

Article

Ensuring the Validity of the Results by Participating in ILC Schemes—Case Study: The Determination of the Water-Soluble Chromium (VI) Content of Cement

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Abstract: The paper presents the mode in which an accredited laboratory, according to SR EN ISO/IEC 17025, monitors its performance by comparing the results with the results of other laboratories. This article aims to analyse the results of the participation of an accredited laboratory in two ILC schemes, one organized in France and the other in Romania, on cement, discussing only the results of the determinations of the water-soluble hexavalent chromium content. Although chromium (VI) is not present in large amounts in cement, it is responsible for allergic reactions on the skin of workers. Thus, in EU countries, the maximum amount of water-soluble Cr (VI) in bagged cement or in the products based on cement is limited to a maximum of 0.0002% by mass of cement. The Chromium (VI) results obtained by the lab must meet the requirements of the standard SR EN 196-10 for the repeatability and, where appropriate, the reproducibility. Questions about the validity of the results arise when the laboratory obtains satisfactory results in the ILC scheme, but the standard deviation of the scheme is higher than that recommended in the standard method. The elements of the novelty of this paper are the interpretation of water-soluble Cr (VI) results and the use of information obtained from participating in interlaboratory testing schemes to improve the validity of laboratory results.

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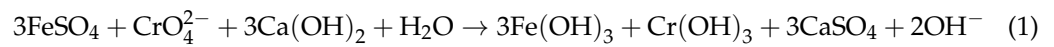
Keywords: water-soluble hexavalent chromium content; ILC scheme; standard deviation validity of the results

1. Introduction

Cement is one of the most used construction materials in the world, and this causes users who are not always properly equipped to come into direct contact with cement-containing products to be prone to contact dermatitis. Wet cement is basic, with a pH of 12.5, and it can change the stratum corneum of the skin by facilitating the penetration of water-soluble substances. The skin contacts with the alkaline cement-water suspension results in irritation, thus increasing the absorption of chromium VI. Due to this, there are directives in EU countries that limit the water-soluble hexavalent chromium content in bagged cement or cement-based products delivered to the bag to a maximum of 0.0002% by mass of cement. This restriction does not occur in controlled closed or totally automated processes [1–3].

The Cr (VI) content of the cement depends on the chromium content, mostly Cr (III) of the raw materials, but it can also come from the furnace lining and the abrasion of the steel alloyed with chromium during the grinding process. The oxidation of Cr (III) to Cr (VI) occurs during clinker production at temperatures between 1400 and 1500 °C. The addition of Cr (VI) reducing agents to Cr (III) (such as ferrous sulphate) in cement causes the Cr (VI) to precipitate in the form of chromium hydroxide in the alkaline mixture of cement and water, which has very low solubility in the water, see reaction (1). This is why water-soluble chromium in ferrous sulphate-containing cement samples does not appear to

be determined by chemical determination. Moreover, chromium hydroxide is practically insoluble in human perspiration [1].



For the determination of the water-soluble hexavalent chromium content, the reference determination method is presented in the standard SR EN 196-10 [4]. In the case of accredited laboratories, whether they are a third party or owned by the manufacturer, the recommended method is the reference one. If another method is used, it must be validated and demonstrated that the results obtained are equivalent to those obtained by the reference method [5,6].

However, even if the use of the reference method meets all the conditions to ensure the validity of the results specified in the accreditation standard, SR EN ISO/IEC 17025 pt. 7.7, periodically, the laboratory management must check and evaluate both the equipment used and the personnel involved, including participation in competency tests [6]. Usually, the evaluation of the results obtained within the competence schemes remains at the level of primary interpretation by framing the results as satisfactory or not. However, a greater inclination of the laboratory management over the obtained results would bring an added value to the activity of its own lab.

2. Method

The laboratory management must monitor the performance of the results obtained compared to other laboratories, this being an important step in demonstrating the validity of the results. This performance monitoring is a complex process that starts with choosing the Proficiency Testing (PT)/Interlaboratory Comparisons (ILC) scheme according to certain criteria that the laboratory establishes, then follows the planning of participation so that the procedure is not overcrowded and the tests are performed in the same regime as well as the other samples normally tested [7]. The final stage is the analysis of the performance of the results, which begins after receiving the report from the organizer of the ILC/PT scheme [6].

The parameters used by the management of the laboratory for the evaluation of the performance of the results are the standard deviation for proficiency assessment (σ_{pt}), the coefficient of variation (CV) and the standardized measure of laboratory bias, calculated using the assigned value and the standard deviation for proficiency assessment (z or z -score) [8].

$$\sigma_{pt} = 1.134 \cdot \sqrt{\sum (x_i^* - x_{pt})^2 / (p - 1)} \quad (2)$$

$$CV = \frac{\sigma_{pt}}{x_{pt}} \cdot 100 \quad (3)$$

$$z_i = \frac{x_i - x_{pt}}{\sigma_{pt}} \quad (4)$$

where:

- p the number of laboratories that took part in interlaboratory tests;
- x_i the result reported by one participant laboratory i ;
- x^* robust average of the results reported by all participant laboratories, calculated according to algorithm A method;
- x_{pt} assigned value (consensus value);
- σ_{pt} standard deviation for proficiency assessment;
- CV coefficient of variation;

The evaluation of the results is usually made according to SR EN ISO/IEC 17043:

- satisfactory, when $|z| \leq 2$;
- questionable, when $2 < |z| < 3$;
- unsatisfactory, when $|z| \geq 3$ [7].

If following the analysis of the performance of the results, it is found that the results were unsatisfactory, the procedure for monitoring the validity of the results is resumed, trying to identify the factors that led to obtaining those results and remedying the non-compliance [6,9]. The corrective actions that can be taken are: checking that the staff understand and follows the measurement procedure, checking that all of the details of the measurement procedure are correct, checking the calibration of equipment and the composition of reagents, and replacing suspect equipment or reagents or comparative tests of staff, equipment and/or reagents with another laboratory [7].

Achieving satisfactory results is always the goal of every laboratory. However, what happens when the results obtained in the competency scheme are classified as satisfactory, but after a more detailed analysis, it is found that the standard deviation of the test exceeds the value of the standard method? Does the chosen competency scheme provide the necessary confidence for the participating laboratories, or is the method very sensitive? These two questions are always raised by the management of the laboratory when obtaining such results.

In the case study presented in this paper, the laboratory received well-homogenized and tightly packed cement samples for water-soluble Cr (VI) determination, among other determinations that are part of the schemes. After recording the samples, the person in charge of the determination prepares the cement mortar in accordance with SR EN 196-1 [10] and performs the determination in accordance with SR EN 196-10 [4].

3. Results

The case study presented in this paper refers to the performance of the results of the determination of water-soluble Cr (VI) in cement. The evaluation of the results was carried out over a period of 10 years, where results were available.

Further on, in the text of the article, the two intercomparison schemes will be identified by a letter, so the scheme organized in France will be noted by "F", and the scheme organized in Romania will be noted by "R".

In the case of scheme "F", where the water-soluble Cr (VI) determination was introduced later in the scheme, a smaller number of results are available. The statistical parameters of the ILC scheme "F" and the results obtained by the lab during the scheme are presented in Table 1 [11]. Furthermore, Table 2 presents the statistical parameters of the ILC scheme "R" and the results obtained by the lab during the scheme [12].

Table 1. The statistic parameters of the ILC scheme "F" and the accredited lab performance.

Round		2016	2017	2018	2019	2020	2021
ILC scheme "F"	$x_{pt}, \%$	0.00085	0.00011	0.00015	0.00024	0.000069	0.000036
	$\sigma_{pt}, \%$	0.0042	0.00014	0.00011	0.00106	0.000063	0.000023
	CV, %	488.6	124.2	73.2	439.2	91.4	64.6
	p	44	67	100	88	79	89
Lab results at ILC scheme "F"	$x_i, \%$	0.00017	0.00006	0.00033	0.00011	0.00006	0.00005
	z-score	-0.2	-0.4	1.6	-0.1	-0.1	0.6

Table 2. The statistic parameters of the ILC scheme "R" and the accredited lab performance.

Round		2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021
ILC scheme "R"	$x_{pt}, \%$	0.0018	0.00002	0.00043	0.00263	0.00087	0.00026	0.00037	0.00038	0.00035	0.00072	0.00001
	$\sigma_{pt}, \%$	0.0003	0.00002	0.00012	0.00051	0.00025	0.00006	0.00006	0.00011	0.00005	0.00006	0.00002
	CV, %	17.64	108.62	28.78	19.36	28.38	24.81	15.53	28.01	14.15	8.95	141.81
	p	11	11	17	12	15	14	14	17	16	20	15
Lab results at ILC scheme "R"	$x_i, \%$	0.0022	0.00002	0.0005	0.003	0.001	0.0003	0.0004	0.0005	0.0004	0.0006	0.00005
	z-score	1.44	-0.1	0.54	0.72	0.52	0.6	1.13	1.16	0.97	-1.24	1.64

Figure 1 represents the evolutions of the z scores obtained by the own laboratory in both ILC schemes. For a correct evaluation compared to the specifications of the standard SR EN 196-10 are represented only the scores obtained in the editions in which the maximum value of the hexavalent chromium was 0.0005%. Moreover, those editions in which the standard deviation for reproducibility was at a maximum of 0.00004% according to SR EN 196-10 [4] are highlighted.

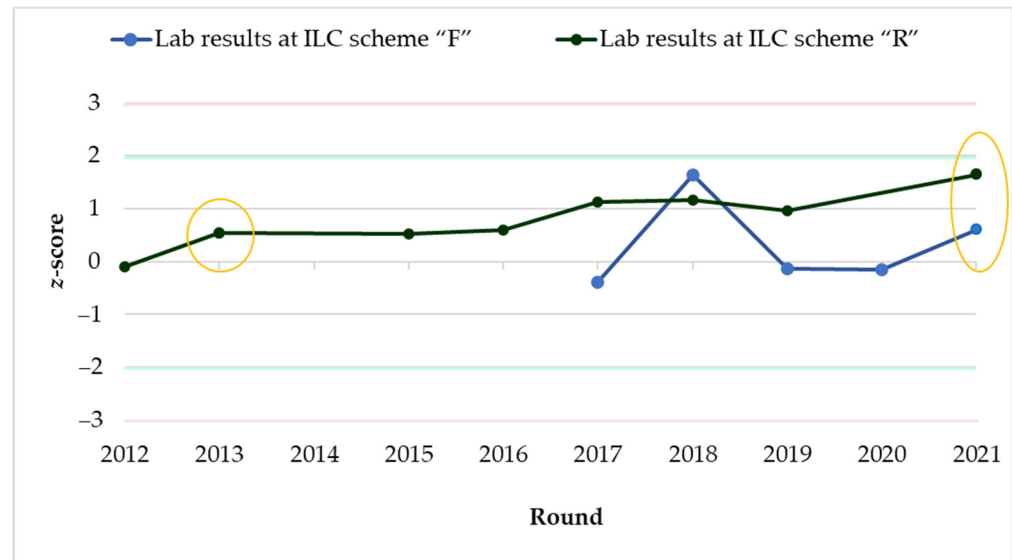


Figure 1. The representation of the z-score evolution obtained at the ILC schemes "F" and "R" in the rounds in which the cement sample had the water-soluble Cr (VI) content under 0.0005%.

4. Discussion

Regarding the values recorded for reproducibility presented in Tables 1 and 2 (standard deviation for proficiency assessment), obtained over a period of 10 years under two ILC schemes and comparing them with the value specified in SR EN 196-10 [4] raises some questions about the validity of this imposed reproducibility and the ability to be obtained in practice.

As can be seen from Figure 1, there are not many editions in which the reproducibility conditions of the method of testing have been fulfilled. The conditions were only met in 3 out of a total of 13 rounds. Thus, within the ILC scheme "F", only in one edition was the condition fulfilled, and in the case of the ILC scheme "R" in two cases. At the same time, it can be observed that all the results obtained by the laboratory are classified as satisfactory, the score z obtained being less than $|2|$ [7].

The simplified evaluation of the laboratory's performance by means of the z score provides important information such as:

- performing well or badly, but also about enabling the laboratory to learn from its participation in ILC schemes and to use this information to improve the quality of its measurements;
- an educational tool using the scheme results to give feedback to staff and in the improvement process;
- tool for monitoring the reliability of measurements in the process of implementing quality control measures [13], but a simplified assessment is not always enough.

Another statistical parameter that provides important information to participants in ILC schemes is the coefficient of variation. The coefficient of variation is a statistical measure of the dispersion of data points in a data series around the mean. It is a useful statistic for comparing the degree of variation from one data series to another, even if the means are drastically different from one to another. The higher the coefficient of variation,

the greater the level of dispersion around the mean. The coefficient of variation represents the homogeneity of the obtained results and it is influenced by several factors, such as the number of participants in the scheme, the participants' experience both in the domain and in the ILC participation, and the sensibility of the method [14]. Analysing the name of the participants from the beginning of the reports, it seems that the variation in the participants was not important. From one round to another, it seems to be the same participants, but the value of the CV is great and fluctuant.

Taking into account the fact that each participant represents an accredited laboratory or a laboratory belonging to a manufacturer, i.e., participants have sufficient experience; one factor remains to be investigated that can strongly influence the values obtained: the stability of the method.

The measures that can be taken at the level of the management of each laboratory so that the results obtained have a high degree of probability are the supply of the client together with the obtained value (y), the expanded measurement uncertainty (U), as $y \pm U$ [15].

$$U = k \times u_{COM} \quad (5)$$

where:

k coverage factor. $k = 2$, which for a normal distribution provides a level of confidence of 95%.

u_{COM} combined standard uncertainty.

In the calculation of the expanded measurement uncertainties, it is recommended that in addition to the components usually introduced by each laboratory: the component related to the operating mode of the personnel (u_{rep}) and the component that takes into account the equipment used (u_{trac}), to take into account a third component—the results of the ILC scheme [16,17]. This third component can be used to estimate the standard deviation of measurements reproducibility (u_{pt}) that can be directly used as the standard measurement uncertainty. This is especially advisable when the uncertainty associated with the assigned value is small compared to the observed spread of the results [15].

$$u_{COM} = \sqrt{u_{rep}^2 + u_{trac}^2 + u_{pt}^2} \quad (6)$$

$$u_{pt} = \frac{u(x_{pt})}{x_{pt}} \quad (7)$$

$$u(x_{pt}) = \frac{\sigma_{pt}}{\sqrt{p}} \quad (8)$$

where:

u_{rep} relative standard uncertainty of the repeatability;

u_{trac} relative standard uncertainty of the traceability;

u_{pt} relative standard uncertainty of the scheme;

$u(x_{pt})$ standard uncertainty of the scheme.

In the present case, the results obtained in the two ILC schemes for the water-soluble Cr (VI) determination are suitable for the use of the third component in the calculation of the measurement uncertainty. However, in practice, laboratories do not use this type of calculation of the extended measurement uncertainty, either because they do not know this calculation method or because they find it more complex and give up or do not participate with sufficient frequency in ILC schemes.

For example, the measurement uncertainty could increase by up to four times if the uncertainty obtained from the ILC schemes is also used in the calculation. If, at first, it seems to be a high value, regarding the obtained variation of the water-soluble Cr (VI) content values in the ILC schemes, it can be concluded that this value is more appropriate. Moreover, then it depends on the client who commands this type of analysis to understand the result obtained, to really use the measurement uncertainty, taking into account that no value obtained by testing is absolute.

5. Conclusions

Participation in ILC schemes is an ongoing process that lab management must maintain as a priority. In Romania, the accreditation body requires that the accredited laboratories testing construction materials participate in ILC/PT schemes with a frequency of two participations per accreditation cycle. For economic reasons, the management chooses to meet this minimum condition of participation even if they know that not all determinations have the same degree of complexity. Moreover, the evaluation of performance is done superficially only on the basis of the *z* score. Thus, problems arise when between accredited laboratories, for example, there are quite large differences between the values provided, especially when the uncertainty of the extended measurement is not provided to the customer.

The measures taken by the laboratories in these cases are to verify the traceability of the sample, of the equipment and to retrain the personnel. If the results of the verification do not indicate irregularities, the conclusion is usually that the sample is inhomogeneous. However, a better understanding of performance evaluation sometimes requires a greater focus on issues that may be beyond the scope of the laboratory at first glance.

Another problem that the laboratories face when they want to compare their values with each other is the inconsistency that the reference brings in this evaluation. In the case study presented in the paper, it was shown how the reproducibility value specified in the standard method of determining the water-soluble hexavalent chromium is almost impossible to achieve in practice. This leads to the idea that perhaps it would be better to revise the limits of reproducibility with the revisions of the method standards so that it reflects the practical realities that the testing laboratories face.

Strategies to make better use of the results obtained from ILC schemes can be found in the documents related to the management of the laboratory, such as the EA guidelines, but also by consulting sites such as <https://www.eurachem.org> (accessed on 3 April 2022) or <https://www.pt-conf.org> (accessed on 3 April 2022).

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