

Application / archive No. 20-20-0033

,,Cement Ring Tests 2020“ final report
No.: 20-20-0033

Organizer: Building testing and research institute, Bratislava branch
Sampling material: Portland-composite cement EN 197-1 – CEM II/B-S 42,5 N
Test methods: STN EN 196 – parts 1, 2, 3, 4, 6, 7, 8, 10

Participant's 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: 05. 06. 2020

Coordinator: Dipl. Eng. Marián Kubíš

Analyst of testing: Dipl. Eng. Ladislav Gilányi, PhD.

Head of testing laboratories: Dipl. Eng. Daniel Peťo

Director of Bratislava branch: Dipl. Eng. Patrik Ševčík

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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 2020 was attended by 22 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) (12)

Cement Hranice akciová společnost; Bělotínská 288; 753 01 Hranice I - Město - ČR
Cemex Czech Republic, s.r.o. (mlýnice Dětmarovice); Areál Edě č.p. 1216; 735 71 Dětmarovice - ČR
CEMEX Czech Republic, s.r.o.; Tovární 296; 538 04 Prachovice - ČR
Ceskomoravsky cement a.s.; Mokra 359; 664 09 Mokra-Horakov
ČESKOMORAVSKÝ CEMENT A.S.; K Cementárně 1261/25; 15302 Praha Radotín - ČR
Lafarge Cement a.s.; Čížkovice 27; 411 12 Čížkovice - ČR
Technický a zkušební ústav stavební Praha, s. p., Centrální laboratoř - zkušebna Brno; Hněvkovského 77; Brno - ČR
TECHNICKÝ A ZKUŠEBNÍ ÚSTAV STAVEBNÍ PRAHA, s.p.- pobočka Teplice; Tolstého 447; Teplice 415 03 - ČR
VŠB-Technická univerzita Ostrava, Centrum Nanotechnologií; 17. listopadu 2172/15; 708 00 Ostrava-Poruba - ČR
Výrobní závod Kotouč Štramberk; Libotín 500; 742 66 Štramberk - ČR
Výzkumný ústav maltovin Praha, s.r.o.; Na Cikánce 614/2; Praha 5 – Radotín - ČR
Výzkumný ústav stavebních hmot, a.s.; Hněvkovského 30/65; 617 00 Brno – ČR

Slovak Republic (SK) (10)

BetónRacio, s.r.o., Skúšobné laboratórium, Pracovisko Trnava; Skladová 2; 917 01 Trnava
CEMMAC a.s.; Cementárska 14; 91442 Horné Srnie
CRH (Slovensko) a. s., 044 02 Turňa nad Bodvou; Slovenská republika
CRH (Slovensko) a.s.; Senická cesta; 906 38 Rohožník
Považská cementáreň, a. s.; ul. J. Kráľa; 018 63 Ladce; Slovenská republika
QUALIFORM SLOVAKIA s.r.o.; Pasienková 9 D; 821 06 Bratislava
TESScontrol,s.r.o., oblastné laboratórium Bratislava; Ľubochňianska 1/A; 831 04 Bratislava
TESScontrol,s.r.o., oblastné laboratórium Zvolen; Hronská 1; 960 93 Zvolen
Technický a skúšobný ústav stavebný, n. o., skúšobné laboratórium Bratislava; Studená 3; 821 04 Bratislava
ZEOCEM, a.s. Bystré; Bystré 282; 094 34 Bystré, okr. Vranov nad Topľou

To compare the test results homogenized Portland-composite cement EN 197-1 – CEM II/B-S 42,5 N (according to STN EN 197-1) was used. The test results were evaluated according to STN ISO 5725-2, 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

Organizer:	Building Testing and Research Institute, (abbrev: TSÚS) Bratislava branch Studená 3, 821 04 Bratislava
Cement Manufacturer:	unreported (information archiving by organizer)
Evaluator:	Building Testing and Research Institute, director's department Studená 3, 821 04 Bratislava

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 Kušík

Character of the tests: study according to STN 73 2031;
Type of tests: STN EN 196 - parts 1, 2, 3, 4, 6, 7, 8, 10;

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,
Director's department,
Studená 3, 821 04 Bratislava

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

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)
ISO 13528: 2015	Statistical methods for use in proficiency testing by interlaboratory comparison
STN ISO 16269-6: 2007	Statistical interpretation of data. Part 6: Determination of statistical tolerance intervals [Štatistická interpretácia dát. Časť 6: Stanovenie štatistických tolerančných intervalov] (01 0233)
STN ISO 5725-1: 2000/C1: 2006	Accuracy (trueness and precision) of measurement methods and results. Part 1: General principles and definitions [Presnosť (správnosť a zhodnosť) metód a výsledkov merania. Časť 1: Všeobecné zásady a definície] (01 0251)
STN ISO 5725-2: 2000/ C1: 2010	Accuracy (trueness and precision) of measurement methods and results. Part 3: Intermediate measures of the precision of a standard measurement method [Presnosť (správnosť a zhodnosť) metód a výsledkov merania. Časť 2: Základná metóda stanovenia opakovateľnosti a reprodukoveľnosti normalizovanej metódy merania] (01 0251)
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 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 stálosťi (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

STN EN 196-10: 2019	[Metódy skúšania cementu. Časť 8: Stanovenie hydratačného tepla. Rozpúšťacia metóda] (72 2100) 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 šestmocného 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: 2016 STN 73 2031: 1985	Cement. Part 2: Conformity evaluation [Cement. Časť 2: Hodnotenie zhody] (72 2101) Testing of structures, building constructions and elements. Common regulations [Skúšanie stavebných objektov, konštrukcií a dielcov. Spoločné ustanovenia] (73 2031)

1.4 List of references

- [1] Likeš J., Laga J.: Základní statistické tabulky, SNTL – Nakladatelství technické literatury, Praha 1978
- [2] Jílek M.: Statistické toleranční meze, SNTL – Nakladatelství technické literatury, Praha 1988
- [3] MSA – L/14: Stanovenie rozsahu a frekvencie účasti v skúškach spôsobilosti, Metodická smernica na akreditáciu, SNAS, Bratislava 2013
- [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 2020

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 and Slovak Republic. Laboratories involvement was based on experience from previous years.

Preparation of testing materials

For execution of comparative tests approximately 250 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 questionnaire in which they established physical units, number of decimal digits and form of presentation include testing instruction.

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

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

Dispersion parameters

v Coefficient of variation / Variance

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

s Standard deviation of a sample

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

s_0 Standard deviation

$$s_0 = \sqrt{\frac{1}{p} \sum_{i=1}^p (x_i - x_m)^2} \quad (2.4)$$

x_{\min} Minimum value

x_{\max} Maximum value

R Sample range

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

Standard Skewness

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

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

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:

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

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

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 $\leq -2; +2 \geq$, 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's method or Dan-Dixon's 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:

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

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

Or in accordance with [1] :

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

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

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

The Grubbs' 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:

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

where

$$t_{(a/(2n), n-2)}$$

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

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:

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

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

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

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

$$\lambda_\alpha(n) = 11,58849 - 10,752151 \cdot \exp(-0,30788516 \cdot n^{(-0,67230923)}) \quad (2.17)$$

For regression curve the Weibull model was used, where:

$$y=a-b \cdot \exp(-c \cdot x^d)$$

with parameters:

$$\begin{aligned} a &= 11,58849 \\ b &= 10,752151 \\ c &= 0,30788516 \\ d &= -0,67230923 \end{aligned}$$

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 $\alpha=0,05$ as a result of applying Student's dividing for $N=(n-1)$ degree of freedom:

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

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

where

L_m 95% Lower confidence limits after elimination of outliers.

L_M 95% Upper confidence limits after elimination of outliers.

For evaluation of deviation ε following equation was applied:

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

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:

$$C = \frac{s_{\max}^2}{\sum_{i=1}^p s_i^2} \quad (2.21)$$

where

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

Z-SCORE

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

Z-SCORE1 is defined as:

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

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

Z-SCORE2 is defined as:

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

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

- if $|Z_i| \leq 2$, than the result is satisfactory,
- if $2 < |Z_i| < 3$, than the result is questionable,
- if $|Z_i| \geq 3$, than the result is unsatisfactory.

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

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.

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 ₂ O content	K ₂ O content	Slag content	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	2,735	0,072 **	3,510	0,590	0,220	0,510 **	26,25 **	6,10
2	2,795	0,089	3,555	0,680	0,220	0,705 *	30,25	6,10
3	2,800	0,089	3,565	0,745	0,225	0,755	30,35	6,25
4	2,805	0,090	3,575	0,760	0,230	0,760	33,00	6,53
5	2,850	0,091	3,575	0,775	0,230	0,775	35,00 **	7,90
6	2,855	0,092	3,585	0,775	0,230	0,775	-	8,10
7	2,875	0,093	3,585	0,780	0,245	0,775	-	8,25
8	2,885	0,094	3,605	0,785	0,245	0,785	-	8,45
9	2,895	0,094	3,610	0,790	0,250	0,790	-	8,75
10	2,900	0,095	3,620	0,795	0,260	0,790	-	9,00
11	2,950	0,095	3,625	0,825	0,260	0,795	-	10,00
12	2,955	0,096	3,640	0,850	0,265	0,800	-	11,75 **
13	3,000	0,097	3,645	0,860	0,280	0,810	-	-
14	3,015	0,097	3,655	0,900	0,320	0,820	-	-
15	3,095	0,098	3,670	1,025	0,330	0,840	-	-
16	3,165	0,098	3,690	1,080	0,930 **	0,840	-	-
17	3,495 **	0,099	3,720	1,190 **	-	-	-	-
18	-	-	3,775 **	-	-	-	-	-
19	-	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-	-
21	-	-	-	-	-	-	-	-
22	-	-	-	-	-	-	-	-
Average	2,9109	0,0942	3,6135	0,8134	0,2540	0,7936	31,20	7,766

Note:

Values marked with single star (*) are considered as biased values.

Values marked with two stars (**) are considered as outliers.

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 (J/g)	Grinding fineness		Setting time		Water for standard consistency (% by mass)	Volume soundness (mm)
		Specific surface (m ² /kg)	Specific gravity (g/m ³)	Initial setting time (min)	Final setting time (min)		
		y ₁	y ₂	y ₃	y ₄	y ₅	y ₆
1	209 **	385,4	2,91	18 **	206	28,0	0,0
2	265	392,6	2,93	20 **	220	28,4	0,0
3	279	393,7	2,94	130	225	28,4	0,0
4	293	399,1	2,98	145	230	28,5	0,0
5	-	401,2	2,99	167	230	28,6	0,2
6	-	402,9	2,99	175	230	28,6	0,2
7	-	405,2	2,99	180	240	28,8	0,3
8	-	408,5	2,99	182	250	28,8	0,4
9	-	409,1	3,00	185	250	28,8	0,5
10	-	411,9	3,01	187	260	28,8	0,5
11	-	413,0	3,04	190	272	29,0	0,5
12	-	416,8	3,04	199	275	29,0	0,5
13	-	420,6	3,04	200	275	29,3	0,5
14	-	422,0	3,07	200	280	29,6	0,6
15	-	430,6	-	200	290	30,0	1,0
16	-	-	-	206	300	30,0	1,0
17	-	-	-	207	300	30,2	1,5
18	-	-	-	220	301	30,5	1,5
19	-	-	-	225	310	30,8	1,5
20	-	-	-	225	360 *	31,0	2,0 *
21	-	-	-	-	-	-	-
22	-	-	-	-	-	-	-
Average	279,0	407,51	2,994	190,2	260,2	29,26	0,56

Note:

Values marked with single star (*) are considered as biased values.

Values marked with two stars (**) are considered as outliers.

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 (MPa)	28 days (MPa)	2 days (MPa)	28 days (MPa)
z_k	z₁	z₂	z₃	z₄
1	3,02	6,05 */○	14,25 **	48,54
2	3,30	7,20	15,82	48,97
3	3,63	7,25	17,82	49,23
4	3,70	7,27	18,18	49,30
5	3,78	7,73	18,32	51,08
6	3,80	8,57	18,68	51,26
7	3,80	8,73	18,73	51,35
8	3,90	8,77	18,82	51,42
9	3,92	8,78	18,93	51,93
10	4,02	9,05	19,69	52,42
11	4,10	9,07	19,69	52,54
12	4,10	9,27	19,86	53,23
13	4,17	9,30	19,86	53,34
14	4,20	9,38	19,98	53,76
15	4,25	9,52	20,07	54,13
16	4,28	9,57	20,13	54,48
17	4,57	9,85	20,13	54,68
18	4,58	9,90	20,58	54,84
19	4,65	10,33	20,94	55,55
20	4,93	10,45	22,26	56,37
21	5,43 **	10,47	23,85 / ○	59,11 */β
22	-	-	-	-
Average	4,035	9,023	19,617	52,421

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 "○" 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 ₂ O content	K ₂ O content	Slag content	Chromium (VI) content
x _j	x1	x2	x3	x4	x5	x6	x7	x8
1	1,17	3,34 **	1,76	1,68	0,44	3,39 **	1,43 *	1,17
2	0,83	0,62	1,05	1,07	0,44	0,85	0,22	1,17
3	0,81	0,62	0,90	0,62	0,41	0,20	0,19	1,08
4	0,78	0,46	0,74	0,52	0,38	0,13	-0,62	0,92
5	0,53	0,30	0,74	0,41	0,38	-0,06	-1,22 *	0,12
6	0,50	0,14	0,59	0,41	0,38	-0,06	-	0,00
7	0,39	-0,02	0,59	0,38	0,30	-0,06	-	-0,09
8	0,33	-0,18	0,27	0,35	0,30	-0,19	-	-0,21
9	0,28	-0,18	0,20	0,31	0,27	-0,26	-	-0,38
10	0,25	-0,34	0,04	0,28	0,21	-0,26	-	-0,53
11	-0,03	-0,34	-0,04	0,07	0,21	-0,32	-	-1,11
12	-0,05	-0,50	-0,27	-0,10	0,18	-0,39	-	-2,13 **
13	-0,30	-0,66	-0,35	-0,17	0,09	-0,52	-	-
14	-0,39	-0,66	-0,51	-0,44	-0,14	-0,65	-	-
15	-0,83	-0,82	-0,74	-1,30	-0,20	-0,91	-	-
16	-1,22	-0,82	-1,05	-1,67	-3,68 **	-0,91	-	-
17	-3,05 **	-0,98	-1,52	-2,43 **	-	-	-	-
18	-	-	-2,38 **	-	-	-	-	-
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.

Bar charts of Z-SCORE for results are illustrated in the Annex.

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 ₂ O content	K ₂ O content	Slag content	Chromium (VI) content
x _j	x1	x2	x3	x4	x5	x6	x7	x8
1	1,532	6,789 **	1,949	1,897	1,004	10,734 **	3,174 *	1,253
2	1,009	1,590	1,101	1,133	1,004	3,354	0,609	1,253
3	0,966	1,590	0,913	0,581	0,856	1,461	0,545	1,140
4	0,922	1,284	0,725	0,454	0,709	1,272	-1,154	0,929
5	0,530	0,979	0,725	0,326	0,709	0,704	-2,437 *	-0,101
6	0,487	0,673	0,537	0,326	0,709	0,704	-	-0,251
7	0,313	0,367	0,537	0,284	0,266	0,704	-	-0,364
8	0,226	0,061	0,160	0,241	0,266	0,326	-	-0,514
9	0,138	0,061	0,066	0,199	0,118	0,136	-	-0,740
10	0,095	-0,245	-0,122	0,156	-0,177	0,136	-	-0,928
11	-0,341	-0,245	-0,217	-0,099	-0,177	-0,053	-	-1,680
12	-0,384	-0,550	-0,499	-0,311	-0,325	-0,242	-	-2,995 **
13	-0,776	-0,856	-0,593	-0,396	-0,768	-0,621	-	-
14	-0,907	-0,856	-0,781	-0,735	-1,949	-0,999	-	-
15	-1,603	-1,162	-1,064	-1,797	-2,244	-1,756	-	-
16	-2,213	-1,162	-1,440	-2,264	-19,959 **	-1,756	-	-
17	-5,087 **	-1,468	-2,005	-3,198 **	-	-	-	-
18	-	-	-3,041 **	-	-	-	-	-
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.

Bar charts of Z-SCORE for results are illustrated in the Annex.

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	Grinding fineness		Setting time		Water for standard consistency	Volume soundness
		Specific surface	Specific gravity	Initial setting time	Final setting time		
y _j	y ₁	y ₂	y ₃	y ₄	y ₅	y ₆	y ₇
1	1,43 **	1,81	1,86	2,68 **	1,55	1,44	1,08
2	-0,10	1,22	1,42	2,65 **	1,18	0,98	1,08
3	-0,48	1,13	1,20	0,74	1,05	0,98	1,08
4	-0,86	0,69	0,31	0,48	0,92	0,86	1,08
5	-	0,52	0,09	0,10	0,92	0,75	0,74
6	-	0,38	0,09	-0,03	0,92	0,75	0,74
7	-	0,19	0,09	-0,12	0,66	0,52	0,57
8	-	-0,08	0,09	-0,15	0,40	0,52	0,40
9	-	-0,13	-0,13	-0,21	0,40	0,52	0,23
10	-	-0,36	-0,35	-0,24	0,14	0,52	0,23
11	-	-0,45	-1,01	-0,29	-0,18	0,29	0,23
12	-	-0,76	-1,01	-0,45	-0,26	0,29	0,23
13	-	-1,07	-1,01	-0,47	-0,26	-0,05	0,23
14	-	-1,19	-1,67	-0,47	-0,39	-0,39	0,06
15	-	-1,89	-	-0,47	-0,65	-0,85	-0,62
16	-	-	-	-0,57	-0,91	-0,85	-0,62
17	-	-	-	-0,59	-0,91	-1,08	-1,46
18	-	-	-	-0,81	-0,94	-1,42	-1,46
19	-	-	-	-0,90	-1,17	-1,77	-1,46
20	-	-	-	-0,90	-2,48	-2,00	-2,31 *
21	-	-	-	-	-	-	-
22	-	-	-	-	-	-	-

Note:

Values marked with single star (*) are considered as questionable values.

Values marked with two stars (**) are considered as unsatisfactory values.

Bar charts of Z-SCORE for results are illustrated in the Annex.

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	Grinding fineness		Setting time		Water for standard consistency	Volume soundness
		Specific surface	Specific gravity	Initial setting time	Final setting time		
y _j	y ₁	y ₂	y ₃	y ₄	y ₅	y ₆	y ₇
1	5,000 **	1,808	1,850	6,814 **	1,699	1,442	1,100
2	1,000	1,220	1,410	6,735 **	1,260	0,984	1,100
3	0,000	1,130	1,189	2,382	1,103	0,984	1,100
4	-1,000	0,688	0,308	1,789	0,947	0,870	1,100
5	-	0,516	0,088	0,918	0,947	0,755	0,707
6	-	0,377	0,088	0,602	0,947	0,755	0,707
7	-	0,189	0,088	0,404	0,633	0,526	0,511
8	-	-0,081	0,088	0,324	0,320	0,526	0,314
9	-	-0,130	-0,132	0,206	0,320	0,526	0,118
10	-	-0,359	-0,352	0,127	0,006	0,526	0,118
11	-	-0,449	-1,013	0,008	-0,370	0,297	0,118
12	-	-0,760	-1,013	-0,348	-0,464	0,297	0,118
13	-	-1,071	-1,013	-0,388	-0,464	-0,046	0,118
14	-	-1,185	-1,674	-0,388	-0,621	-0,389	-0,079
15	-	-1,889	-	-0,388	-0,934	-0,847	-0,864
16	-	-	-	-0,625	-1,248	-0,847	-0,864
17	-	-	-	-0,665	-1,248	-1,076	-1,847
18	-	-	-	-1,179	-1,279	-1,419	-1,847
19	-	-	-	-1,377	-1,561	-1,762	-1,847
20	-	-	-	-1,377	-3,129	-1,991	-2,829 *
21	-	-	-	-	-	-	-
22	-	-	-	-	-	-	-

Note:

Values marked with single star (*) are considered as questionable values.

Values marked with two stars (**) are considered as unsatisfactory values.

Bar charts of Z-SCORE for results are illustrated in the Annex.

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	2,00	2,39 *	2,55 **	1,58
2	1,48	1,42	1,77	1,42
3	0,87	1,38	0,77	1,32
4	0,74	1,36	0,59	1,29
5	0,60	0,97	0,52	0,62
6	0,56	0,26	0,34	0,56
7	0,56	0,13	0,32	0,52
8	0,37	0,09	0,27	0,50
9	0,34	0,09	0,22	0,30
10	0,15	-0,14	-0,16	0,12
11	0,00	-0,16	-0,16	0,07
12	0,00	-0,33	-0,25	-0,18
13	-0,13	-0,35	-0,25	-0,23
14	-0,18	-0,42	-0,31	-0,38
15	-0,28	-0,54	-0,35	-0,52
16	-0,33	-0,58	-0,38	-0,65
17	-0,87	-0,82	-0,38	-0,73
18	-0,89	-0,86	-0,61	-0,79
19	-1,02	-1,22	-0,79	-1,06
20	-1,53	-1,32	-1,45	-1,36
21	-2,46 **	-1,34	-2,24	-2,39 *
22	-	-	-	-

Note:

Values marked with single star (*) are considered as questionable values.

Values marked with two stars (**) are considered as unsatisfactory values.

Bar charts of Z-SCORE for results are illustrated in the Annex.

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	2,219	2,917 *	3,221 **	1,698
2	1,607	1,789	2,279	1,510
3	0,885	1,740	1,079	1,396
4	0,732	1,720	0,862	1,366
5	0,557	1,269	0,778	0,587
6	0,514	0,445	0,562	0,508
7	0,514	0,288	0,532	0,469
8	0,295	0,248	0,478	0,438
9	0,251	0,238	0,412	0,215
10	0,033	-0,026	-0,044	0,000
11	-0,142	-0,046	-0,044	-0,052
12	-0,142	-0,242	-0,146	-0,354
13	-0,295	-0,272	-0,146	-0,402
14	-0,361	-0,350	-0,218	-0,586
15	-0,470	-0,488	-0,272	-0,748
16	-0,536	-0,537	-0,308	-0,901
17	-1,169	-0,812	-0,308	-0,988
18	-1,191	-0,861	-0,578	-1,058
19	-1,344	-1,283	-0,794	-1,369
20	-1,956	-1,400	-1,586	-1,728
21	-3,049 **	-1,420	-2,541	-2,927 *
22	-	-	-	-

Note:

Values marked with single star (*) are considered as questionable values.

Values marked with two stars (**) are considered as unsatisfactory values.

Bar charts of Z-SCORE for results are illustrated in the Annex.

6 SUMMARY OF THE RESULTS

The results of the Cement Ring Tests 2020 are summarised in Table 6.1.

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

Sample without outliers	Average (Arithmetic mean)	Precision of a measure of the mean	Ratio $\frac{2*\varepsilon}{\bar{x}}$	Lower confidence	Upper confidence	Ratio $\frac{L_M - L_m}{\bar{x}}$	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)	2,9109	0,0632	0,04342	2,6662	3,1556	0,1681	0,1148	3,9	16
Chloride content (% by mass)	0,0942	0,0018	0,03822	0,0872	0,1012	0,1486	0,00327	3,5	16
Loss on Ignition (% by mass)	3,6135	0,0261	0,01444	3,5009	3,7261	0,2664	0,05311	1,5	17
Insoluble residue (% by mass)	0,8134	0,0648	0,15933	0,5624	1,0644	0,6172	0,11775	14,5	16
Na ₂ O content (% by mass)	0,2540	0,0194	0,15276	0,1814	0,3266	0,5717	0,03387	13,3	15
K ₂ O content (% by mass)	0,7936	0,0158	0,03982	0,7365	0,8507	0,1439	0,02642	3,3	14
Slag content (% by mass)	30,97	4,58	0,29577	21,810	40,130	0,5915	3,2994	10,7	5 ⁺
Chromium (VI) content (ppm)	7,766	0,937	0,24131	4,802	10,730	0,7633	1,3301	17,1	11
Hydrating heath (J/g)	261,5	67,65	0,51740	144,32	378,68	0,8962	36,819	14,1	4 ⁺
Specific surface (m ² /kg)	407,51	7,01	0,03440	381,29	433,73	0,1287	12,226	3,0	15
Specific gravity (g/m ³)	2,994	0,027	0,01804	2,896	3,092	0,0655	0,0454	1,5	14
Initial setting time (min)	190,2	12,9	0,13565	136,9	243,5	0,3661	25,27	13,3	18
Final setting time (min)	260,2	15,8	0,12145	193,2	327,2	0,5150	31,90	12,3	19
Water for standard consistency (% by mass)	29,26	0,42	0,02871	27,43	31,09	0,1251	0,874	3,0	20
Volume soundness (mm)	0,56	0,25	0,89286	0	1,63	2,9107	0,509	90,9	19
Flexural strength - 2 days (MPa)	4,035	0,220	0,10905	3,077	4,993	0,4748	0,4575	11,3	20
Flexural strength - 28 days (MPa)	9,023	0,489	0,10839	6,890	11,156	0,4728	1,0191	11,3	20
Compressive strength - 2 days (MPa)	19,617	0,800	0,08156	16,130	23,104	0,3555	1,6661	8,5	20
Compressive strength - 28 days (MPa)	52,421	1,097	0,04185	47,638	57,204	0,1825	2,2854	4,4	20

+) Remark: Outliers are included due to the very small count of results.

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Checked by: Dipl. Eng. Michal Bačuvčík

Date: 05. 06. 2020

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	(16+14+8)xA4