AN OVERVIEW ON INTERLABORATORY TESTS FOR CEMENT ORGANIZED BY THE TESTING LABORATORY OF CEPROCIM S.A, IN THE LAST 11 YEARS

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Abstract

CEPROCIM S.A. laboratory has organised yearly, since 1988, Interlaboratory Tests for cement, with over 40 laboratories representing Research institutes, Cement plants, Precast units, Hydro plant construction companies, Industrial companies, Building companies etc. from Romania, Republic of Moldova, Croatia, Serbia, Macedonia, Bulgaria, Hungary, Ukraine and Lebanon.

The subject of the Interlaboratory Tests for cement were twelve chemical determinations (Loss on ignition, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CaO, MgO, SO$_3$, Free CaO, Insoluble residue, Na$_2$O, K$_2$O, Cl$^-$), seven physical tests (Residue on the 90 µm sieve, Density, Specific surface area, Standard consistency, Initial setting time, Final setting time, and Soundness) and nine mechanical tests (Weight at demoulding; Flexural strength at 1, 2, 7, and 28 days; and Compressive strength at 1, 2, 7, and 28 days), the last ones done with two types of sand.

An analysis of the efficiency of Interlaboratory Tests for cement made for the last 11 years shows a positive trend for the standard deviation of reproducibility or variation coefficient for SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CaO or Compressive strength to 28 days respectively, determinations which were shown as examples.

Key words

Interlaboratory tests, Cement

1 INTRODUCTION

The Interlaboratory Tests proficiency testing represent the most efficient means of self-evaluation for testing laboratories, and are a key item in establishing a common language between national and foreign partners. S.C. CEPROCIM S.A. has
organised yearly, since 1988, Interlaboratory Test for cement, with over 40 laboratories representing Research institutes, Cement plants, Precast units, Hydro plant construction companies, Industrial companies, Building companies etc. from Romania, Republic of Moldova, Croatia, Serbia, Macedonia, Bulgaria, Hungary, Ukraine and Lebanon.

Repartition of the participants by types of companies and institutions over the period from 1989 till now is presented in Figure 1 [1-12].

![Figure 1 - The participant’s repartition in time](image)

2 CONDITIONS AND PROCEDURES

Yearly, the cement meant for the interlaboratory tests, represents a quantity of about 1 tone. Its homogeneity was tested at CEPROCIM. The values of the chemical, physical and mechanical characteristics, obtained by CEPROCIM’s laboratory on 10 (ten) cement samples confirmed the homogeneity of cement. Figure 2 presents the homogeneity results obtained for the particle size distribution at the edition 2005-2006.
Figure 2 – An example of particle size distribution of the cement (the LASER method)

The sand being made available to the 7th edition of interlaboratory tests participants originates from the Société Nouvelle du Littoral, France. It has a particle size distribution according to the requirements in SR EN 196–1:1995. See for example the particle size distribution of the sand used at the edition 2005-2006 of the Interlaboratory Tests, in the Figure 3.
The cement was divided into 100 bags, and the polygrained sand was divided into 100 packets including 4 bags of 1350 g each. This samples were send to the participants.

The 37 chemical, physical and mechanical determinations carried out by the participants are:
- Loss on ignition, SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, SO₃, Free CaO, Insoluble residue, Na₂O, K₂O, and Cl–, according to SR EN 196-2:1995 and SP 18-5:2004;
- Residue on the 90 µm sieve, Density, Specific surface area, Standard consistency, Initial setting time, Final setting time, and Soundness, according to SR EN 196-3: 1995 and SR EN 196- 6:1994;
- Weight at demoulding; Flexural strength at 1, 2, 7, and 28 days; and Compressive strength at 1, 2, 7, and 28 days according to SR EN 196-1:1995;

3 INTERPRETATION OF THE RESULTS

The statistical interpretation of the results allows each participant to appreciate his own results, for the same test, in comparison with the whole of the participants or in comparison with CEPROCIM's. In the last 3 years, the evaluation of the results was carried out according to ISO/IEC GUIDE 43–1:1997 [12-15] by the Z score calculation. Subsequently, the results were considered:
- Satisfactory, when $|Z| \leq 2$
- Questionable, when $2 < |Z| < 3$, and
- Unsatisfactory when $|Z| \geq 3$. 

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Fig. 3 - Particle size distribution of the polygrained sand used in the 2005-2006 edition
As an example figures 4 and 5 presents the Gauss distribution and the Z score for compressive strength of cement at 28 days.

The results for the 28-day compressive strength had a normal Gauss distribution as it can be seen in figure 4.

![Gauss distribution of 28-day compressive strength for all the participants at the edition 2005-2006](image)

**Figure 4 - Gauss distribution of 28-day compressive strength for all the participants at the edition 2005-2006**

Following the Z score evaluation, out of a total number of 42 laboratories 40 laboratories obtained satisfactory results, one laboratory obtained a questionable result, and two others unsatisfactory results (Figure 5).
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Figure 5 - Evaluation of the results for the 28-day compressive strength by using the Z score
4 EVALUATION OF THE STATISTICAL PARAMETERS IN THE LAST 11 YEARS

Below is presented an analysis of the efficiency of the Interlaboratory Tests on cement for 5 of the 37 determinations. There are shown the values of the standard deviation of reproducibility or the variation coefficient compared to the values prescribed by the method standards. The values covers only the last 11 years from the all 19, because since 1995 the national standard methods were replaced by the European ones.

4.1 Evolution of the results for chemical determinations

Figures 6-9 shows the standard deviation values of reproducibility obtained by the participants and standard deviation values of repeatability obtained by CEPROCIM, during the last 11 editions, for the main oxides SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ and CaO.

Figures 6-9 – Evolution of the standard deviation of repeatability and reproducibility for the main oxides: SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ and CaO respectively

The values presented were calculated in the second step, after the elimination of the unsatisfactory results.
SiO$_2$ shown in figure 6 presents frequently overpassing of the prescribed limits of reproducibility with 0.02-0.33 %. These overpassing claim a closer look for this
because the method contains many steps that could influence the results. Among this are the temperatures of insolubilization and ignition the time of insolubilization, and so on.

For Al₂O₃, presented in figure 7, the standard deviation of reproducibility is usually under the prescribed limit of 0.25 % and it ranges 0.14-0.25 %. At the edition 2003-2004 is an exception with an over passing of 0.15 %.

Fe₂O₃, presented in figure 8, shows that the results are very close to the mean, 6 values of the standard deviation of reproducibility being under 0.10 %.

In the case of CaO, presented in figure 9, the standard deviation of reproducibility is on or under the prescribed limit of 0.43 %, but it presents large variation between 0.25-0.43 %.

For the standard deviation of reproducibility, the more permissive interpretation of the results in the last 3 editions, when Z score was used, and the relatively small number of participants (between 15-18), conducted to an increase of the standard deviation of reproducibility.

The standard deviation of repeatability was under the prescribed limits, for all the main oxides presented in figures 6-9. There were some variations due to the use of cements with admixtures to the editions 1997-1998 and 1999-2000.

### 4.2 Evolution of the results for the 28 days compressive strength

The variation coefficients of repeatability and reproducibility for the compressive strength at 28-days – chosen as example for the mechanical determinations – are plotted in figure 10.

![Figure 10 – Evolution of the standard deviation of repeatability and reproducibility for 28-day compressive strength](image-url)
It can be seen that during the last 11 editions the coefficient of variation for repeatability obtained by CEPROCIM range between 0.15 – 1.91%, values that are lower than the value of 1-3% required by the standard of method SR EN 196-1:1995. At the edition 1995 – 1996, the value of 1.91 % was due both to the replacing of the Romanian standards with the European standards as well as to the new methods implementation. The variation coefficients of repeatability start decreasing in time and 7 values were even lower than 1%, which demonstrates that better performance was achieved, according to the last new requirements in SR EN 196-1:2006. The variation coefficients of reproducibility obtained by the participants with CEPROCIM’s sand, calculated after the unsatisfactory results elimination, decrease in time from the values of about 9.9 – 7.4 up to values of 4.4 – 6.6 which are closer to the value of 6%* required by SR EN 196-1:1995. Despite a similar trend can be observed for the variation coefficients of reproducibility with the participants’ own sand, the existence of different sand sources in different countries keeps the above mentioned values slightly higher than the required one.

*Note: At the present the requirement of SR EN 196-1:2006 is 4%.

5 CONCLUSIONS

a) S.C. CEPROCIM S.A. has organised yearly, since 1988, Interlaboratory Test for cement, with over 40 laboratories representing Research institutes, Cement plants, Precast units, Hydro plant construction companies, Industrial companies, Building companies etc. from Romania, Republic of Moldova, Croatia, Serbia, Macedonia, Bulgaria, Hungary, Ukraine and Lebanon.

b) Each edition had its own batch of approx. 1 tonne of cement. The homogeneity of the batch was verified by chemical, physical and mechanical determinations and delivered to all participants.

c) The results obtained for the 37 chemical, physical and mechanical determinations, received from the participants were statistically interpreted using Z score.

d) For the examples discussed, the statistical parameters for the last 11 years shows:
   - For the standard deviation of reproducibility, the results for the main oxides are under the superior limit in case of Al₂O₃, Fe₂O₃ and CaO but presents frequent overpassing in case of SiO₂.
   - In the case of the chemical determinations, the more permissive interpretation of the results in the last 3 editions, when Z score was used, and the relatively small number of participants (between 15-18), conducted to an increase of the standard deviation of reproducibility.
   - The variation coefficients of reproducibility obtained by the participants with CEPROCIM’s sand, calculated after the unsatisfactory results elimination, decrease in time from the values of about 9.9 – 7.4 up to values of 4.4 – 6.6 which are closer to the value of 6% required by SR EN 196-1:1995.

REFERENCES

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