Express Forecast of Portland Cement Strength Using Conductimetric and Thermogravimetric Analyses

Yefimenko Yu.V. 1

1 Candidate of Technical Sciences, Deputy Head of the Research Center "Building Materials and Technologies", Ministry of Construction of the Russian Federation branch of FGBU "TSNIIP Russian Ministry of Construction" DalNIIS, ul. Borodinskaya, 14, Vladivostok, 690033, RF

E-mail: t.rusanova@dalniis.ru

Abstract. Questions of express (within 15 minutes or 24 hours) instrumental forecast of Portland cement strength by means of conductivity and (or) gravimetric measurements are considered. It is shown that the specific resistivity of the sample of cement-sand mortar of standard composition (1:3, W/C=0.5) or the determination of the degree of hydration of cement stone (W/C=0.3-0.32) for interval losses during thermogravimetric analysis in the period of 24 hours provides fairly reliable results in the range of 40 to 70 MPa for R 28 and 12-30 MPa for R3 days during the first 15 minutes.

A comparison of the different nature of the forecast methods adequacy for Portland cement durability (for "ion" power and transformation of cement-framework of grains) demonstrates the compatibility of these practices and ensures the convergence of the strength results. The use of these different techniques also provides additional information about a number of important construction and technical characteristics (the period of cement setting in the solution, the number of mineral additives, the content of Ca(OH)2, etc.).

1. Introduction

The strength of concrete (C) is not a stochastic characteristic and according to the rules for selecting concrete composition is determined by the type of portland cement (PC) and water-cement ratio [1, 3, 22].

However, in a number of cases (non-regulated storage, using cements of foreign supply, the use of unknown grade cement), there is a need to determine the cement grade very quickly.

The hardening of practically all inorganic binders is caused by the formation [2, 3], the intergrowth and interlacing of crystalline hydrates (for example, for portland cement in the form of portlandite, hydrogarnets of the type CSHn, AFtm, C3AFHn) in the electrolytic medium [3, 5, 7, 16].

The composition of the formed hydrating portland cement compounds depends on the mineralogical composition of the clinker, the ratio of the solid and liquid phases, the hardening temperature, etc. The technical properties resulting from the hardening of the cement stone are formed in the interstitial fluid with high electrical conductivity [4, 16] and depend on the mineralogical composition of the clinker (mainly C3S) in portland cement and obey the rules of mixture and the W / C law [5, 10, 14, 17].

The known proportionality of the cement materials (Cm) strength [1, 2, 3, 14, 15] on the content of the C3S alite in the clinker is also confirmed for the electrolytic characteristics of the Cm-electrical conductivity [4, 5]. According to our calculations of the data [4], the fraction of electrical conductivity of C3S is about 80% of the calculated additive electrical conductivity of the interstitial fluid for the cement (liquid) phase.

For our case, this was the basis for choosing the structurally sensitive methods of structure recognition in the form of the conductimetric analysis method (CMA) (ion concentration in the
interstitial fluid and its volume [5, 20]) and thermogravimetric (TGA) - (type and amount of hydrated compounds) [18, 19, 23, 24].

In DalNIIS conductimetric studies of cement materials began in the 60s of the XX century after the launch of one of the first in the country line for electric heating for expanded-clay concrete exterior wall panels [9]. Over the long period, a large volume of studies on the adequacy of the conductimetric evaluation of the cements and concretes quality was carried out and it was obtained that the value of specific resistivity (SR) and its dynamics characterize the correspondence of these changes to the basic laws and rules of mixtures and technologies, including "thermal" maturity [21].

It was determined that the changes in the composition of Cm (dough, mortar, concrete) on W / C, type and concentration of chemical additives, the porosity of the aggregate with sufficient statistical capacity (R^2 to 0.8-0.85) causes a corresponding adequate change in p_{min} Om cm at the stage of the mixture (the period before setting) and its relative value \( \beta = p_{1}/p_{min} \), rel. units - in the process of hardening.

A relationship between the dynamics of the electrical specific resistivity (SR) and the strength of concrete was found out [17].

Our experimental data [8, 17-20, 24] are in many respects consistent with the results of studies by other authors on conductimetric studies of the setting processes diagnostics [5, 7], hardening [5], composition effects [6], chemical and antifreeze additives [8] and etc.

The proposed techniques for the use of conductometry [13] for predicting individual physico-mechanical properties of C are rather complex, time-consuming, and carried out with the use of unrealistic samples in the form of suspensions.

Therefore, CMA, as a relatively simple and instrumentally available method, has long been used [6, 7, 8, 11, 12] to solve various problems of monitoring the technical characteristics of cement materials of real compositions. In this paper we studied a genetically justified forecast of the strength of mature cement material according to the results of measurements for cement material samples of the real composition at the stage of the mixture.

The changes in hardening of cement materials registered with the help of CMA are associated with transformations in their framework of grains (accumulation of hydrates), which we fix by means of thermogravimetric analysis (TGA). In the process of hardening, the increase in the concentration of new formations monitored by TGA is subject to a logarithmic relationship (as well as for strength).

### 2. Methods of research

**Conductimetric analysis (RCL P5030 measuring instrument, f = 1 kHz).**

The analytical sample is a standard cement-sand mortar \( C: S = 1: 3, W / C = 0.5 \), laid with vibration into the measuring cell.

Measurements and calculations of the specific resistivity (RS) were carried out according to the usual rules [20], taking into account individually measured values (in 0.1N KCl solution) of the "constant" cell \( K_c = 0.42 \pm 0.02 \text{ cm}^{-1} \) for manufactured cells (two conical nickel-plated rod fixed in the center of a cylindrical Teflon container).

**Thermogravimetric analysis (OD-102 and Q1500 derivatographs).**

Analytical sample - cement paste W / C = 0.30-0.32, compacted (with tipping) in a plastic lid and stored at 20 ± 1 °C over water in a darkened desiccator. Preparation in acetone (chemically pure) in a stream of warm air (50-60 °C).

Calculations of the hydrated phases were carried out according to known and accepted in our practice formulas [18, 19, 24, 25]. It is considered that the indicator \( X_3 \) (weight loss from 20 to 300 °C) is represented by 70-80% by evaporating water from CSH and AF_t, m hydrates.

**Formulas for forecast strength calculations** were obtained as a result of tests and measurements carried out jointly with the Central Laboratory of “Spasskcement” JSC for 40-45 cement batches of Novospassky plant - PC of 500 D0 and Spasskiy Plant - PC 500 D0 and PC 400 D0 D20. The test was carried out directly in the Central laboratory of “Spasskcement” JSC (freshly prepared PC) and in the laboratory of DalNIIS (7-20 days after delivery of cement samples from the plant).
The obtained statistically significant equations of the relationship between specific resistivity (RS) and TGA parameters of the mixture with the strength of $R_{28}$ are given in Table 1.

**Table 1.** Formulas for calculating the forecast strength $R_{28}$ based on the results of conductimetric (CMA) and thermogravimetric (TGA) measurements

| No. Of Formula | CMA method | Formula | Range | $R^2$ statistical indicator |
|---------------|------------|---------|-------|----------------------------|
| 1             | For PC D0-20 | $R = 74,7 - 0,055 \cdot \rho$, MPa | $\rho: 370 - 750$, Om cm | 0,75 |
| 2             | For PC D0   | $R = 63,4 - 0,02 \cdot \rho$, MPa | $\rho: 360 - 630$, Om cm | 0,60 |

b) for thermogravimetric analysis of cement stone $W / C = 0,30 - 0,32$ at the age of 24 hours

| TGA method | Formula |
|------------|---------|
| 3          | $X_3$   | $R = X_3 \cdot 5,15 + 9$ |
| 4          | $X_{cn}$ | $R = X_{cn} \cdot 3,78 + 20$ |
| 5          | $X_{xcb}$ | $R = X_{xcb} \cdot 2,93 + 17$ |

*Note*

- $X_3$ - weight loss (%) with TGA in the range of 20-300 °C;
- $X_{cn}$ - the amount of $Ca(OH)_2$, %;
- $X_{xcb}$ - the content of chemically bound water, %,

$XCB = TT20 - 900^\circ C - 0,41 \cdot TT600 - 850^\circ C$, %

where $TT20 - 900^\circ C$ and $TT600 - 850^\circ C$ - weight loss in the temperature ranges, respectively, 20-900 °C and 600-850 °C.

The values $X_{cn}$ and $X_{xcb}$ are taken in consideration of their content in the original (unhydrated cement).

Results of research and verification of the proposed method.

Examples of a comparative strength forecast of various cements according to CMA data (15 min.) and TGA (24 hours) are presented in Tables 2-4.

**Table 2.** Comparison of the “forecast” strength values of PC obtained by the results of CMA and TGA (Portland cement of Novospassky Plant PC 500-D0)

| Parameter                        | Conductimetric analysis (CMA) | Thermogravimetric analysis (TGA) in the period of 24 hours |
|----------------------------------|--------------------------------|---------------------------------------------------------|
|                                  | $p 0,25$ hour, Om cm | $p min$, Om cm | $X_3$, % | $XCB$, % | $Ca(OH)_2$, % |
| Measured value                   | 530                           | 456           | 8,88    | 12,6     | 7,5             |
| Forecast strength $R_{28}$, MPa  | $R_{28} = 52,2$               | -             | 54,7    | 54       | 54,3            |
| Actual strength (GOST 310.4)     | $R_{28} = 52$                 |               |         |          |                 |
Note: $X_3$ - interval weight loss up to $300^\circ$C., XCB - chemically bound water.

From Table 2 it can be seen that for the PC 500 D0, forecast values of $R_{28}$ for individual indicators of CMA and TGA have practically the same values of $R_{28} = 52 \pm 1$ MPa, which characterizes the coherence of the methods used to determine the forecast strength of cement.

### Table 3. Comparison of the “forecast” and actual strength values of PC obtained from the results of CMA (Formula 1) and TGA (formulas 3, 4, 5) for Portland cement with an additive (China).

| No. of PC | Parameter                        | Conductimetric analysis (CMA) | Thermogravimetric analysisis (TGA) in the period of 24 hours |
|-----------|---------------------------------|------------------------------|-------------------------------------------------------------|
|           |                                 | $p_{0.25}$, Om cm | $p_{min}$, Om cm | $X_3$, % | XCB, % | Ca(OH)$_2$ |
| PC1       | Measured value                  | 567*                      | 450             | 6,1     | 8,64   | 3,7       |
| (No. 1223) | Forecast strength, MPa          | 42,6                       | 42              | 40,4    | 42,3    | 40        |
| Actual strength, MPa (GOST 310.4) |                           |                             | 41,1          |
| PC2 2     | Measured value                  | 371*                      | 320             | 7,7     | 11,1   | 6,0       |
| (No. 1221) | Forecast strength, MPa          | 52                         | 54              | 49      | 47     | 48,7      |
| Actual strength, MPa (GOST 310.4) |                           |                             | 49,9        |

* extrapolated values

Conductimetric studies of these PC 1 and PC 2 determined that the change in the SR of these cements is characterized by an unusual increase in this characteristic during 2 hours, followed by a normal decrease up to 4-5 hours (by the period of cement setting in the solution). Such an anomalous change in the SR is especially fixed for PC 1.

Based on the results of the TGA, in the samples of the initial cements along with the usual for non-hydrated PC compounds in the form of CSH$_{0,5-2}$ and the products of the Ca(OH)$_2$ and CaCO$_3$ (0.5-3%), exothermic TGA effects of 590 and 960 $^\circ$C were recorded and they are especially strong for PC 1. For PC 1 (sample No. 1223) a small (0.5-0.6%) temporary weight increment at a temperature of 500 $^\circ$C was recorded (thermal oxidation of the additive, its reaction with CaO from Ca(OH)$_2$ at the time of TGA analysis) and weight increment in the range 850-920 $^\circ$C (additions of furnace dust and blast-furnace granulated slag). The presence of these effects is attributed to the presence of furnace dust and probably blast furnace granulated slag, while the content of furnace dust and slag in the cement PC 1) is higher.

Thus, for PCs 1 and 2, the forecast values of strength (28 days) according to the CMA data (42 MPa and 53 MPa for PCs 1 and 2, respectively) and according to TGA method (41 MPa and 48 MPa for PCs 1 and 2, respectively) practically coincide with the results of tests in accordance with GOST 310.4 (41 MPa and 49.9 MPa respectively).

### Table 4. Results of thermogravimetric strength forecast (formulas 3-5) of Portland slag cement (North Korea, Rason, code MW959, No. 3111).

| Parameter                        | Thermogravimetric analysisis (TGA) in the period of 24 hours |
|---------------------------------|-------------------------------------------------------------|
| Indicator Value                 | $X_3$, % | XCB, % | Ca(OH)$_2$ |
| Forecast strength, MPa          | 3,84    | 5,36   | 3,27       |
| Actual strength, MPa (GOST 310.4) | 29      | 32     | 38         |
|                                 | 39,9    |        |            |
For this cement (sample No. 3117), the reduced accuracy of the TGA forecast (deviation up to -20 ... -27%) is due to the increased content of the granulated slag, which is significantly different from the clinker in the chemical-mineralogical composition and hydration activity.

The given examples of the use of CMA-and TGA methods for strength forecast for three different cements of domestic and foreign manufacturers characterize the normal convergence of different methods and their compliance with the results of standard tests in accordance with GOST 310.4. This confirms the coherence of the electric (SR) and mineral-phase (TGA) express methods for forecasting the cement grade.

Conclusions
1. The electrolytic model of cement strength and the relationship of this indicator with the products of hydration based on thermogravimetric analysis is substantiated.
2. Correlations between the specific resistivity (in 15 minutes) and the phase composition of the cement material (at the age of 1 day), measured in analytical samples of the real composition, with the strength of the cement material at the age of 28 days are proposed.
3. Sufficient convergence of the two methods for forecasting the strength of cement has been obtained, and the use of these methods allows obtaining additional information on a number of important building and technical characteristics (the period of setting the cement in a real solution, the amount of mineral additives, the content of Ca(OH)_2, etc.).

Reference
[1] Krylov B A 1985 Electroconductive properties of concrete with plasticizing additives Concrete and reinforced concrete No 12 pp 6-7
[2] Dorf V A Romanchuk V E 1984 Determination of cement content in a concrete mixture by a conductometric method Concrete and reinforced concrete No 2 pp 13-14
[3] Kalinkin B A 1985 Forecast of grade strength based on 4-day strength of concrete in normal storage Concrete and reinforced concrete No 1 p 11
[4] Yefimenko Yu V 1975 About colloid-chemical effects of cement-water systems Journal of Applied Chemistry No 5 pp 1135-1137
[5] Efimenko Yu V Nekipelov I N Mikhaylov A D 1986 Features of the structure and properties for concrete of immediate demoulding operation Concrete and reinforced concrete No 9 pp 10-12
[6] Bazhenov Yu M 1978 Technology of concrete Moscow High school publ p 455
[7] Volzhensky A V 1986 Mineral binders (technology and properties) Textbook for high schools Moscow SI Publ p 464
[8] Lee F M 1961 Chemistry of cement and concrete Moscow SI Publ p 645
[9] Babushkin V I 1968 Physicochemical processes of corrosion of concrete and reinforced concrete Moscow SI Publ p 187
[10] Akhverdov I N Margulis L N 1975 Nondestructive quality control of concrete by conductivity "Science and technology Publ " Minsk p 174
[11] Wegener R V 1953 Electroheating of concrete and reinforced concrete structures SI Publ Moscow
[12] Tasmas F Farkas E Roy D 1984 Electrical Conductivity of Pastes Made of Clinker + Gypsum Proceeding Britain Ceramic Society - No 35 pp 237-248
[13] Repyov E N Toroptsev A V 1968 Electroheating of expanded-clay concrete external wall panels Proceedings of RILEM Moscow SI Publ pp 300-304
[14] Alekseev S N 1976 Rosenthal Corrosion resistance of reinforced concrete structures in an aggressive industrial environment Moscow SI Publ p 207
[15] Moskvin V M 1980 Corrosion of concrete and reinforced concrete methods of their protection Moscow SI Publ p 536
[16] Stupachenko P P Efimenko Yu V Tsuprik V G 1992 Structure properties and durability of materials based on mineral binders Vladivostok Publishing House of the Far Eastern University p 144
[17] Butt Yu M and others 1965 Technology of binders Moscow Higher Schoolp p 619
[18] Larionova Z M 1971 Formation of the structure of cement and concrete Moscow SI Publ p 161
[19] Ershov L D 1956 Effect of phase composition and petrographic structure of clinker on the properties of cement stone Proceedings of the meeting on chemistry of cement Moscow Promstroyizdat p 500
[20] Rakhimov Sh M Smirnova E A 2005 Method for forecasting the grade strength of cement stone Bulletin of BSTU No 9 pp 293-296
[21] Yefimenko Yu V 1978 On the issue of electrical modeling of the strength of cement-water systems Hydration and hardening of cements Collection of scientific works No 3 Chelyabinsk p 136
[22] Efimenko Yu V Kuznetsova L A Antropova V A Nekipelov I N Structure and properties of fine-grained ceramsite concrete in the presence of microsilica Proceedings of the international conference on concrete and reinforced concrete Moscow DIPAK vol 4 Lightweight and cellular concrete pp 61-67
[23] Yefimenko Yu V Nekipelov I N 2008 Effect of mineral additives on the structure and phase composition of cement materials Collection of works of the international conference "Environment construction security" Vladivostok p 312 (pp 113-120)
[24] Yefimenko Yu V 1969 To the technique of measuring the electrical conductivity of cement systems Factory laboratory No 4
[25] Antropova V Efimenko Y Koneva N 1997 On the corrosion resistance of the sea water for mixing (Ibausil) 13th Intern Baustoff 924 band 2 Weimar pp 2-0307-2-0313