermal stability up to 530°, when it starts to decompose, eliminating SiF_4 [6]. In the water glass mixtures, the integral consumption of Na_2SiF_6 in the glass-hardening process is obvious.

The kinetics of water loss from the water glass - fluorosilicate mixtures depends upon the contact time of the components, the presence of fine powders based on SiO_2, etc.; as the contact time increases, the constitution

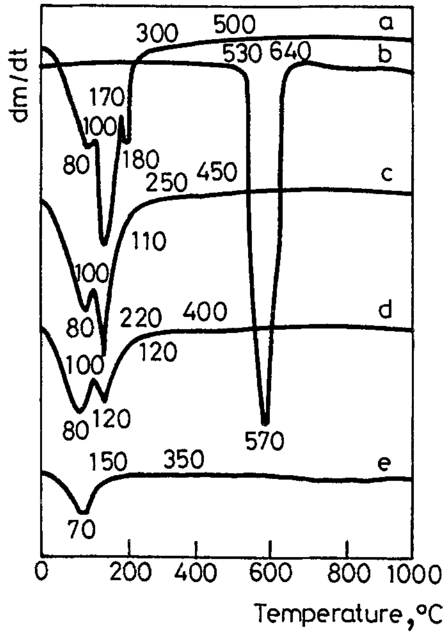

Fig. 3 Derived thermal gravimetry curves comparatively presented in order to evidence the part played upon hardening by the following factors: Na_2SiF_6, time, finely ground sand.
a) - water glass solution ($\rho = 1.4$ g/cm^3); b) - Na_2SiF_6: c) - water glass + Na_2SiF_6 (5%) immediately after mixing; d) - water glass + Na_2SiF_6 (5%) after 2-day hardening;
e) - water glass + Na_2SiF_6 (5%) + sand (10%) after 2-day hardening

water loss is completed at a lower temperature (500-350°) (Fig. 3, curves *a*, *c*-*e*). Curve *e* shows particular water loss kinetics and the quickest cross-linking owing to the presence of the finely-ground sand.

The very fine powders containing SiO_2 (sand, silica gel or UFS) added to the glass matrix play several roles: they promote the hardening, because they react with the OH groups of the matrix, accelerating polysilicate formation; they contribute to the formation of crystalline compounds; and they play the part of microfillers and of degreasing substances, preventing glass expansion during heating [3].

The parts played by other promoters, such as NH_4Cl, silica gel and UFS added in an amount of 5% and after a 2-day hardening, were also studied in comparison with the fluorosilicate hardener by means of derived thermal gravimetry (Fig. 4).

Experimentally, NH_4Cl was found to gelify the silica sol at the highest rate, possibly because of the HCl released in the hydrolysis reaction, which rapidly neutralizes the deflocculant. Figure 4, curve *c* shows that NH_4Cl is thermally decomposed within the temperature range from 150° to 380°, with maximum rate at 280° [6]. In curve *h*, the decomposition effect of NH_4Cl no longer appears, which demonstrates that it was integrally consumed.

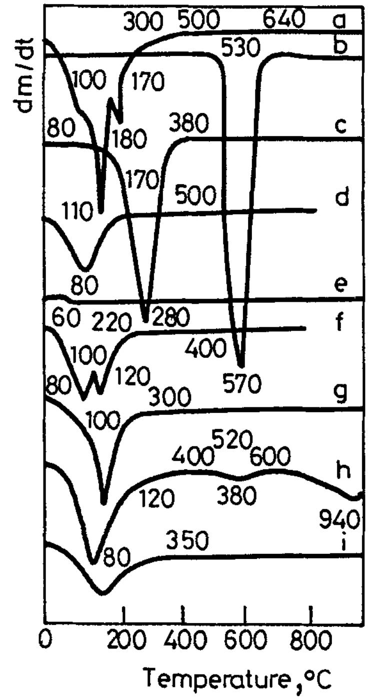

Fig. 4 Derived thermal gravimetry curves compare the influence of different hardeners on the hardening of water glass binder.
a) - water glass solution ($\rho = 1.4$ g/cm^3); b) - Na_2SiF_6; c) - NH_4Cl; d) - silica gel; e) - UFS; f) - glass hardened with Na_2SiF_6; g) glass hardened with silica gel; h) - glass hardened with NH_4Cl; i) - glass hardened with UFS

This curve also reveals the presence of NaCl resulting from the neutralization reaction, followed by melting at 800°, and evaporation, occurring with maximum rate at 940°. The mass loss effect with maximum rate at 580° represents the destruction of NaCl crystals by atomization, a process which is practically non-thermal [7].

As concerns the action of silica gel and UFS (Fig. 4, curves *g* and *i*), we assume that they gelify the sol by rapid water adsorption because of their high specific area, but they act predominantly in the cross-linking process; the proof is that after a 2-day storage at room temperature, the constitution water loss takes place at a temperature 100-150 deg lower than that for water glass hardened in the presence of CO_2 in air (Fig. 4, curve *a*).

Applications

The hardening promoters studied in this work were used in the composition of some thermal tracing paints based on water glass.

The crystalline component $Na_2O \cdot 2SiO_2$ and SiO_2 (from water glass added) form a eutectic mixture melting at 790°, which enabled us to use water glass for the ceramic hardening of some artificial cluster granules by heating at 800°.

Conclusions

Thermal analysis permitted a contribution to the formulation of hypotheses on the mechanism of hardening of the water glass binder at room temperature and at 800° and to the parts played by the hardening promoters (Na_2SiF_6, NH_4Cl, silica gel and UFS).

References

1 I. Teoreanu, V. Moldovan and M. Georgescu, Physical and Chemical Fundamentals on the Hardening of Inorganic Binders, Editura didactica si pedagogica (Didactical and Pedagogical Publishing House), Bucharest 1972, p.349.
2 C. D. Nenitescu, General Chemistry, Editura didactica si pedagogica, Bucharest 1979, p.841.
3 A. Petzold and M. Röhrs, Beton für hohe Temperaturen, Veb, Verlag für bauwessen, Berlin 1971, pp.50-53, 198.
4 S. Tilenschi, Chimie coloidala, Editura technica (Technical Publishing House), Bucharest 1964, p.418.
5 V. Moldavan, Aditivi în betoane, Editura technica, Bucharest 1978, p.51.
6 Dictionar de chimie Editura technica, Bucharest 1964, pp.193, 308.
7 J. Simon, S. Gál and L. Erdey, Acta. Chim. Acad. Sci. Hung., 53(1967) 105.

Zusammenfassung — Die durch Thermoanalyse und Röntgendiffraktion gewonnenen Daten ermöglichten die Nutzung eines eutektischen Gemisches aus $Na_2O \cdot 2SiO_2$ und SiO_2 mit einem Schmelzpunkt von 790°C. Auf dieser Basis wurde Wasserglas als Bindemittel zur Herstellung von künstlichen Cluster-Granulaten genutzt, die bei 800°C keramisch gehärtet wurden. Dieser Härtungsprozess von Wasserglas in Gegenwart von Härtemitteln wie z.B. Na_2SiF_6, NH_4Cl, Silikagel und ultrafeiner Kieselerde wurde mittels Thermoanalyse untersucht. Im ersten Schritt der Gelbildung aus dem SiO_2-Sol erfolgt die Neutralisation des NaOH-Deflokulanten, während der zweite Schritt durch Polykondensation eine dreidimensionale Vernetzung umfaßt, die durch SiO_2-reiche Pulver unterstützt wird.