Some Recent Concepts on Portland Cement Hydration and Hardening

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The subject of hardening of cement paste is one of our most complicated problems, one having great practical value. Many research workers, including such prominent scientists as A. Lavoisier, H. Le Chatelier, D. Mendeleev, W. Michaelis, A. Baikov, D. Bernall, P. Rebinder, N. Belov and others, have studied the problem, and progress has been achieved in understanding the essence of the process of hardening of binding materials. However, some primary questions of the theory of hardening have not yet been answered and hence still are controversial. Some of these questions are discussed here on the basis of experimental and theoretical considerations. New data on composition of the liquid phase formed during hardening of portland cement pastes, obtained with a specially constructed filter press at ages of 2 min to 28 days, are given. The possibility of cement hydration by top chemical pattern on the basis of microscopic evidence showing formation of short-life unstable primary products is discussed. The structure of new formations is considered a general aspect of the hardening process, taking into account the presence of structure-forming processes along with destructive ones, thus suggesting that the process of cement hardening is "internally contradictory." Some experimental and theoretical aspects of extra-rapid hardening concretes are considered. At the age of 15 to 30 min such concretes develop strength necessary for stripping and transportation, thus permitting the optimum design of an automated plant for production of reinforced-concrete articles.

Composition of the Liquid Phase of Cement Pastes and Suspensions

As waste gas composition discloses the process of fuel burning, so the composition of the liquid phase formed during hardening of cement paste makes possible some important conclusions concerning the process of cement hydration. Works of Baikov (1), Roller (2), Lerch (3), Hansen and Pressler (4), Kuhl (5) and Hedin (6) should be mentioned in this connection. However, further study of the liquid phase of hardened pastes is needed, but is hampered by the immense difficulty of extracting the liquid from capillaries of a sound cement stone. Such an extraction requires a specially designed filter-press, able to transmit pressure on the stone in the range of 1500 kg/cm², and provide for exclusion of atmospheric CO₂, which will change the composition of the liquid phase (7). Such an installation was employed to extract the liquid phase from portland cement and blast-furnace slag cement suspensions at ages in the range of 2 min to 28 days. Suspensions for the principal experiments had w/c = 0.5. Others had various w/c ratios, some in particular with w/c = 20; in this case the filter-press was not used. Experimental filtrates were analyzed for SiO₂, Al₂O₃, Fe₂O₃, CaO, R₂O(K₂O + Na₂O) and SO₃ contents.

According to Baikov, the liquid phase has no silica; however, according to Strelkov (7), all samples of liquid phase contained SiO₂ in amounts ranging from 2 to 25 mg/liter.

Al₂O₃ and Fe₂O₃ in the course of the first day were absent and appeared just when SO₃ in the liquid phase disappeared. Al₂O₃ contents in the liquid phase, depending on the amount of SO₃, has been reported by Budnikov and Lezhoev (8) in studies of sulfate cements. The w/c ratios of suspensions greatly influence the amount of calcium hydroxide in the liquid phase, which explains the divergence of data obtained by various workers. According to Strelkov (7) the liquid phase from a paste having w/c = 0.5
contains the greatest amount of CaO (1.4 g/l) at 2 min age; in the course of time the concentration of Ca(OH)$_2$ drops, reaching the value of 0.2 g/l at the age of 3 days.

The CaO content in diluted suspensions made with w/c = 20 changed quite differently. At the age of 2 min it amounted to 1 g/l, at the age of 6 hr it increased to 1.95 g/l and then dropped to 1.3 g/l at the age of 7 days, this value remaining at more prolonged ages. This difference of solubility of Ca(OH)$_2$ is explained by the effect of hydroxides of alkalies, the concentration of which depends on w/c (a well-known fact, but in some works it is not taken into consideration). Concentration of R$_2$O in the liquid phase of a suspension of w/c = 20 was 0.2 g/l, and it did not change in the period of time ranging from 2 min up to 28 days; at w/c = 0.8 the amount of R$_2$O in the liquid phase of a suspension at 2-min age was nearly 4 g/l and increased almost 5 g/l at the age of 1 day. Because of this the concentration of calcium hydroxide drops. However, it is not yet known why such a relatively small change of general R$_2$O content of the liquid phase caused such a large drop in CaO concentration. It is clear that it is connected with the fact that at different ages of hardening of portland cement paste, the alkali exists in different forms. Considering data obtained by various workers, one can suppose that at first the alkali sulfate form prevails and later it is completely converted into alkali hydroxide.

In the works of Strelkov (7) and of some other authors (1, 3, 4, 5), the liquid phase composition was expressed in the form of its general content of separate oxides; some authors, instead of the general content of separate oxides, calculate the ions (2). However, in both cases it is still not clear how cations of calcium and alkaline metals are distributed among anions of SO$_4$ and OH$^-$. In order to clear the pattern of distribution of cations, a procedure permitting concentrations of Ca(OH)$_2$, CaSO$_4$, ROH and R$_2$SO$_4$ in the liquid phase was worked out (9, 10). This procedure is based on complete solubility of hydroxides and sulfates of the alkaline metals in 50 percent ethyl alcohol and of practically full insolubility of CaSO$_4 \cdot 2$H$_2$O in it. To use the properties of these compounds, water is evaporated from a given volume of the liquid phase. The precipitate is treated with ethyl alcohol. The analysis of the resulting solution and of the solid insoluble residue gives the data from which one can easily calculate the compounds named.

The amounts of SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ are determined from a separate aliquot of a given liquid phase.

Such a process was employed to study the liquid phase of different commercial and laboratory portland cements—the last ones being prepared by laboratory grind of commercial clinkers with additions of gypsum. The most important data of some cements studied are given in Table 1.

Tables 2, 3 and 4 contain the data on the composition of the liquid phase. The liquid phase of the suspension having w/c = 0.5 was extracted with the help of a filter-press (7) when the pressure of 1500 kg/cm$^2$ was enough to drive out the necessary amount of the liquid phase. The age of samples varied from 2 min to 28 days, or a lesser period (3 or 7 days) if the samples were too strong.

From suspensions having w/c = 1, the liquid phase was separated at ages from 30 sec to 1 hr using a vacuum filter. At these ages the pastes were not yet hardened enough to require the filter press.

One can see from Tables 2 and 3 that the concentration of Ca(OH)$_2$ in the liquid phase, expressed as CaO content, varied from 1.51 to 0.03 g/l. Note that in all cases the higher concentrations correspond to the lower sample ages. CaO concentration is independent of the specific surface in the range of 2000-3500 cm$^2$/g. Specific surface was determined by Tovarov's method of air permeability (11).

The solubility of Ca(OH)$_2$ is decreased with increasing concentration of the hydroxides of alkaline metals, as would be expected. The higher concentrations of CaSO$_4$ in liquid phases of commercial cement at the start of their hardening (Table 2) is due to presence of hemihydrate. In laboratory cements made with gypsum, the CaSO$_4$ content did not exceed 2 g/l (Table 3) compared to 3.1 to 6.4 g/l for the extracts from commercial cement. These observations are in accord with the results of thermographical studies (13) and the studies of the liquid phase by Hansen (14).
Results on extracts from suspensions having w/c = 1 (Table 4) supply information on concentration at earlier ages, namely at 30 and 60 sec, not obtainable with the filter-press. According to data of Tables 1 and 2, SiO₂ was always present in the liquid phase, in agreement with previous data (7).

In the liquid phase of pastes of commercial cements, Al₂O₃ was absent up to 1, 3 or even 7 days. In the liquid phase of laboratory-ground cements the time for first appearance of Al₂O₃ depended on the specific surface of the cement—for specific surfaces of 2000, 2300 and 3500 these times were 2 hr, 30 min and 3 min, respectively (Table 2).

The values obtained lead us to suppose that, in suspensions of cements, calcium hydroaluminate is always formed, its amount being a function of the specific surface of the cement. In laboratory cements the amount of calcium sulfate cannot be more than 2 g/l, independent of the fineness of cement. Such a concentration can provide sulfate to bind hydroaluminate into hydrosulfoaluminate only in pastes of coarse-ground cement. Commercial cements contain hemihydrate which provides for sufficiently high content of CaSO₄ to convert all calcium hydroaluminate into insoluble calcium hydrosulfoaluminate.

These suppositions probably can partially explain different concentrations of Fe₂O₃ in liquid phases extracted from suspensions of commercial and laboratory cements.

It is necessary to stress that CaO content of the liquid phase can depend on the hydration reaction of calcium alumoferrite, since hydroaluminates, hydroferrites and hydrosulfoaluminate contain more lime than is in the initial alumoferrite.

FORM AND INTERNAL STRUCTURE OF THE NEW FORMATIONS

According to Le Chatelier (15), hardened plaster, portland cement and other binding materials are composed of newly formed and irregularly located acicular crystals. Kühl's study of portland cement paste microsections has shown that the light microscope does not clearly show the crystalline pattern prior to 20 years of curing (16). Similar studies of other workers (17, 18, 19), who investigated set cement pastes under the microscope, have shown that at the age of one or several months, hexagonal crystals of calcium hydroxide...
TABLE 2
COMPOSITION OF AQUEOUS EXTRACTS FROM PASTES OF LABORATORY GROUND PORTLAND CEMENTS

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Sample Age of</th>
<th>mg/l</th>
<th>g/l</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SiO₂</td>
<td>Al₂O₃</td>
<td>Fe₂O₃</td>
<td>Ca(OH)₂ (as CaO)</td>
<td>CaSO₄</td>
<td>R₂SO₄</td>
</tr>
<tr>
<td>416</td>
<td>Cement H₃, Specific Surface 2033 cm²/g, R₂O = 0.37 Percent</td>
<td>2.4</td>
<td>trace</td>
<td>trace</td>
<td>0.68</td>
<td>1.75</td>
<td>1.37</td>
</tr>
<tr>
<td>417</td>
<td>30 min</td>
<td>2.4</td>
<td>trace</td>
<td>trace</td>
<td>0.82</td>
<td>1.7</td>
<td>1.37</td>
</tr>
<tr>
<td>422</td>
<td>2 hr</td>
<td>2.3</td>
<td>0.17</td>
<td>0.34</td>
<td>0.74</td>
<td>1.8</td>
<td>1.53</td>
</tr>
<tr>
<td>423</td>
<td>6 hr</td>
<td>2.3</td>
<td>0.47</td>
<td>0.35</td>
<td>0.74</td>
<td>2.04</td>
<td>1.19</td>
</tr>
<tr>
<td>424</td>
<td>1 day</td>
<td>2.6</td>
<td>0.86</td>
<td>1.3</td>
<td>0.72</td>
<td>1.73</td>
<td>1.38</td>
</tr>
<tr>
<td>425</td>
<td>3 days</td>
<td>5.1</td>
<td>1.45</td>
<td>0.02</td>
<td>0.14</td>
<td>0.03</td>
<td>0.1</td>
</tr>
<tr>
<td>430</td>
<td>7 days</td>
<td>6.6</td>
<td>3.3</td>
<td>0.10</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>440</td>
<td>28 days</td>
<td>4.2</td>
<td>2.7</td>
<td>3.0</td>
<td>0.12</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

| 418      | Cement H₄, Specific Surface 2300 cm²/g, R₂O = 0.37 Percent | 3.0 | trace | trace | 0.41 | 1.94 | 2.16 | 2.04 |
| 419      | 30 min | 2.4 | 0.4 | trace | 0.42 | 2.11 | 1.68 | 2.55 |
| 422      | 2 hr   | 2.3 | 0.24 | 0.54 | 0.63 | 1.56 | 2.52 | 2.15 |
| 429      | 6 hr   | 2.5 | 0.44 | 0.60 | 0.34 | 2.19 | 1.54 | 2.55 |
| 431      | 1 day  | 3.2 | 0.52 | 0.20 | 0.10 | 1.50 | 2.4 | 3.0 |
| 425      | 3 days | 6.2 | 1.29 | trace | 0.04 | 0.02 | 0.14 | 6.1 |
| 427      | 7 days  | 6.6 | 2.6 | 3.3 | 0.12 | 0 | 0 | 6.5 |
| 421      | 28 days | 13.8 | 1.2 | 4.9 | 0.03 | 0 | 0 | 6.5 |

| 440      | Cement H₅, Specific Surface 3500 cm²/g, R₂O = 0.37 Percent | 2.6 | 1.7 | 4.2 | 0.70 | 1.70 | 1.78 | 1.75 |
| 444      | 30 min | 1.8 | 1.3 | 4.3 | 0.77 | 2.04 | 0.91 | 2.21 |
| 443      | 2 hr   | 6.2 | 1.0 | 1.5 | 0.63 | 1.85 | 1.12 | 1.84 |
| 441      | 3 days | 8.6 | not measured | 0.19 | 0.08 | 0.51 | 4.36 |

| 555      | Cement D, Specific Surface 2809 cm²/g, R₂O = 0.04 Percent | 2.0 | 0 | 0.1 | 1.51 | 1.92 | 0.16 | 0.14 |
| 563      | 6 hr   | 1.8 | 1.3 | 4.3 | 0.77 | 2.04 | 0.91 | 2.21 |
| 570      | 24 hr  | 6.2 | 1.0 | 1.5 | 0.63 | 1.85 | 1.12 | 1.84 |
| 571      | 7 days  | 8.6 | not measured | 0.19 | 0.08 | 0.51 | 4.36 |

°w/c = 0.5.

TABLE 3
COMPOSITION OF AQUEOUS EXTRACTS FROM PASTES OF COMMERCIAL PORTLAND CEMENT

| Test No. | Cement Designation | Age of Sample | mg/l | g/l | | | |
|----------|-------------------|---------------|-----|-----| Ca(OH)₂ (as CaO) | CaSO₄ | ROH (as R₂O) | R₂SO₄ |
| 474      | K                 | 2 min         | 2.0 | 0   | 0.1 | 0.72 | 6.41 | 0.51 | 1.18 |
| 478      | K                 | 6 hr          | 4.6 | 0   | 0.14 | 0.97 | 1.55 | 0.49 | 0.44 |
| 469      | K                 | 1 day         | 2.2 | 0   | 0.08 | 0.98 | 1.63 | 0.95 | 0.99 |
| 483      | K                 | 3 days        | 5.6 | 0   | — | 0.32 | 0 | 3.18 | 0.26 |
| 472      | K                 | 7 days        | 16.8 | 0   | — | 0.22 | 0 | 4.27 | 0.32 |
| 475      | Kp                | 2 min         | 6.8 | 0   | 0.16 | 0.41 | 3.06 | 0.62 | 0.45 |
| 477      | Kp                | 6 hr          | 3.2 | 0   | 0.22 | 0.91 | 1.27 | 0.54 | 0.89 |
| 470      | Kp                | 1 day         | 1.2 | 0   | 0 | 0.75 | 0 | 2.19 | 0.04 |
| 481      | Kp                | 3 days        | 5.4 | 0.36 | — | 0.32 | 0 | 3.18 | 0.26 |
| 473      | Kp                | 7 days        | 9.8 | 0.48 | — | 0.10 | 0 | 6.0 | 0.16 |
| 524      | H                 | 2 min         | 3.4 | 0   | 0 | 0.55 | 4.74 | 1.59 | 4.72 |
| 530      | H                 | 6 min         | 1.6 | 0   | 0.15 | 0.64 | 1.07 | 2.40 | 4.23 |
| 526      | H                 | 1 day         | 2.4 | 0   | 0 | 0.82 | 0.73 | 2.55 | 5.20 |
| 528      | H                 | 3 days        | 1.6 | 2.6 | — | 0.12 | 0 | 6.95 | 0.36 |
| 532      | H                 | 7 days        | 12.2 | 1.8 | 0.2 | 0.10 | 0 | 7.90 | 0.24 |
| 522      | H                 | 28 days       | 9.0 | 2.0 | 0.4 | 0.10 | 0 | 8.52 | 0.24 |

°w/c = 0.5.
TABLE 4

HYDROXIDE AND SULFATE CONTENT OF LIQUID PHASE OF SUSPENSIONS OF COMMERCIAL CEMENTS

Table: Table 4

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Cement Designation</th>
<th>Age of Sample</th>
<th>Content (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ca(OH)$_2$ (as CaO)</td>
</tr>
<tr>
<td>490</td>
<td>K</td>
<td>30 sec</td>
<td>1.30</td>
</tr>
<tr>
<td>491</td>
<td>K</td>
<td>1 min</td>
<td>1.29</td>
</tr>
<tr>
<td>492</td>
<td>K</td>
<td>2 min</td>
<td>1.20</td>
</tr>
<tr>
<td>493</td>
<td>K</td>
<td>5 min</td>
<td>1.17</td>
</tr>
<tr>
<td>495</td>
<td>K</td>
<td>10 min</td>
<td>1.12</td>
</tr>
<tr>
<td>494</td>
<td>K</td>
<td>20 min</td>
<td>1.30</td>
</tr>
<tr>
<td>487</td>
<td>K</td>
<td>1 hr</td>
<td>1.42</td>
</tr>
<tr>
<td>500</td>
<td>H 17/18</td>
<td>2 min</td>
<td>0.60</td>
</tr>
<tr>
<td>501</td>
<td>H 17/18</td>
<td>5 min</td>
<td>0.61</td>
</tr>
<tr>
<td>502</td>
<td>H 17/18</td>
<td>10 min</td>
<td>0.66</td>
</tr>
<tr>
<td>488</td>
<td>Kp</td>
<td>2 min</td>
<td>1.22</td>
</tr>
<tr>
<td>489</td>
<td>Kp</td>
<td>1 hr</td>
<td>1.39</td>
</tr>
</tbody>
</table>

$w/c = 1.$

and calcium hydroaluminate can be found in small numbers. Calcium hydrosilicates in such pastes, cured at ordinary temperature, are a highly dispersed gel, whose form and dimensions cannot be defined except by electron microscopy under favorable conditions. In connection with this many investigators supposed that portland cement stone consists mainly of amorphous gel and crystalline Ca(OH)$_2$.

Earlier electronographic studies started by Eitel (20) in 1937, later continued by many scientists (21), made Bernal (21) conclude that even calcium hydrosilicates have the form of extremely thin crystalline needles. This conclusion was based particularly on Grudemo's electronographic studies (22) of hydration products arising in highly diluted suspensions.

Grudemo's further studies (23) of concentrated portland cement suspensions have shown that even over 10 years of common curing, new formations are mainly in the amorphous state. All this agrees with X-ray and electronographic studies of other investigators (24-28).

Thus it can be proved that calcium hydrosilicates comprising binding components of concrete hardening at ordinary temperature are either in an amorphous state or in a poorly crystalline form for a long time. Probably at the beginning of hardening the rest of the hydration products are in an amorphous state, the duration of which is different for separate newly formed products.

Outer shapes of newly formed products are of great interest. Numerous electronographic studies have shown that particles of Ca(OH)$_2$ can have the form of globules, hemispheres, needles, scales, hexagonal plates and fibrils. In hydration of C$_2$S and C$_3$S, spheric, plate, leaf, acicular, fibrous and prismatic particles have been revealed. In C$_3$A hydration hexagonal plates, globules (separate and chained), acicular planks and cubes have been observed. At the interaction of C$_4$AF with water, hexagonal plates and chains of spheric formations have been observed. In the course of the study of hydration products of portland cements, the same forms of particles have been found that are found in the hydration of the separate clinker minerals.

Some authors suppose that among new formations of hardened portland cement spheric particles prevail (24, 27, 29, 30, 31, 32, 36).

In his paper devoted to the chemistry of cement hydration presented at the Seventh Conference on Silicate Industry (Budapest, June 1963), Taylor made an observation of possible morphological types occurring in new formations in the course of portland cement hardening. In his opinion, three main morphological types of new formations have been found by means of electronographic study. These types are as follows:

1. Scales of Ca(OH)$_2$, diameter of which is often more than 1 micron; they are very thin and give a good diffraction picture, inherent in crystalline calcium hydroxide.
2. Fibrils up to 1 micron long and of some hundreds Å width; these fibrils sometimes give scattered monocrystal diffraction pictures, inherent in tobermorite phase.

3. Disorderly masses of small plates having diameter of some hundreds of Å, and maximum thickness of 30 Å; their form is slightly distorted, their diffraction pictures showing some separate scattered rings.

Opinions differ concerning quantitative fractions of the second and third forms listed. Taylor agrees with Grudemo, in whose opinion disorderly masses prevail and the amount of fibrils is relatively small. In his paper Taylor notes that the tobermorite-like gel which forms at the hardening of portland cement at ordinary temperatures is nearly an amorphous substance.

Microscopic study by Strelkov and his co-workers (32) has shown that the primary structural elements of concentrated (and sometimes of diluted) suspensions of portland cement, finely ground lime and even plaster of Paris are spherical particles (Figs. 1 and 2). This coincides with Bogue's previously mentioned opinion (31) concerning the possible prevalence of spherical particles in portland cement hydration products.

At first glance this seems to be ununderstandable. Concerning this it is necessary to note that the formation of spherical products of hydration agrees with new concepts about the form of the primary colloidal particles.

Kargin and Berestneva (33) have experimentally demonstrated and theoretically proved that amorphous globular particles are formed first in colloidal systems of highly supersaturated solutions. In the course of time they, as a result of interglobular crystallization, transform into a great amount of crystallites, and the latter unite in the secondary structure—threads, nets and others. The transformation of globules of some sols into small crystallites can be explained by their limited strength, which is not sufficient to withstand crystal pressure. However, there are colloidal particles of globular form which do not change their form in the course of crystallization (34).

All this makes it possible to regard spherical products of hydration of binding substances as a gel strong enough to retain the initial globular structure. One can also suppose that at the beginning of their existence new formations of globular configuration were in amorphous state (35, 36). Detailed electronographical studies of calcium hydroxide forming from supersaturated solutions of gel have confirmed such a supposition. Figures 3a and 3b show that, at first, globular particles of calcium hydroxide were in amorphous state, and then, with no change of their forms, converted into crystalline Ca(OH)₂. The presence of particles, presumably Ca(OH)₂, with split ends was also detected (Figs. 3c and 3d). Their microdiffraction (Fig. 3e) proves, however, these particles to be CaO. It is interesting that similar particles were observed by Grudemo (22) in his study of diluted C₃S suspensions and were identified as hydrosilicate. Figure 3f shows the photo of the structure obtained by Grudemo. Appearance of acicular particles of CaO which can form net-like structures is explained by the action of the electron beam on some definite particles and by the influence of high vacuum. Dimensions of such particles in hydration products of binding materials are probably in the range of 0.1-2 microns. Coarse particles absorbing a great amount of heat energy from the electron beam can be heated up to some thousands of degrees C (37). This can be followed not only by destruction of Ca(OH)₂ but even by evaporation of CaO. With some heat treatment the surface of globular particles deteriorates, resulting in the formation of a castellated pattern of the surface and some "bridges" or interconnections between separate particles (Fig. 3g). The particles of CaO breaking from separate coarse globules turn into threads or "needles" (Fig. 3h). At some combination of conditions (definite vacuum, location of the particles among other areas being irradiated) disintegration, evaporation, and consequent condensation on the areas of low temperature result, forming either net-structures (Fig. 3i), "margins" around thread-like particles or needles (Figs. 3c and 3h), or particles with split points (Fig. 3d).

It is quite natural that CaO identified in such forms in electronographic study of Ca(OH)₂ has no relation to the structure of hardened lime and portland cement paste; conditionally these forms can be referred to as "pseudo-forms" of cement stone. It follows that these pseudo-forms can form in the course of electronographic study of the hydration process of calcium silicates, and generally, of any binding agents. That is
Figure 1. Sample of plaster of Paris, 13 min after mixing, 5 min of intensive stirring, water-gypsum ratio = 5 (microphoto, magnified 500 times).

Figure 2. Thin microsection of cement stone from concrete after 20 years of normal hardening (microphoto, magnified 1000 times).
Figure 3. Electronography of the products of CaO hydration: a and b—globular particles of Ca(OH)$_2$; c and d—particles with split ends, magnified 6000 and 7000 times; e—their microdiffraction; f—calcium hydrosilicate seen by Grudemo at C$_3$S hydration; g—bridges between globular particles of Ca(OH)$_2$, magnified 9000 times; h—the first stage of decomposition of a globular particle, magnified 22,000 times; i—the net of threads, magnified 7000 times.
why we suppose that pseudo-forms appearing at various conditions of electronographic study are one of the reasons for differences among the data of various authors.

As far as our opinion is concerned, the primary objective of recent studies is to reveal how fibrous formations, observed at hardening, reflect real structure of new formations. It is of special importance to find the relationship between fibrous structure and calcium hydrosilicates which, in the course of hardening, correspond to tobermorite of high lime content. Tobermorite belongs to polymers which have fibrous and, therefore, acicular or thread-like structure. However, it is necessary to remember that, according to Kargin and Markova (34), polymers can have globular form. Hence it is possible that globules can be the primary structural element of hydration products of any cements. They can hardly be detected in binding components of concrete even with the help of the electron microscope. The explanation lies partly in the difficulties of sample preparation but mainly in the tendency of concentrated suspensions of globules to form secondary structures making oval particles, chains, rings and plates of regular and irregular shapes and of different dimensions. Sometimes discs and hexagonal plates can form. Such forms, despite their being rarely observed, have been traced by Toropov and Sokolova (38) in the course of their study of calcium hydroaluminates. In our opinion, flakes of crystalline \( \text{Ca(OH)}_2 \) represent one of the most common examples of a disorderly agglomeration or coalescence of several globules of amorphous \( \text{Ca(OH)}_2 \) later transformed into crystalline state.

Thus we suppose that portland cement stone can be referred to as a gel whose primary structural element is an amorphous globular particle. Acicular and, generally, elongated new formations play a subsidiary role; it is possible that they result from disintegration of samples studied with the electron microscope.

POSSIBILITY OF TOPOCHEMICAL REACTIONS

There are two general concepts of cement-water interaction. According to the first, the clinker minerals dissolve without chemical reactions. According to the second, the clinker minerals react chemically at first without dissolution and disperse in the aqueous phase; it is the reaction products that dissolve. A great many studies have been devoted to this problem; a survey of them is presented in Hansen's papers (14, 39). In the USSR, the second point of view was advanced by A. A. Baikov in his work of 1923-1932 (1, 40).

The authors of this paper assume that the second point of view, which admits topochemical reactions, is preferable to the first. Here we do not aim to give complete consideration of the question in point, but shall confine ourselves to some remarks and shall show some experimental data which confirm our concept.

It is necessary to distinguish between two- and three-dimensional topochemical reactions. The most difficult to explain are three-dimensional topochemical reactions because, for them to occur, the crystalline lattice of the initial substance should have rather big channels for free access of water. Such a phenomenon is quite possible, as is proved by the structure of hemihydrated gypsum (41).

The products of topochemical reactions can be referred to as primary hydrates, to distinguish them from the secondary hydrates precipitated from the solution (42).

We suppose that hardening of binding materials and their attainment of technically useful strength are based on the formation of secondary hydrates. This, however, does not exclude the possibility that the primary hydrates exist for such a short period of time that it is difficult to detect them; their time of existence will be determined by their relative rates of formation and solution. If the rate of solution of the primary hydrates is greater than or equal to the rate of their formation, they would not be detected. Ordinarily, in aqueous suspensions of cement the primary hydrates cannot be seen. The particles of cement clinker are clad with a crust made of new formations, formed during storage; this crust retards the diffusion of water to the clinker minerals.

When mixing cement particles with water this crust can be seriously damaged, thus making the "cores" of cement grains more accessible to water. If this is accompanied by increasing the rate of chemical reaction, by heating, for example, then it can be expected that primary hydrates can be discovered by microscopic study. But even under
these conditions the clinker grains would eventually become clad with a new film, consisting of the secondary hydrates, impermeable enough to limit the diffusion of water to the area of reaction. Then the rate of formation of the primary hydrates would be less than that of their dissolution and they would no longer be detected.

Therefore, it may appear at first glance that only dissolution of clinker minerals takes place although, as a matter of fact, dissolution of the product of topochemical reaction can take place, at a rate greater than or equal to the rate of formation of the primary hydrates.

It is clear from the above that under certain conditions it is possible to detect primary hydrates with light microscopy. Because they are now soluble, they should, in the course of time, convert into secondary hydrates. To confirm this, various portland cements, separate clinker minerals and plaster of Paris were tested. It was decided to have w/c = 0.7. To test the powder under study it was mixed from 5 sec to 20 min. The resulting paste was placed on a glass slide and inspected with the light microscope, the sample being slightly heated during the test. After some minutes the portland cement samples contained a great amount of fibrous thread-like formations (Fig. 4). These threads were not observed if the mix was agitated for only 5 sec or if not agitated at all. Prolonged observation of the same area of a sample would reveal the character of changes in the structure of newly formed particles in the course of time. Figure 5 shows some microphotographs of a series of portland cement samples prepared at various lengths of mixing; all the photos were taken at certain intervals after the mixing had been completed. As is clear from Figure 5, the most distinct fibrous new formations are revealed when a portland cement sample was mixed with water for 10 sec. However, even at 20 min mixing, fibrous structures can be distinctly seen.

As mentioned, the primary hydrates, due to their high solubility, transform into the secondary ones, this being proved by the appearance of oval and chain-like particles on the spots occupied by fibrous new formations. It is necessary to stress that fibrous formations can appear at several times. They can reappear due to the break in the secondary hydrate film, which creates the conditions for the primary hydrates to appear at such a spot. The break in the film and intensification of the topochemical process should cause an increased release of heat in the cement paste. That is why we suppose that the accelerated release of heat at some periods of portland cement hydration, shown by Lerch (3), signifies a topochemical reaction between C₃A and water.
Figure 5. Portland cement paste samples, w/c = 0.7, made by mixing for 5 sec to 20 min; microphotographs taken 2–120 min after mixing has been completed (magnified 360 times).
The appearance of fibrous, highly soluble new formations occurred in tests of samples of C₃S, C₅S, and C₃A as well. CaO samples showed a weak appearance of fibrous matter, and plaster samples showed none. The results obtained probably verify that under the conditions of our tests the rate of solution of primary hydrates of such materials as plaster and calcium oxide is higher than the rate of their formation.

Topochemical hydration of binding materials can be observed in the stage when hydration products are not completely soluble.

According to Baikov (1) and Roller (2), silica is not present in the liquid phase of portland cement suspensions. However, our present studies, in the course of which SiO₂ content was determined by modern colorimetric methods, have shown that, as a matter of fact, hydroxides dissolve and are present both at the beginning of cement and water mixing and at later ages as well. It is clear from the above, however, that the presence of SiO₂ in the liquid phase gives no ground to assert, contrary to some authors (4), that there is no topochemical stage in the course of hydration of silicates.

HARDENING OF CEMENTS AS AN INTERNALLY CONTRADICTORY PROCESS

Corrosion of concrete is accompanied by a destructive process that lowers its strength. Free lime in cement also lowers its strength. Thus an opinion is widely held that destruction phenomena occur in concrete structures when made of poor quality cement with high free lime content. However, on the basis of some considerations and facts one can suppose that destructive processes can develop along with structural ones in concrete made with cement of normal composition and cured under standard conditions.

In connection with this, Strelkov (42, 44) has advanced the hypothesis that hardening of binding materials is an internally contradictory phenomenon. Later, Budnikov and Kravchenko (45), Rebinder and Segalova (46), Mchedlov-Petrosyan and Babushkin (47) have come to similar conclusions.

Excluding stresses resulting from temperature changes, one may assume that the two most important sources of negative stresses are: (a) "hydration dispersion" into primary hydration products followed by coalescence of these products into cement stone (42), and (b) crystalline pressure. Hydration dispersion is defined as the conversion of the macroscopic primary hydration products, such as shown in Figure 5, into new solid particles which are very much smaller than the primary products. This process is accompanied by a negative internal stress. Hydration dispersion may be regarded as a kind of chemical grinding and is considered to be the most important phenomena in the hydration of binding materials. Widely known electronographic results show the size of cement products to fall in the range of 0.01 to 1.00 micron. The mean size of particles of modern cement clinkers is in the range of 15 to 20 microns. It follows, therefore, that one particle of cement of average size may possibly create thousands (to billions?) of newly formed particles going through the topochemical formation of primary hydrates which convert to secondary hydrates constituting cement stone.

Following hydration dispersion, agglomeration of the smallest particles of hydration products occurs in the region that had been occupied by the solid cement particle, the agglomeration having much greater volume than that of a particle of cement. Such an increase in the volume of the solid phase, called a "volume hydration effect," depends on an increase in the absolute volume of the solid particles.

Besides this volume increase, spaces between agglomerates are formed and these spaces inevitably appear in the course of disintegration of a solid body into powder. The increase in volume of the solid phase during hydration has been studied extensively by Powers (48, 49). According to his data, 1 cc of cement after hydration makes not less than 2.4 cc of hydration product. It is necessary to stress that volume effect of hydration is not a constant value, but depends on the rate of hydration (42). It is quite understandable if one considers that a given rate of filling of a volume with solid particles corresponds to a certain hydration rate. The higher the rate of filling of a given volume with a large number of particles, the less compacted the particles will be. That is why, all other conditions being equal, the greater the rate of introduction of particles into a volume, the greater is the bulk volume the powder will occupy.
Following hydration an increase in the volume of the solid phase around the cement grains takes place, thus naturally causing hydration dispersion pressure to develop. Development of such pressure is inevitably connected with hydration; it makes new formations pack closer. That is why hydration dispersion pressure contributes to increase in strength. However, if this pressure rises too fast, it decreases strength. An example of the negative effect that hydration dispersion pressure can produce is seen in the case of a too high hydration speed at higher fineness of a cement, especially in cements with an increased content of active clinker minerals—C₃S and C₃A. The strength of cement paste increases with increase in its fineness up to a certain limit; at fineness above the critical value, the strength of cement paste drops. As an example we can say that normal consistency cement paste samples, where the fineness of cements was increased from 4000 to 9500 cm²/g, showed a considerable drop in compressive strength (42).

As we have already said, hydration dispersion pressure is a function of the volume effect of hydration. Hence it follows that, if the size of particles of the primary binding material and that of its hydration products are of the same order, neither volume effect nor hydration dispersion pressure should develop. This conclusion has been proved both by Osin's study of lime (50) and by the well-known fact that the smaller the size of MgO grains in the clinker, the less harmful is its negative effect on strength of the cement. In case all MgO is in glassy matter of the clinker, i.e., it is of nearly molecular dispersity, it does not cause a strength decrease.

As we have already said, the second source of the internal negative stresses is connected with crystalline pressure. According to Scheftal' (51), until all the given layer of a growing crystal is filled with the ions necessary, the next layer will not begin. The value of crystalline pressure varies from a few tenths of a gram up to dozens of kilograms per square centimeter. It particularly depends on the amount of supersaturation at which crystallization takes place (52).

When considering the problems of hardening, it is evidently necessary to distinguish between crystalline pressure arising at the interface between crystals of the same chemical composition and structure that causes their coalescence, and crystalline pressure arising at the interface between growing crystals of different structure. In the second case the coalescence of crystals is practically impossible; however, it can be observed in the hardening of portland cement pastes. It can occur on the contacts of growing crystals of calcium hydroxide and silicate calcium hydrate only if they are in a crystalline state and meet each other in a position favorable for coalescence. This is very important, since these hydrates can be in an amorphous state. In addition, Belov et al. (53) report that Ca(OH)₂ and hillebrandite can intergrow where they contact each other with unipolar layers which contain calcium and hydroxyl ions.

Decrease of strength due to the crystalline pressure can greatly reduce the efficiency of hydrothermal treatment. Therefore, in order to increase strength values of cement and concrete, it is necessary to minimize destructive phenomena.

Taking all this into consideration, optimum mineralogical composition for portland cement of 800 kg/cm² compressive strength was found. It was found that two cements of almost equal C₃A and C₄AF content and equal fineness, but of different C₃S and C₂S content, had equal strength at one day of hardening and quite different ones at the age of 28 days.

The cements were ground to nearly 6,000 cm²/gr Tovarov fineness and were tested according to the USSR State Standard, GOST 310-41. One cement having 74 percent C₃S showed one-day strength of 436, and 28-day strength of 670 kg/cm². The second cement, with 51 percent C₃S, had strength values 404 and 821 kg/cm², respectively.

At present, hydration dispersion pressure is not yet measured sufficiently, and we do not have enough data concerning negative stresses arising at hardening. Nevertheless, taking into consideration the data available, we can draw some conclusions about its value. For example, Kuntsevich (55) has experimentally measured the pressure of extension, which is approximately equal to the algebraic sum of all the internal stresses arising in the course of hardening of binders. According to his data the pressure arising at the hardening of lime is equal to 140 kg/cm², of gypsum-aluminous expanding cement and of plaster of Paris it is approximately equal to 30 kg/cm².
Some idea concerning the hydration dispersion pressure is given by the results of a test made by Strelkov (7). Two sets of samples were prepared from a neat paste of fine-ground quicklime containing 30 percent water. The samples were made small enough that one set could be stored in air under such conditions that the heat developed by hydration was dissipated so rapidly that their temperature remained constant. Their one-day strength was equal to 15 kg/cm². The second batch was immersed in water after 30 min of molding and showed, at 24 hr of water curing, strength of 95 kg/cm². The linear extension of water-cured samples amounted to 10-11 percent, no cracks being detected; their water content rose up to 70 percent. The higher strength of the second batch of samples signifies that internal stresses in these samples were partly eliminated.

All this shows that, in the course of hardening of binding materials, not only negative stresses arise but that there are some ways to minimize them.

Besides the ways mentioned to decrease negative stresses at hardening, there is another effective one—additional wet grinding of cements. Its role is to create super rapid hardening concrete, and will be discussed below.

SUPER RAPID HARDENING CONCRETE

According to Le Chatelier (15), the hardening of binding materials is caused by surface adhesion of elongated newly formed crystalline substance (primary particles which are soluble); according to Michaelis (56), it is caused by the adhesion of colloidal hydrates. If the cement hardening is caused only by surface adhesion of newly formed particles, then it is difficult to explain their high water resistance. Therefore Baikov's point of view (1), according to which hardened binders make a crystalline coalescence, is more acceptable. Baikov, however, has not said anything about the kinetics of this process. According to Segalova and Rebinder (57), newly formed particles intergrow in a highly supersaturated solution, thus making a lattice. Consequent growth in strength of this lattice is obtained by continued growth of its members.

Another explanation of the kinetics of the building up of newly formed particles has been offered by Strelkov (35, 44). According to his concept, crystalline or amorphous hydrates are building up in the zone of saturated solution due to their coming into close proximity. Microcapillary cracks form to make thermodynamically unstable areas in which the surrounding solution, saturated with respect to macrocapillaries, becomes supersaturated with respect to the microcapillaries. New particles precipitate to join the particles they meet. Building up of crystalline hydrates is similar to self-healing of microcracks of crystals, the theory of which has been worked out by Lemmlein (59).

On the basis of supposed kinetics of the building up of newly formed particles Strelkov has concluded that, when making concrete units by means of mechanical compaction, the cement paste can be forced to harden very rapidly, missing the negative stresses (59).

To provide for such a super rapid hardening, a certain amount of newly formed particles in the cement suspension should accumulate. According to experimental data by Strelkov et al. (60), cement suspensions of w/c = 0.35-0.5 should contain not less than 15-20 percent hydration products. The total surface area of a suspension in a dehydrated state should be 5, 500-6, 000 cm²/g Tovarov (11). The cement having such characteristics is referred to as an extremely prehydrated one.

The process of extensive prehydration of a cement can be achieved by various means: additional wet grinding either in a vibration mill or short high-speed ball mill vibromatic, ultrasonic treatment, etc. When 15-20 percent of newly formed particles are obtained, the preliminary hydration can be achieved in the very short time necessary for the outer mechanical forces to bring the secondary hydrates or their aggregations closer together since the very process of their coalescence occurs practically instantly. For partial extraction of water, intensification of hydration, and elimination of volume stresses, it is advisable to submit a cement suspension or concrete mix to an intensive heating. These theoretical considerations have been proved by laboratory and pilot plant tests (56-61).
It is necessary to stress that gypsum powder wetted with a small amount of water is just calcium sulfate hemihydrate that is 100 percent preliminarily hydrated. That is why dihydrate powder can show high strength after being pressed, its value depending on the pressure used and the size of specimens. Laboratory specimens of pressed gypsum of 400 kg/cm² compressive strength have been made. However, such products do not increase in strength since they are fully hydrated. Portland cement, submitted to an additional wet grinding until it has 15-20 percent of newly formed particles, will continue hardening even after a hot pressing—especially if the unit is moistened in order to compensate for partial water loss. During the hot pressing a super speed hardening, due to the agglomeration of newly formed particles, takes place. Further hardening takes place because of consequent hydration of clinker minerals. In other words, the hardening of compacted, preliminarily deeply hydrated cement takes place according to a complex pattern.

Not only concrete but asbestos cement can be submitted to super-speed hardening. Under laboratory conditions small-sized units of asbestos cement have been made, their tensile strength being up to 500 kg/cm².

Here it is necessary to note that additional wet grinding, concrete mix compaction and heat treatment of units have long been widely known. Nevertheless, all these methods have never been used as a single technological complex. That is why here we have a completely new technology—the so-called super-speed hardening which takes neither days nor even hours but minutes to complete.

The possibility of super-speed hardening of large-sized concrete units was proved in 1959 in a pilot plant making concrete slabs of 320 by 40 by 4 (or 15) cm (61). The strength of these slabs at the age of 15 min reached as much as 60-100 and even 140 kg/cm²; at the age of 1 hr it amounted to 170-200 kg/cm². The cement used had strength of 400-500 kg/cm², its consumption being 360-400 kg/cm². At 15 min the strength of the slabs permitted their stripping and transportation. After having been moistened they continued to harden intensively and at the age of 30-45 days their strength was 700-800 kg/cm². The molding of these slabs was performed on a base plate with vertically movable side and butt shields. The base plate and side shields had been pre-heated to 60-70 °C; the concrete mix was vibrated for some minutes and then it was compacted by vibrators having a temperature of 150-200 °C. There were interstices between separate plates of vibro-units into which a small amount of water was introduced in order to prevent excessive drying of the concrete. These vibro-units supplied an additional load in the range of 150-300 g/cm². Duration of vibration was, for any point being vibrated, nearly 2 min. Due to it the temperature of the concrete mix increased from 30-35 °C up to 65-70 °C. After the stripping, which was performed 15 min after the unit had been molded, it did not show cracks.

The consumption of cement can be reduced by 15-25 percent by preliminary deep hydration; the duration of hydrothermal cure can be reduced by as much as 2-4 times.

THE ROLE OF GYPSUM

Kühl notes (62) that Lafuma, Bogue, Lerch, Taylor and Brown support Le Chatelier's opinion, according to which the action of gypsum depends on the formation of hydro-sulfoaluminate forms. Formation of hydrosulfoaluminates in a nonhardened cement paste is helpful—indeed of the way it appears. If hydrosulfoaluminate is formed from a solution, then it is harmless. But if hydroaluminate appears due to a "solid-state" reaction, then internal extending stresses can arise in hardening cement stone and they would decrease the strength of the concrete (65).

According to Blondiau (63), different action of gypsum is connected with its influence on the solubility of calcium hydrosulfoaluminate which stipulates the sizes of calcium hydrosulfoaluminate crystals. Budnikov and his co-workers also support this concept (8, 64, 65, 66, 68).

According to Kalousek (67), in the process of hardening of portland cement containing gypsum, formation of hydrosulfoaluminate excludes the possibility of formation of calcium hydroaluminate. The data mentioned earlier concerning the composition of the liquid phase of pastes show that calcium hydroaluminate can be present even in the presence of gypsum.
In connection with this we exclude the possibility that calcium hydrosulfoaluminate is formed by "solid-state" reactions. However, the size of its particles and the density of their packing depend on the solubility of hydroaluminates, hydrosulfoaluminate, and on the rate of hydrosulfoaluminate formation. The smaller the particles of calcium hydrosulfoaluminate and the higher the speed of their formation, the bigger is the volume necessary for their dislocation and the greater are the extended stresses arising in cement stone.

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