ALROSA GROUP
INNOVATION CENTER
BOUREVESTNIK
RESEARCH ✦ DESIGN ✦ PRODUCTION

Lab report

X-ray diffraction monitoring of product quality in cement industry

Cement is rightly considered to be the basic material in modern construction field. There are a lot of various cements depending on mineralogical composition, clinker type, use and other criteria. All stages of cement production need continuous monitoring of its quality control.

One of the main tasks in cement quality control is the accurate determination of mineralogical composition of raw meal, clinker and cement itself.

For example, regular clinker contains the following 4 calcium-based minerals, which concentrations are responsible for Portland cement properties:

C_3S (full nomination is $3CaO \cdot SiO_2$) – alite or tricalcium silicatет;

C_2S (full nomination is $2CaO \cdot SiO_2$) – belite (larnite) or dicalcium silicate;

C_3A (full nomination is $3CaO \cdot Al_2O_3$) – tricalcium aluminate;

C_4AF (full nomination is $4CaO \cdot Al_2O_3\ Fe_2O_3$) – tetracalcium aluminoferrite.

The higher alite concentration is, the more difficult to burn clinker, the higher temperature should be. Increase in the content of C_3A and C_4AF facilitates sintering of clinker and improve coating formation. Mineral composition also affects the productivity of cement mills. Presence of C_3S impoves grinding capacity of cements, whereas presence of C_2S ydegrades it because of higher hardness and lower fragility of belite. Clinkers with higher aluminoferrite contents also have lower grinding capacity.

Knowledge of clinker mineral composition allows predicting properties of Portland cements, such as speed of strengthening at different hardening conditions, resistivity to fresh and mineral waters, heat emission at hardening etc. Depending on building and its environmental peculiarities one can select cement with required composition.

With properly prepared raw meal clinker should contain less than 1% of free lime CaO and less than 5% of periclase MgO because of concrete cracking after its solidification.

To slow down cement hardening one should add minor quantity of gypsum minerals (up to 3%). To improve particular properties of Portland cement and for its cost reduction various mineral additives are used.

Calcite $CaCO_3$, dolomite/ankerite $Ca(Mg,Fe)(CO_3)_2$, quartz SiO_2, alkaline feldspars $KAlSi_3O_8$, plagioclase $NaAlSi_3O_8$ and some other common minerals can occur as minor impurities in clinkers and cements.

X-ray diffraction in mineralogy of cements.

XRD is the most fast and reliable nondestructive technique for examination of mineralogical composition. It allows determination of not only main components of clinkers and cements but can also recognize minor impurities, including undesirable ones, for example, free lime CaO. Moreover, XRD can directly distinguish different polymorphic modifications of certain minerals, for example, cubic and orthorhombic tricalcium aluminates C3A, that can't be done with calculations.

XRD measurements, data processing and analysis.

Current application note shows analytical abilities of DRON-8 multifunctional diffractometer in qualitative and quantitative phase analysis of powder samples from various cement factories.

Measurements of samples and their analyses have been performed in the X-ray diffrcation laboratory of Bourevestnik Innovation Centre.

Experimental setup.

DRON-8 multifunctional diffractometer equipped with 2.5 BSV-27 Cu X-ray tube and Mythen 2R 1K linear stripped position-sensitive detector has been used for mesurements.

Sample preparation.

Powder samples were pressed into low-bacskground cuvettes CUT from silicon (911) single crystals. Sample surface was aligned with cuvette border.

Measurement conditions.

High regime of X-ray tube operation – 40 kW, 20 mA;

Scanning method - Θ-Θ;

Scanning mode – discrete;

Angular 2Θ range of scanning – 10-65 deg.;

Scanning step – 0.05-2 deg.;

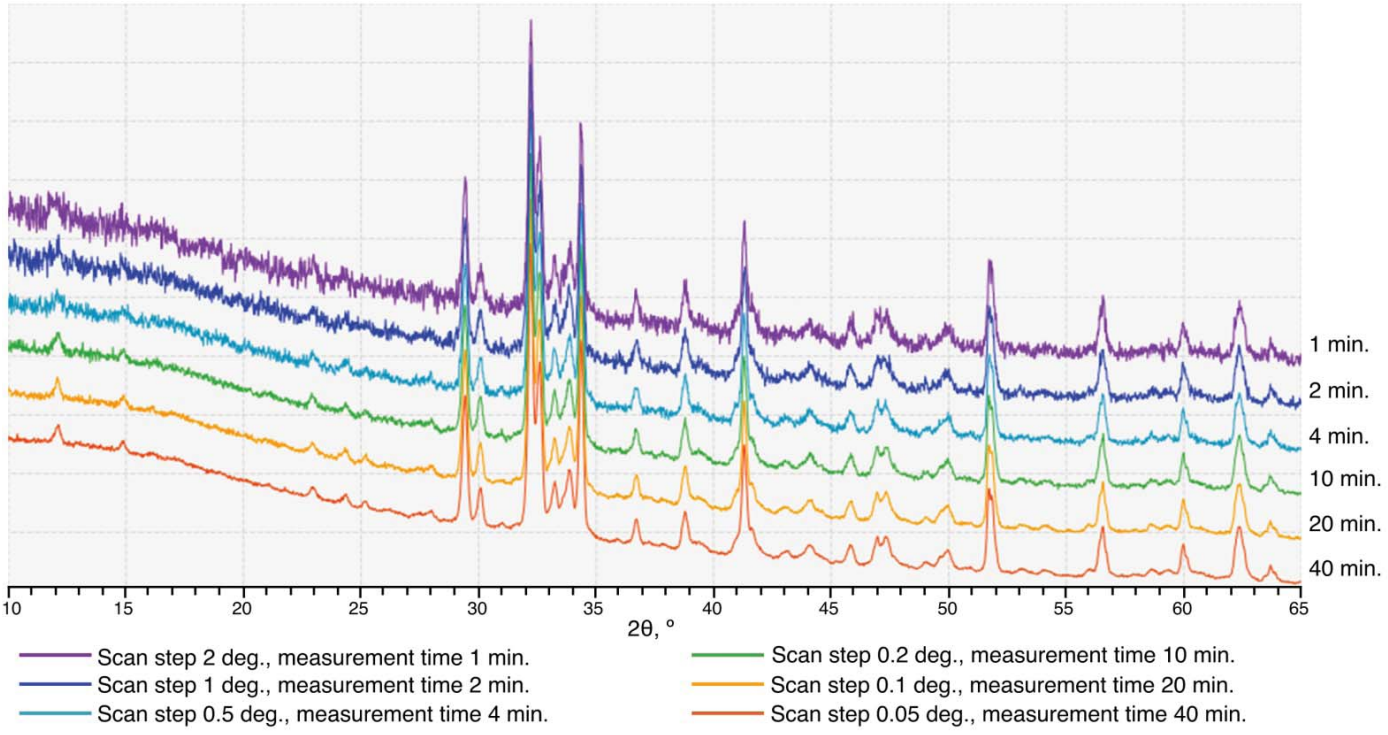
Exposure – 1 sec per point;

Number of active measuring channels – 1000;

Sample in-plane rotation – switched on;

Measuring time was from 1 to 40 min depending on step size of scanning.

Fig. 1 X-ray diffraction pattern of clinker measured from 1 to 40 min with different step size in 2Θ range of 10-65 deg.



Data obtained within 1-5 minutes are essential for identification of main components at qualitative phase analysis. To recognize minor components 20 minutes of measurements is recommended. Quantification by Rietveld refinement requires at least 40 minutes of measurement.

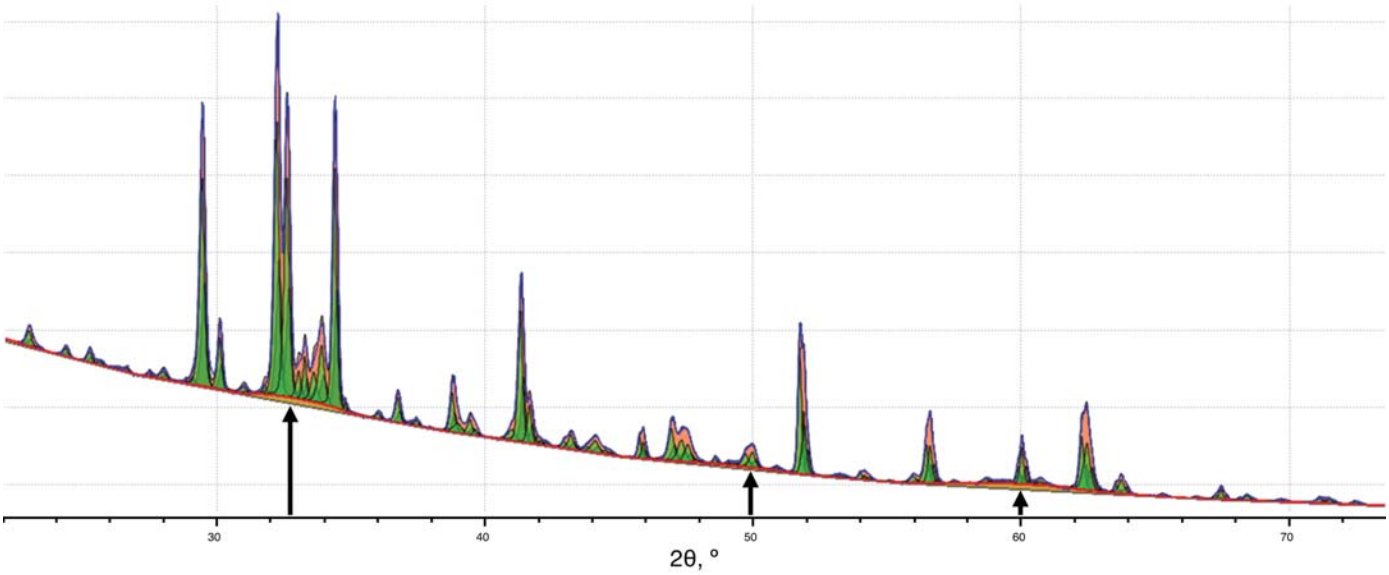
Preliminary processing of measured data.

X-ray diffraction patterns obtained in digital form have been processed with DrWin program (developed by Bourevestnik JSC).

The following procedures have been carried out:

- background approximation with a polynomial of n^{th} degree or with user curve;
- separation of Kα-doublets;
- determination of angular positions of diffraction maxima;
- approximation of peak profiles with pseudo-Voigt function (for the whole pattern and separately for each peak);
- calculation of linear and integral intensities of reflections;
- calculation of FWHM of reflections;
- determination of amorphous phase content.

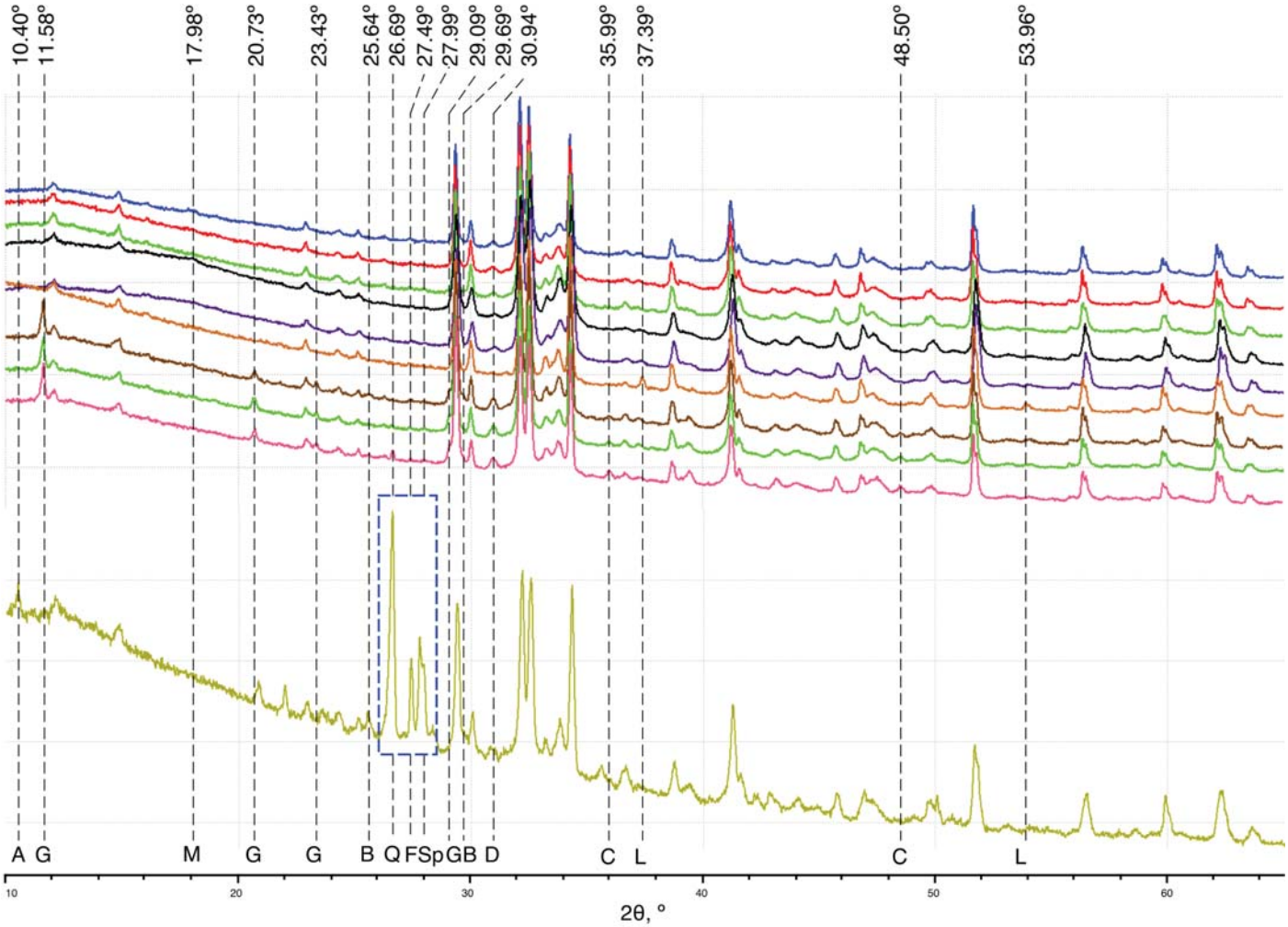
Fig. 2 Preliminary processing of diffraction pattern of cement, containing 5% of amorphous phase (indicated with arrows)



Qualitative and semi-quantitative phase analysis by RIR (Reference Intensity Ratio) method.

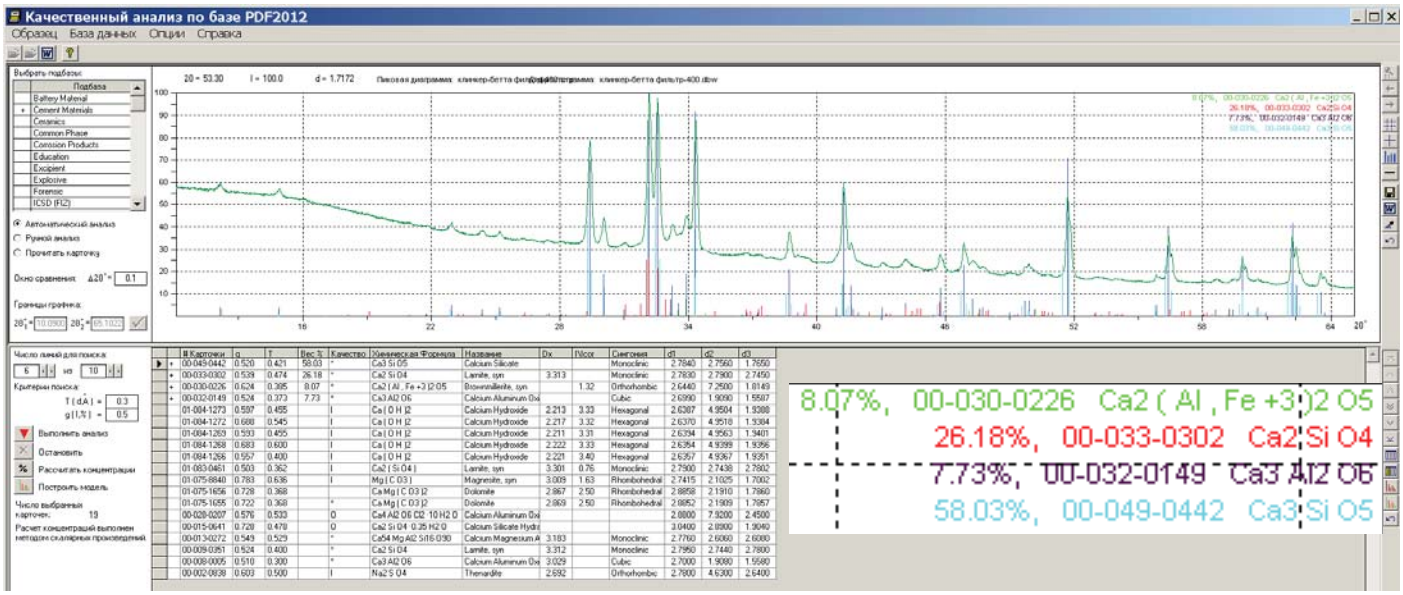
Tabulated data obtained from processing of diffraction pattern have been used for qualitative analysis of clinkers and cements from PDF-2 database with the help of Retrieve&Search-Match software suit. Using RIR's for the components available in the database, one can quantify mixture within the accuracy of 2-3 wt.%.

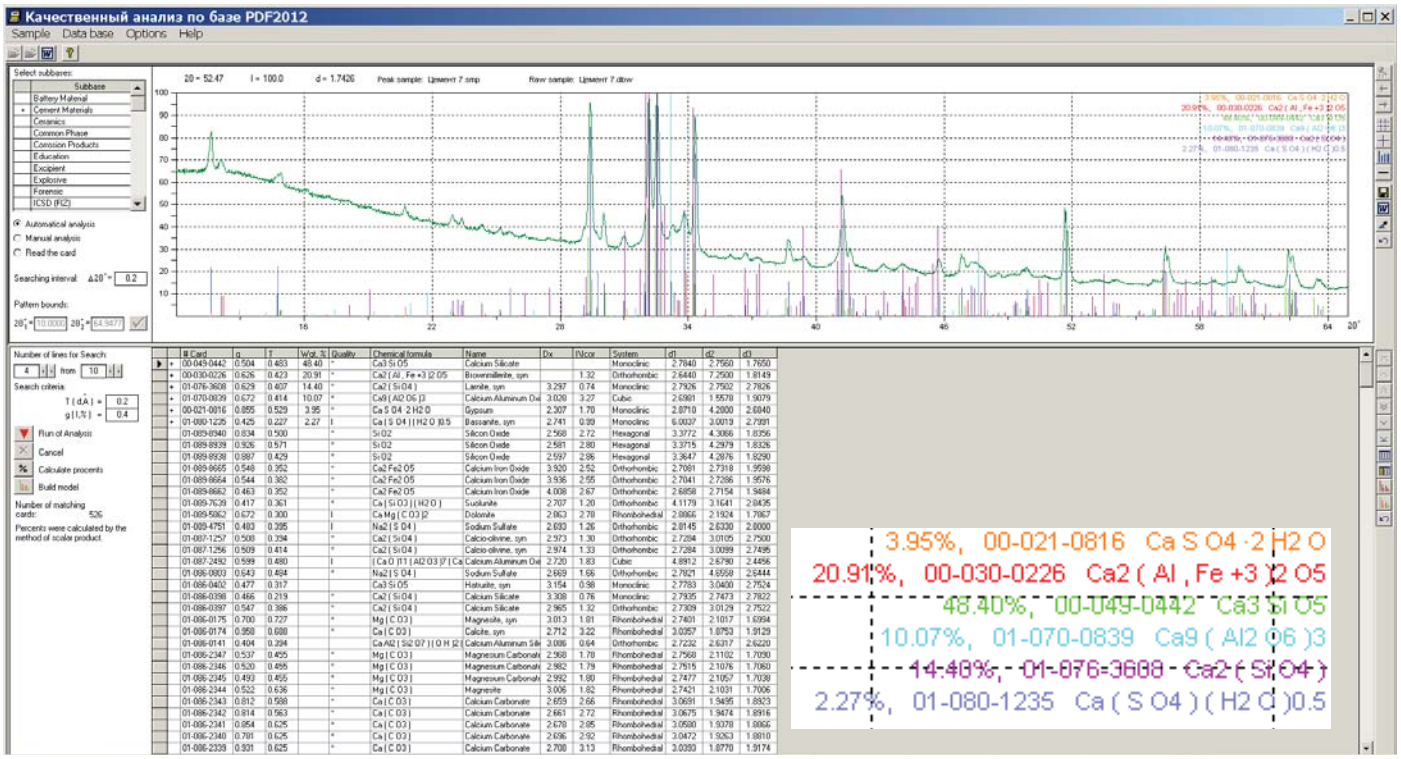
Fig. 3 Comparative analysis of measured XRD data for clinkers and cements.



Nomination of analytical lines of minor impurities and accessory minerals: G – gypsum, M – mayenite, B – bassanite, Q – quartz, FSp – alkaline feldspars, D – dolomite, C – calcite, L – lime (calcium oxide).

Рис. 4 Qualitative and semi-quantitative analysis of clinker and cement.





RIR for alite, one of the main components of clinker, is not available in PDF-2 database, therefore quantification by RIR method is not correct and shows lower concentration of alite.

Simulation of powder diffraction patterns of mineral mixtures has been carried out with TheorPattern program (developed by Bourevestnik JSC).

The following parameters have been set:

- geometrical parameters of X-ray optical system (goniometer radius, focus size of X-ray tube, widths and divergencies of collimation slits, distances between collimating elements, tube focus and receiving slit of the detector etc.);
- X-ray radiation, angular range, step size;
- profile function for peak approximation and background curve;
- average crystallite size (in microns) to simulate degree of crystallinity;
- atomic co-ordinates, thermal parameters and occupations of crystallographic positions in crystal structures of mixture components (available in CIF*-files in ICSD** or COD*** databases;
- concentrations of components in a mixture.

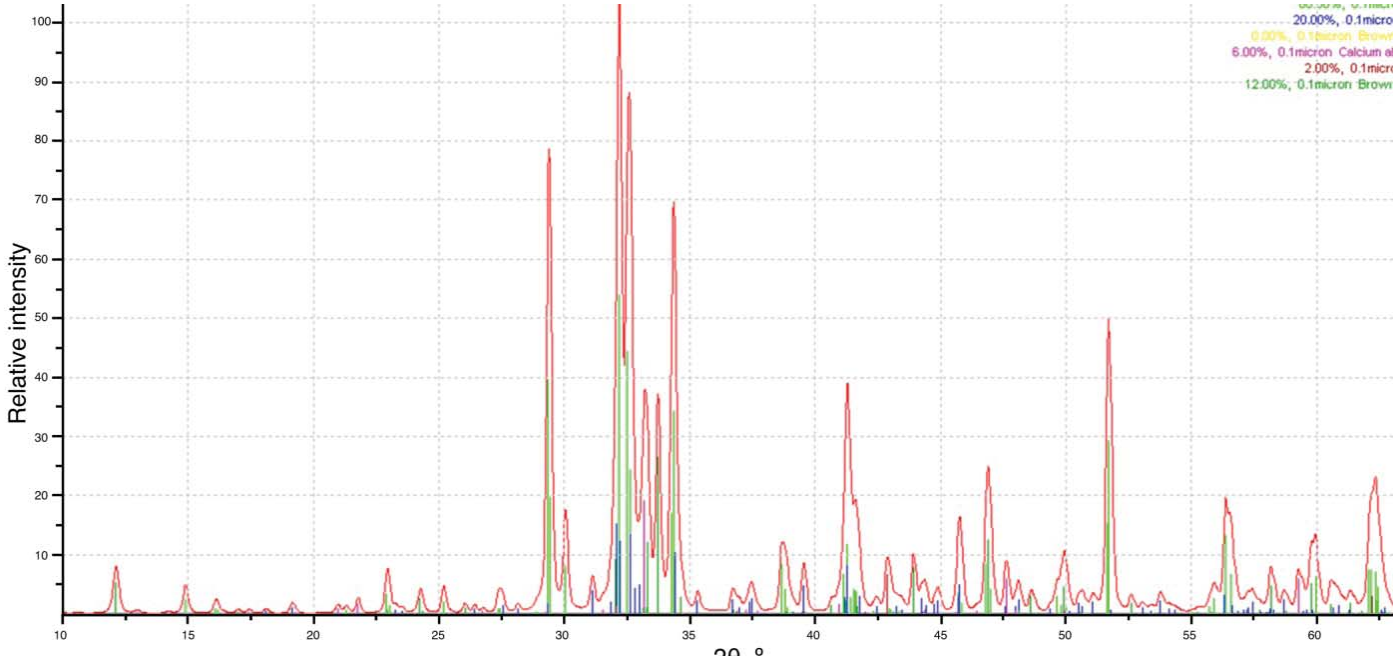
Notes:

***CIF – Crystallographic Information File*

***ICSD – Inorganic Crystal Structure Database/Developed by FZK Karlsruhe;*

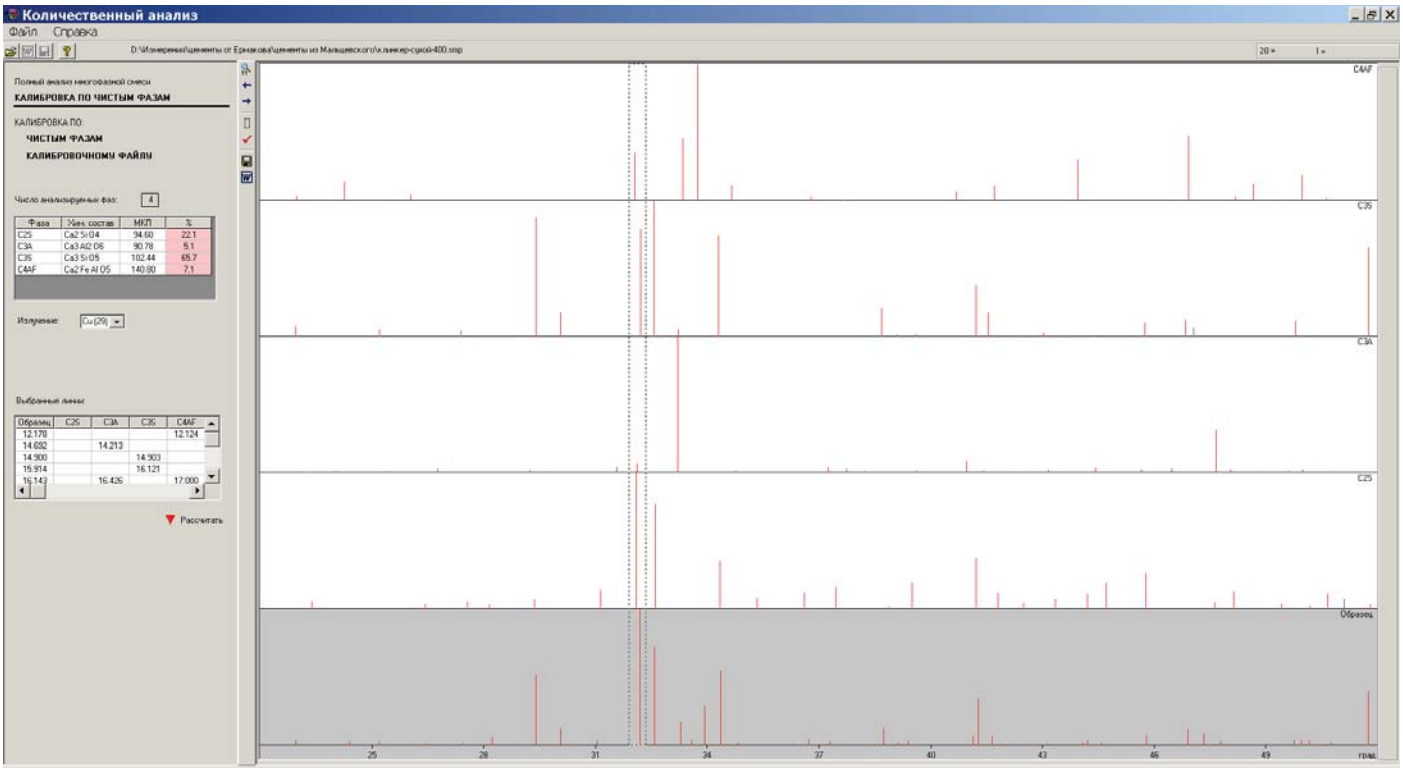
****COD – Crystallography Open Database http://www.crystallography.n*

Fig. 5 Simulated diffraction pattern of a clinker containing five minerals with average crystallite size of 0.1 μm



Quantification of mixtures by standard calibration has been performed with Quan program (developed by Bourevestnik, Inc.). Standard powder patterns for calibration have been calculated with with TheorPattern program from structural data taken from ICSD database..

Fig. 6 Quantification of clinker by standard calibration



Quantification of mixtures by Rietveld refinement has been carried out with Rietveld program (developed by Bourevestnik, Inc.). To calculate XRD pattern of mixture the structural data for components as CIF files from ICSD database have been set. The following parameters have been refined:

- zero shift and background polynomial coefficients, which are common for the whole pattern;
- peak profile parameters, unit cell constants, texture coefficient (if necessary), which are specific for each component;
- concentrations of components in a mixture.

Results of quantification are shown in Table 1.

Table 1. Results of quantification of clinkers and cements by Rietveld refinement

Smp-No	Type I/II*	Concentrations of minerals, wt. %											
		C_3S	C_2S	C AF	C_3A	G***	B	L	Q	C	D	M	A
1	K	63.5	21	11.5	4.5	-	-		-	-	-	-	-
2	K	65	16.5	12	6.5	-	-		-	-	-	-	-
3	K	66.2	15.3	14.2	4.3	-	-		-	-		-	-
4	K	66.7	6.0	13.3	2.8	-	-	-	-	-	1.7	6.9	2.6
5	K	63.9	15.4	11.6	3.4	-	-	-	-	-	-	4.0	1.6
6	K	80.3	-	11.8	6.0	-	-	1.9	-	-	-	-	-
7	Ц	60.2	14.2	11.9	5.1	4.6	1.4	-	-	2.6	-	-	-
8	Ц	57.7	16.9	9.3	6.7	5.4	0.6	-	-	3.4	-	-	-
9	Ц	57.6	13.3	10.4	5.1	5.1	0.6	-	0.8	7.1	-	-	-

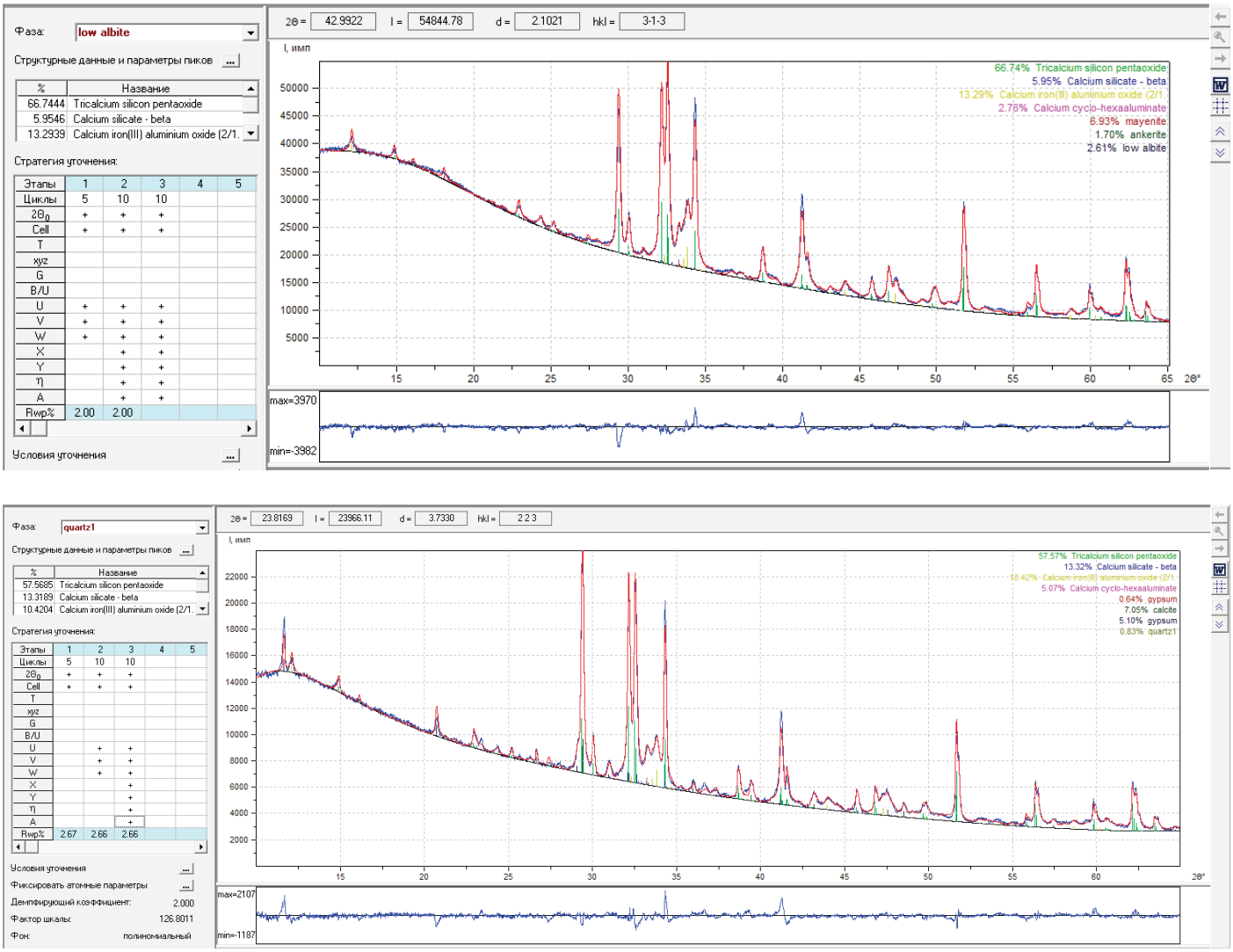
*I – clinker, II – cement

***Nomination of accessory minerals: G – gypsum, B – bassanite, L – lime (calcium oxide), Q – quartz, C – calcite, D – dolomite, M – mayenite, A – albite.

Table 2. Comparison of clinker quantification by different methods

Clinker		RIR (except alite)	Standard calibration	Rietveld refinement
	Alite Ca_3SiO_5	58	65	63.5
	Belite (larnite) Ca_2SiO_4	26	21.5	22.5
	Brawnmillerite $Ca_2(Al,Fe)_2O_5$	8	7.3	7.5
	Calcium aluminate (cub.) $Ca_3Al_2O_6$	8	6.2	6.5

Fig. 7 Quantification of clinker (a) and cement (b) by Rietveld refinement



Results and Discussion.

It is demonstrated that qualitative and quantitative phase analyses of cement products can be carefully done with DRON-8 multifuncional X-ray diffractometer developed by Bourevestnik Innovation Centre.

All the studied samples are polymineral mixtures (see Table 1), which contain various additives and minor impurities to the four basic cement minerals.

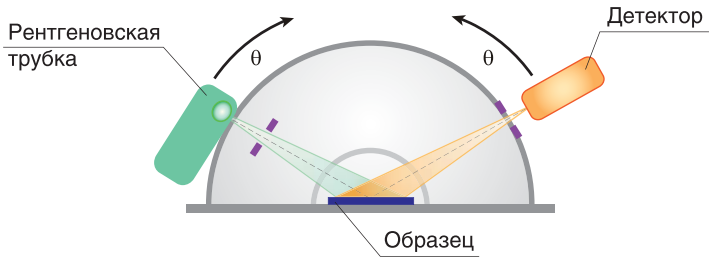
Accurate determination of minor impurities with concentrations below 3 wt% is acheivable from reliable diffraction data measured with linear stripped position-sensitive detector.

RIR method of express quantification gives in general lower accuracy of determination of component concentrations (2-3 wt%), therefore it is not recommended for quantification of clinkers and cements because of absence of RIR for alite in PDF-2 database.

Quantifications of cement products have been performed by two other well-known methods of analysis – by standard calibration and by Rietveld refinement. Comarison of the results is given in Table 2, which shows good agreement of data – within 1 wt% for main compomemts of clinker. Both methods require standard data on each component of mixture, which can be obtained with calcuation fron structural data. It is recommended to perform preliminary calculations of standard XRD patterns and to simulate patterns of mixtures from them to compare with measured patterns and to select the most reliable structural data for further analyses.

Technical data of diffractometer DRON-8.

Basic configuration

Goniometer		
Goniometer type		Vertical θ–θ
X-ray optical scheme		 Bragg-Brentano/Debye-Sherrer/paral-lel-beam
Radius R, mm		180 – 250
Angular range, deg	2θ	-10 - 165
	θ_F	-5 - 165
	θ_D	-5 - 95
Scanning modes		discrete/ continuous
Scanning methods		θ–θ, θ, Ω, 2θ-Ω, ψ, $\sin^2\psi$
Smallest addressable increment, deg		0.0005 (0.0001 - optional)
Scanning rate, deg/min		0.1 - 50
Reproducibility, deg		±0.001 (0.0001 - optional)
Maximum angular speed, deg/min		600 (2000 - optional)
Registration system (basic):		
Detector type		scintillation NaI (Tl)
Counting rate, count/sec		up to 500 000
High voltage power supply:		
Output power, kW		3
Output voltage, kV		0-60
Anode current, mA		0-80
Long term stability, %		0,01
Cooling agent		air
X-ray tube (basic):		
Type		2,5БСВ-27Cu
Cooling agent		water (3 l/min.)
Focus size, mm		10 x 1.6

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