

Determination of the chloride content of concrete and execution of a Round Robin test in two steps

Summary

Chloride analysis have a great technical and economical importance. Because of partially bad experiences a 2-phase Round Robin test and additional laboratory experiments have been carried out in order to gain better provisions for the different steps of the chloride analysis and to deduce propositions for the necessary revision of the recommendation SIA 162/2 "Determination of the chloride content in concrete".

Within the 1st phase of the Round Robin test the 17 participating laboratories had to analyse according their own standard operating procedures: chloride contaminated samples of 11 sorts of concrete (maximum grain size of aggregate: 16 mm) and of one ready mix mortar. The reproducibility and detection rate (portion of the true or nominal value) were very unsatisfactory. For the 2nd phase of the Round Robin test the laboratory had two chloride containing solutions, two concrete powders (ingress of the chlorides by suction) and three concrete cores (chlorides added to the mixing water) to analyse. Additional provisions have made for the analysis. The results of the Round Robin tests can be summarised as follows:

- Not all of the possible combinations of the methods for the extraction and analysis are appropriate for the daily laboratory routine. There are obvious difficulties with the calibration of the analysis.
- Commercial instruments are on the market and in use which are not suitable for quantitative chloride analysis.
- The provisions for the preparation of the samples for the 2nd phase of the Round Robin test were sufficient.
- The detection rate is higher for the extraction with nitric acid (95%) than for the hot water extraction (88%). (Note: By the 1st phase of Round Robin test the detection rate was significantly lower: app. 65% for the hot water and 90% for the nitric acid extraction, respectively.)
- The standard deviation depends on the chloride content and increases for chloride contents below 0.4 M.%/Z (chloride content in respect to cement).
- For the 2nd phase of the Round Robin test the relative standard deviations (standard deviation related to the corresponding average value) were for chloride contents >0.4 M.%/Z – depending on type of concrete and chloride content – and for both extraction methods between app. 8 and 18%, for the hot water extraction between app. 8 and 13%, for the nitric acid extraction between app. 11 and 17%. The reasons for the larger scatter for the acid extraction are not clear.
- The standard deviation is larger if it is calculated based on the results of nitric acid and hot water extraction (detection rate is different).
- The "relative repeatability" (standard deviation of the results of the various samples determined by one single laboratory have been calculated by the normalisation of the single values) of the 2nd phase of the Round Robin test were for both extraction methods – depending on type of concrete and chloride content – between app. 3 and 16%, for the hot water extraction between app. 3 and 10%, for the nitric acid extraction between app. 5 and 14%.

- The analysis of concrete, intended to be homogeneously contaminated with chloride, might result in slightly varying chloride contents along the length of concrete cores. For a concrete with a maximum grain size of 16 mm the deviation was around 2 to 3% when the centre part of the concrete cores was analysed. The differences might be even a little bit higher when the outermost parts of concrete cores is analysed.

The above mentioned statement, that not all of the possible combinations of the methods for the extraction and analysis are equally suitable, is of special importance. With some of the methods of the analysis unsatisfactory results have been gained, since e.g.:

- they need well educated and experienced laboratory personnel
- they are carried out with inappropriate equipment available on the market
- the calibration curves necessary for the analysis are determined in inappropriate solutions (other ions).

The actual findings are summarised in **table Z.1**. It has to be pointed out here very clearly, that different laboratories got correct and sound results even with those combinations of methods of extraction and analysis which are categorised in this table as “sensitive”. A precondition is a practised and appropriate quality management system and well educated, experienced laboratory personnel, who is familiar with the difficulties of the whole analysis in all the details.

Method of analysis	Method of extraction		Remarks
	Hot water extraction	Acid-extraction	
Titration	appropriate	appropriate	
Photometry	(appropriate)	sensitive	calibration curve, susceptibility to errors, experience
Ion sensitive electrode	sensitive	sensitive	calibration curve, experience, cross sensitivity
Ion chromatography	??	inappropriate	cross sensitivity
X-ray fluorescence (no extraction necessary)	appropriate		calibration curve

Table Z.1 Qualitative assessment of the various methods of chloride extraction and analysis.

The higher scatter of the chloride contents determined after the extraction with nitric acid compared to those determined after the extraction with hot water is remarkable. Additional investigations might be necessary in order to find out the reasons for this result.

The Round Robin test and the additional investigations in the laboratory of the TFB led further to the following conclusions:

- The most important sources of errors is related to the type of calibration needed for the analysis and – at least partly – very likely to the lack of laboratory routines of the personnel.
- The chloride contents determined after hot water extraction are significantly lower than those determined after acid extraction (ratio app. 0.9).
- The type of chloride ingress (internal: addition to the mixing water, external: by suctioning of chloride containing water), the type of cement, the water/cement ratio, the type of salt (CaCl₂, NaCl) are of minor importance.
- Considering the scatter after hot water and acid extraction a fineness of the concrete powder <0.5 mm is sufficient.

- For the extraction with nitric acid a medium acid concentration should be used. Temperature and extraction time is of minor importance.
- For the extraction with hot water the extraction time is of minor importance.
- The chloride analysis of polymer modified mortar and concrete needs special care to make sure that the total chloride content is determined and the scatter remains low.

Chapter 8 contains some propositions for the revision of the recommendation SIA 162/2 as well as to the question of the appropriate reference concrete materials.

The laboratories should participate on Round Robin tests on a regular base in order to check and, eventually, to improve the quality of their analysis and the quality management system.

Dr. F. Hunkeler, H. Ungricht und F. Deillon, TFB, Wildegg

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Order information: VSS, Seefeldstrasse 9, 8008 Zürich.