TECHNICKÝ A SKÚŠOBNÝ ÚSTAV STAVEBNÝ, n. o.
BUILDING TESTING AND RESEARCH INSTITUTE, Slovak Republic
Studená 967/3, 821 04 Bratislava

Application / archive No. 20-24-0012

„Cement Ring Tests 2024“ final report

No.: 20-24-0012

Organizer: Building testing and research institute, Bratislava branch
Sampling material: Portland-composite cement EN 197-1 – CEM II/B-M (S-LL) 42,5 N
Test methods: STN EN 196 – parts 1, 2, 3, 6, 8, 9, 10 and STN P ENV 196-4

Participant’ code:

Chemical analyses	Physical tests	Mechanical tests
x1, x2, x3, x4, x5, x6, x7, x8	y1, y2, y3, y4, y5, y6, y7	z1, z2, z3, z4

Date of issue: 10. 07. 2024

Coordinator: Dipl. Eng. Marián K u b i š .....

Analyst of testing: Dipl. Eng. Ladislav G i l á n y i, PhD. .....

Head of testing laboratories: Dipl. Eng. Daniel P e t h ő .....

Director of Bratislava branch: Dipl. Eng. Patrik Š e v č í k .....

CONTENT

1 SCOPE

Main objective of the final report is evaluation of the comparative tests of participating laboratories. These tests entitled as "Cement Ring Tests" are alternately organized by laboratories TZÚS Prague and TSÚS Bratislava. The Cement Ring Test 2024 was attended by 17 laboratories include laboratories working in building material industry and laboratories operating as independent testing institutes. Invitation to these comparative tests was accepted by following laboratories (*written in alphabetical order*):

Czech Republic (CZ) (08)
Cemex Czech Republic, s. r. o. (mlýnice Dětmarovice); Areál Edě č. p. 1216; 735 71 Dětmarovice, CZ
CEMEX Czech Republic, s. r. o..; Tovární 296; 538 04 Prachovice, CZ
Heidelberg Materials CZ, a. s., [Českomoravský cement, a. s.]; závod Mokrá; Mokrá 359; 664 09 Mokrá-Horákov, CZ
Heidelberg Materials CZ, a. s., [Českomoravský cement, a. s.]; závod Radotín; K Cementárně 1261/25; 153 02 Praha Radotín, CZ
HOLCIM Česko), a.s., [Lafarge Cement], a. s.; Čížkovice 27; 411 12 Čížkovice, CZ
Technický a zkušební ústav stavební Praha, s. p., pobočka Teplice; Tolstého 447; Teplice 415 03, CZ [abbreviated TZÚS]
Výzkumný ústav maltovin Praha, s. r. o.; Na Cikánce 614/2; Praha 5 – Radotín, CZ
Výzkumný ústav stavebních hmot, a. s.; Hněvkovského 30/65; 617 00 Brno, CZ

Slovak Republic (SK) (08)
BetónRacio, s. r. o., Skúšobné laboratórium, Pracovisko Trnava; Skladová 2; 917 01 Trnava, SK
CEMMAC, a. s.; Cementárska 14; 914 42 Horné Srnie, SK
Danucem Slovensko, a. s., závod Rohožník; Senická cesta; 906 38 Rohožník, SK
Danucem Slovensko, a. s., závod Turňa nad Bodvou; 044 02 Turňa nad Bodvou, SK
Považská cementáreň, a. s.; ul. J. Kráľa; 018 63 Ladce, SK
STACHEMA Bratislava, s. r. o., 900 41 Rovinka 411, SK
Technický a skúšobný ústav stavebný, n. o., pobočka Bratislava; Studená 967/3; 821 04 Bratislava, SK [abbreviated TSÚS]
ZEOCEM, s. r. o., Prešovská 282/1, 094 34 Bystré, SK

Hungary (HU) (01)
SZIKKTI LABOR, Kft.; Bécsi út 122-124. D épulet, 1301 Pf.: 81.; 1034 Budapest, HU

To compare the test results homogenized Portland-slag cement EN 197-1 – CEM II/B-M (S-LL) 42,5 N (according to STN EN 197-1) was used. The test results were evaluated according to STN ISO 13528: 2023 and TNI CEN/TR 10345: 2014, while comparisons of the deviations were performed within the participated laboratories.

For this testing, cement, which contains not reduced content of water-soluble chromium (VI) was chosen.

1.1 Test data

Ordering party / organizer: (proficiency testing provider)	Building Testing and Research Institute, (abbrev: TSÚS), Studená 3, 821 04 Bratislava
Cement Manufacturer:	unreported (information archiving by organizer)
Evaluator:	Building Testing and Research Institute, director's department Studená 967/3, 821 04 B r a t i s l a v a

Competence and authorization of the test provider / organizer:
TSÚS is Notified body No.:1301 according to Regulation (EU) No 305/2011 – Construction products, regards to building materials and Construction.

TSÚS, testing laboratory Bratislava has developed system of quality according to requirements of STN EN ISO/IEC 17025: 2018, article 1.2 as holder of Certificate of accreditation No.: S-045 valid until 20. 12. 2024, is acting as independent testing and research institute.

Head of tests (coordinator): Dipl. Eng. Marián K u b i š

Character of the tests: study according to STN 73 2031;
Type of tests: STN EN 196 - parts 1, 2, 3, 6, 8, 9, 10; STN P ENV 196-4

The tests were performed according to standard test methods in a range of organizer's requirements whilst following a test schedule.

1.2 Statistic execution

Organizer: Building testing and research institute (TSÚS),
Bratislava branch, Studená 967/3, 821 04 Bratislava

Analyst of the tests: Dipl. Eng. Ladislav Gilányi, PhD,

1.3 Background to execution of the tests and results of the evaluation

Quoted standards and technical regulations

STN ISO 2602: 1993 Statistical interpretation of test results. Estimation of the mean. Confidence interval [*Štatistická interpretácia výsledkov skúšok. Odhad priemeru. Interval spoľahlivosti*] (01 0231)

TNI CEN/TR 10345: 2014 Guideline for statistical data treatment of inter laboratory tests for validation of analytical methods [*Návod na štatistické spracovanie údajov medzilaboratórnych skúšok na validáciu analytických metód*] (01 0240)

STN ISO 13528: 2023 Statistical methods for use in proficiency testing by interlaboratory comparison [*Štatistické metódy používané pri skúšaní spôsobilosti založenom na medzilaboratórnom porovnaní*] (01 0241)

STN EN ISO/IEC 17025: 2018 General requirements for the competence of testing and calibration laboratories [*Všeobecné požiadavky na kompetentnosť skúšobných a kalibračných laboratórií (ISO/IEC 17025: 2017)*] (01 5253)

STN EN ISO/IEC 17043: 2023 Conformity assessment - General requirements for the competence of proficiency testing providers [*Posudzovanie zhody. Všeobecné požiadavky na kompetentnosť poskytovateľov skúšok spôsobilosti*] (01 5257)

STN EN 196-1: 2019 Methods of testing cement. Part 1: Determination of strength [*Metódy skúšania cementu. Časť 1: Stanovenie pevnosti*] (72 2100)

STN EN 196-2: 2013 Methods of testing cement. Part 2: Chemical analysis of cement [*Metódy skúšania cementu. Časť 2: Chemický rozbor cementu*] (72 2100)

STN EN 196-3: 2020 Methods of testing cement. Part 3: Determination of setting time and soundness [*Metódy skúšania cementu. Časť 3: Stanovenie času tuhnutia a objemovej stálosti (Konsolidovaný text)*] (72 2100)

STN P ENV 196-4: 1996 Methods of testing cement. Part 4: Quantitative determination of constituents [*Metódy skúšania cementu. 4. časť: Kvantitatívne stanovenie hlavných zložiek*] (72 2100)

STN EN 196-6: 2020 Methods of testing cement. Part 6: Determination of fineness [*Metódy skúšania cementu. Stanovenie jemnosti mletia*] (72 2100)

STN EN 196-7: 2008 Methods of testing cement. Part 7: Methods of taking and preparing samples of cement [*Metódy skúšania cementu. Časť 7: Postupy na odber a úpravu vzoriek cementu*] (72 2100)

STN EN 196-8: 2010 Methods of testing cement. Part 8: Heat of hydration. Solution method [*Metódy skúšania cementu. Časť 8: Stanovenie hydratačného tepla. Rozpúšťacia metóda*] (72 2100)

STN EN 196-9: 2010	Methods of testing cement. Part 9: Heat of hydration. Semi-adiabatic method [*Metódy skúšania cementu. Časť 9: Stanovenie hydratačného tepla. Semiadiabatická metóda*] (72 2100)
STN EN 196-10: 2019	Methods of testing cement. Part 10: Determination of the water-soluble chromium (VI) content of cement [*Metódy skúšania cementu. Časť 10: Stanovenie obsahu vo vode rozpustného šesťmocného chrómu (VI) v cemente*] (72 2100)
STN EN 197-1: 2012	Cement Part 1: Composition, specifications and conformity criteria for common cements [*Cement. Časť 1: Zloženie, špecifikácie a kritériá na preukazovanie zhody cementov na všeobecné použitie*] (72 2101)
STN EN 197-2: 2021	Cement. Part 2: Conformity evaluation [*Cement. Časť 2: Hodnotenie zhody*] (72 2101)

1.4 List of references

[1] Likeš J., Laga J.: Základní statistické tabulky, [*Basic statistical tables*]; SNTL – Nakladatelství technické literatury, Praha 1978

[2] Jílek M.: Statistické toleranční meze, [*Statistical tolerance limits*]; SNTL – Nakladatelství technické literatury, Praha 1988

[3] MSA – L/14: Stanovenie rozsahu a frekvencie účasti v skúškach spôsobilosti, Metodická smernica na akreditáciu, [*Determination of the scope and frequency of participation in competency tests*], [*Methodological guideline for accreditation*], SNAS, Bratislava, júl 2021

[4] K. Kersting, J. Wehde, W. Leimbrock, D. Breuer: Bestimmung des Chrom(VI)-Gehaltes in Zementen, in: Gefahrstoffe -Reinhaltung der Luft 62 (2002) Nr. 7/8

2 ELIGIBILITY OF THE TEST

2.1 Requirements of compliances of the tests

Organization of the Cement Ring Test 2024

These tests are organized alternately by the laboratories of TSÚS, Bratislava branch and TZÚS, Teplice branch since 1996.

Laboratories recruitments

To attend the comparative tests, the laboratories of cement manufacturers from Slovak republic were invited as well as laboratories of cement manufacturers and independent testing institutes from Czech Republic, Slovak Republic and Hungary. Laboratories involvement was based on experience from previous years.

Preparation of testing materials

For execution of comparative tests approximately 100 kg of homogenized cement was used.

Verification of stability and homogeneity of testing material: Previous to transport organizer of the tests confirmed homogeneity of testing material according to STN EN 196-7.

Selection of the test methods

Subject of comparison was based on standard testing method such as chemical analyses, physical methods and stability of cement according to EN 196. In addition alternative test methods were offered.

Instructions for participants of international laboratories comparative tests

Test attendants received a spreadsheet indicating the name of the property being tested, the required values with units and an opportunity to comment on deviations from the procedure.

Based on previous experience, the test results are presented in such form that each participating laboratory is able to find only its own results. The overall review of the test results can be seen in section 4 and 5 in a following form:

Chemical analyses	Physical tests	Mechanical tests
x1, x2, x3, x4, x5, x6, x7, x8	y1, y2, y3, y4, y5, y6, y7	z1, z2, z3, z4

Where:

x1, x2, x3, x4, x5, x6, x7, x8	are row numbers in table 4.1 and 5.1.1, 5.1.2
y1, y2, y3, y4, y5, y6, y7	are row numbers in table 4.2 and 5.2.1, 5.2.2
z1, z2, z3, z4	are row numbers in table 4.3 and 5.3.1, 5.3.2

The code numbers will be announced to each laboratory separately.

2.2 Statistics analyse of the test compliance

Basic statistics for evaluation of the tests

p Sample size / Count

Central trend parameters

$\bar{x}$ Average, arithmetic mean

$$\bar{x} = \frac{1}{p} \sum_{i=1}^{p} x_i \qquad (2.1)$$

Dispersion parameters

v Coefficient of variation / Variance

$$v(\%) = \frac{s \cdot 100}{|\bar{x}|} \qquad (2.2)$$

s Standard deviation of a sample

$$s = \sqrt{\frac{1}{p-1} \sum_{i=1}^{p} (x_i - \bar{x})^2} \qquad (2.3)$$

s_o Standard deviation

$$s_o = \sqrt{\frac{1}{p} \sum_{i=1}^{p} (x_i - \bar{x})^2} \qquad (2.4)$$

x_{min} Minimum value

x_{max} Maximum value

R Sample range

$$R = x_{max} - x_{min} \qquad (2.5)$$

Standard Skewness

Skewness is symmetry ratio of distribution of dividing function
Skewness is defined with regards to central moment of third degree:

$$SK_{est} = \frac{1}{n \cdot s^3} \sum_{i=1}^{p} (x_i - \bar{x})^3 \qquad (2.6)$$

which is mean value of divided cubature Z-score.

Standard Kurtosis

Kurtosis is commonly defined as the fourth cumulant divided by the square of the variance of the probability distribution.

Excess is defined as:

$$\gamma_2 = \beta_2 - 3 \qquad (2.7)$$

$$\beta_2 = \frac{1}{n \cdot s^4} \sum_{i=1}^{p} (x_i - \bar{x})^4 \qquad (2.8)$$

where:

s is decisive deviation of a sample.

Note: Values of skewness and kurtosis were formally evaluated without any precise analyse of dividing. In case that statistic values are out of interval ≤ -2; +2 ≥, a higher consideration should be taken since these values represent significant deviations from standard dividing.

Tests of outlier observations

outlier (accordance with ISO 13528: 2015): member of a set of values which is inconsistent with other members of that set

Note 1 to entry: An outlier can arise by chance from the expected population, originate from a different population, or be the result of an incorrect recording or other blunder.

Note 2 to entry: Many schemes use the term outlier to designate a result that generates an action signal. This is not the intended use of the term. While outliers will usually generate action signals, it is possible to have action signals from results that are not outliers

To test outlier of the results STN ISO 5725-2, Grubbs' method, Irwin' method or Dan-Dixon' tests were used.

Occurrence of one outlier observation was evaluated according Grubbs' statistic G_p, and G_1 respectively:

Definitions of Grubbs' tests are based on hypothesis H_0 against H_a where:

H_0: no outlier in a sample

H_a: at least one outlier in a sample

Grubbs' test statistic is defined as:

$$G_p = \frac{(x_p - \bar{x})}{s} \qquad (2.10)$$

$$G_1 = \frac{(\bar{x} - x_1)}{s} \qquad (2.11)$$

Or in accordance with [1] :

$$k_{vyp} = \frac{x_{max} - \bar{x}_n}{s_n} \geq k_{krit} = k_\alpha(n) \qquad (2.12)$$

$$k_{vyp} = \frac{x_{min} - \bar{x}_n}{s_n} \geq k_{krit} = k_\alpha(n) \qquad (2.13)$$

where $\bar{x}_n$ and s_n are mean values and decisive deviation.

The Grubb´s test statistic is the largest absolute deviation from a sample mean value in units of a sample standard deviation.

Significance Level:
critical region: The hypothesis of no outliers is rejected if:

$$G > \frac{(n-1)}{\sqrt{n}} \sqrt{\frac{t^2_{(\alpha/(2n),n-2)}}{n-2+t^2_{(\alpha/(2n),n-2)}}} \qquad (2.14)$$

where

$t_{(\alpha/(2n),n-2)}$

is the critical value of the t-distribution with (N-2) degrees of freedom and a significance level of α /(2N).

In the above formulas for the critical regions, the Handbook follows the convention that is the upper critical value from the t-distribution and is the lower critical value from the t-distribution. Note that this is the opposite of what is used in some texts and software programs. In particular, Data plot uses the opposite convention.

Irwin test, in which the biased of two the closest elements on the edge of ordered selection is verified according to:

$$\lambda_{vyp} = \frac{x_n - x_{n-1}}{s_n} \geq \lambda_\alpha(n) \qquad (2.15)$$

$$\lambda_{vyp} = \frac{x_2 - x_1}{s_n} \geq \lambda_\alpha(n) \qquad (2.16)$$

$(x_1 \leq x_2 \leq x_3 \leq x_4 \leq \ldots \leq x_i \leq \ldots \leq x_{n-1} \leq x_n)$

Critical value was approximately calculated for number of elements *n* as:

$$\lambda_\alpha(n) = 11{,}58849 - 10{,}752151 \cdot \exp(-0{,}30788516 \cdot n^{(-0.67230923)}) \qquad (2.17)$$

For regression curve the Weibull model was used, where:

y=a-b·exp(-c·x^d)

with parameters:

a = *11,58849*
b = *10,752151*
c = *0,30788516*
d = *-0,67230923*

Significance of outlier value and biased value correspond to definitions within STN ISO 5725-2: 2000.

As a result of relatively small number of participating laboratories added to not fulfilled condition of standard distribution measurements in some cases (Cl-content, Natriumoxid content, Potassium content, Chrome content, volume of soundness, initial setting time) it seems to be more appropriate to apply calculation of robust algorithms.

Intervals of confidence for outlier values were evaluated as minimum L_m and maximum L_M at level of α=0,05 as a result Student's distribution was applied' dividing for N=(n-1) degree of freedom:

$$L_m = \bar{x} - s \cdot t_{(n-1)} \qquad (2.18)$$

$$L_M = \bar{x} + s \cdot t_{(n-1)} \qquad (2.19)$$

where

$L_{m\ 95\%}$ Lower confidence limit safter elimination of outliers.

$L_{M\ 95\%}$ Upper confidence limit safter elimination of outliers.

For evaluation of deviation ε following equation was applied:

$$\varepsilon = \frac{s}{\sqrt{(n-1)}} \cdot t_{(n-1)} \qquad (2.20)$$

where

$t_{(n-1)}$ is value of Student's dividing for N=n-1 degree of freedom when level of significance is selected.

Test of interlaboratory dispersion

Cochran's test for evaluation interlaboratory dispersion was used according to article 7.3.3 of STN ISO 5725-2.

Cochran's statistic is given by equation:

$$C = \frac{s^2_{max}}{\sum_{i=1}^{p} s_i^2} \qquad (2.21)$$

where

s_{max} is the highest decisive deflection from given data set
p is set rate of selected decisive deflections (laboratory count).

Z-SCORE

z-score Standardized measure of performance, calculated using the participant result, assigned value and the standard deviation for proficiency assessment.

The Z-SCORE (standard score) indicates how many standard deviations an element is from the mean.

Z-SCORE1 is defined as:

$$\text{Z-SCORE1} = \frac{(x_i - \bar{x})}{s} \qquad (2.22)$$

where $\bar{x}$ and s are calculated for the complete sample.

Z-SCORE2 is defined as:

$$\text{Z-SCORE2} = \frac{(x_i - \bar{x}_2)}{s_2} \qquad (2.23)$$

where $\bar{x}_2$ and s_2 are calculated for the sample without outliers.

if $|Z_i| \leq 2,0$ then the result is satisfactory/is considered to be acceptable,
if $2,0 < |Z_i| < 3,0$ then the result is questionable and biased/is considered to give a warning signal,
if $|Z_i| \geq 3,0$ then the result is unsatisfactory and outlier/is considered to be unacceptable (or action signal).

3 PARTIAL RESULTS

Summary of statistic comparative results testing methods is illustrated in the Annex.
The results are presented in tables in Section 4.
The Z-SCORE1, Z-SCORE2 of the results is presented in tables in Section 5.

The result selection:
each laboratory has received code which consists of 3 number series: - x_i / y_j / z_k.

The **first number cluster** represents the code of lines for the results and Z-SCORE presented in Table 4.1 and 5.1.1, 5.1.2 resp.,

the **second number cluster** represents the code for the results and Z-SCORE presented in Table 4.2 and 5.2.1, 5.2.2 resp., and

the **third number cluster** represents the code for the results and Z-SCORE presented in Table 4.3 and 5.3.1, 5.3.2 resp.

NOTE
Blunder removal by ISO 13528: 2022, Clause 6.3
6.3.1 ISO/IEC 17043:2010 section B.2.5 and the IUPAC Harmonized Protocol recommend removing obvious blunders from a data set at an early stage in an analysis, prior to use of any robust procedure or any test to identify statistical outliers. Generally, these results would be treated separately (such as contacting the participant). It can be possible to correct some blunders, but this should only be done according to an approved policy and procedure. Occasionally (especially in proficiency testing that is offered for the first time) a single participant (or multiple participants) will make several such blunders in reporting, perhaps due to misunderstanding of instructions or report forms. In such cases all results from that participant should be removed from the analysis, including any results that may not be obvious blunders.
NOTE Obvious blunders, such as reporting results in incorrect units or switching results from different proficiency test items, occurs in most rounds of proficiency testing, and these results only impair the performance of subsequent statistical methods.

When processing the results, we corrected obvious errors from rewriting.

4 SUMMARY OF THE RESULTS

4.1 Results of chemical analysis

The results of chemical analyses are presented in Table 4.1

Table 4.1 - The results of chemical analysis

Laboratory key numbers	Sulfate content (as SO_3)	Chloride content	Loss on Ignition	Insoluble residue	Na_2O content	K_2O content	Slag content microscopically	Chromium (VI) content
	(% by mass)	(% by mass)	(% by mass)	(% by mass)	(% by mass)	(% by mass)	(% by mass)	(ppm)
x_j	x1	x2	x3	x4	x5	x6	x7	x8
1	***2,985 *****	***0,067 *****	7,615	1,470	0,210	***0,586 *****	***11,65 [m] *****	***1,15 ****
2	3,170	0,077	7,615	1,495	0,215	0,665	15,55 [m]	2,02
3	3,180	0,077	7,625	1,520	0,220	0,680	17,65 [m]	2,17
4	3,220	0,079	7,650	1,545	0,226	0,710	22,35 [m]	2,92
5	3,225	0,080	7,655	1,620	0,244	0,715	***23,50 [m] *****	3,40
6	3,245	0,081	7,670	1,630	0,250	0,720	-	3,44
7	3,255	0,081	7,695	1,635	0,270	0,720	-	3,45
8	3,255	0,081	7,715	1,675	0,275	0,730	-	3,50
9	3,260	0,082	7,735	1,685	0,285	0,740	-	3,65
10	3,345	0,082	7,780	1,710	0,290	0,745	-	4,39
11	3,345	0,085	7,780	1,715	0,300	0,745	-	5,10
12	3,355	0,086	7,830	1,760	0,320	0,751	-	-
13	3,360	0,088	7,885	1,780	***0,455 *****	0,765	-	-
14	3,440	0,092	7,970	1,785	-	-	-	-
15	3,450	0,094	***8,520 *****	-	-	-	-	-
16	-	-	-	-	-	-	-	-
17	-	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-	-
21	-	-	-	-	-	-	-	-
22	-	-	-	-	-	-	-	-

Note:
Values marked with single star (*) are considered as biased values.
Values marked with two stars (**) are considered as outliers.
[w] – tested by wet way (We do not present the results for a small number of participants.),
[m] – tested microscopically.

4.2 Results of physical tests

The results of physical tests are presented in Table 4.2.

Table 4.2 - The results of physical tests

Laboratory key numbers	Hydrating heat D), S)	Grinding fineness		Setting time		Water for standard consistency	Volume soundness
		Specific surface	Specific gravity	Initial setting time	Final setting time		
	(J/g)	(m^2/kg)	(g/m^3)	(min)	(min)	(% by mass)	(mm)
y_j	y1	y2	y3	y4	y5	y6	y7
1	265 S	***466,8 ****	2,87	180	250	26,90	0,0
2	266 D	476,6	2,88	180	265	26,90	0,0
3	272 D	478,2	2,91	186	275	27,20	0,0
4	-	498,0	2,93	187	277	27,40	0,0
5	-	501,8	2,97	198	277	27,48	0,0
6	-	502,5	3,00	215	278	27,50	0,2
7	-	505,2	3,00	218	280	27,50	0,2
8	-	509,0	3,01	218	288	27,60	0,3
9	-	509,0	3,01	220	293	27,65	0,3
10	-	510,3	3,02	220	293	28,20	0,5
11	-	512,4	3,03	223	295	28,25	0,5
12	-	515,0	3,03	225	295	28,50	0,5
13	-	524,1	3,03	231	300	28,55	0,5
14	-	-	3,05	236	300	28,75	0,7
15	-	-	-	243	312	28,80	***1,0 *****
16	-	-	-	248	***423 *****	29,00	***1,0 *****
17	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-
21	-	-	-	-	-	-	-
22	-	-	-	-	-	-	-

Note:
Values marked with single star (*) are considered as biased values.
Values marked with two stars (**) are considered as outliers.
D) – tested by dissolution metod,
S) – tested by semidiabatic metod (We cannot present any results).

4.3 Results of mechanical tests

The results of mechanical tests are presented in Table 4.3.

Table 4.3 - The results of mechanical tests

Laboratory key numbers	Strength			
	Flexural strength		Compressive strength	
	2 days	28 days	2 days	28 days
	(MPa)	(MPa)	(MPa)	(MPa)
z_k	z1	z2	z3	z4
1	3,70	***6,37*** **	18,30	47,46
2	3,87	7,28	18,72	48,00
3	3,88	7,52	18,86	48,16
4	3,88	7,73	19,18	49,03 / **β**
5	3,93	7,77	19,35	49,12
6	3,93	7,88	19,38	49,19
7	4,03	8,01	19,98	49,28
8	4,03	8,02	19,98 / **β**	49,57 / **β**
9	4,06	8,13	20,03 / **o**	50,36
10	4,07	8,22	20,20	50,53
11	4,08	8,26	20,35	50,54
12	4,10	8,27	20,35	50,68
13	4,23 / **β**	8,45	20,41	51,10 / **β**
14	4,27	8,48	20,45	51,52
15	4,43	8,48	21,50	52,34
16	4,49	8,71	21,95	52,95 / **β**
17	4,57	9,04	***23,07*** **	53,38
18	-	-	-	-
19	-	-	-	-
20	-	-	-	-
21	-	-	-	-
22	-	-	-	-

Note:
Values marked with single star (*) are considered as biased values.
Values marked with two stars (**) are considered as outliers.
Values marked with "β" are considered as biased values for the interlaboratory deviations due to Cochran´s test.
Values marked with "o" are considered as outliers for the interlaboratory deviations due to Cochran´s test.

5 Z-SCORE EVALUATION

5.1 Z-SCORE for chemical analysis

The Z-SCORE1 for chemical analyses is presented in Table 5.1.1

Table 5.1.1 – Z-SCORE1 for chemical analysis

Laboratory key numbers	Sulfate content (as SO_3)	Chloride content	Loss on Ignition	Insoluble residue	Na_2O content	K_2O content	Slag content microscopically	Chromium (VI) content
x_j	x1	x2	x3	x4	x5	x6	x7	x8
1	***-2,452 *****	***-2,316 *****	-0,733	-1,668	-0,986	***-2,689 *****	***-1,328 *****	***-1,854 ****
2	-0,875	-0,782	-0,733	-1,430	-0,909	-1,019	-0,530	-1,067
3	-0,790	-0,782	-0,689	-1,191	-0,832	-0,702	-0,100	-0,931
4	-0,449	-0,475	-0,580	-0,952	-0,739	-0,068	0,862	-0,252
5	-0,406	-0,322	-0,558	-0,235	-0,461	0,038	***1,097 *****	0,182
6	-0,236	-0,169	-0,492	-0,140	-0,368	0,144	-	0,218
7	-0,151	-0,169	-0,383	-0,092	-0,059	0,144	-	0,227
8	-0,151	-0,169	-0,296	0,290	0,019	0,355	-	0,272
9	-0,108	-0,015	-0,208	0,386	0,173	0,567	-	0,408
10	0,616	-0,015	-0,012	0,625	0,250	0,672	-	1,078
11	0,616	0,445	-0,012	0,673	0,405	0,672	-	1,720
12	0,701	0,598	0,207	1,103	0,714	0,799	-	-
13	0,744	0,905	0,447	1,294	***2,801 *****	1,095	-	-
14	1,426	1,518	0,818	1,342	-	-	-	-
15	1,511	1,825	***3,221 *****	-	-	-	-	-
16	-	-	-	-	-	-	-	-
17	-	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-	-
21	-	-	-	-	-	-	-	-
22	-	-	-	-	-	-	-	-

Note:
Values marked with single star (*) are considered as questionable values.
Values marked with two stars (**) are considered as unsatisfactory values.

The Z-SCORE2 for chemical analyses is presented in Table 5.1.2

Table 5.1.2 – Z-SCORE2 for chemical analysis

Laboratory key numbers	Sulfate content (as SO_3)	Chloride content	Loss on Ignition	Insoluble residue	Na_2O content	K_2O content	Slag content microscopically	Chromium (VI) content
x_j	x1	x2	x3	x4	x5	x6	x7	x8
1	***-3,444 *****	***-3,121 *****	-1,066	-1,668	-1,336	***-4,737 *****	***-1,972 *****	***-2,454***
2	-1,377	-1,195	-1,066	-1,430	-1,199	-2,021	-0,852	-1,507
3	-1,265	-1,195	-0,974	-1,191	-1,062	-1,506	-0,249	-1,343
4	-0,818	-0,809	-0,742	-0,952	-0,898	-0,474	1,101	-0,527
5	-0,762	-0,617	-0,695	-0,235	-0,405	-0,303	***1,431 *****	-0,004
6	-0,539	-0,424	-0,556	-0,140	-0,241	-0,131	-	0,039
7	-0,427	-0,424	-0,325	-0,092	0,307	-0,131	-	0,050
8	-0,427	-0,424	-0,139	0,290	0,444	0,213	-	0,105
9	-0,371	-0,231	0,046	0,386	0,717	0,557	-	0,268
10	0,579	-0,231	0,464	0,625	0,854	0,729	-	1,073
11	0,579	0,347	0,464	0,673	1,128	0,729	-	1,846
12	0,691	0,539	0,927	1,103	1,676	0,935	-	-
13	0,746	0,925	1,437	1,294	***5,372 *****	1,416	-	-
14	1,640	1,696	2,225	1,342	-	-	-	-
15	1,752	2,081	***7,325 *****	-	-	-	-	-
16	-	-	-	-	-	-	-	-
17	-	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-	-
21	-	-	-	-	-	-	-	-
22	-	-	-	-	-	-	-	-

Note:
Values marked with single star (*) are considered as questionable values.
Values marked with two stars (**) are considered as unsatisfactory values.

5.2 Z-SCORE for physical tests

The Z-SCORE1 for physical tests is presented in Table 5.2.1.

Table 5.2.1 – Z-SCORE1 for physical tests

Laboratory. key numbers	Hydrating heath [1)]	Grinding fineness		Setting time		Water for standard consistency	Volume soundness
		Specific surface	Specific gravity	Initial setting time	Final setting time		
y_j	y1	y2	y3	y4	y5	y6	y7
1	- [1)]	***-2,017 ****	-1,862	-1,571	-1,164	-1,431	-1,062
2	- [1)]	-1,433	-1,695	-1,571	-0,765	-1,431	-1,062
3	- [1)]	-1,338	-1,191	-1,296	-0,500	-0,996	-1,062
4	-	-0,160	-0,856	-1,250	-0,446	-0,705	-1,062
5	-	0,067	-0,185	-0,746	-0,446	-0,589	-1,062
6	-	0,108	0,319	0,032	-0,420	-0,560	-0,472
7	-	0,269	0,319	0,169	-0,367	-0,560	-0,472
8	-	0,495	0,487	0,169	-0,154	-0,415	-0,177
9	-	0,495	0,487	0,261	-0,021	-0,342	-0,177
10	-	0,573	0,654	0,261	-0,021	0,456	0,413
11	-	0,698	0,822	0,398	0,032	0,528	0,413
12	-	0,852	0,822	0,490	0,032	0,891	0,413
13	-	1,394	0,822	0,765	0,165	0,964	0,413
14	-	-	1,158	0,994	0,165	1,254	1,003
15	-	-	-	1,314	0,484	1,326	***1,888 ****
16	-	-	-	1,543	***3,433 ****	1,617	***1,888 ****
17	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-
21	-	-	-	-	-	-	-
22	-	-	-	-	-	-	-

Note:
[1)] - We do not present the results for a small number of participants.
Values marked with single star (*) are considered as questionable values.
Values marked with two stars (**) are considered as unsatisfactory values.

The Z-SCORE2 for physical tests is presented in Table 5.2.2.

Table 5.2.2 – Z-SCORE2 for physical tests

Laboratory. key numbers	Hydrating heath [1)]	Grinding fineness		Setting time		Water for standard consistency	Volume soundness
		Specific surface	Specific gravity	Initial setting time	Final setting time		
y_j	y1	y2	y3	y4	y5	y6	y7
1	- [1)]	***-2,630 ****	-1,862	-1,571	-2,245	-1,431	-1,066
2	- [1)]	-1,928	-1,695	-1,571	-1,288	-1,431	-1,066
3	- [1)]	-1,813	-1,191	-1,296	-0,651	-0,996	-1,066
4	-	-0,395	-0,856	-1,250	-0,523	-0,705	-1,066
5	-	-0,123	-0,185	-0,746	-0,523	-0,589	-1,066
6	-	-0,072	0,319	0,032	-0,459	-0,560	-0,246
7	-	0,121	0,319	0,169	-0,332	-0,560	-0,246
8	-	0,393	0,487	0,169	0,179	-0,415	0,164
9	-	0,393	0,487	0,261	0,497	-0,342	0,164
10	-	0,486	0,654	0,261	0,497	0,456	0,984
11	-	0,637	0,822	0,398	0,625	0,528	0,984
12	-	0,823	0,822	0,490	0,625	0,891	0,984
13	-	1,475	0,822	0,765	0,944	0,964	0,984
14	-	-	1,158	0,994	0,944	1,254	1,803
15	-	-	-	1,314	1,709	1,326	***3,033 ****
16	-	-	-	1,543	***8,788 ****	1,617	***3,033 ****
17	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-
21	-	-	-	-	-	-	-
22	-	-	-	-	-	-	-

Note:
[1)] - We do not present the results for a small number of participants.
Values marked with single star (*) are considered as questionable values.
Values marked with two stars (**) are considered as unsatisfactory values.

5.3 Z-SCORE for mechanical tests

The Z-SCORE1 for mechanical tests is presented in Table 5.3.1.

Table 5.3.1 – Z-SCORE1 for mechanical tests

Labor key numbers	Strength			
	Flexural strength		Compressive strength	
	2 days	28 days	2 days	28 days
z_k	z1	z2	z3	z4
1	-1,643	***-2,725 *****	-1,512	-1,599
2	-0,929	-1,237	-1,164	-1,283
3	-0,887	-0,844	-1,047	-1,189
4	-0,887	-0,501	-0,782	-0,679
5	-0,676	-0,435	-0,640	-0,626
6	-0,676	-0,255	-0,615	-0,585
7	-0,256	-0,043	-0,117	-0,533
8	-0,256	-0,026	-0,117	-0,363
9	-0,130	0,154	-0,076	0,100
10	-0,088	0,301	0,066	0,200
11	-0,046	0,366	0,190	0,206
12	0,038	0,383	0,190	0,288
13	0,584	0,677	0,240	0,534
14	0,752	0,726	0,273	0,780
15	1,424	0,726	1,145	1,260
16	1,676	1,103	1,519	1,618
17	2,013	1,642	***2,449 *****	1,870
18	-	-	-	-
19	-	-	-	-
20	-	-	-	-
21	-	-	-	-
22	-	-	-	-

Note:
Values marked with single star (*) are considered as questionable values.
Values marked with two stars (**) are considered as unsatisfactory values.

The Z-SCORE2 for mechanical tests is presented in Table 5.3.2.

Table 5.3.2 – Z-SCORE2 for mechanical tests

Labor key numbers	Strength			
	Flexural strength		Compressive strength	
	2 days	28 days	2 days	28 days
z_k	z1	z2	z3	z4
1	-1,643	***-3,942 *****	-1,697	-1,599
2	-0,929	-1,916	-1,262	-1,283
3	-0,887	-1,382	-1,117	-1,189
4	-0,887	-0,915	-0,785	-0,679
5	-0,676	-0,826	-0,609	-0,626
6	-0,676	-0,581	-0,578	-0,585
7	-0,256	-0,292	0,045	-0,533
8	-0,256	-0,269	0,045	-0,363
9	-0,130	-0,024	0,096	0,100
10	-0,088	0,176	0,273	0,200
11	-0,046	0,265	0,428	0,206
12	0,038	0,287	0,428	0,288
13	0,584	0,688	0,490	0,534
14	0,752	0,755	0,532	0,780
15	1,424	0,755	1,621	1,260
16	1,676	1,266	2,087	1,618
17	2,013	2,001	***3,248 *****	1,870
18	-	-	-	-
19	-	-	-	-
20	-	-	-	-
21	-	-	-	-
22	-	-	-	-

Note:
Values marked with single star (*) are considered as questionable values.
Values marked with two stars (**) are considered as unsatisfactory values.

6 SUMMARY OF THE RESULTS

The results of the Cement Ring Tests 2024 are summarised in Table 6.1.

Table 6.1 - Results summary (without biased values and without outliers)

Sample without outliers	Average (Arithmetic mean)	Precision of a measure of the mean	Ratio (2*ε) / $\bar{x}$	Lower confi-dence	Upper confi-dence	Ratio (L_M - L_m) / $\bar{x}$	Standard deviation of a sample	Coefficient of variation (%)	Count (Sample size)
	$\bar{x}$	ε		$L_{m95\%}$	$L_{M95\%}$		$s_{(n-1)}$	v	n
Sulfate content (as SO_3) (% by mass)	3,2932	0,0536	0,0326	3,0998	3,4866	0,1175	0,08950	2,7%	14
Chloride content (% by mass)	0,0832	0,0031	0,0745	0,0720	0,0944	0,2692	0,00519	6,2%	14
Loss on Ignition (% by mass)	7,7300	0,0646	0,0167	7,4970	7,9630	0,0603	0,10785	1,4%	14
Insoluble residue (% by mass)	1,6446	0,0627	0,0762	1,4185	1,8707	0,2750	0,10465	6,4%	14
Na_2O content (% by mass)	0,2588	0,0242	0,1870	0,1784	0,3392	0,6213	0,0365	14,1%	12
K_2O content (% by mass)	0,7238	0,0193	0,0533	0,6598	0,7878	0,1768	0,0291	4,0%	12
Slag content (% by mass)	18,140	6,784	0,7480	4,572	26,760	1,2232	4,8868	26,9%	5 +)
Chromium (VI) content (ppm)	3,404	0,6930	0,4072	1,3260	5,482	1,2209	0,9186	27,0%	10
Hydrating heath (J/g)	269,0	-	-	-	-	-	-	-	2 ++)
Specific surface (m^2/kg)	503,51	9,2600	0,0368	472,79	534,23	0,1220	13,959	2,8%	12
Specific gravity (g/m^3)	2,981	0,0360	0,0242	2,8520	3,110	0,0865	0,0596	2,0%	14
Initial setting time (min)	214,3	12,00	0,1120	167,7	260,9	0,4349	21,84	10,2%	16
Final setting time (min)	285,2	9,00	0,0631	251,6	318,8	0,2356	15,68	5,5%	15
Water for standard consistency (% by mass)	27,886	0,38	0,0272	26,42	29,355	0,1054	0,6891	2,5%	16
Volume soundness (mm)	0,26	0,15	1,1538	-	0,79	4,0769	0,244	93,8%	14
Flexural strength - 2 days (MPa)	4,091	0,126	0,0616	3,586	4,596	0,2469	0,2380	5,8%	17
Flexural strength - 28 days (MPa)	8,141	0,247	0,0607	7,183	9,099	0,2354	0,4493	5,5%	16
Compressive strength - 2 days (MPa)	19,937	0,531	0,0533	17,881	21,993	0,2062	0,9645	4,8%	16
Compressive strength - 28 days (MPa)	50,189	0,904	0,0360	46,571	53,807	0,1442	1,7065	3,4%	17

+) Remark: Outliers are included also due to the small number of results.
++) Remark: We do not present the results for a small number of participants.

Elaborated by: Dipl. Eng. Ladislav Gilányi, PhD.

Date: 10. 07. 2024

Dipl. Eng. Patrik Ševčík
Director of Bratislava branch

List of annexes

Annex No.	Content of annex	Form
1	Summary statistics and bar charts of frequency distribution, part x, y, z	(24+18+12)xA4