75. H. O. House, P. P. Wickham, and H. C. Müller, J. Amer. Chem. Soc., 84, 3139 (1962).
76. S. Rossi, W. Butta, and C. Valvo, Farmaco (Pavia), Ed. Sci., 14, 666 (1959).
77. W. Schneider and H. Götz, Annalen, 653, 85 (1962).
78. E. Anet, G. K. Hughes, D. Marmion, and E. Ritchie, Austral. J. Sci. Research, A 3, 330 (1950).
79. S. F. Birch, W. J. Oldham, and E. A. Johnson, J. Chem. Soc., 818 (1947).
80. L. M. Rice and C. H. Grogan, J. Org. Chem., 22, 185 (1957).
81. C. H. Grogan and L. M. Rice, J. Org. Chem., 22, 1223 (1957).
82. R. Griot, Helv. Chim. Acta, 42, 67 (1959).
83. G. Schmidt, German P. 1086703 (2nd February 1961).
84. W. E. O'Malley, G. W. Haemmerli, L. M. Rice, and C. F. Geschickter, J. Amer. Pharmaceut. Assoc. (Pract. Pharmaceut. Edn.), 47, 263 (1958).
85. M. Tiffeneau and K. Fuhrer, Bull. Soc. chim. France [4], 15, 162 (1914).
86. J. V. Braun and A. Nelken, Ber., 55, 2059 (1922).
87. J. V. Braun and F. Zöbel, Annalen, 445, 247 (1925).
88. Bulei Sukural, Bull. Chem. Soc. Japan, 7, 155 (1932).
89. E. Hope and F. Lauskshear, Proc. Chem. Soc., 29, 224 (1913).
90. E. W. Cook and W. G. France, J. Phys. Chem., 36, 2383 (1932)
91. A. Uffer and E. S. Schlitter, Helv. Chim. Acta, 31, 1397 (1948).
92. L. M. Rice, C. H. Grogan, and E. E. Reid, J. Amer. Chem. Soc., 75, 4911 (1953).
93. L. M. Rice, C. H. Grogan, and E. E. Reid, J. Amer. Chem. Soc., 77, 616 (1955).
94. W. E. O'Malley, G. Winkler, L. M. Rice, and C. F. Geschickter, J. Amer. Pharmaceut. Assoc. (Pract. Pharmaceut. Edn.), 46, 346 (1957).
95. C. H. Grogan and L. M. Rice, U. S. P. 2784199 (5th March 1957).
96. L. M. Rice and C. H. Grogan, J. Org. Chem., 25, 393 (1960).
97. K. Alder and K. H. Backendorf, Annalen, 535, 101 (1938).
98. R. B. Woodward and H. Baer, J. Amer. Chem. Soc., 70, 1161 (1948).
99. K. Alder and H. F. Rickert, Ber., 70, 1354 (1937).
100. O. Diels and S. Olsen, Annalen, 490, 243 (1931).
101. G. I. Poos, M. M. Lehman, E. B. Landis, and J. D. Rosenau, J. Medicin. Pharmaceut. Chem., 5, 883 (1962).
102. K. Alder, F. W. Chambers, and W. Trimborn, Annalen, 566, 27 (1950).
103. G. I. Poos and J. D. Rosenau, J. Org. Chem., 28, 665 (1963).
104. K. Takedac et al., Ann. Report Shionogi Res. Lab., 10, 1 (1960).
105. T. Minesta et al., Ann. Report Shionogi Res. Lab., 10, 15 (1960).
106. Monabu Fujimoto and Keiko Okabe, Chem. Pharm. Bull. (Tokyo), 10, 714 (1962).
107. L. M. Rice and C. H. Grogan, J. Org. Chem., 22, 1100 (1957).
108. L. M. Rice and C. H. Grogan, J. Org. Chem., 24, 7 (1959).
109. R. C. Fuson and W. Cole, J. Amer. Chem. Soc., 60, 1237 (1938).
110. E. R. Buchman, A. O. Reims, T. Skei, and M. J. Schlatter, J. Amer. Chem. Soc., 64, 2696 (1942).
111. L. M. Rice, J. Org. Chem., 24, 1520 (1959).
112. C. A. Kerr, J. Amer. Chem. Soc., 51, 614 (1929).
113. M. Conrad and M. Guthzeit, Ber., 17, 1185 (1884).
114. W. H. Perkin and J. F. Thorpe, J. Chem. Soc., 75, 48 (1899).
115. T. Izzo, J. Org. Chem., 28, 1713 (1963).
116. R. Kuhn and H. Trischmann, Annalen, 611, 117 (1958).
117. R. Baltzly, N. B. Mehta, P. B. Russell, R. E. Brooks, E. M. Grivsky, and A. M. Steinberg, J. Org. Chem., 27, 213 (1962).

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POLYMERISATION CONCEPTS IN THE CHEMISTRY OF CEMENTS

Yu. S. Cherkinskii

1. INTRODUCTION

The chief chemical elements present in cements are silicon, aluminium, oxygen, and calcium. In the inorganic world, silicon exhibits a remarkable ability to form polymeric chains[1]. These include the homochain polymer formed by elementary silicon, and a large number of heterochain polymers, of which the silicic acids and their salts — the silicates — are most widely encountered in nature and also in practical applications[2-8].

Aluminium is a metallic element but the great majority of its oxygen compounds, e.g. compounds such as corundum and hydrargillite, are heterochain polymers[2,9-13].

Oxygen in the polymeric chains formed by various elements acts as a bridge, and only in the peroxides is it capable of forming a homochain, consisting of two atoms[1].

Calcium on the other hand behaves as a cation.

Since the chief elements present in cements are capable of forming inorganic polymer chains, there is every justification for assuming that polymerisation and depolymerisation processes will also take place in the preparation and hardening of cement.

The ideas of Le Châtelier, subsequently developed by many workers, made it possible to understand the basis of the mechanism of the hardening of inorganic binding agents. In most work devoted to this question, the substance taken as standard model was gypsum — a compound which is not polymeric in character. In some cases, macromolecular compounds were also used as models. While drawing the analogy between the mechanisms of the hardening of cement and joiners' glue or silica gel, however, the supporters of the colloid theory (Michaelis and Kühl) saw in these substances only the high degree of dispersion, the high specific surface, and the ability to take part in sorption processes[14,15].

Modern theoretical views on the mechanism of the hydration hardening of cement are based on the concepts of physicochemical mechanics, whose basis principles were developed by Rebinder[16,17].

Work by Bernal[18], Belov and coworkers[19,20], and others established that the products of the hydration hardening of Portland cement contain isolated units of calcium hydrosilicates and compounds containing chains of condensed silicon–oxygen tetrahedra, i.e. polysiloxane chains. The periodicity of the manifestation of binding properties, related to Mendeleev's Table, was established by Zhuravlev[21] and confirmed by Moshchanskii[22].

In an examination of cement and concrete from the viewpoint of the chemistry of macromolecular compounds, Korshak and Mozgova[2] put forward the idea that "cement and concrete contain inorganic silicate polymers". The suggestion that silicate cements be regarded as three-dimensional polymers had been put forward earlier, in

less explicit form[11]. More recently the question of polymerisation has been raised with increasing frequency in papers devoted to inorganic binding agents[23-29].

The basic questions of the chemistry of Portland cement and alumina cement are considered below from the viewpoint of polymerisation reactions.

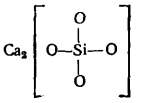
2. PORTLAND CEMENT

The raw material used for the preparation of Portland cement contains, firstly, elements capable of forming macromolecular compounds with oxygen (chiefly silicon and aluminium) and, secondly, an element (calcium) which acts as a cation.

Silicon and aluminium are introduced into the charge in the form of natural (clays, loams, or clay shales) or synthetic (e.g. the waste materials from the production of aluminium from nephelite) macromolecular compounds whose structure has a definite influence on the preparation of the clinker[30-33]. Calcium is introduced into the charge in the form of lime or limestone.

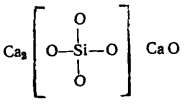
Preparation of cement. It is possible to distinguish the following main stages in the firing of the charge: (1) drying and preheating; (2) depolymerisation; (3) ionic solution; (4) cooling. From the viewpoint of polymerisation theories, the second and third stages are the most important and the most complex.

The second stage, which gives a monomeric silicon–oxygen compound by the thermal depolymerisation of the original polysiloxane (polyaluminosiloxane) in the presence of oxygen and calcium ions, is a *necessary* stage in the preparation of the binding agent, but this stage is still *insufficient* for the preparation of a binding agent which hardens rapidly. The process taking place in the solid phase[34] at this stage leads to the formation of belite, the chief component of which is calcium orthosilicate — a monomeric silicon–oxygen compound[35-38]



or $2CaO \cdot SiO_2$.

The preparation of the highly active binding agent alite, whose chief component is again the monomeric silicon–oxygen compound $3CaO.SiO_2$ or[38-42]



takes place in the third stage as a result of a liquid-phase process. This stage can be defined more precisely as the ionic solution stage[43-47]. This subdivision of the process of clinker preparation is not contradicted by a large amount of experimental data[48-54].

In the preparation of Portland cement, the macromolecular component of the charge — clay — is heated to a high temperature. Clay also forms ceramic tile. In the preparation of Portland cement, however, the clay is converted not into water-resistant ceramic but into a substance which exhibits new binding properties.

What is changed during the high-temperature transformation of the clay and at what stage does the change take place?

The first stage in the transformation of the original polyaluminosiloxane (the clay minerals) is evidently of the same general type in both cases and involves thermal depolymerisation.

The two processes differ in the subsequent stage, in which in the first case the products of the degradation of the polyaluminosiloxane are converted into inorganic macromolecular compounds of a new type as a result of thermal polymerisation (polyrecombination) on cooling. These include a vitreous phase, mullite, and certain other substances which form the basis of ceramics and porcelain. Depolymerisation in the case of kaolinite, for example, begins in the range of the endothermic effect (520–600°), whereas polyrecombination takes place at 900–1000° and is responsible for a sharp exothermic effect[55-59].

In the preparation of cement, the changes in the polymers taking place in a medium of calcium ions (and oxygen) stops at the depolymerisation stage, and the resulting monomeric silicon–oxygen groups (and polyaluminooxane chains) are fixed by the calcium ions, which prevent polymerisation in the melt during cooling.

Thus the changes in the silicon–oxygen component of a Portland cement charge are described by the left-hand side of the scheme illustrated in Fig. 1.

Clinker. The hydraulic activity of Portland cement clinker is determined chiefly by the presence of monomeric silicon–oxygen compounds taken in the form of the calcium salts (or strontium or barium salts[21]). Increase in the defect nature of the structure leads to an increase in the activity of the binding agent[41,60].

Reaction with water. The reaction of cement with water (with chemistry of the hardening process) is described by the right-hand side of the scheme (Fig. 1).

In the reaction of clinker (here and subsequently we shall refer to the silicate component, namely dicalcium silicate, but it should be noted that the aluminate and ferrite components also play some part in Portland cement) with water leads, as a result of the hydrolysis of calcium orthosilicate, to the formation of orthosilicic acid[61-63]:

$$Ca_2SiO_4 + 4H_2O \rightarrow 2Ca^{2+} + 4OH^- + H_4SiO_4, \quad (1)$$

which is an extremely unstable compound.

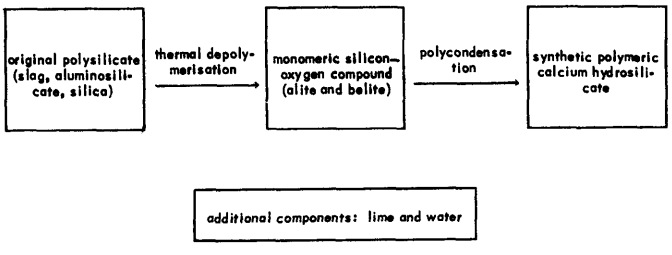


Fig. 1. Polymeric changes undergone by the silicate component of Portland cement.

Under the conditions of setting, the orthosilicic acid formed takes part in reactions of salt formation and polycondensation.

a. Salt formation:

$$\equiv Si-O^-H^+ + Ca^{2+} + 2OH^- \rightleftarrows \equiv Si-O^-Ca^{2+} + OH^- + H_2O. \quad (2)$$

This reaction involves the calcium ions which were liberated as a result of the hydrolysis of calcium orthosilicate, and also the "excess of lime" in C_3S. [64-66]. Under ordinary conditions, however, the hydrolysis is irreversible and reaction (2), when orthosilicate is taken as the original silicic acid, leads to the formation of acid salts of the afwillite type [67]. Orthosilicate is formed only under conditions of extremely high temperatures and pressures [67-68].

b. The polycondensation reaction is represented in general form by the equation

$$HO-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-OH + HO-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-OH \rightleftarrows HO-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-O-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-OH + H_2O, \quad (3)$$

or, in the limit,

$$n Si(OH)_4 \rightleftarrows (SiO_2)_n (OH)_m + p H_2O, \quad (4)$$

where $m \rightarrow 0$ and $p = \frac{4n - m}{2}$.

Opinions differ regarding the details of the mechanism of the polycondensation reaction [69-73] and the probability of condensation of $H_3SiO_4^-$ ions in alkaline medium has also been noted [74,75].

Reactions (2) and (3) take place simultaneously and the direction of the chemical reactions is decided by competition between these two types (ionic and molecular) of chemical change.

A vast amount of practical experience and experimental and theoretical data [76] indicate that the tendency of orthosilicic acid to undergo polycondensation is so great that this molecular reaction is one of the chief reactions determining the chemistry of the aqueous hardening of Portland cement and, in particular, the behaviour of cement block kept in water.

The equilibrium for the polycondensation reaction always tends to be displaced towards the formation of polymeric silicates; this takes place at the first opportunity, and in the limit leads to the formation of silica $(SiO_2)_n$. In the presence of calcium ions, however, monomeric calcium hydrosilicates (acid salts of orthosilicic acid), e.g. afwillite and the alpha-hydrate of C_2S, and polymeric hydrosilicates (salts of di- and poly-silicic acids) are formed. According to the phase diagram for the $CaO-SiO_2-H_2O$ system at normal temperature [18], hydrosilicates with a molar $CaO : SiO_2$ ratio less than 5 : 3 are polymeric, although polymeric calcium silicates (hillebrandite) with higher $CaO : SiO_2$ ratios are also known.

Calcium hydrosilicates. The composition and structure of individual calcium hydrosilicates in a number of cases have been established with certainty and in other cases they have been assumed [20,77,78]. On the basis of polymerisation principles, calcium hydrosilicates can be divided into two main groups: low-molecular and macromolecular (or simply polymeric).

Low-molecular calcium hydrosilicates include compounds with a monomeric or dimeric silicon–oxygen anion.

a. Compounds containing a monomeric silicon–oxygen anion include, for example, afwillite $Ca_3[SiO_3(OH)].2H_2O$ [79] and the alpha-hydrate of C_2S. [38] Afwillite and other calcium hydrosilicates containing an individual silicon–oxygen group and consisting of a definite combination of Si tetrahedra and hydroxide and calcium ions are the first members of a polymer homologous series of calcium polyhydrosiloxanates, whose existence is possible under conditions where the active degrading action of the calcium ions is a maximum.

b. Compounds with a dimeric silicon–oxygen anion include those of the cuspidine type $Ca_4[(Si_2O_7)(OH, F)_2]$. [80,81]

These hydrosilicates can be regarded as the second members of the above polymer homologous series. Calcium hydrosilicate containing a diorthosilicate anion obeys the crystal-chemical laws covered by the second chapter of "The Crystal Chemistry of Silicates Containing Large Cations". [19] It can therefore be regarded as the first member in a series of crystallographically and chemically similar calcium hydrosilicates in which the individual or linked diorthosilicate units are situated in the electric field of the calcium ions.

It is possible to assume the existence of the various [67] subsequent members of the polymer homologous series of calcium polyhydrosiloxanates, but it is more important to turn attention to the macromolecular compounds whose molecular or, more accurately, ionic weight amounts to several thousand units.

Macromolecular calcium hydrosilicates have ordered or disordered structures. Compounds with ordered structure include xonotlite $Ca_6(Si_6O_{17})(OH)_2$, [82,83] nekoite $Ca_3(Si_6O_{15}).2H_2O$, [84] and tobermorite $Ca_{10}(Si_{12}O_{31}).(OH)_6.nH_2O$. [66,85,86]

The first type of hydrosilicate has a polymeric silicon–oxygen anion in the form of linked six-unit rings [82]; the silicon–oxygen chain of hydrosilicates of the nekoite type consists of alternating eight-membered and double five-membered rings [84]. The chain in tobermorite is made up of doubled xonotlite chains which fit over one another in the condensation process to form corrugated layers [80].

Examination of polymeric calcium hydrosilicates shows that the structure of the silicon–oxygen chain may be comparatively simple or extremely complex.

The even greater complexity of the structure of the silicon–oxygen polymeric anion produced in the polycondensation process or on rearrangement of the ordered structure makes it impossible to determine the structure by existing crystallographic and chemical methods. These calcium hydrosilicates are combined in a subgroup of polymers with disordered structure. They include the gel-like phase and the X, Y, and Z phases [77,78].

Polymeric hydrosilicates and some properties of concrete. Belov attributes the cementing properties to polymeric hydrosilicates of the xonotlite type [42,80]. On the other hand, it has been noted [20] that the strength of cements decreases with the formation and increase in the quantity of the low-molecular readily-crystallising afwillite and the alpha-hydrate of C_2S.

The concentration of polymeric calcium hydrosilicates can be increased artificially; this increases the bending strength of the concrete but decreases the rate of hardening[87,88]. In practice, this is usually achieved by introducing, with the clinker, substances capable of forming polymeric hydrosilicates under the conditions of setting. These substances include silica gel, pozzolana, and diatomite, i.e. familiar mineral additives.

The chemical changes undergone by these additives are also defined by the scheme given in Fig. 1 with the fundamental difference that in this case the depolymerisation of the polysiloxane takes place as a result of the hydrolysis (hydrolytic depolymerisation) of the –Si–O–Si– siloxane bond under the influence of aqueous calcium hydroxide solution[89-93]. The depolymerisation leads to the formation of orthosilicic acid, which condenses according to the mechanism described above; the excess of the silicon–oxygen component makes it possible to increase the quantity of polymeric phase. Similar processes also take place in the preparation of autoclave silicate concretes[77]; the activation of the silicon–oxygen component as a result of the increase in temperature makes it possible to utilise effectively both calcium orthosilicate and metasilicate as well as silica[94].

The most important property of Portland cement — its hydraulic resistance — is determined by the ability of the original clinker materials and their hydrolysis products to form polymeric compounds — polymeric calcium hydrosilicates — since of the ionic and covalent bonds present in the products obtained by hydration hardening, only the covalent bond is sufficiently resistant to the action of the polar solvent water. Although in actual fact the quantity of polymeric silicates (crystalline silicates and the "amorphous" gel-like phase) in cement block is small, the thick network of siloxane chains formed when the cement block comes into contact with water is capable of blocking to a considerable extent the ionogenic components — lime and calcium ions; these are chemisorbed by the polymeric silicate, which prevents them from coming into contact with water and dissolving.

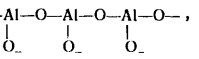
Methods of increasing the quantity of polymeric phase. One possible method of increasing the concentration of polymeric calcium hydrosilicates in concrete involves the use of active mineral additives. Autoclave silicate concretes and limestone–pozzolana concretes also contain a high concentration of polymeric calcium hydrosilicates.

The polymerisation reaction scheme (Fig. 1) may facilitate the search for other methods of preparing inorganic polymeric materials of the silicate–concrete type.

3. ALUMINA CEMENT

Raw material. The raw materials used for the preparation of alumina cement[38,95,96] include, firstly, polymeric coordination compounds of aluminium, such as hydrargillite, boehmite, and diaspore[9,11,12,97-104], and, partly, of iron (haematite), together with a small quantity of a silicate component which we shall not consider in this Section. The second component is lime (limestone).

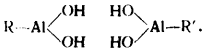
Preparation of cement. After the first preliminary stage involving drying, the second stage of the preparation of cement at temperatures up to approximately 500–600° involves the removal of water from hydrated forms of aluminium, i.e. deolation of hydrargillite (polyaluminodiolane) takes place. With further heating in the presence of Ca^{2+} ions and oxygen, thermal depolymerisation takes place (see scheme in Fig. 2), accompanied by a change in the coordination number (c.n.) of the aluminium atoms from 6 to 4 and leading to the formation of calcium polyaluminooxanate (c.n. Al = 4) containing the chain



or, which is the same thing: $CaO.Al_2O_3$, CA, or $Ca(AlO_2)_2$. The formation of $Ca(AlO_2)_2$ takes place in the liquid phase and it is suggested[105] that the melt contains complex ions. Cooling of the melt is accompanied by thermal polymerisation of calcium aluminooxanates.

Clinker. The instability of oxygen compounds of aluminium with c.n. Al = 4 and their tendency to undergo conversion into stable oxygen compounds with c.n. Al = 6 are the chief factors determining the activity of alumina cement clinker, in which the chief component is calcium polyaluminooxanate (c.n. Al = 4).

Reaction with water. The first stage in the reaction of calcium aluminate (calcium polyaluminooxanate) with water involves rupture of the $^4Al–O–^4Al$ aluminooxane bond as a result of hydration, or more accurately as a result of the olation reaction specific for coordination compounds of aluminium (c.n. Al = 4).[98] During olation, the aluminooxane bond is first converted into the diol bond $R–Al<^{OH}_{OH}>Al–R'$, after which chain rupture takes place with the formation of two hydroxyl groups at the ends of the chain



During olation, the coordination number of the aluminium atom increases from 4 to 6 and the calcium ions go into solution.

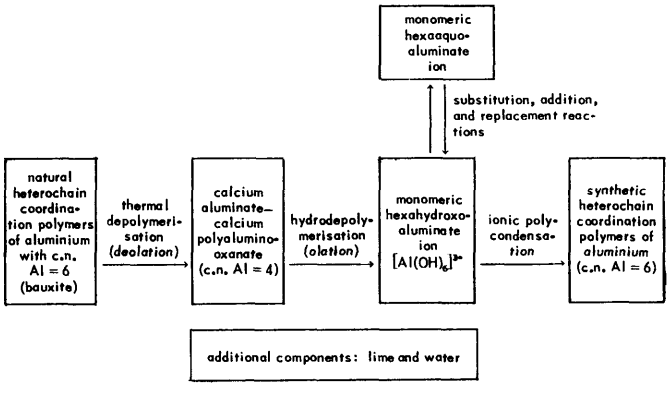


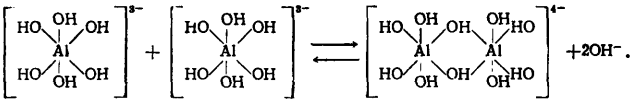
Fig. 2. Polymeric changes undergone by the aluminate component of alumina cement.

At the end of the first stage, further development of the olation process takes place, leading in the limit to the complete degradation of the polyaluminooxane (c.n. Al = 4) with the formation of a monomeric hydrated compound of aluminium with c.n. Al = 6, namely the $[Al(OH)_6]^{3-}$ anion.

Main reactions and compounds obtained. In order to picture the possible reactions in which the hexahydroxoaluminate ion may take part, we may recall that according to the modern theory of hydro-complexes [98,106,107], the amphoteric nature of aluminium hydroxide (hydrargillite) is expressed by the equation

$$[Al(OH)_6]^{3-} \overset{H_3O^+}{\rightleftharpoons} [Al(OH)_3(H_2O)_3] \overset{H_3O^+}{\rightleftharpoons} [Al(H_2O)_6]^{3+}.$$
$$\Big\| \; n\,[Al(OH)_3]_n$$
hydrargillite

The hexahydroxoaluminate ions undergo ionic condensation, probably according to the equation [108]



The dimeric ion undergoes further condensation with a monomeric ion with the formation of a trimer, hexamer, etc.; the hexamer undergoes ring closure and in the limit forms aluminium hydroxide — hydrargillite — a planar polymer with a reticulate structure made up of linked six-membered rings.

Both the monomeric and the more complex anions react with cations, particularly the Ca^{2+} ion, to form salts, some of which are listed in Table 1, which gives complex compounds of aluminium in which the aluminium atom is present in a complex anion and in which only the limiting member of the series — hydrargillite — is neutral.

Hydrargillite exhibits one other characteristic feature. It is the most stable hydrated compound of aluminium in the biosphere [109].

It may therefore be stated that in the limit the reaction of calcium aluminate with water when Ca^{2+} ions are deficient, leads to the formation of hydrargillite.

In an examination of the behaviour of the monomeric $[Al(OH)_6]^{3-}$ ion, it should be noted that the OH^- groups in the inner coordination sphere of the aluminium atom may be replaced by univalent (Cl^-, F^-) or multivalent anions.

An important case in the chemistry of cement is that where the ligand is orthosilicic acid. In this case, inner-sphere substitution taking place under hydrothermal conditions [110] leads to the formation of a separate series of hydrogarnets and, in the limit, of the garnet grossular [the fraction indicates the proportion of the $(SiO_4)^{4-}$ ligand corresponding to one Al atom in the complex] (see p. 456).

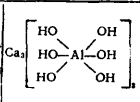
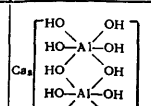
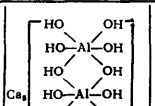
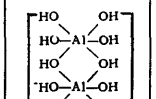
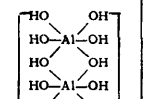
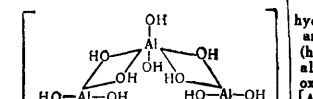
$$[Al(OH_6)]_2Ca_3 \equiv 3CaO \cdot Al_2O_3 \cdot 6H_2O \rightarrow$$
$$\rightarrow [(OH)_6Al(SiO_4)_{1/4}]_2Ca_3 \equiv 3CaO\ Al_2O_3 \cdot {}^1/_3SiO_2 \cdot 5H_2O \rightarrow$$
$$\rightarrow [(OH)_4Al(SiO_4)_{2/4}]_2Ca_3 \equiv 3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O \rightarrow$$
$$\rightarrow [(OH)_2Al(SiO_4)_{3/4}]_2Ca_3 \equiv 3CaO \cdot Al_2O_3 \cdot 1^1/_2SiO_2 \cdot 3H_2O \rightarrow$$
$$\rightarrow [(OH)_2Al(SiO_4)_{1/4}]_2Ca_3 \equiv 3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow$$
$$\rightarrow [(OH)\,Al(SiO_4)_{3/4}]_2Ca_3 \equiv 3CaO \cdot Al_2O_3 \cdot 2^1/_2SiO_2 \cdot H_2O \rightarrow$$
$$\rightarrow [Al(SiO_4)_{6/4}]_2Ca_3 \equiv 3CaO \cdot Al_2O_3 \cdot 3SiO_2.$$

That this process is correct is confirmed by the preparation of the first, third (plazolite), fourth, fifth, and seventh compounds [111-113]; compounds with compositions close to those of the second [114,115] and sixth [111] compounds have also been prepared. The second and subsequent garnets are polymeric: the inner coordination spheres of the Al atom are joined by $(SiO_4)^{4-}$ groups.

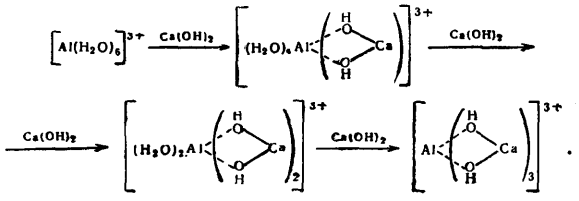
In addition, because of the amphoteric nature of aluminium, formation of the $[Al(H_2O)_6]^{3+}$ ion is also possible (see scheme in Fig. 2).

The behaviour of the $[Al(H_2O)_6]^{3+}$ cation, which is capable of forming salts with anions, differs fundamentally from that of $[Al(OH)_6]^{3-}$. First of all it should be noted that in calcium hydroxide and calcium sulphate solutions coordination compounds are formed, as a result of inner-sphere substitution, in which two aquo-groups in the inner-sphere

TABLE 1. Series of aluminodiolanes.

Type	Anion						
	monomeric	dimeric	trimeric	tetrameric	pentameric	hexameric	polymeric
Ratio OH/Al	6	5	4.67	4.5	4.4	4	3
"Oxide formula"	$3CaO \cdot Al_2O_3 \cdot 6H_2O$	$2CaO \cdot Al_2O_3 \cdot 5H_2O$	$5CaO \cdot 3Al_2O_3 \cdot 14H_2O$	$3CaO \cdot 2Al_2O_3 \cdot 9H_2O$	$7CaO \cdot 5Al_2O_3 \cdot 22H_2O$	$CaO \cdot Al_2O_3 \cdot 6H_2O$	$Al_2O_3 \cdot 3H_2O$
Chemical structural formula							hydrargillite (hydrated aluminium oxide) $[Al(OH)_3]_n$

of the central atom are replaced by one molecule of calcium hydroxide, which occupies two coordination positions:



The calcium hydroxide molecules present in the inner coordination sphere of the Al atom in the calcium hydroaluminates formed during the hydration of alumina cement can be characterised as "combined lime".

When the complex cation is considered from the viewpoint of the octahedral model, a number of possibilities arise. The two calcium hydroxide molecules may be present in the complex in either the *trans*- or *cis*-positions; in the latter case, optically active forms are produced.

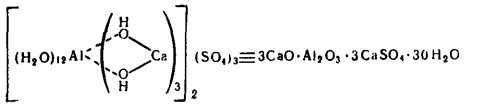
The complex containing three calcium hydroxide molecules should also exist in the form of mirror isomers or a racemate.

The $[Al(H_2O)_6]^{3+}$ cation or its derivatives containing calcium hydroxide molecules react with anions to give compounds with $[Al(OH)_6]^{3-}$, OH^-, Cl^-, SO_4^{2-}, etc. in the outer coordination sphere.

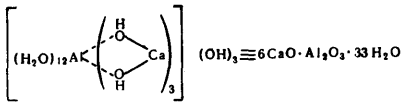
Table 2 gives complex cations which contain a central aluminium atom and can be regarded as derivatives of the $[Al(H_2O)_6]^{3+}$ ion. Thus the water present in the "oxide" formulae should be regarded as water of constitution, removal of which (particular attention must be paid to the possibility of hydrate isomerism) leads to breakdown of the coordination compound.

Calcium hydroaluminates containing much larger quantities of water are also known.

Deval's salt [116]



and hexacalcium hydroaluminate

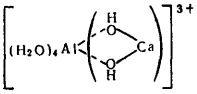
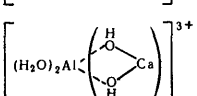
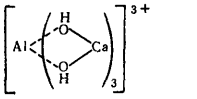


are super-complex compounds [117] in which the coordination sphere of the Al atom contains 12 "additional" water molecules.

Thus in the products of the hydration hardening of monocalcium aluminate it is necessary to distinguish the following [118].

1. Products of the incomplete hydration (olation) of monocalcium aluminate — calcium polyaluminooxanate with c.n. Al = 4.

TABLE 2. Most important hydroaluminates containing the Al atom in a complex cation.

Cation	Anion			
	$[Al(OH)_6]^{3-}$	$(OH)^-$	Cl^-	$(SO_4)^{2-}$
$[Al(H_2O)_6]^{3+}$	$Al(OH)_3$ (hydrargillite)	$Al(OH)_3$ (hydrargillite)	$AlCl_3 \cdot 12H_2O$	$Al_2(SO_4)_3 \cdot 12H_2O$
	$CaO \cdot Al_2O_3 \cdot 8H_2O$	$2CaO \cdot Al_2O_3 \cdot 13H_2O$	—	$2CaO \cdot Al_2O_3 \cdot 3H_2SO_4 \cdot 7H_2O$
 *trans*- and *di-cis*-forms	$2CaO \cdot Al_2O_3 \cdot 7H_2O$	$4CaO \cdot Al_2O_3 \cdot 11H_2O$ (α-, β-, and γ-forms, hydrocalumite)	—	$CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 8H_2O$
 *di-cis*-forms	$3CaO \cdot Al_2O_3 \cdot 6H_2O$	$6CaO \cdot Al_2O_3 \cdot 9H_2O$	$3CaO \cdot Al_2O_3 \cdot 3CaCl_2 \cdot 6H_2O$	$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 6H_2O$

2. Coordination compounds of aluminium in which the aluminium atom (c.n. Al = 6) is present in a complex *anion*: (a) aluminolanes — monomeric (cubic $3CaO.Al_2O_3.6H_2O$), dimeric, and in the limit polymeric (hydrargillite) coordination compounds of aluminium; (b) inner-sphere substitution products in which the inner coordination sphere of the aluminium atom contains the ligands Cl^-, $(SiO_4)^{4-}$ — in the latter case the products are garnets and hydrogarnets (it is necessary to distinguish polymeric forms).

3. Coordination compounds of aluminium in which the aluminium is present in a complex *cation*, surrounded by H_2O and $Ca(OH)_2$ ligands. This group includes hydrocalumite, calcium hydrochloroaluminate and hydrosulphoaluminate, etc.

4. Products obtained as a result of the deolation of hydrargillite, e.g. boehmite.

Additives to the cement. Since the polymeric components of concrete based on alumina cement are polyaluminodiolanes, hydrated forms of aluminium are used as characteristically active hydraulic additives to alumina cement.

Tervalent iron, like aluminium, is capable of forming polymeric coordination compounds [118], so that hydrated and oxide forms of iron, and also calcium ferrites, have no harmful action in alumina cement.

SUMMARY

The ability of oxygen compounds of silicon and aluminium to undergo polymerisation and depolymerisation has a marked influence on the preparation of cement clinker, the reaction of the latter with water, and the properties of concretes. Polymeric compounds are present in the products of hydration hardening and also in the original raw material and the hydraulic additives. It is these polymeric compounds which determine to a considerable extent the technological methods for the processing of the raw material and the properties of cements and concretes. All this indicates that macromolecular compounds and inorganic binding agents (cements) are similar in character. The

main characteristic feature common to these two groups of substances is the presence of chains formed by covalently bound atoms.

In view of the important part played by polymeric substances in cements and concretes, the chemistry of Portland cement and alumina cement is an important field of the chemistry of silicon and aluminium polymers. The chemistry of cements leads to new synthetic procedures in the chemistry of macromolecular compounds.

Cements have their own characteristic features, shown only by this type of substance, so that the group of inorganic binding agents includes both cements and gypsum, magnesia, and lime binding agents.

During the hydration hardening of all inorganic binding agents, a fundamentally new disperse phase — new formations — not previously present in the system are formed from aqueous solution (the water not only acts as a dispersion medium but also takes direct part in the chemical reaction). The part played by the processes leading to the formation of the crystalline aggregate, in particular cement block, in the technological processes for the production of concretes is so great that up to the present the main attention has been directed to these processes. The similarity of these processes for a variety of substances has led to their classification as inorganic binding agents.

At the same time it is convenient to distinguish inorganic binding agents according to the possibility of formation and actual formation of polymeric chains; the latter are characteristic of Portland cement and alumina cement but not of gypsum.

Thus in an examination of inorganic binding agents (cements) it is necessary to take account of the dual nature of the chemical bonding (ionic and covalent) as a result of which the atoms joined to one another are capable of forming polymeric chains in these substances, and also of the chemical and physicochemical processes taking place during the preparation and hydration hardening of the binding agent. This becomes possible if cements are approached from the viewpoint of polymerisation and crystallisation theories[28]. A one-sided approach to cements will not reveal the great variety in their properties.

1. "Itogi Nauki. Khimiya i Tekhnologiya Sinteticheskikh Vysokomolekulyarnykh Soedinenii" (Science Reviews. The Chemistry and Technology of Synthetic Macromolecular Compounds), Vol. 3, No. 2, Izd. Akad. Nauk SSSR, 1959; Vol. 7, 1961.
2. V. V. Korshak and K. K. Mozgova, Uspekhi Khim., 28, 783 (1959).
3. D. I. Mendeleev, "Osnovy Khimii" (Principles of Chemistry), 1871 Edn.; see also "Osnovy Khimii" (Princples of Chemistry), Parts I and II, 13th Edn., Goskhimizdat, 1947.
4. B. S. Shvedov, "Vvedenie v Khimiyu Kremniya" (Introduction to the Chemistry of Silicon), Gizlegprom, Moscow, 1934.
5. B. N. Dolgov, "Khimiya Kremneorganicheskikh Soedinenii" (The Chemistry of Organosilicon Compounds), Goskhimtekhizdat, Leningrad, 1933.
6. V. V. Tarasov, "Novye Voprosy Fiziki Stekla" (New Problems in the Physics of Glass), Gosstroiizdat, 1959.
7. N. S. Evstrop'ev and N. A. Toropov, "Khimiya Kremniya i Fizicheskaya Khimiya Silikatov" (The Chemistry of Silicon and the Physical Chemistry of the Silicates), Promstroiizdat, Moscow, 1950.
8. G. Lundgren, Arkiv Kemi., 10, 397 (1957).
9. I. Haiduc, Uspekhi Khim., 30, 1124 (1961) [Russ. Chem. Rev., 498 (1961)].
10. J. C. Bailar and D. H. Busch (Editors), "The Chemistry of the Coordination Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1960.
11. A. F. Wells, "Structural Inorganic Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1948.
12. J. D. Bernal and G. Megou, Proc. Roy. Soc., A 151, 384 (1935).
13. R. C. Evans, "An Introduction to Crystal Chemistry" (Translated into Russian), Goskhimizdat, 1948.
14. H. Kühl, Zement-Kalk-Gips, No. 12, 525 (1958).
15. H. Kühl, "Cement Chemistry" (Translated into Russian), GNTI, Leningrad, 1931.
16. P. A. Rebinder, "Fiziko-Khimicheskaya Mekhanika" (Physicochemical Mechanics), Izd. Znanie, 1958.
17. P. A. Rebinder, "Sbornik Posvyashchennyi Pamyati Akademika P. P. Lazareva" (Symposium Dedicated to the Memory of Academician P. P. Lazarev), Izd. Akad. Nauk SSSR, 1956, p. 13.
18. J. D. Bernal, "Proceedings of the Third International Congress on the Chemistry of Cement" (Translated into Russian), Gosstroiizdat, 1958, p. 37.
19. N. V. Belov, "Kristallokhimiya Silikatov s Krupnymi Kationami" (The Crystal Chemistry of Silicates Containing Large Cations), Izd. Akad. Nauk SSSR, 1961.
20. Kh. S. Mamedov, Azerbaidzhan. Khim. Zhur., No. 2, 105 (1962).
21. V. F. Zhuravlev, "Khimiya Vyazhushchikh Veshchestv" (The Chemistry of Binding Agents), Goskhimizdat, 1951.
22. N. A. Moshchanskii, Doctoral Thesis, TsNIPS, Moscow, 1953.
23. V. V. Volkonskii and M. M. Sychev, Tsement, 2, 5 (1964).
24. Ya. M. Syrkin and M. B. Frenkel', "Khimiya i Tekhnologiya Shlakoportlandtsementa" (The Chemistry and Technology of Slag Portland Cement), Gosstroiizdat, Ukrain. SSSR, Kiev, 1962.
25. P. P. Budnikov, I. M. Petrovykh, and V. G. Savel'ev, Trudy AzNIITsement, Chimkent, No. 1, 1 (1962).
26. O. P. Mchedlov-Petrosyan, Trudy Khar'kov Inst. Inzh. Zheleznodorozh. Transp. im. Kirova, Khar'kov, No. 39, 5 (1962).
27. O. P. Mchedlov-Petrosyan, Trudy Khar'kov Inst. Inzh. Zheleznodorozh. Transp. im. Kirova, Khar'kov, No. 54, 5 (1962).
28. Yu. S. Cherkinskii, "O Edinstve Prirody Vysokomolekulyarnykh Soedinenii i Mineral'nykh Vyazhushchikh Veshchestv. Otchet VNIINSM AS i A SSSR, Mai, 1962, Reg. No. 30616 Goskomiteta po Delam Izobretenii i Otkrytii pri SM SSSR" (The Common Character of Macromolecular Compounds and Mineral Binding Agents. Report of the All-Union Research Institute for New Constructional Materials, Academy of Building and Architecture of the USSR, May, 1962, Reg. No. 30616, USSR Council of Ministers' State Committee for Inventions and Discoveries).
29. Yu. S. Cherkinskii, "Sbornik Nauchno-Tekhnickeskoi Informatsii VNIINSM" (Scientific and Technical Information, All-Union Research Institute for New Constructional Materials), No. 4, 1963, p. 97.
30. W. Eitel, "The Physical Chemistry of the Silicates" (Translated into Russian), Inostr. Lit., 1962.
31. G. Gigi and F. Gouier, "Proceedings of the Third International Congress on the Chemistry of Cement" (Translated into Russian), Gosstroiizdat, 1958, p. 346.
32. A. I. Avgustinik, "Keramika" (Ceramics), Gosstroiizdat, 1957.
33. V. A. Kargin, "Osnovnya Problemy Khimii Polimerov" (Fundamental Problems in the Chemistry of Polymers), Izd. Akad. Nauk SSSR, Moscow, 1958.
34. P. P. Budnikov and A. M. Gistling, "Reaktsii v Smesyakh Tverdykh Veshchestv" (Reactions in Mixtures of Solids), Gosstroiizdat, 1961.
35. N. A. Toropov, "Khimiya Tsementa" (The Chemistry of

Cement), Promstroiizdat, 1956.
36. R. Ners, "Proceedings of the Third International Congress on the Chemistry of Cement" (Translated into Russian), Gosstroiizdat, 1958, p. 27.
37. P. P. Budnikov, V. A. Bron, and L. B. Khoroshavin, Trudy Moskov. Khim.-Tekhnol. Inst. im. Mendeleeva, No. 36, 15 (1961).
38. F. M. Lea and C. H. Desch, "The Chemistry of Cement and Concrete" (Translated into Russian), Gosstroiizdat, 1961.
39. H. O'Daniel, T. Hahn, and H. Müller, Neues. Jahrb. Mineral., Monatsh., 1 (1953).
40. H. O'Daniel and E. Hellner, Neues. Jahrb. Mineral., Monatsh., 108 (1950).
41. D. Jeffrey, "Proceedings of the Third International Congress on the Chemistry of Cement" (Translated into Russian), Gosstroiizdat, 1958, p. 5.
42. N. V. Belov, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 5, 686 (1960).
43. O. A. Esin, Uspekhi Khim., 26, 1374 (1957).
44. V. I. Malkin, "Fizicheskaya Khimiya Rasplavlennykh Solei i Shlakov" (The Physical Chemistry of Fused Salts and Slags), Metallurgizdat, 1962, p. 376.
45. O. A. Esin, "Voprosy Shlakopererabotki" (Problems of Slag Treatment), Chelyabinsk, 1960, p. 81.
46. V. I. Malkin, "Metallurgicheskie Shlaki i Primenenie ikh v Stroitel'stve" (Metallurgical Slags and Their Use in Building Construction), Gosstroiizdat, 1962, p. 81.
47. M. I. Temkin, Zhur. Fiz. Khim., 20, 105 (1946).
48. V. N. Yung, "Vvedenie v Tekhnologiyu Tsementa" (Introduction to the Technology of Cement), Gosstroiizdat, Moscow–Leningrad, 1938.
49. V. N. Yung, "Trudy Soveshchaniya po Khimii Tsementa" (Proceedings of the Conference on the Chemistry of Cement), Promstroiizdat, 1956, p. 14.
50. S. M. Royak and O. K. Aleshina, Tsement, No. 2, 11 (1962).
51. G. S. Val'berg, Tsement, No. 5, 20 (1957).
52. O. P. Mchedlov-Petrosyan and V. I. Babushkin, "Novoe v Khimii i Tekhnologii Tsementa" (Progress in the Chemistry and Technology of Cement), Gosstroiizdat, 1962, p. 187.
53. V. N. Yung and N. I. Fateeva, Tsement, No. 3, 11 (1954).
54. P. F. Rumyantsev and N. A. Toropov, "Voprosy Khimicheskoi Tekhnologii" (Problems in Chemical Technology), Goskhimizdat, 1957, p. 20.
55. O. P. Mchedlov-Petrosyan, "Fiziko-Khimicheskie Osnovy Keramiki" (The Physicochemical Principles of Ceramics), Promstroiizdat, 1956, p. 95.
56. E. K. Keler and A. I. Leonov, Uspekhi Khim., 22, 334 (1953).
57. P. P. Budnikov and O. P. Mchedlov-Petrosyan, Dokl. Akad. Nauk SSSR, 134, 349 (1960).
58. P. F. Konovalov and A. I. Efremov, "Trudy Soveshchaniya po Khimii Tsementa" (Proceedings of the Conference on the Chemistry of Cement), Promstroiizdat, 1956, p. 106.
59. I. D. Sedlitskii, "Metody Opredeleniya Kolloidno-Dispersnykh Mineralov" (Methods for the Determination of Colloidal Dispersed Minerals), Izd. Kiev. Gos. Univ. im. T. Shevchenko, Kiev, 1955.
60. P. P. Budnikov and M. I. Strelkov, Zhur. Prikl. Khim., 19, 343 (1946).
61. G. N. Sivertsev, "Trudy Soveshchaniya po Khimii Tsementa" (Proceedings of the Conference on the Chemistry of Cement), Promstroiizdat, 1956, p. 201.
62. M. I. Streklov, *ibid.*, p. 183.
63. S. Yatabe, J. Chem. Soc. Japan, Ind. Chem. Sect., 63, 236 (1960); Ref. Zhur. Khim., 1k-327 (1961).
64. V. N. Yung and V. V. Timashev, Tsement, No. 1, 4 (1957).
65. S. Brunauer, J. Amer. Chem. Soc., 80, 761 (1958).
66. L. E. Kopeleind, D. L. Kantro, and G. Cerbeck, "Abstracts of Reports to the 4th International Symposium on the Chemistry of Cement, Washington, 1960" (Translated into Russian).
67. E. Thilo, H. Funk, and E. Wichmann, "The Physical Chemistry of the Silicates" (Translated into Russian), Inostr. Lit., Moscow, 1956, p. 5.
68. Yu. M. Butt, L. M. Rashkovich, and N. K. Sudina, "Khimiya i Prakticheskoe Primenenie Silikatov" (The Chemistry and Practical Application of Silicates), TsBTI, Leningrad, 1960, p. 115.
69. W. D. Treadwell and W. Wieland, Helv. Chim. Acta, 13, 842 (1930).
70. R. K. Ayler, "The Colloid Chemistry of Silica and the Silicates" (Translated into Russian), Gosstroiizdat, 1959.
71. W. A. Weyl, "A New Approach to Surface Chemistry and to Heterogeneous Catalysis", 1951, pp. 46–48.
72. R. Shvarts, Uspekhi Khim., 26, 923 (1957).
73. E. Thilo, Makromol. Chem., 34, 179 (1959).
74. E. N. Egorova, "Metody Vydeleniya Kremnevoi Kisloty i Analiticheskoe Opredelenie Kremnezema" (Methods for Isolating Silicic Acid and the Analytical Determination of Silica), Izd. Akad. Nauk SSSR, 1959.
75. Tai An-pang and Chiang Lung, Acta Chim. Sinica, 23, 90 (1957).
76. N. V. Belov, Khim. Nauka i Prom., 3, No. 1, 46 (1958).
77. Yu. M. Butt and L. N. Rashkovich, "Tverdenie Vyazhushchikh pri Povyshennykh Temperaturakh" (The Hardening of Cements at Elevated Temperatures), Gosstroiizdat, Moscow, 1961.
78. H. Taylor, "Abstracts of Reports to the 4th International Symposium on the Chemistry of Cement, Washington, 1960" (Translated into Russian).
79. H. D. Megaw, Acta Cryst., 5, 477 (1952).
80. N. V. Belov, "Mineralogicheskii Sbornik L'vovskogo Geologicheskogo Obshchestva" (Mineralogical Symposium of the Lvov Geological Society), No. 13, Izd. L'vov. Univ., 1959, p. 23.
81. Kh. S. Mamedov, R. F. Klevtsov, and N. V. Belov, Dokl. Akad. Nauk SSSR, 126, 151 (1959).
82. Kh. S. Mamedov and N. V. Belov, Dokl. Akad. Nauk SSSR, 121, 901 (1958).
83. Kh. S. Mamedov and N. V. Belov, Dokl. Akad. Nauk SSSR, 123, 741 (1958).
84. Kh. S. Mamedov and N. V. Belov, Dokl. Akad. Nauk SSSR, 121, 720 (1958).
85. S. Brunauer, Amer. Scientist, 50, 210 (1962).
86. H. G. Kurczyk and H. E. Schwiete, "Abstracts of Reports to the 4th International Conference on the Chemistry of Cement, Washington, 1960" (Translated into Russian).
87. V. A. Kind, S. D. Okorokov, and L. V. Frolov, "Putstsolanovye Tsementy" (Pozzolana Cements), VNIITs, Leningrad, 1936, p. 333.
88. S. M. Royak, *ibid.*, p. 367.
89. Yu. S. Cherkinskii, "Sbornik Nauchno-Tekhnicheskoy Informatsii VNIINSM" (Scientific and Technical Information, All-Union Research Institute for New Constructional Materials), No. 5, 1963, p. 111.
90. N. G. Krasil'nikov and A. V. Kiselev, in "Sbornik Nauchnykh Rabot po Vyazhushchim Materialam" (Collected Papers on Cements), Promstroiizdat, 1949, p. 141.
91. Yu. G. Shteinberg, Zhur. Prikl. Khim., 20, 927 (1947).
92. V. A. Mikhal'chenko, Zhur. Prikl. Khim., 19, 1364 (1946).
93. S. A. Greenberg, J. Phys. Chem., 61, 373 (1957).
94. P. I. Bozhenov, V. I. Kavalerova, V. S. Sal'nikova, G. F. Suvorova, and L. I. Kholopova, "Tsementy Avtoklavnogo Tverdeniya i Izdeliya na ikh Osnove" (Autoclave-Hardened Cements and Articles Made from Them), Gosstroiizdat, 1963.
95. I. V. Kravchenko, "Glinozemistyi Tsement" (Alumina Cement), Gosstroiizdat, 1961.
96. I. V. Kravchenko, "Rasshiryayushchiesya Tsementy" (Expanding Cements), Gosstroiizdat, 1962.

97. A. I. Lainer, "Proizvodstvo Glinozema" (The Production of Alumina), Metallurgizdat, Moscow, 1961.
98. T. Parker, "Proceedings of the Third International Congress on the Chemistry of Cement" (Translated into Russian), Gosstroiizdat, 1958, p. 307.
99. A. E. Fersman, "Geokhimiya" (Geochemistry), Vol. IV, Goskhimizdat, 1939.
100. G. Erwin and E. Osborn, "Experimental Studies in the Field of Petrography and Ore-Formation" (Translated into Russian), Inostr. Lit., 1954.
101. I. S. Lileev, "Khimiya i Tekhnologiya Okisi Alyuminiya" (The Chemistry and Technology of Aluminium Oxide), Part 1, Leningrad.Tekhnol. Inst. im. Lensoveta, Leningrad, 1940.
102. K. M. Fedot'ev and S. S. Batsanov, Zap. Vses. Miner. Obshch., 86, No. 4 (1957).
103. L. Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, 1947.
104. S. I. Kuznetsov, "Proizvodstvo Glinozema" (The Production of Alumina), Metallurgizdat, Sverdlovsk, 1956.
105. A. M. Samarin and L. A. Shvartsman, Zhur. Fiz. Khim., 20, 189 (1946).
106. P. Pfeiffer, Ber., 40, 4036 (1908).
107. A. Werner, "Neuere Aussthauungen in anorganischen Chemie" (Translated into Russian), ONTI, 1936.
108. V. A. Pazukhin, "Metallurgiya Tsvetnykh Metallov, Sbornik Trudov Moskovskogo Instituta Met. i Zolota im. M. K. Kalinina i VNITO Metallurgov" (The Metallurgy of Non-Ferrous Metals, Collected Papers of the Kalinin Moscow Institute for Metals and Gold and the All-Union Scientific, Engineering, and Technical Society for Metallurgists), Metallurgizdat, 1952, p. 159.
109. V. I. Vernadskii, "Ocherki Geokhimii" (Essays on Geochemistry), Gosizdat, Moscow–Leningrad, 1927.
110. S. A. Mironov, O. M. Astreeva, and L. A. Marinina, Tsement, No. 2, 9 (1957).
111. D. Roy and R. Roy, "Abstracts of Reports to the 4th International Conference on the Chemistry of Cements, Washington, 1960" (Translated into Russian).
112. P. Niggli, "Stereochemistry" (Translated into Russian), Inostr. Lit., Moscow, 1949.
113. N. V. Belov, "Mineralogicheskii Sbornik L'vovskogo Geologicheskogo Obshchestva" (Mineralogical Symposium of the Lvov Geological Society), Lvov, 1962, No. 16, p. 14.
114. V. A. Tikhonov and Z. G. Klimenko, "Issledovaniya Vyazhushchikh Veshchestv i Izdeliya na ikh Osnove" (Studies of Cements and Articles Made from Them), Nos. 2 and 3, Lvov, 1962, p. 10.
115. Z. G. Klimenko and V. A. Tikhonov, "1-ya Nauchnaya Konferentsiya po Khimii i Khimicheskoi Tekhnologii" (First Scientific Conference on Chemistry and Chemical Technology), Izd. L'vov. Univ., Lvov, 1963, p. 41.
116. P. P. Budnikov, "Gips" (Gypsum), Izd. Akad. Nauk SSSR, Leningrad, 1933.
117. A. A. Grinberg, "Vvedenie v Khimiyu Kompleksnykh Soedinenii" (Introduction to the Chemistry of Complex Compounds), Goskhimizdat, 1945; *ibid.*, 1951 Edn.
118. Yu. S. Cherkinskii, "Neorganicheskie Polimernye Stroitel'nye Materialy. Otchet VNIINSM, 1963, Reg. No. 42 050, Goskomiteta po Delam Izobretenii i Otkrytii pri SM SSSR." (Inorganic Polymeric Building Materials. Report of the All-Union Research Institute for New Constructional Materials, 1963, Reg. No. 42 050, USSR Council of Ministers' State Committee for Inventions and Discoveries).

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U. D. C. 547.458.81

GRAFT COPOLYMERS OF CELLULOSE AND ITS DERIVATIVES

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I. INTRODUCTION

The controlled modification of the properties of cellulose and its derivatives by the synthesis of graft copolymers based on them undoubtedly provides one of the most promising and effective methods for improving the quality and extending the range of application of cellulosic materials.

Several cellulosic materials possessing valuable new properties have already been obtained by the synthesis of graft copolymers. For example, cellulosic materials which are completely resistant to the action of microorganisms can be prepared by grafting on various carbon-chain polymers, and improved stability to light and heat is achieved by the synthesis of graft copolymers with polyacrylonitrile. Non-flammable cellulosic materials can be obtained by the grafting on of polymers containing phosphorus or chlorine; the grafting of water-repellent carbon-chain or silicon-containing polymers confers water-repellent properties and improved resistance to acids. The synthesis of graft copolymers of cellulose with a definite class of synthetic polymers makes it possible to