

# X-RAY QUANTITATIVE PHASE ANALYSIS OF RESIDUES OF THE REFERENCE PORTLAND CLINKERS

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*Residues obtained from the chemical treatment of three Reference Portland clinkers (8486, 8487 and 8488) were analyzed by SEM and X-ray Rietveld quantitative phase analysis. It was found that the chemical treatment was not fully selective. Calculated weight fractions were compared to the weight fraction intervals obtained from a previous analysis of complete clinkers. It was found that in general the refinements based on the diffraction patterns of residues performed better than those based on the patterns of complete clinkers, even though the calculated weight fraction ratios lie mostly within the intervals reported previously. The most important conclusion for daily practice is that if one just wishes to achieve more reliable results in X-ray quantitative phase analysis the improvement is not worth the time and work invested into the chemical treatment of the clinkers.*

## INTRODUCTION

The phase composition of Portland clinkers is quite complex and, up until now, more than 30 constituting phases have been identified. Despite the large variety of phases in clinker only four of them are, in common practice, of real importance - tricalciumsilicate or  $C_3S$ , dicalcium silicate,  $C_2S$ , tetracalcium aluminate ferrite,  $C_4AF$  and tricalcium aluminate,  $C_3A$ . However, due to the presence of various impurities in the raw materials, which are responsible for formations of various solid solutions, the chemical compositions given above are rather idealized, especially in the  $C_4AF$  case [1,2]. Since the final properties of a cement strongly depend on the phase composition of a clinker, accurate quantitative phase analysis is one of the crucial points in every cement production process. Probably the oldest, but in common practice enduring method, is the so-called Bogue phase calculation, which is based on chemical analysis and the assumption that the system has reached equilibrium at high temperatures [3]. Even though this assumption is evidently a weak point of Bogue phase calculation, the method is still widely used with only minor modification - replacement of wet chemical analysis by X-ray fluorescence analysis. An alternative to the Bogue calculation is the examination of phase composition by optical microscopy, but this method can reliably determine only calcium silicates and has been,

until recently, rather difficult to automate. On the other hand, X-ray powder diffraction represents a fast and a highly automated method, which has been used across many fields of material science for decades and has also found many industrial applications [4,5,6]. X-ray diffraction phase analysis of clinkers is however not an easy-to-accomplish procedure, because powder diffraction patterns of many clinker phases overlap almost completely, and it is thus quite impossible to obtain accurate values of integrated or peak intensities. For example, X-ray powder patterns of  $C_3S$  and  $C_2S$  overlap almost completely, leaving unaffected just a weak diffraction of  $C_2S$  at  $\sim 2.87\text{\AA}$  [7].

A more recent alternative to the classic X-ray quantitative phase analysis, the Rietveld method [8], which is based on total observed and calculated (using structural data) diffraction patterns rather than on extracted individual integrated intensities, provides a partial remedy to this problem. Although the Rietveld method has shown its strength in many situations, in the case of clinkers it faces several serious problems. Firstly, some clinker phases may appear in several polymorphic forms, which cannot be, due to several correlations, included into calculations simultaneously. Secondly, the crystal structures of "real" clinker phases can significantly differ from those obtained from single crystals, etc.. Because a large complexity of diffraction patterns of clinkers prevents accurate phase analysis, it is desir-

able to reduce it e.g. by a chemical pretreatment - a selective extraction [9]. For instance, by dissolving a clinker in a mixture of KOH/sucrose "silicate" phases are concentrated, while a solution of salicylic acid/methanol provides calcium aluminates and calcium ferrites. With 7% HNO<sub>3</sub> in methanol one obtains a residue containing ferrites and periclase, etc. [10]. In our previous study [11] we analyzed the phase composition of three reference Portland clinkers, 8486, 8487 and 8488 delivered by the National Institute of Standards and Technology by means of X-ray Rietveld quantitative phase analysis. A comparison of the estimated individual weight fractions (*w*) and the certified values eluded to the fact that few absolute errors reached ~20%, and some relative errors (e.g. in C<sub>3</sub>A case) even exceeded 100%.

The aim of this study was to analyze residues obtained from a selective extraction of the reference clinkers by X-ray Rietveld quantitative phase analysis and to compare the estimated weight fractions, *w*, to those obtained by the analysis of complete clinkers. Some additional information on the elemental composition of the residues was obtained by electron microprobe analysis.

## EXPERIMENTAL

Reference clinkers were first grounded to fine powders (< 20 μm) and then chemically treated to obtain two groups of residues. In the first group, obtained by the extraction in KOH/sucrose solution (KOSH heretofore), calcium silicates dominated, whilst the second group, obtained by extraction into a solution of salicylic acid in methanol (SAM), contained mainly calcium aluminates and calcium ferrites. In this way five residues were obtained. The available amount of 8487 clinker was, however, too small and therefore only KOSH extraction was done. All five samples were scanned within 10-80° 2θ using CoKα<sub>1</sub> radiation with a transmission STOE Stadi P diffractometer. Quantitative phase analysis was done in the two series of Rietveld refinements based on the following crystal structures: monoclinic C<sub>3</sub>S and C<sub>2</sub>S [12,13], orthorhombic C<sub>4</sub>AF [2] and C<sub>3</sub>A [14] and cubic C<sub>3</sub>A [15,16] and MgO [17]. All Rietveld refinements were done using the FullProf program [18].

The strategy of all refinements lay in a stepwise addition of relevant phases starting with the most abundant and proceeding towards the phase with the smallest expected weight fraction (*w*). Just like in our previous study [11] two series of refinements were done - one with the atomic parameters fixed and one with all possible atomic parameters relaxed. The maximum number of simultaneously refined parameters reached 19

(KOSH) and 15 (SAM) if the atomic parameters were held fixed and 92/69 with them relaxed. In a different manner to our previous calculations an attempt was made to estimate the weight fraction of calcium aluminate not only using the cubic structure [15,16], but also with a more complicated orthorhombic[14] one. The motivation behind this approach was the fact that this polymorph was said to be present in the reference clinkers [19], but was not identified by us in the diffraction patterns of the untreated clinkers. The chemical composition of all five residues was examined by an electron microprobe. In five randomly selected points the amounts of Ca, Si, Al, Fe, Mg and K were determined. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were used for the structural studies. SEM observations were performed using a JEOL 5310 electron microscope operated at the accelerating voltage of 15 kV. EDX analyses were performed using a Kevex Delta class IV spectrometer.

## RESULTS AND DISCUSSION

### SEM analysis - KOSH residues

The dominating elements were in all analyzed points, as expected, calcium and silicon (figure 1). The two exceptions were a point on the 8486 clinker, where a significant amount of Mg indicated either presence of periclase or a Mg for Ca substitution, and a point on 8488 with a larger amount of K indicating the presence of alkali sulphate (not shown in the figure 1). It should be noted that although the "trace elements" (Fe, Al and K) were in fact detected in all analyzed points, their amounts were so small that they could not have significantly influenced the results of X-ray quantitative phase analysis. The amounts of Ca and Si detected in the individual points are for 8486/8487 in very good agreement with the reference values, but in the 8488 case the amount of Si is more- and the amount of Ca seriously underestimated. This fact may point to a bias in the reference values. Traces of Al and Fe observed in the majority of cases indicate that the chemical treatment is not a fully selective procedure.

### SEM analysis - SAM residues

The fact that Si was detected in almost all analyzed points suggests either contamination by a silicon oxide or imperfection of the decomposition procedure. As the inspection of diffraction patterns did not show any presence of crystalline silicon oxide, the hypothesis on imperfection is more probable. Fortunately, the amounts of Si were too small to have any impact on the X-ray

phase analysis. A good amount of Mg, detected in two points on 8486, proves that the original clinker must have contained more periclase than the other two clinkers. The elemental compositions found for the individual points (figure 1) selected within two SAM residues imply, in contrast to the KOSH residues, a rather variable phase composition. Of particular note is the large variation found for the Fe:Al ratios, which suggests that the  $C_4AF$  phase introduced to refinements was at maximum an average representative of all phases - solid solutions with the composition  $C_xA_yF_z$ . The situation is even more complicated by the fact that a significant amount of "C<sub>4</sub>AF" and  $C_3A$  is assumed to appear in the amorphous phase. As a consequence, X-ray diffraction and SEM analyses need not necessarily provide identical pictures of a sample.

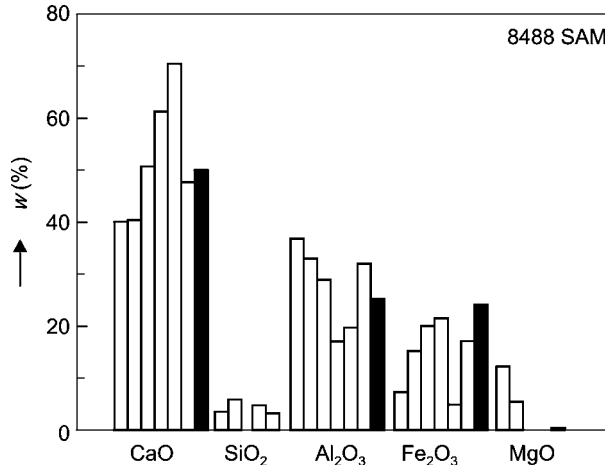
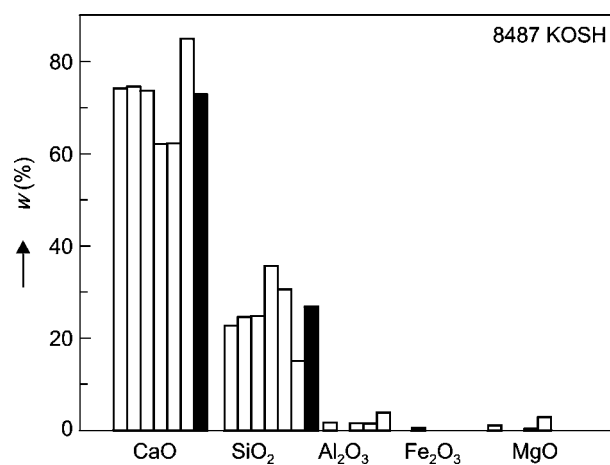
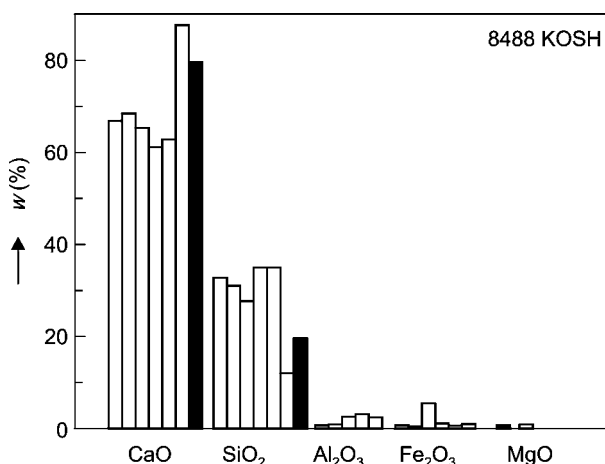
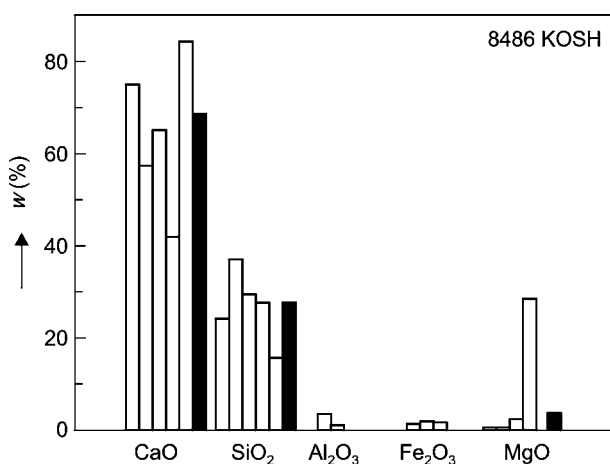
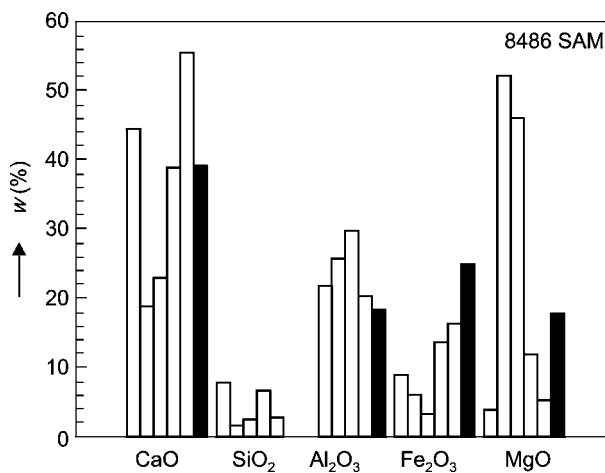


Figure 1. Distributions of analyzed elements in the selected points expressed in weight percentages of the corresponding oxides. Full bars indicate the expected values delivered by the producer. KOSH and SAM abbreviations are defined in the text.

## X-ray quantitative phase analysis

All calculated weight fractions are summarized in tables 1 and 2, examples of fits are in figures 2 and 3. In order to keep the mathematical models as small as possible, and in accordance with the results of SEM analyses (figures 1), only the major expected phases were introduced into the calculations:  $C_3S$ ,  $C_2S$ ,  $MgO$  (KOSH treatment) and  $C_3A$ ,  $C_4AF$ ,  $MgO$  (SAM treatment), respectively. Even though some amounts of crystalline  $MgO$  could have been detected in some residues, attempts to refine its contents mostly led to numerically unstable calculations. It is therefore reasonable to expect, that  $w(MgO)$  in 8487 and 8488 is  $< 5\%$ . The occurrence of K atoms indicated the possible presence of potassium sulphate, however, it was not unambiguously identified and therefore its  $w$  value was not estimated.

When comparing the refinements based on a) the patterns with different complexity<sup>1</sup>, and b) the structural models significantly differing by the number of simultaneously optimized parameters, one would intu-

itively expect the "best" results for the simple patterns and many optimized parameters. Simple patterns in this context imply the patterns without a heavy overlap of diffractions and not influenced e.g. by very variable chemical composition of possible present solid solutions. Quite naturally, it is expected that the patterns of residues will provide more accurate results than the patterns of complete clinkers.

Due to the nature of the least squares procedure, the refinements with the atomic parameters relaxed (i.e. with much more free parameters) are expected to provide more accurate results than those with the atomic parameters fixed. Inspection of figure 4 shows that while this is evident for 8486 and 8488, but, quite unexpectedly, not for the  $C_3A$ -rich 8487 clinker. However, even in this case the ratios  $w(C_3S) : w(C_2S)$  are closer to the expected values than the intervals found in our previous study [11]. A large variation in weight fraction ratios obtained for the 8487 case, either for complete clinkers or for the residue, thus point to some inadequacies in the mathematical models. The results obtained for the 8488 clinker in addition indicate that the com-

Table 1. Weight fractions ( $w$ ) obtained in the calculations with the atomic parameters fixed. The upper indices (1, 2) indicate which structure of  $C_3A$  was used to calculate the pattern: 1 - cubic [15,16], 2 - orthorhombic [14].

	8486		8487		8488		
	KOSH	SAM <sup>1</sup>	SAM <sup>2</sup>	KOSH	KOSH	SAM <sup>1</sup>	SAM <sup>2</sup>
$C_3S$	74			91	82		
$C_2S$	22			9	18		
$C_4AF$		66	49			72	57
$C_3A$ cub.						26	
$C_3A$ ortho.		17	39				43
$MgO$	4	17	12			2	

Table 2. Weight fractions ( $w$ ) obtained in the calculations with the atomic parameters relaxed. The upper indices (1, 2) indicate which structure of  $C_3A$  was used to calculate the pattern: 1 - cubic [15,16], 2 - orthorhombic [14].

	8486		8487		8488		
	KOSH	SAM <sup>1</sup>	SAM <sup>2</sup>	KOSH	KOSH	SAM <sup>1</sup>	SAM <sup>2</sup>
$C_3S$	66			87	79		
$C_2S$	27			12	21		
$C_4AF$		69	73			75	78
$C_3A$ cub.						23	
$C_3A$ ortho.		16	13				21
$MgO$	7	15	14	1		2	1

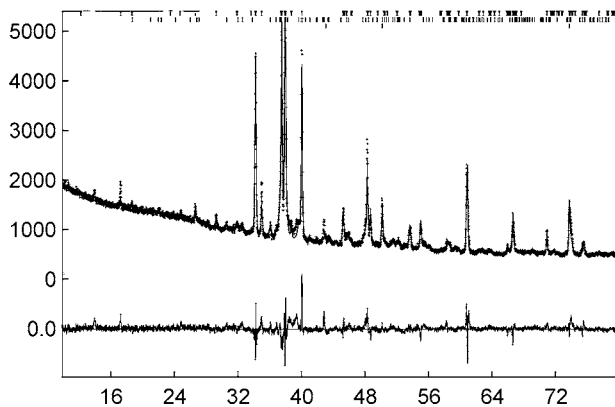


Figure 2. Rietveld fit for the KOSH residue of the 8486 clinker. The markers (vertical bars) in the upper part correspond (top to bottom) to  $C_3S$ ,  $C_2S$  and  $MgO$ .

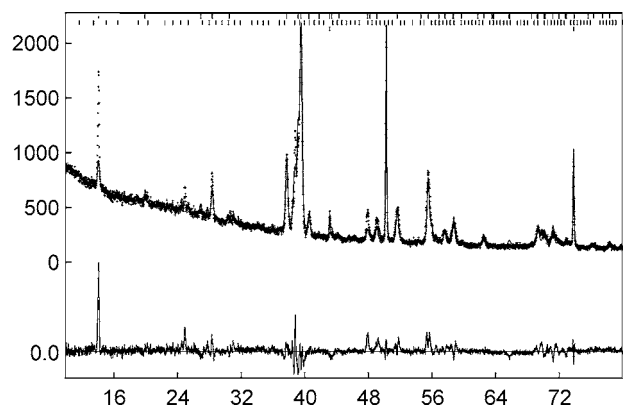


Figure 3. fit for the SAM residue of the 8486 clinker. The markers (vertical bars) in the upper part correspond (top to bottom) to  $C_4AF$ ,  $C_3A$  and  $MgO$ .

plexity of the diffraction patterns had not any important impact on the refinements because the estimated values lie within the original intervals, i.e. nothing was gained by the chemical pretreatment. In the 8486 case the picture is mixed, but the refinements based on the diffraction pattern taken from the residue provided results, which are closer to the expected values.

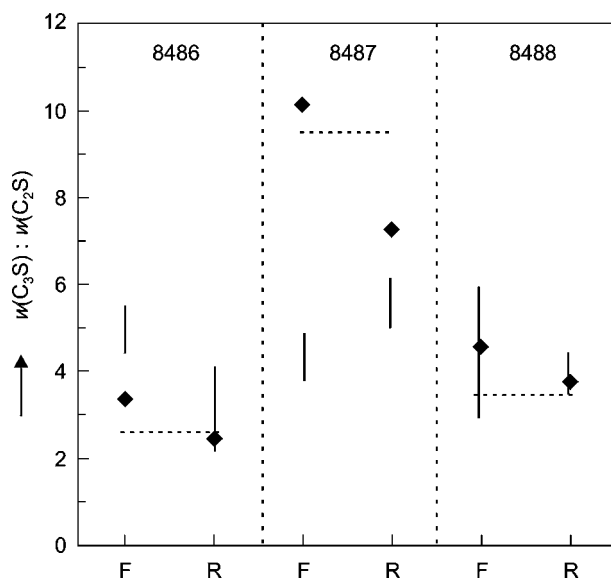


Figure 4. Weight fraction ratios  $w(C_3S) : w(C_2S)$  obtained by our calculations. Filled diamonds represent the values found in this study, while vertical lines mark the intervals of values found in our previous study [11]. Broken horizontal lines denote the expected values based on the NIST's certificate. F, R - calculations done with the atomic parameters fixed (F) or relaxed (R).

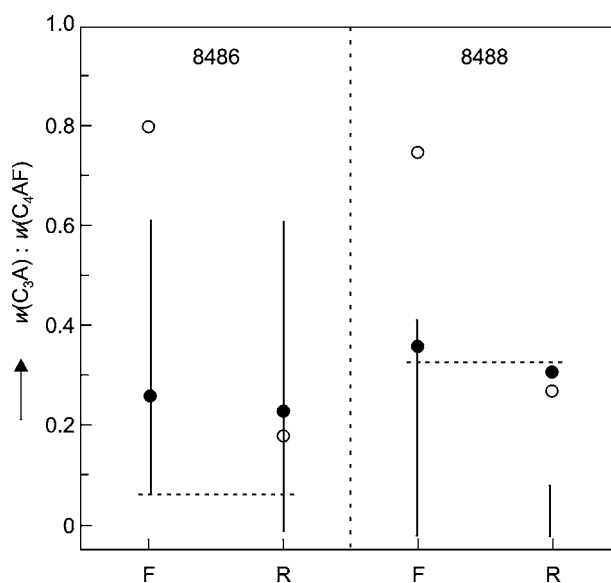


Figure 5. Weight fraction ratios  $w(C_3A) : w(C_4AF)$  obtained by our calculations. Open bullets indicate the values found with orthorhombic, while filled bullets with cubic  $C_3A$  structure. Meaning of other symbols is defined in the legend for figure 4.

Figure 5 shows that in the refinements with the atomic parameters fixed, cubic  $C_3A$  performed better than  $C_3A$  orthorhombic. With the atomic parameters relaxed both phases worked equivalently, i.e. introduction of more free parameters did not lead to any significant improvement of accuracy. The main source of variability here is the structural model used to account for calcium aluminium ferrite, because in clinkers more solid solutions belonging to the C-A-F system have been identified.

## CONCLUSIONS

The phase composition models proposed in this study worked quite well for the 8488 and 8486 Reference clinkers. There is, however, no straightforward explanation why it worked much worse for 8487, because no "missing phases" have been identified. Similarly, there is no clear answer to the question of why the calculations with the atomic parameters fixed behaved better than those with the parameters relaxed. It was found that the refinements based on the diffraction patterns of the residues in general performed better than those based on the patterns of complete clinkers, even though the calculated weight fraction ratios mostly lie within the intervals reported previously [11]. Introduction of a more complicated structural model for  $C_3A$  did not lead to any significant improvement of the overall fit. The most important conclusion for daily practice is that if one just wishes to achieve more reliable results in X-ray quantitative phase analysis, total improvement is not worth the time and work invested into the chemical treatment of the clinkers.

### Notation:

<sup>1</sup> A total number of contributing diffractions, degree of their overlap, influence of the so called real structure like size and strain effects, preferred orientation of particles, etc...

## References

1. Colville A. A., Geller S.: *Acta Cryst.* B27, 2311 (1971).
2. Colville A. A., Geller S.: *Acta Cryst.* B28, 3196 (1972).
3. Taylor H.F.W.: *The Chemistry of Cements*, Volume I, p.120, Academic Press, London and New York 1964.
4. Scarlett N.V.Y., Madsen I.C.: *Powder Diffraction* 16, 71 (2001).
5. Möller H.: *World Cement* 9, 75 (1995).
6. Neubauer J., Pollmann H., Meyer H. W. in: 10<sup>th</sup> International Congress on the Chemistry of Cement, Vol. 3, 3v007, Gothenburg 1997.

7. Chung H.F., Smith D.K.: *Industrial applications of x-ray diffraction*, p.415-440, Marcel Dekker Inc. 2000.
  8. Rietveld H. M.: *J.Appl.Cryst.* 2, 65 (1969).
  9. Gutteridge W. A.: *Cem.Concr.Res.* 9, 319 (1979).
  10. Stutzman P. E.: NISTIR 5755, 1996.
  11. Pritula O., Smrčok L., Baumgartner B.: *Powder Diffraction* 18, 16 (2003).
  12. Mumme W. G.: *N. Jb.Miner.Mh.* 4, 145 (1995).
  13. Mumme W. G., Hill R. J., Bushnell - Wye G., Segnit E. R.: *N. Jb.Miner.Abh.* 169, 35 (1995).
  14. Nishi F., Takeuchi Y.: *Acta Cryst.* B31, 1169 (1975).
  15. Mondal P., Jeffery J.W.: *Acta Cryst.* B31, 689 (1975).
  16. Takeuchi Y., Nishi F., Maki I.: *Zeit.Krist.* 152, 259 (1980).
  17. Schmahl N. G., Eikerling G. F.: *Zeit.Phys.Chem.* 62, 268 (1968).
  18. Rodriguez-Carvajal J.: *Personal communication.*
  19. Taylor J.C., Hinczak I., Matulis C.E. : *Powder Diffraction* 15, 7 (2000).
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KVANTITATÍVNA RTG FÁZOVÁ ANALÝZA REZIDUÍ  
REFERENČNÝCH PORTLANDSKÝCH SLINKOV

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Reziduá získané chemickou úpravou troch referenčných Portlandských slinkov (8486, 8487 a 8488) sme analyzovali na zariadení SEM/EDX a Rietveldovou rtg kvantitatívnu fázovú analýzou. Zistili sme, že chemické úpravy slinkov nie sú úplne selektívne. Vypočítané hmotnostné zlomky sme porovnali s intervalmi hmotnostných zlomkov, ktoré sme získali spresňovaniami zo záznamov nerozložených slinkov. Výpočtami založenými na záznamoch reziduí slinkov sme vo všeobecnosti dosiahli lepšie výsledky ako pri spresňovaniach zo záznamov pôvodných slinkov. Hodnoty hmotnostných zlomkov stanovené zo záznamov reziduí však ležia v intervaloch hodnôt stanovených pre nerozložené slinky. Najdôležitejším výsledkom pre dennú prax preto je, že pri potrebe dosiahnuť spoľahlivejšie výsledky v rtg kvantitatívnej fázovej analýze nie je zlepšenie úmerné času ani práci, ktorá bola vynaložená na chemické spracovanie slinkov.