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# COMPOSITION RECONSTITUTION OF CONCRETE AND MORTARS BASED ON PORTLAND AND EXPANSIVE CEMENTS

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Abstract. Preliminary research aiming at the reconstitution of concrete and mortar substrate composition with the application of classical analytical methods and XRF is described. Approximate calculations of the substrate composition have been performed on the basis of an algorithm that consists in determining content proportions of calcium oxide, silica, alumina, iron oxide, sulfur trioxide and chlorides in substrates and products, elaborating linear equations with material balance for individual oxides in substrates and products, setting equation systems of two unknowns (cement, sand) for mortars and three unknowns (cement sand, coarse aggregate) for concretes, and finally solving all possible arrangements of equations with the use of a computer software. Mean values of all possible solutions have been accepted as final results. The determined initial composition is close to the real one with maximum differences of about 3%. The elaborated algorithm cannot be applied to calculate substrate composition when sulfur oxides and aluminum occur simultaneously in the balance equation.

keywords: cement binders, concrete mix composition, chemical analysis of cementitious materials

# 1. Introduction

Artificial stone, that is materials produced on the basis of cement, is the most often used material in construction engineering. Mortars and concretes belong to that group. They form, as a result of setting and hardening, a mixture which basic components are cement, aggregate and mixing water combined in adequate proportions. Hazard condition assessment and analysis of concrete construction damages that would lead to the determination of causes of those damages make an essential problem (Jamrozy, 2008). Cementitious materials compose or enter the composition of structural (load-bearing) elements and that is why they should exhibit adequate strength properties that considerably depend on their chemical composition (Czarnecki, 2004; Kurdowski, 2000). For that reason determination of chemical and mineral composition of concretes or mortars makes possible to find out many of their properties and thereby to establish some technical characteristics (physical-chemical and mechanical

properties). Chemical composition of cement as well as many other construction materials can be determined by means of chemical analysis methods (classical or instrumental) with the application of modern computational techniques that can be referred to as chemometry (Mazerski, 2000; Massart et al., 1998).

Although cementitious materials are very popular and the knowledge of their production technologies is very extensive, it happens that the end products do not meet designed strength standards or undergo unexpected corrosion (Czarnecki and Emmons, 2002). In such cases it is necessary to reconstitute the composition of the mixture out of which the faulty material has been produced (Jakubowska et al., 2009). Such analysis is not an easy task as the tested materials, that is concretes and mortars, are not uniform. Successful reconstitution of composition depends on numerous data concerning origin and kinds of the applied substrates as well as of the products whose initial composition is to be determined.

Within the presented research project, cement-based materials have been designed and produced under laboratory conditions. Their raw-material composition has been reconstituted with the application of chemical analysis methods and mathematical calculations that consist in the elaboration of many material-balance equation systems for individual determined components (CaO, MgO, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>, Cl) where substrate components (e.g. cement, sand, aggregate) are the unknowns. The calculations have been performed with the use of computer software and the obtained results have been compared to the real data.

The experiments on raw-material composition reconstitution have been performed for mortars and concrete produced on the basis of portland cement and expansive cement (Krol and Tur, 1999; Peukert, 2000).

## 2. Characteristics of the tested materials: substrates and products

Mineral materials with a hydraulic binder (cement) as their main component have been tested.

#### 2.1 Cements

Presently, among cements the portland cement is the most often used in the building industry. A variety of strength values and curing rates characterize that kind of cement (Kurdowski, 1991). It is produced in special kilns out of natural rock materials like limestone, clay, marlstone, chalk, diatomaceous earth, or high-silica sand. After having been processed the mentioned raw materials assume a form of porous baked nodules whose dimensions do not exceed 20 mm and are called portland cement clinker. In order to control the setting behavior gypsum is added during the clinker grinding process. The ground mixture of clinker and gypsum is referred to as portland cement. Portland cement clinker makes also a basis for the production of other cement varieties. Its properties influence physical-chemical characteristics of the

final product. That is the reason why it is essential to adequately proportion individual raw materials, make them uniform and process properly.

Properly prepared rawmix should include components shown in Table 1. The components can be found in limestone and clay or in marlstone, in a bonded form.

No.	Component	Proportion in the portland cement composition (%)
1	CaO	60-70
2	SiO <sub>2</sub>	18-25
3	$Al_2O_3$	4-9
4	$Fe_2O_3$	1-5
5	MgO	1-5
6	$SO_3$	1-3
7	$Na_2O + K_2O$	0.5 - 1.8

Table 1. Main chemical components of cement (Jamrozy, 2008)

The following four mineralogical phases can be distinguished in the final product:

– alite –  $C_3S$  or tricalcium silicate  $3CaO \cdot SiO_2$ , participates in the formation of initial mechanical strength, longtime strength also depends on the mineral, content from 30 to 65%

– belite –  $C_2S$  or dicalcium silicate 2CaO·SiO\_2, it sets slower than  $C_3S,$  content from 15 to 45%

– tricalcium aluminate (celite) –  $C_3A$  or  $3CaO \cdot Al_2O_3$ , the quickest reaction with water, content from 5 to 15%

- brownmillerite  $-C_4AF$  or tetracalcium aluminoferrite  $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ , one of the ferrites (there are also  $C_6A_2F$ ,  $C_6AF_2$ ), content from 5 to 15%.

Individual minerals differ in the way they undergo the hydration process (different reactivity with water) as well as in their share in the formation of chemical resistance and mechanical strength of the hardened cement paste.

Three characteristic processes that change structures of individual minerals can be distinguished as the process of setting and hardening runs (Kurdowski, 2008): dissolution of some minerals in water, hydrolysis, that is a chemical reaction of the mineral with water that makes the mineral decompose into constituent elements, and hydration, that is chemical binding of water by the mineral.

The addition of gypsum makes sulfate ions  $SO_4^{2-}$  react with already hydrating  $C_3A$ , which forms a layer of ettringite ( $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ ) on its surface that inhibits the disadvantageous process of  $C_3A$  hydration and makes hydration of calcium silicates (mainly of alite) run in an undisturbed way. The reaction produces a phase denoted by the formula CSH. It makes the main component of most cement pastes and the most essential factor that determines strength of the hardening mix. At the same time calcium hydroxide (portlandite) forms.

## 3. Experimental

#### 3.1. Results and discussion

The presented research project has aimed at elaborating an algorithm for the determination of an initial raw-material composition of concretes and mortars and evaluating its accuracy by the comparison of the obtained substrate content values to the quantities real-time used for the product production.

The testing range has included tests on the content proportions of basic elements in substrates (cements, mixing water, sand, aggregate) and in products (mortars and concretes). The following components have been determined: CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub> and chlorides.

Quantitative analysis testing has been performed by classical methods concordant with operative standards and partly by means of XRF techniques with the application of an x-ray fluorescence spectrometer, manufactured by Philips, model PW 1606.

Chemical-analysis techniques that meet the PN-EN 206-1:2006 standard requirements and concern cement testing are of the status of standard model methods or alternative ones. Some of instrumental methods can be alternatively applied but only in the case when they use certified calibration patterns, Within the presented research work testing of all raw-material components as well as of mortar and concrete (after 28 days of the setting period) has been performed by classical methods described in the PN-EN standard while cement analyses have been done by both kinds of methods as only for that case calibration patterns have been available.



Fig. 1. Analysis results for expansive cement (Krol and Tur, 1999) sampled from the store of the Lublin University of Technology and tested by classical and instrumental (XRF) methods

The use of XRF techniques for chemical testing of building materials yields fast and accurate results but requires the application of calibration patterns that presently are not available for aggregates, mortars and concretes and that is why chemical composition of those materials cannot be determined that way. Chemical testing of building materials performed by classical methods recommended in the PN-EN 206-1:2006 Standard is characterized by lower accuracy and is more time-consuming but makes possible to determine chemical composition not only of cements bur also of aggregates, mortars and concretes with their samples adequately prepared prior to the testing.



Fig. 2. Analysis results obtained by classical and XRF methods for portland cement CEM I 32,5 R of Chelm Cement Plant

Accuracy of the results depends mainly on a kind of the performed analysis, the determined component, applied reagents, and careful preparation of the sample. Some of the needed reagents are expensive and hard to obtain. Additionally, some of them can be a source of contamination. The performed testing has shown that the most inaccurate result has been obtained for a sample of aluminum oxide. For that reason additional calculations have been performed using interpolation of the obtained concentrations of individual materials determined both by classical and XRF methods.

Reconstitution of initial composition shown by the example of concretes and expansive mortars

Determination of the initial chemical composition for concretes and mortars with the application of research methods starts at the assumption that oxide constitutions of individual substrates and products are already known.

Table 2 presents oxide constitution of substrates and expansive products. An analysis of the presented materials indicates that there are also other compounds that enter their constitution. Notably, a coarse aggregate (gravel) sample has included carbonate rock chips. In the course of pyroprocessing its mass decrement of ca 20% has occurred and has complemented component balance of the aggregate as well as of the concrete with bonded water taken into account.

For the determination of raw-material composition of cementitious materials an algorithm in the form of an equation system has been proposed. It uses mathematical apparatus including matrix determinants. Calculations have been performed with the use of the Microsoft Office Excel software.

Based on the obtained results concerning oxide constitution of cement, sand, and gravel as well as of concrete and mortar material balance has been elaborated for each of the components. For concrete, many alternative equation arrangements in systems, of three equations with three unknowns representing components required for its manufacture (cement, sand, gravel) have been elaborated. In the case of mortar the

elaborated systems included two equations with two unknowns representing percent proportions of cement and sand. The following symbols have been used in the equations to denote the unknowns:

c – percentage of portland or expansive cement in a product (concrete or mortar)

p – percentage of sand in a product (concrete and mortar)

z – percentage of gravel in a product (only concrete).

Table 2. Chemical composition of the tested materials obtained by means of classical analyses

Chemical	Expansive concrete	Expansive mortar	Sand	Gravel
composition	Content (%)			
CaO	24.27	27.82	3.2	20.37
$SiO_2$	47.74	45.59	87.74	53.27
$Al_2O_3$	3.88	5.71	0.58	1.19
$Fe_2O_3$	0.96	0.94	0.44	1.17
$SO_3$	1.17	2.1	0.02	0.08
Cl	0.1	0.07	0.15	0.15
Sum	78.12	82.23	92.13	76.23

For the sake of clarity in presenting all the arrangements composed of equations for individual chemical components, the following notation has been used to represent the components in each of the tables:

 $\overline{C}$  – calcium oxide (CaO); S – silica (SiO<sub>2</sub>); A – alumina (Al<sub>2</sub>O<sub>3</sub>); F – iron oxide (Fe<sub>2</sub>O<sub>3</sub>);

S – sulfur trioxide (SO<sub>3</sub>); Cl – chloride ions (Cl<sup>-</sup>).

In the equations, water components have been neglected considering their low concentrations. In final calculations, water quantity has been established as the remaining part when from the sample whole a total of the calculated components has been subtracted.

A number of all possible arrangements has been calculated (Nahorska, 2002):

$$C_k^n = \frac{n!}{k! \cdot (n-k)!},$$

where: n – number of all possible equations, k – number of equations in a system. Respectively:

- for concretes: 
$$C_3^6 = \frac{6!}{3!(6-3)!} = 20$$
  
- for mortars:  $C_2^6 = \frac{6!}{2!(6-2)!} = 15$ 

Equation systems have been elaborated with the use of computer software (MathCad and Microsoft Office Excel).

Below given are example balance equations for expansive concrete and expansive mortar analyzed by classical methods: for concrete:

0.6169c + 0.0320p + 0.2037k = 24.2700 calcium oxide 0.1274c + 0.0058p + 0.0119k = 3.8800 alumina 0.1711c + 0.8774p + 0.5327k = 47.7400 silica, boundary conditions: c + p + k < 100, c > 0, p > 0, k > 0,solution of the equation system: c = 25.787, p = 27.037, k = 36.804,where: c, p, k – percent proportions of expansive cement, sand, coarse aggregate in expansive concrete. For mortar: 0.1274c + 0.0058p = 5.7100 alumina

0.1214c + 0.0036p = 3.7100 additional 0.1711c + 0.8774p = 45.5900 silica c + p < 100, c > 0, p > 0

solution of the equation system: c = 42.834, p = 43.607, where: c, p – percent proportions of expansive cement and sand in expansive mortar.

Tables 3 and 4 present example balance arrangements and solutions of equation systems. Percent proportions of individual concrete or mortar components have been calculated as arithmetic means of results obtained for all the arrangements. In all the elaborated equations water fraction has been neglected as it contains only minute quantities of the balanced chemical components. Two repeating arrangements of equations for concrete:  $CaO + SO_3 + Al_2O_3$  and  $CaO + SO_3 + Fe_2O_3$ , have been rejected because of a disproportionate difference in the results.

All the equations systems have been solved with the use of matrix determinants. In the case of concrete (three variables), at calculating main determinants W for individual equation systems Sarrus rule has been applied and values of all the unknowns (c, p, z) have been calculated based on Cramer formulas (Krysicki and Wlodarski, 2005). Determinants for all the equation systems, both for mortar and concrete, have been calculated using software of the Microsoft Office Excel 2003.

Both for mortar and concrete, correct solutions have been obtained only by equation systems with a non-zero main determinant that is by determined systems that have only one solution in the form of the searched values of unknowns with all those calculated values (c, p, z for concrete and c, p for mortar) meeting earlier determined boundary conditions. It has been noted that results obtained for expansive and portland cements by the C+S+A i C+S+F arrangements (Table 3) do not meet boundary conditions which means that mathematical equations.

It has been noted that results obtained for expansive and portland cements by the C+S+A i C+S+F arrangements (Table 3) do not meet boundary conditions which means that mathematical equations with the calcium sulfate participation are more implicit.

Figures 3 and 4 present raw-material composition of expansive materials – concrete and mortar. It has been calculated on the basis of chemical analyses and the elaborated algorithm. Percent proportions of individual mix components obtained with

the use of classical analytic methods and with classical + instrumental methods have been marked. The calculated results have been compared to real-time raw-material composition. Figures 5 and 6 present results obtained for mortar and concrete based on portland cement CEM I 32,5 R.

Classical methods		Classical and instrumental analytical methods				
Arrangements	Cement (%)	Sand (%)	Gravel (%)	Cement (%)	Sand	Gravel
					(%)	(%)
A+S+C	25.787	27.037	36.804	25.892	27.140	35.629
$A+S+\underline{S}$	-	-	-	-	-	-
A+S+Cl	25.889	27.856	35.424	25.918	27.364	35.251
A+S+F	25.913	27.973	35.227	25.857	26.842	36.161
$C+S+\underline{S}$	23.051	22.08	45.852	22.994	21.883	45.321
S+C+Cl	26.184	27.773	35.469	26.000	27.335	35.269
S+C+F	26.695	28.701	33.776	25.607	26.622	36.583
$C+\underline{S}+Cl$	23.059	17.039	46.62	23.002	16.918	46.082
$C+\underline{S}+F$	-	-	-	23.019	6.808	47.619
$C+\underline{S}+A$	-	-	-	22.095	1.152	33.410
<u>S</u> +Cl+F	23.119	21.961	41.69	23.047	20.601	42.392
<u>S</u> +Cl+A	-	-	-	-	-	-
<u>S</u> +Cl+S	23.201	28.639	35.001	23.141	28.336	34.645
Cl+F+A	25.911	28.095	35.184	25.846	26.256	36.366
Cl+F+S	25.814	27.881	35.411	26.342	27.215	35.343
Cl+F+C	26.929	30.332	32.81	25.450	25.427	37.249
F+A+C	25.965	23.621	36.785	25.839	28.393	35.597
$F+A+\underline{S}$	-	-	-	-	-	-
A+Cl+C	25.838	26.538	36.705	25.899	26.984	35.633
$F+\underline{S}+S$	23.126	25.38	40.394	23.055	24.563	40.891
mean	25.10	26.07	37.54	24.93	25.46	37.91

Table 3. The obtained results set by arrangements based on analyses performed for expansive concrete with the use of classical methods only and with classical methods + XRF method

It needs to be noted that he value defined as "water" that has been obtained by subtracting the total of determined components from the whole is not exactly the amount of water that has been used to produce expansive concrete and expansive mortar. Practically, it is a total of the amount of water participating in the setting process, of water remaining in the pores, of evaporated water and also of carbon dioxide  $CO_2$  bonded in the process of the binder carbonization.

	Classical methods		Classical methods + instrumental methods	
Balance equations	Cement (%)	Sand (%)	Cement (%)	Sand(%)
A+S	42.834	43.607	42.920	42.612
A+C	42.821	43.934	43.157	37.395
A+ <u>S</u>	42.611	48.549	42.605	49.522
A+Cl	42.838	43.555	42.607	49.499
A+F	42.884	42.556	42.210	58.228
S+C	42.838	43.612	42.427	42.720
S+ <u>S</u>	42.631	43.652	42.632	42.675
S+Cl	43.764	43.431	46.683	41.793
S+F	42.609	43.657	46.673	41.795
C+ <u>S</u>	42.613	47.936	42.649	38.378
C+Cl	42.841	43.555	42.445	42.363
C+F	42.895	42.512	41.496	60.857
<u>S</u> +Cl	42.631	43.583	42.634	42.338
<u>S</u> +F	42.631	43.567	42.619	43.797
Cl+F	42.627	43.583	43.001	42.288
mean	42.81	44.09	43.05	45.04

 Table 4. The obtained results set by arrangements based on analyses performed for expansive mortar with the use of classical methods only and with classical methods + XRF methods



S Classical method 
Classical method +XRF 
Real-time composition



Classical method Classical method +XRF C Real-time composition

Fig. 3. Raw-material composition of expansive concrete

Fig. 4. Raw-material composition of expansive mortar





Fig. 6. Raw-material composition of ordinary concrete

## 4. Determination of concrete composition by the Gawlicki method

Determination of concrete and aggregate content proportions has been also performed by a method described by Gawlicki (Malolepszy, 2000). The method has been elaborated for an ordinary concrete, where Portland cement has been used as a binder without any additives. The presented research work attempts a reconstitution of the portland and expansive concrete composition taking into account that aggregate contains carbonate rock chips.

Table 5. Composition of ordinary concrete					
	Cement	Sand + gravel			
Real-time value (%)	15.00	77.50			
Calculated value (%)	11.81	75.72			
Difference in results (%)	21.27	2.30			
Table 6. Composition of expansive concrete					
	Cement	Sand + gravel			
Real-time value (%)	25.00	65.00			
Calculated value (%)	17.27	68.13			
Difference in results (%)	30.92	4.59			

# 5. Conclusions

Quantitative analyses of cement performed by classical methods according to the operative standards seem to be less accurate than analyses performed by X-ray fluorescence techniques. Alumina concentration sets a particular example of that. In the case of portland cement it is of 12.74% (Fig. 2) and the value is too high as compared to the standard values of 4-9% (Table 1). Percent proportions of the remaining chemical components calculated by the both kinds of methods do not exceed content value ranges given by the standards. Analytic results obtained by classical methods and by the instrumental one approach each other and their distribution do not exceed a few per cent. The greatest differences occur in the case of chlorides and in that case exorbitant values obtained by classical methods can result from the chloride contamination of reagents applied to the analyses. In each case it is important that samples to be analyzed are adequately prepared with their homogenization to be particularly careful. The applicability of instrumental methods to quantitative analyses of building materials is limited as they can be used for that purpose only when adequate calibration patters exist. The application range of classical chemical-analysis methods is wider and includes assessment of the corrosion hazard for those materials and other expertise projects with the reconstitution of quantitative composition of concrete mixtures in that number. With interpolation applied to determine concentrations of chemical components required for the reconstitution of the real-time composition of cementitious materials it is possible to obtain more accurate results in the case of mortars and concretes based on Portland and expansive cements.

Estimated amounts of individual substrates calculated with the elaborated algorithm based on the results obtained by classical methods as well as by the XRF techniques approach real-time composition of concretes and mortars, ordinary and expansive ones, tested within the presented research project. In order to generalize the above observation 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). However, it should be emphasized that substrate water cannot be balanced for the end product. Practically, it is a total of the amount of water participating in the setting process, of water remaining in the pores, of evaporated water and also of a new component, that is carbon dioxide  $CO_2$  bonded in the process of the binder carbonization.

The elaborated algorithm to be used for the reconstitution of real-time composition of concretes and mortars is characterized by relatively high accuracy. In order to enhance its reliability it is enough to minimize sources of faulty solutions of the balance equation systems. The most important are efficient methods of chemical analysis that make possible to accurately determine chemical composition of individual materials.

In the case of calculating mixture composition of both kinds of concretes, strikingly disproportionate results have been obtained with equation systems that included A+S, both for classical methods and instrumental techniques. It can be related to the occurrence of ettringite,  $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ , in the composition of concretes. Further investigations of a similar kind are necessary in order to describe that relation in the form of a mathematical equation.

Results obtained by the method of Gawlicki (Malolepszy, 2000) show differences between real-time and calculated values of the order of a few percent for sand and gravel and of over 20 and 30% for cements (Table 5 and 6).

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