MONITORING THE STRENGTH PROPERTIES OF CEMENT CLINKER ON THE BASIS OF MEASUREMENTS OF ELECTRICAL RESISTIVITY

1D.Stackelberg, 1B.Wilge, 1S.Boiko
1Concretect Ltd., Jerusalem, Israel

2P.Martauz, 2J.Strigac
2Považska cementareň plant, Ladce, Slovakia

Abstract
Považska cementareň plant’s laboratory has used Concretect Ltd. Company’s technology in its second year to assess the quality of cement clinker. The basic of technology is the continuous measurement of the electrical resistivity of hardening of the standard C:S-mortar during 22-24 hours.

The proposed report sets out the fundamental principles and results of the practical use of the algorithm evaluation of the stability of strength characteristics of clinker.

Originality
The implementation of the algorithm has a certain sequence of operations:
- analysis of the kinetic curve \( R = f(\tau) \) and appointment to the optimal time of determining the structural parameter;
- this parameter is correlated with the properties of cement clinker.

From April 2008 to August 2009 the laboratory staff of the plant, along with standard tests, measured the electrical resistivity of the standard "clinker-sand" mortar. Results were tested on more than 300 batches of clinker.

Chief contributions
1. Company Concretect Ltd. developed and proposed to use an algorithm for reducing the coefficient of variation of early strength in cement clinker production process.
2. The algorithm is based, formulated and implemented on the principle of “reference group of samples”.
   According to this principle, a sufficiently long time period, the production set, samples (party) clinker are characterized by minimum variation values of early 1-day and 2-day strength coefficients.
3. This group of samples is considered as "reference" set, for it defines the basic statistical parameters; properties of all the other samples are correlated with the properties of “reference”.
4. The correlation between the values of the early strengths of clinker and the structural parameter - the values of resistivity,
   are measured at an early stage of hardening in terms of 14 to 20 hours after mixing clinker with water.
5. Comparison of properties of samples of the entire array with the properties of the samples “reference group” allows,
   by measuring the electrical resistivity, at an early age (in 14 - 20 hours) to identify samples of clinker, this increases the coefficient of variation and creates the possibility of an early detection and elimination of the causes of destabilizing process of manufacture.
6. This method predicts the early strength of clinker on the measurements of the electrical resistivity at an early age. Use this method on Považska cementareň plant for predicting the strength of more than 350 parties, cement clinker showed good agreement with the results of standard tests for the following values coefficients of variation: 2.15% for 1-day strength and 6.70% for 2-day strength.

Keywords: Clinker, strength, electrical resistivity, structure parameter.

Introduction
Cement clinker production - is a complex process, whose stability is determined by a combination of parameters such as feedstock materials, fuel, technological equipment’s level and its operating modes, etc. The inevitable variations of these parameters determine fluctuations in the finished product’s properties, and above all, the clinker’s strength.
The purpose of this paper – is the creation of algorithm estimates of cement clinker’s strength on the basis of new principles of monitoring hardening and strengthening of cement-concrete compositions, formulated and developed by Concretex Ltd. [1,2,3].

The solution of the problem is solved by:

a) Revealing in a certain period of time series of tested clinker samples – the samples group – which have minimal variation coefficients at early 1-day and 2-day’s strength, i.e. selecting a so called “reference group” of samples;
b) Establishing correlations [4] between the values of the early clinker’s strengths and the effective or apparent resistivity – hereinafter "resistivity", measured at an early stage of the hardening process;
c) Estimating the 1-day and 2-day cement clinker’s strength, according to Concretex Ltd.’s technology, based on early resistivity measurements of hardened standard mortar.

Clinker’s time series strength analysis and the “reference group” samples selection

During the production’s process at Považská cementáreň plant in April - May 2008, a set of 37 samples were obtained for the clinker’s strength variation analysis. In laboratory tests the standard compressive strength at the age of 1, 2 and 28 days (Fig. 1) was determined. It can be seen that between the curve \( S(1) = f_1(\theta) \) and \( S(2) = f_2(\theta) \) there is a good correspondence, (where \( \theta \) is the testing’s current date) but the curve \( S(28) = f_3(\theta) \) differs significantly from them.

A measurement of resistivity standard "clinker-sand" mortar is carried out continuously during the first 24 hours of hardening (Fig. 2). Trying to represent all the experimental curves \( R = f(\tau) \) on one graph is not only impossible but meaningless as well. Therefore Fig. 2 shows the experimental values of the field bounded by the curves \( (Average + 2StDev) = f_1(\tau) \) and \( (Average - 2StDev) = f_2(\tau) \), and at the central part the 37 measurements’ average of the curve \( Average = f_3(\tau) \) (where \( \tau \) is the measuring time of resistivity during the hardening process).

The strength parameters’ stability is estimated by the coefficients of variation:

- For the entire array of samples: \( C_{VAR}[S(1)] = 11.6, C_{VAR}[S(2)] = 8.9, C_{VAR}[S(28)] = 3.1 \);
- For the “reference group” samples: 
  \[ C_{VAR}[S(1)] = 2.9, \quad C_{VAR}[S(2)] = 3.6, \quad C_{VAR}[S(28)] = 2.1. \]

It is obvious, that given such periods for the total time of production makes it possible to determine the "reference" period, characterized by the most efficient statistical indicators. The convergence of the parameters’ averages values to "reference" should reduce the coefficient of variation and, as a result, improve the stability of clinker production.

**Measurements of resistivity and their relationship to the early strength of cement clinker**

To establish the correlations "Strength - Resistivity" an analysis of the kinetic curves \( R = f(\tau) \) was performed. Fig. 3 shows the resistivity changes for the 6 clinker samples in a "reference period" – from 12.04.08 to 18.04.08.

It can be seen, that a stable increase in the resistivity, corresponding to clinker’s crystallization strengthening initial process, begins 10 - 11 hours after completion of molding "clinker-sand" mortar samples. Stable increase in resistivity is caused by a good correlation between the conducting properties changes of the material to develop its structure.

At this stage, the developed crystallization "post-ettringite" and "post-portlandite" structure of the clinker’s has been well defined in its structural and mechanical properties (including strength), and the resistivity is almost uniquely determined by these properties. Therefore, the value of resistivity \( R(\tau) \), measured in a predetermined time, directly characterizes the level of the emerging structure’s development, and therefore is in essence a structural parameter.

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**Fig. 3. Resistivity’s change for “reference group” samples during the first days of “clinker-sand” mortar hardening process.**

Fig. 4 shows 1-day and 2-day clinker samples’ strength produced during the test period, compared with the same samples’ resistivity measurements at the age of 20 hours. It can be seen that the variations of the parameter \( R(20h) \) well corresponds to the variations of early strength \( S(1) \) and \( S(2) \). It should also be noted
that the resistivity measurements made at an earlier age (17 and even 14 hours) also provide a close similarity between the curves $S(1) = f_1(\theta)$, $S(2) = f_2(\theta)$ and $R = \varphi(\theta)$.

\[
S(1) = 0.1035R(20) + 4.0537 \quad (1)
\]
\[
S(2) = 0.1059R(20) + 14.631 \quad (2)
\]

Fig. 4. 1-day, 2-day strength values and resistivity values changes measured at the age of 20 hours.

The comparison of the standard determinations’ results of early strengths $S(1), S(2)$ and resistivity measurements for the entire array (37 samples) showed that the “Strength - Resistivity” relation is approximated by the following linear equations:

The algorithm of cement clinker early strength’s prediction is implemented as follows.

1. During the daily clinker testing at the plant’s laboratory, in parallel to the standard prisms samples manufacturing, 2 sensors – containers [3] are filled with the same “clinker-sand” mortar, which continuously measure the resistivity of hardened mortar within 24 hours.

2. A specialized computer software, previously fed with the equations (1) and (2) coefficients, at a predetermined time (in our case, 20 hours after the beginning of measurements) calculates and displays forecasted strengths $S(1)$ and $S(2)$ values.

During the years 2008-2009 at the Považskà cementàreň cement plant, more than 350 clinker batches were tested using this algorithm; the results are summarized in Table 1. In order to save space, the table shows the average dates for a 2-week testing periods. The table shows the results of standard measurements [5] of 1-day and 2-day strength $[S(1)_{ST}, S(2)_{ST}]$ and the corresponding predicted values $[S(1)_{PR}, S(2)_{PR}]$, calculated automatically from the measured value of the parameter $R(20h)$. 

The comparison between the standard tests’ results and the calculated prediction strength values showed that the maximum difference between the average values of the “Standard – Prediction” is for 1-day strength: 1.2 MPa (8.7%), and for 2-day: 2.1 MPa (7.5%). Such deviations are quite acceptable when using non-destructive testing methods.

The statistical processing of the test data for the entire array (354 samples) also showed that the prediction’s accuracy of the cement clinker’s early strength, at the resistivity measurement results corresponds to the accuracy of the strength’s determination by the standard destructive methods.

Table 1

<table>
<thead>
<tr>
<th>Time period</th>
<th>R(20h) [cm²/m]</th>
<th>Compressive Strength [MPa]</th>
<th>1 day</th>
<th>Difference [%]</th>
<th>2 days</th>
<th>Difference [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>05-17/04/08 (13 samples)</td>
<td>145</td>
<td>S(1)_ST: 19.3, S(1)_PR: 18.9</td>
<td>0.4</td>
<td>1.4</td>
<td>30.7</td>
<td>31.1</td>
</tr>
<tr>
<td>18-30/04/08 (13 samples)</td>
<td>152</td>
<td>S(1)_ST: 19.9, S(1)_PR: 19.6</td>
<td>0.3</td>
<td>0.9</td>
<td>30.6</td>
<td>31.7</td>
</tr>
<tr>
<td>01-11/05/08 (11 samples)</td>
<td>136</td>
<td>S(1)_ST: 17.7, S(1)_PR: 18.2</td>
<td>-0.4</td>
<td>-2.7</td>
<td>28.4</td>
<td>30.4</td>
</tr>
<tr>
<td>02-14/06/08 (10 samples)</td>
<td>151</td>
<td>S(1)_ST: 20.1, S(1)_PR: 19.5</td>
<td>0.5</td>
<td>2.0</td>
<td>31.4</td>
<td>31.7</td>
</tr>
<tr>
<td>16-26/06/08 (10 samples)</td>
<td>126</td>
<td>S(1)_ST: 17.0, S(1)_PR: 17.2</td>
<td>-0.3</td>
<td>-2.0</td>
<td>28.7</td>
<td>29.6</td>
</tr>
<tr>
<td>01-16/07/08 (15 samples)</td>
<td>140</td>
<td>S(1)_ST: 18.2, S(1)_PR: 18.5</td>
<td>-0.3</td>
<td>-2.7</td>
<td>30.8</td>
<td>30.8</td>
</tr>
<tr>
<td>17-30/07/08 (14 samples)</td>
<td>155</td>
<td>S(1)_ST: 19.6, S(1)_PR: 19.8</td>
<td>-0.2</td>
<td>-1.7</td>
<td>31.2</td>
<td>31.9</td>
</tr>
<tr>
<td>01-13/08/08 (13 samples)</td>
<td>129</td>
<td>S(1)_ST: 18.3, S(1)_PR: 17.5</td>
<td>0.7</td>
<td>2.7</td>
<td>30.1</td>
<td>29.9</td>
</tr>
<tr>
<td>14-31/08/08 (14 samples)</td>
<td>131</td>
<td>S(1)_ST: 18.5, S(1)_PR: 17.7</td>
<td>0.8</td>
<td>3.8</td>
<td>30.7</td>
<td>30.0</td>
</tr>
<tr>
<td>01-14/09/08 (14 samples)</td>
<td>139</td>
<td>S(1)_ST: 18.4, S(1)_PR: 18.4</td>
<td>0.0</td>
<td>-0.8</td>
<td>30.5</td>
<td>30.7</td>
</tr>
<tr>
<td>15-30/09/08 (16 samples)</td>
<td>142</td>
<td>S(1)_ST: 18.4, S(1)_PR: 18.6</td>
<td>-0.3</td>
<td>-1.9</td>
<td>31.6</td>
<td>30.9</td>
</tr>
<tr>
<td>05-16/10/08 (12 samples)</td>
<td>153</td>
<td>S(1)_ST: 20.3, S(1)_PR: 19.6</td>
<td>0.6</td>
<td>2.4</td>
<td>33.5</td>
<td>31.8</td>
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<tr>
<td>17-31/10/08 (12 samples)</td>
<td>128</td>
<td>S(1)_ST: 17.7, S(1)_PR: 17.5</td>
<td>0.3</td>
<td>0.4</td>
<td>30.4</td>
<td>29.8</td>
</tr>
<tr>
<td>01-14/11/08 (13 samples)</td>
<td>147</td>
<td>S(1)_ST: 19.6, S(1)_PR: 19.1</td>
<td>0.5</td>
<td>2.2</td>
<td>31.4</td>
<td>31.3</td>
</tr>
<tr>
<td>15/11-05/12/08 (19 samples)</td>
<td>132</td>
<td>S(1)_ST: 16.6, S(1)_PR: 17.8</td>
<td>-1.2</td>
<td>-8.7</td>
<td>29.9</td>
<td>30.1</td>
</tr>
<tr>
<td>07-20/04/09 (10 samples)</td>
<td>83</td>
<td>S(1)_ST: 13.9, S(1)_PR: 13.5</td>
<td>0.4</td>
<td>1.5</td>
<td>26.9</td>
<td>26.2</td>
</tr>
<tr>
<td>21-30/04/09 (10 samples)</td>
<td>80</td>
<td>S(1)_ST: 12.6, S(1)_PR: 12.9</td>
<td>-0.3</td>
<td>-2.6</td>
<td>25.2</td>
<td>25.7</td>
</tr>
<tr>
<td>01-18/05/09 (12 samples)</td>
<td>100</td>
<td>S(1)_ST: 15.3, S(1)_PR: 15.0</td>
<td>0.4</td>
<td>2.0</td>
<td>28.3</td>
<td>27.6</td>
</tr>
<tr>
<td>19-30/05/09 (12 samples)</td>
<td>117</td>
<td>S(1)_ST: 15.9, S(1)_PR: 16.4</td>
<td>-0.6</td>
<td>-4.1</td>
<td>29.1</td>
<td>28.9</td>
</tr>
<tr>
<td>01-11/06/09 (11 samples)</td>
<td>102</td>
<td>S(1)_ST: 14.6, S(1)_PR: 15.2</td>
<td>-0.6</td>
<td>-4.4</td>
<td>28.1</td>
<td>27.8</td>
</tr>
<tr>
<td>01-15/07/09 (15 samples)</td>
<td>120</td>
<td>S(1)_ST: 16.1, S(1)_PR: 16.8</td>
<td>-0.7</td>
<td>-4.3</td>
<td>28.5</td>
<td>29.2</td>
</tr>
<tr>
<td>16-31/07/09 (15 samples)</td>
<td>111</td>
<td>S(1)_ST: 15.8, S(1)_PR: 16.0</td>
<td>-0.2</td>
<td>-2.0</td>
<td>28.2</td>
<td>28.4</td>
</tr>
<tr>
<td>01-24/08/09 (18 samples)</td>
<td>114</td>
<td>S(1)_ST: 15.9, S(1)_PR: 16.2</td>
<td>-0.3</td>
<td>-2.9</td>
<td>28.9</td>
<td>28.6</td>
</tr>
<tr>
<td>01-17/09/09 (12 samples)</td>
<td>116</td>
<td>S(1)_ST: 16.2, S(1)_PR: 16.3</td>
<td>-0.1</td>
<td>-1.9</td>
<td>29.0</td>
<td>28.8</td>
</tr>
<tr>
<td>18-30/09/09 (12 samples)</td>
<td>111</td>
<td>S(1)_ST: 15.7, S(1)_PR: 15.9</td>
<td>-0.2</td>
<td>-2.5</td>
<td>28.5</td>
<td>28.4</td>
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<td>01-15/10/09 (13 samples)</td>
<td>105</td>
<td>S(1)_ST: 15.2, S(1)_PR: 15.4</td>
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<td>-2.3</td>
<td>28.1</td>
<td>28.0</td>
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<td>S(1)_ST: 15.6, S(1)_PR: 15.9</td>
<td>-0.3</td>
<td>-2.7</td>
<td>28.5</td>
<td>28.4</td>
</tr>
</tbody>
</table>

Average [MPa]**| 17.4 | 17.5 | 29.9 | 29.8 |
Standard Deviation [MPa] | 2.62 | 2.05 | 2.63 | 1.86 |
Variation Coefficient [%] | 15.01 | 11.73 | 8.82 | 6.23 |

**The basic statistical parameters are defined for the entire array - 354 samples of clinker.

Actually the strength’s variation coefficients are close to their values:

- For 1-day strength: 15.01 (standard) and 11.73 (predicted),
- For 2-day strength: 8.82 (standard) and 6.23 (predicted).
A graphical generalization of the standard determination’s results and prediction for 1-day and 2-day clinker’s strength (see Table 1) is shown in Fig. 5. The graph shows that the predicted values variation of strength $S_{PR1}, S_{PR2}$ clearly correspond to variations of standard values $S_{ST1}, S_{ST2}$.

This data suggests that the early strength prediction’s results not only are accurate enough in magnitude, but they almost uniquely determine the clinker’s strength variation due to fluctuations of different technological parameters.

![Fig. 5. Standard and predicted values of 1-day and 2-day of cement clinker’s strength.](image)

Thus, the monitoring of cement clinker’s early hardening results, using an algorithm developed by Concretc Ltd., reflect the production process’ real state, and the "risk" of the practical use for prediction results is almost minimal.

**Conclusions**

1. Concretc Ltd. Co. has developed an algorithm for monitoring cement clinker’s strengthening in its production process. The algorithm is based on the formulated and implemented principle of "reference groups" samples. According to this principle and in general terms, a sufficiently prolonged and established production’s period for clinker’s samples (batches) is characterized by minimal variations of the early 1- and 2-day strength’s coefficients values.
2. A good correspondence was established between the cement clinker’s resistivity changes and the behavior of its formation for 1-day and 2-day strength.
3. The comparison between the clinker’s properties tested and the samples’ properties of the "reference group" allows the electrical resistivity’s measurements results, at an early age (in 14-20 hours) to assess (predict) the material’s strength properties. This enables the possibility of a prompt detection and elimination of causes that may destabilize the manufacturing process.
4. At the Považská cementárň’s plant more than 350 cement clinker’s production batches were successfully tested using this algorithm.
5. The statistical processing of test data for the entire array (354 samples) also showed that the prediction’s accuracy for cement clinker’s early strength resistivity measurement results corresponds to the strength’s accuracy determination set by standard destructive methods.
6. The early strengthening of cement clinker monitoring results, obtained using an algorithm developed by Concretec Ltd., uniquely determine the clinker’s variation strength and as a result of this, they reflect the real state of the technological process. Therefore, the "risk" of the practical use for prediction results is minimal.

References