Chemical and Instrumental Testing of Cement-Based Materials Leading to the Reconstitution of Their Substrate Composition

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Abstract

The article discusses testing of cement-based materials with the application of chemical analyses as well as of classical techniques according to the Polish standards: PN-EN 196–2:2006: "Methods for cement testing – Part 2: Chemical analysis of cement" and PN-EN 1744–1 "Tests for chemical properties of aggregates. Chemical analysis." The obtained testing results have been verified by means of instrumental methods using X-ray fluorescence spectroscopy (XRF) for materials with certified reference samples. In other cases interpolation techniques have been applied. Estimated substrate composition of the produced cement-based materials has been calculated based on the material balance using a computer program. Final results have been calculated as an arithmetic mean of all possible solutions that meet boundary conditions. Joint application of both the mentioned methods to reconstitute substrate composition of cement-based materials has yielded results that approach the originally applied real composition at the maximum difference of a few percent.

Keywords: concrete, portlandite, calcium silicate hydrate (C-S-H), mixture proportion, X-ray diffraction (XRD)

Introduction

Materials produced on the basis of cement such as mortars and concretes form as a result of setting and hardening processes in an adequately composed mixture, whose basic ingredients are cement, aggregate and mixing water. Cement binder and an adequate selection of the remaining ingredients decide over useful properties of those materials including their useful life and operational safety. Although cement-based materials are very popular and their production technologies are thoroughly recognized, it happens that the end products do not exhibit the designed strength characteristics and undergo unexpected corrosion (Czarnecki and Emmons 2002). In such cases it is necessary to reconstitute the originally applied composition of the mixture, out of which the faulty material has been produced (Jakubowska et al. 2009).

Elaboration of an algorithm to determine the original substrate composition of concrete and cementitious mortars has been the objective of the discussed project. Such an analysis does not make an easy task because the investigated materials are not uniform. Successful reconstitution of the initial composition depends on the information about the origin and kinds of the applied substrates as well as about the obtained end products. It seems necessary to perform such analyses at the quality inspection, at elaborating expertise opinions and at the heritage preservation works in order to determine original composition of the materials, when historical buildings are reconstructed.

The substrate composition reconstitution of the presented project has been realized according to the following procedure. First, cement-based materials have been designed and produced in the laboratory conditions. Then, they have been subjected to chemical analysis in order to determine their composition. Next, mathematical procedures have been used to elaborate many systems of material balance equations for the determined components (CaO, MgO, SiO_2, Fe_2O_3, Al_2O_3, SO_3) both in the substrates and in the products. Substrate ingredients (cement, sand, gravel aggregate)

have been the unknowns in the equations. Computer software has been used to perform the calculations and the obtained results have been compared to the real data. The attempted reconstitution of the original substrate composition has been performed for mortars and concrete based on portland cement as well as on the cement of increased aluminum and gypsum content.

1 Characteristics of the substrates and products

The testing has been performed on mineral materials that are substrates for the production of mortar and concrete and whose main ingredient is hydraulic binder — portland cement The remaining ingredients are: sand, mixing water and additionally, in the case of concrete, lightweight aggregate. Chemical composition of cement and many other building materials can be determined based on chemical analyses using classical or instrumental methods with the application of modern computing techniques that can be referred to as chemometrics (Jakubowska et al. 2009).

1.1 Cements

Presently, it is the portland cement that is the most often applied in the construction industry. Its chemical composition and four phases that can be distinguished in the portland cement is given in table 1.
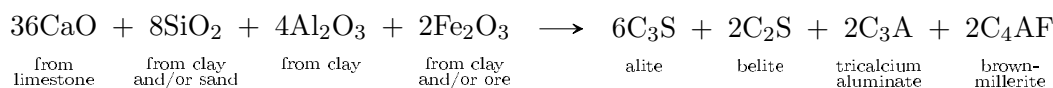
Tab. 1. Main chemical and mineralogical components of the cement

Component	Proportion[a]
CaO (C)	60–70
SiO_2 (S)	18–25
Al_2O_3 (A)	4–9
Fe_2O_3 (F)	1–5
SO_3 ($\bar{S}$)	1–3
$3CaO \cdot SiO_2$ (C$_3$S)	30–65
$2CaO \cdot SiO_2$ (C$_2$S).	15–45
$3CaO \cdot Al_2O_3$ (C$_3$A)	5–15
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (C$_4$AF)	5–15
$CaSO_4$ (C$\bar{S}$)	2–5

Source: Czarnecki and Emmons (2002)
[a]within the portland cement composition (in %)

Summary course of the cement clinker formation reaction:

$$36CaO \ + \ 8SiO_2 \ + \ 4Al_2O_3 \ + \ 2Fe_2O_3 \ \longrightarrow \ 6C_3S \ + \ 2C_2S \ + \ 2C_3A \ + \ 2C_4AF$$

from limestone | from clay and/or sand | from clay | from clay and/or ore | alite | belite | tricalcium aluminate | brown-millerite

The above mentioned mineralogical phases exhibit varied reactivity with water and that is why there is a practice to add some amount of gypsum to portland clinker in order control the setting processes and obtain adequate mechanical strength as well as corrosion resistance of the hydration products (Czarnecki and Emmons 2002). Chemical testing of the cement has been performed according to the Polish standard PN-EN 196–2:2006 "Methods for cement testing – Part 2: Chemical analysis of cement," as well as with the use of instrumental methods.

1.2 Mixing water

Mixing water makes an essential ingredient of concrete as it makes the cement setting processes possible and it influences consistency of the concrete mix. Only insignificant part of the water enters the chemical reaction with cement and most of it is necessary to ensure adequate plasticity of the mix. The operative PN-EN 1008:2002 standard determines chemical properties of water

that can be applied to the concrete production. Experiments of the discussed project have been performed using tap water of the Lublin municipality (Szymura 2006).

1.3 Aggregates for the construction mortars

Aggregate as a filler is a loose material that consists of solid coarse particulates. Chemical composition of selected aggregates, according to J. Piasta and W. Piasta (2002) depends on the area of their origin.

The volume of aggregate in concrete ranges from 60 to 75%. Many essential concrete characteristics depend on the applied aggregate and the most important among them are: compressive strength, thermal conductivity, density and resistance to various factors related to its functional use. Generally, aggregates to be applied as substrates to the production of concrete should exhibit: constancy of their physical characteristics, uniform grain-size distribution and they should not contain any components of negative effect on technical properties of concrete (Osiecka 2005).

Sand is also classified as a mineral aggregate of the grain size smaller than 2 mm. Construction industry uses aggregates of rocks that are characterized by high strength (e.g., granite, basalt, porphyry) for the production of concrete of considerable compressive strength and abrasion resistance as well as aggregates of lower-strength rocks (limestone, dolomite) to produce some concrete products that are used under lesser load. Special aggregates of high-density rocks (over 2600 kg/m^3) are applied to the production of heavy concretes for shielding purposes. For the research purposes of the discussed project lightweight coarse aggregate and sand sampled from the store of the Lu-

Tab. 2. Chemical composition of selected carbonate aggregates

Kind of rocks and the area of their occurrence	Loss on ignition (%)	Chemical composition (%)					Bulk density (kg/dm^3)	Porosity	Absorba-bility (%)	Compressi-ve strength (MPa)
		SiO$_2$	Al$_2$O$_3$	CaO	MgO	SO$_3$				
Compact limestone										
Jaźwica	43,3	1,0	0,5	54,4	0,5	vestige	2,72	1,8	0,89	97
Karwów	43,6	0,8	0,3	53,1	1,7	1,1	2,75	2,1	0,30	98
Kowala	41,8	4,4	1,3	51,4	2,1	0,1				75
Jaworznia	43,5	1,2	0,5	53,9	0,5	-	2,74	1,5	0,21	83
Bielawy	18–55	7–23	0,3	41–52	1,5	0,5–1,2	2,69	3,5	3,70	45
Ostrówka	43,3	0,2	0,1	54,9	0,3	-	2,70	0,4	0,10	140
Borsuki	42,1	21,8		32,8	2,1	vestige	2,67	7,0	5,90	26
Travertine										
Raciszyn	42,9	1,5	0,7	54,3	0,4	0,5	2,70	3,7	0,60	58
Porous limestone										
Trawniki	31,2	23,1	1,0	40,1	0,2	vestige	2,59	41,3	24,1	16
Karsy	27,3	34,7	0,9	34,6	0,4	0,4	2,50	42,0	26,0	15
Pińczów	43,3	3,8	0,9	52,5	0,8	vestige	2,68	35,5	16,3	10
Józefów	43,1	2,0		53,1	0,6	9,4	2,65	45,7	17,7	3

Source: Piasta and Piasta (2002)
Note: [In the journal (in both Polish and English texts) European practice of number notation is followed — for example, 36 333,33 (European style) = 36 333.33 (Canadian style) = 36,333.33 (US and British style). Furthermore in the International System of Units (SI units), fixed spaces rather than commas are used to mark off groups of three digits, both to the left and to the right of the decimal point. — Ed.]

blin University of Technology have been used. Chemical analyses have been performed according to the standard PN-EN 1744–1 "Tests for chemical properties of aggregates. Chemical analysis and the XRF method."

1.4 Concrete

According to the operative standard PN-EN 206–1:2000 "Concrete – Part 1: Specification, performance, production and conformity," ingredients for the designed concrete should be selected so

that the determined physical requirements are met. Requirements concerning chemical composition that are specified in the standard are reduced to the determination of the allowed chloride content in concrete.

All the phenomena concerning water effect on the cement binder are referred to as hydration-hydrolysis processes. They lead to the formation of a phase that is denoted by the acronym CSH (Calcium-Silicate-Hydrate)and the set paste can be described as a non-uniform structure of gel-like, amorphous and crystalline products of hydration of the cement component minerals (Kurdowski 2008a, 2008b). When cement gets mixed with water, chemical changes and physical processes occur at the surface of the cement grains as well as a result of dissolution of cement components and of some reaction products during the liquid phase.

Some component minerals of clinker such as: calcium aluminates and aluminoferrites dissolve congruently (i.e., with no chemical changes): and undergo hydration: $C_3A + 6H \longrightarrow C_3AH_6$ (hydrogarnet). In the presence of gypsum that acts as the setting process retardant, depending on the mole ratio of $C\underline{S}H_2/C_3A$, chemical reactions proceed and their product is ettringite or monosulphate:

$$C_3A + 3C\bar{S}H_2 + 26H \longrightarrow C_6A\bar{S}_3H_{32} \quad \text{or} \quad 2C_3A + C_6A\bar{S}_3H_{32} + 4H \longrightarrow 4C_4A\bar{S}H_{12}$$

In the presence of gypsum, brownmillerite forms the same phases ofettringite $C_6(A,F)\bar{S}_3H_{32}$ or monosulphate $C_4(A,F)\bar{S}H_{12}$.

Alite and belite dissolve in an incongruent way — with decomposition resulting from hydrolysis. In a simplified way, the reactions can be written as follows:

$$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3CH \quad \text{and} \quad 2C_2S + 4H \longrightarrow C_3S_2H_3 + CH$$
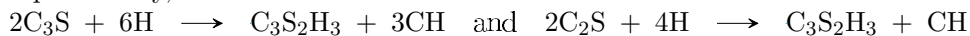
The products of those changes are: calcium hydroxide (CH) and an amorphous gel-like substance that is for short referred to as CSH (calcium silicate hydrate), whose CaO/SiO_2 composition is variable and depends on the concentration of Ca^{2+} ions in the liquid phase (i.e., on the saturation ratio relative to CH).
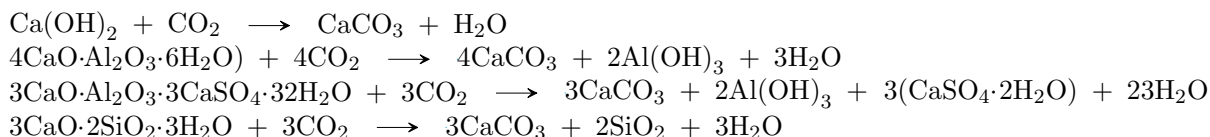
Approximate volumetric composition of the hydrated cement individual phases is the following: 55–65% — gel phase CSH, 15–20% — CH crystals, 8–10% — crystals ofettringiteandmonosulphate, ca. 15% — capillary pores that form as a result of water evaporation.

The CSH phase is the main component of the cement matrix and its content influences basic properties of the cement with its strength and corrosion resistance in particular. This phase is characterized by the prevalent gel-like structure of variable chemical composition and varied degree of crystallinity. It forms when tetrahedra of orthosilicate anions link together forming trimers, pentamers and longer wollastonite chains. This phase exhibits extraordinary properties and for that reason it is an object of vivid interest, many research projects and hypotheses. It follows from the in-depth investigations of many authors that in the CSH gel, depending on the Ca/Si ratio, fibrous or film-like crystallites form, whose structure resembles tobermorite (Kurdowski 2008a, 2008b; Taylor 1993).

Energy of the tobermorite crystal lattice is 26 535 kJ/mol, which is 2,5 times more as compared to alite and over 7 times more in the case of calcium oxide. Richardson and Groves have proposed a generalized model of the solid solution of CH in tobermorite as well as combining the areas of the jennite and tobermorite structures. However, it is gel dispersion that is the basic structure of the CSH phase. Owing to its cohesion forces the forming structure gets compacted and retains plasticity at low stresses (Taylor 1993).

The CSH phase structures also include other macro-components such as Al, S and Fe. According to many researchers, they replace Si in tetrahedra as Mg can isomorphously replace Ca (Bullarda et al. 2011; Kurdowski 2008a, 2008b). Such solid solutions and mixtures with the CAF and $C\bar{S}A$, phases yield significant bonds that influence characteristics of concrete materials. The amount of water in CSH depends on the ambient humidity and can be removed or replenished when the humidity changes (Taylor 1993).

As the time passes, in a humid environment components of the hardened cement paste bind CO_2 from the air.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$
$$4CaO \cdot Al_2O_3 \cdot 6H_2O) + 4CO_2 \longrightarrow 4CaCO_3 + 2Al(OH)_3 + 3H_2O$$
$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3CO_2 \longrightarrow 3CaCO_3 + 2Al(OH)_3 + 3(CaSO_4 \cdot 2H_2O) + 23H_2O$$
$$3CaO \cdot 2SiO_2 \cdot 3H_2O + 3CO_2 \longrightarrow 3CaCO_3 + 2SiO_2 + 3H_2O$$

During a one-year period, a thin layer of concrete of the 0,5÷1 mm thickness undergoes carbonatization.

Balancing of chemical components during the setting processes indicates that the substrate macro-components (Ca, Si, S, Al, Fe) introduced with cement, aggregate and water remain in the concrete. Concentration of those components in water is by three orders lower than in the remaining substrates, which is a value approaching the analytic determination error level and that is why they have been neglected in the balance equations. The substrate content of cement, aggregate and sand remains unchanged in the concrete product, while the amount of water in the concrete differs from the amount of mixing water designed for the concrete mix and depends on the ambient humidity (9).

As well as on the concrete age, which is the reason why it has been neglected in the balance calculations. Its share has been calculated as the 100% complement. In older concretes, CO_2 from the air should be considered as it enters the composition of concrete by the carbonatization processes. Concrete testing of the discussed project has been performed after the lapse of 28 days and the mentioned component could not have any significant effect on the results, so it has been neglected.

2 Chemical analysis methods applied to testing of building materials

Laboratory testing for the chemical composition of building materials is usually performed by classical methods that are recommended by the operative standard for the determination of components in cement, mixing water and aggregate. In specialized laboratories of construction chemistry the analyses are also performed by instrumental methods, with the application of the modern-day apparatus.

The PN-EN 196–2 standard includes a description of classical methods for chemical analyses to be applied for the cement testing purposes, Standard and alternative methods are presented there and results obtained with the alternative methods match the results of the standard procedures. Prior to the chemical analysis procedures, samples for the testing should be adequately prepared according to the PN-EN 196–7 standard.

Among the modern-day measuring techniques that make possible to determine quantitative elemental composition of the tested materials there are methods of atomic spectroscopy. X-ray fluorescence spectroscopy (XRF) is one of the atomic spectroscopy methods that is widely applied for quantitative and qualitative elemental analyses also in the cement plant laboratories.

Another kind of innovative chemical analysis techniques for the testing of building materials is a quite recent and still very expensive application of scanning electron microscopes coupled with automatic systems for elemental microanalysis (e.g., Quantitative Evaluation of Minerals by Scanning electron microscopy QEMSCAN).

3 Experimental

Within the discussed project, an algorithm for the determination of the concrete and mortar substrate composition has been elaborated. Its accuracy has been evaluated by comparing the obtained results to the original composition that has been real-time used to produce the testing samples (mortar and concrete).

The applied laboratory procedures have included sampling of mortar and concrete according to the operative standard with the use of the below given substrate ingredients that have been designed in mass proportions at the consistency correction:
- portlandcement mortar → portland cement : sand : water—3,7 : 5,6 : 1,0
- portlandcement concrete→ portlandcement : sand : gravel : water—2,0 : 3,4 : 6,9 : 1,0

Chemical testing has been performed to determine the content of basic elements in the substrates (cements, mixing water, sand and aggregate) and in the products i.e. in mortars and concretes that have been produced out of the substrates.
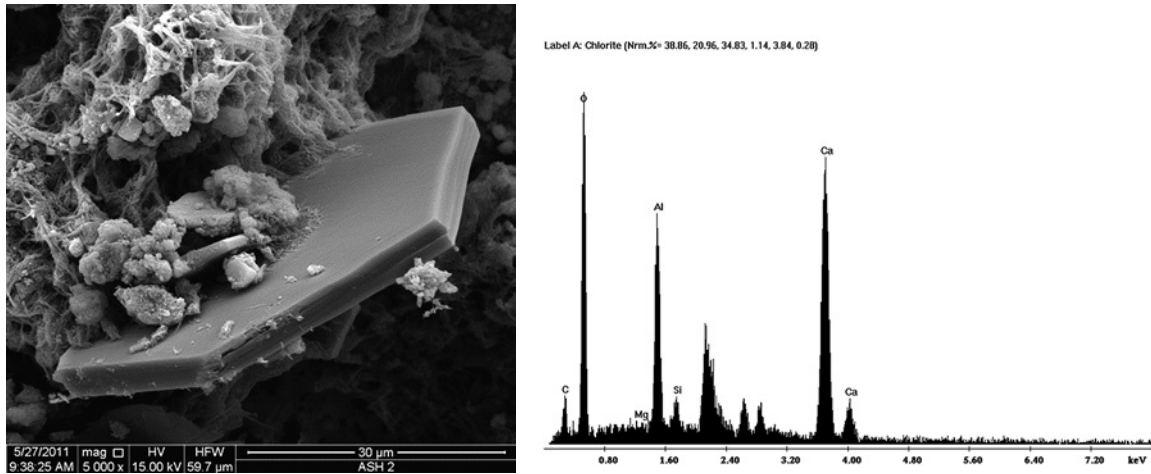

Fig. 1. SEM image of the cement mortar microstructure obtained with the use of a scanning microscope QUANTA FEG 250 (Fei-SEM). At the right — EDS image of a sample of that cement mortar

The following components have been determined: CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3.

Quantitative analyses have been performed with classical methods, according to the operative standards (PN-EN 206–1:2006) as well as using the XRF technique with the application of an X-ray fluorescence spectrometer of the Philips manufacture (model PW 1606).

As far as cement testing is concerned, chemical analysis techniques are classified as standard or alternative methods. Some of the instrumental methods can be applied the alternative way, but only in the case when certified reference samples are used.
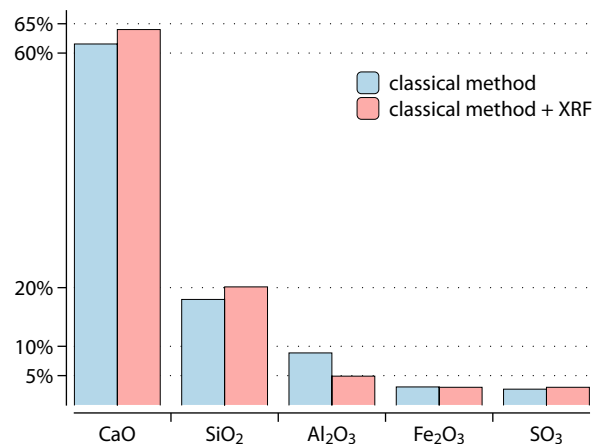

Fig. 2. Results of the portland cement CEM I 32,5 R analysis performed with a classical method as well as with the XRF method

Within the discussed project, analytical testing of all substrate components as well as of the mortar and concrete (when 28 days of the setting period have passed) has been performed with classical methods, according to the aforementioned standard, while cements have been analyzed using both kinds of the methods as only in that case standard reference samples have been available.

The application of X-ray fluorescence (XRF techniques) to chemical analyses of building materials yields fast and accurate results, but as it requires standard reference samples for the calibration purposes it cannot be used to determine chemical composition of aggregates, mortars and concretes. Chemical analyses of building materials performed with the use of classical methods,

according to the standard PN-EN 206–1:2006, are characterized by lower accuracy and are time-consuming, but make possible to determine chemical composition not only of cements, but also of aggregates, mortars and concretes if the samples are adequately prepared prior to the testing. Accuracy of the obtained results depends mainly on a kind of the performed analysis, the applied reagents and very careful sampling.

The procedures require the application of many reagents, which can be a source of contamination. The performed testing has shown that the least accurate result has been obtained for the aluminum oxide (tab. 3). Therefore, additional calculations have been performed using interpolation of the obtained concentrations of individual materials determined both with classical and XRF methods. All the tests have been performed in the laboratory of construction engineering of the Lublin University of Technology and in a laboratory of the cement plant Cemex in Chełm.

Reconstitution of the original substrate composition for mortar and concrete

Determination of the original substrate composition for concretes and mortars with the application of research methods has been done at the assumption that the oxide composition of individual substrates and products is already known owing to the earlier performed chemical analyses (Szymura 2012). Table 3 presents oxide composition of the substrates and table 4 – of the portland cement based products. The performed analyses have shown that composition of the tested materials includes also other chemical compounds than the determined ones. Notably, the sample of coarse aggregate (gravel) has included carbonate rock chips. The decrement of ca 20% of its mass that has occurred in the course of pyroprocessing has complemented the component balance of the aggregate as well as of the concrete with the bound water taken into account.

In order to determine substrate composition of cement-based materials an algorithm has been proposed with the application of chemical analysis techniques and mathematical apparatus including matrix determinants. Calculations have been performed with the use of the Microsoft Office Excel software. In order to reconstitute substrate composition of the tested cement mortar and concrete, material balance has been elaborated for each of their determined constituents. In the equations, water components have been neglected considering their negligibly low concentrations

Tab. 3. Chemical composition of the substrate materials obtained with classical methods (k) and with classical methods + XRF (k+X) (in %)

Component	Cement		Sand		Gravel		Mixing water
	k	k+X	k	k+X	k	k+X	k
CaO	61,55	64,01	3,20	3,20	20,37	20,37	0,020
SiO_2	17,99	20,13	87,74	87,74	53,27	53,27	-
Al_2O_3	8,87	4,91	0,58	0,32	1,19	0,66	-
Fe_2O_3	3,07	3,10	0,44	0,43	1,17	1,17	0,005
SO_3	2,69	3,01	0,02	0,02	0,08	0,08	0,007
Other comp.	5,83	4,84	8,02	8,29	23,92	24,45	99,968

Tab. 4. Chemical composition of the products obtained using classical methods (k) and classical methods + XRF (k+X) (in %)

Component	Mortar		Concrete	
	k	k+X	k	k+X
CaO	22,50	22,50	20,44	20,44
SiO_2	54,95	54,95	54,12	54,12
Al_2O_3	3,29	2,16	2,21	1,45
Fe_2O_3	1,26	1,26	1,16	1,16
SO_3	0,92	0,95	0,45	0,47
Other comp.	17,08	18,18	22,62	22,36

(tab. 3). In the final calculations, the water amount has been established as the remaining part, when from the sample as a whole (100%) a total of the calculated components has been subtracted.

Figures 3 and 4 show substrate composition of mortar and concrete that have been produced on the basis of the portland cement CEM I 32,5R. The values presented in the diagrams have been calculated using chemical analyses and the elaborated algorithm. Content proportions of individual ingredients in the mix are marked at making the distinction between the values obtained using classical testing methods and the ones obtained with classical techniques + instrumental ones. For the sake of comparison, the real-time used ingredient proportions are also shown.

It should be noted that the value defined as "water" in the mortar and concrete is not exactly the amount of water that has been really used to produce those materials. In practice, it is a total amount of water that includes: the water participating in the setting process, the water remaining in the pores, the evaporated water and also carbon dioxide CO_2 bound in the process of the binder carbonatization.
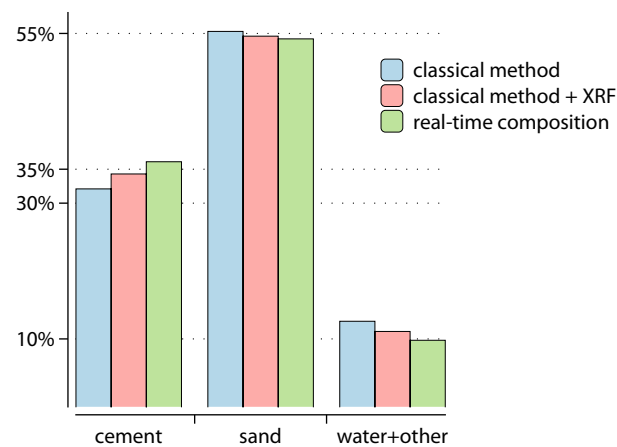

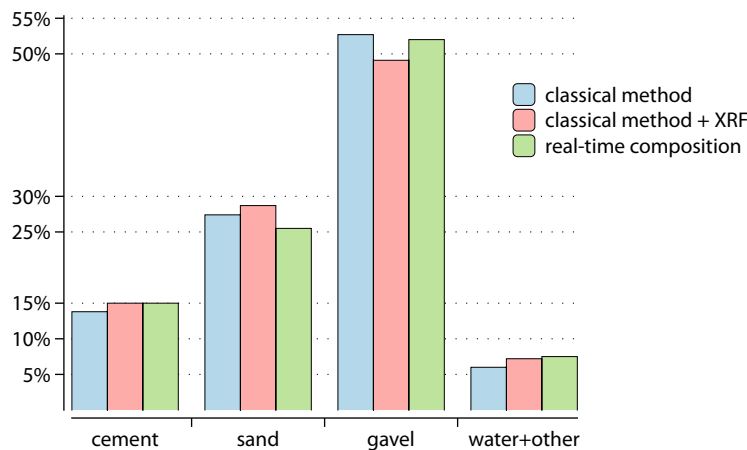**Fig. 3.** Substrate composition of mortar

Fig. 4. Substrate composition of concrete

Recapitulation and conclusions

In the case of cement, the results of quantitative analyses performed with the use of classical methods, according to the operative standards, have been less accurate than the ones obtained with the XRF techniques. It is particularly conspicuous in the case of the alumina concentration. For the Portland cement it amounts to 12,74% (fig. 2), which is a much overestimated value as compared to the standard values 4–9% (tab. 1). A comparative analysis of the content percentage obtained for the remaining chemical components to their standard content interval syndicates that the results of cement analyses performed with the both methods are contained within the allowed limits.

The testing results obtained with the use of classical techniques and with instrumental methods approach one another with the distribution spread not greater than a few percent. In each case, adequate preparation of the samples is of crucial importance, especially their homogenization.

The applicability of instrumental methods to quantitative analyses of building materials is limited as they can be used for that purpose only when adequate standard reference samples are available. The application range of classical methods is wider. With interpolation applied to determine concentrations of chemical components required for the reconstitution of the original composition of cementitious materials it is possible to obtain more accurate results in the case of the portland cement mortars and concretes.

Estimated quantities of individual substrates obtained based on the proposed algorithm with both classical methods and the modified ones with the XRF results taken into account approach the real-time used composition of the ordinary mortars and concretes that have been tested within the discussed project. In order to generalize the above observations over a wider range of cases, it is necessary to perform more extensive testing with the use of extended range of substrates proportioned various ways

At the reconstitution of concrete and mortar substrate composition the greatest discrepancies have been observed for the case of the "water" component (water + the other components). However, it should be emphasized that the substrate water cannot be balanced for the end product. Practically, it is a total amount of water composed of the water participating in the setting process, the water remaining in the pores, the evaporated water and also of a new component, that is carbon dioxide CO_2 bound in the carbonatization process, which makes an added value only in the case of concrete.

Algorithm for the reconstitution of the mortar and concrete substrate composition that has been used for calculations of the discussed project is characterized by comparatively high accuracy (differences of the 3% order). The accuracy can be improved by minimizing the sources of faulty solutions of the balance equation systems. The most important are efficient methods of chemical analysis that can accurately determine chemical composition of individual materials.

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