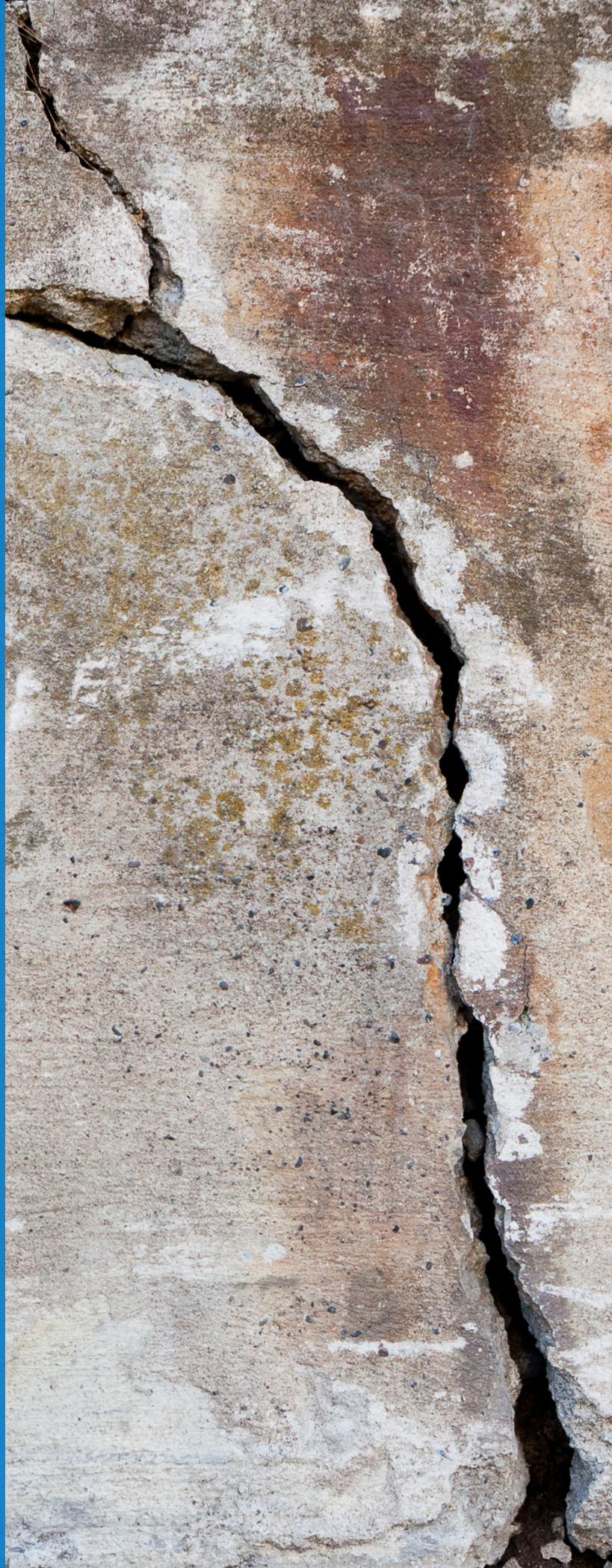




CSA GROUP RESEARCH

Multi-laboratory study of proposed new test for determination of sulphide sulphur content of concrete aggregates

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Executive Summary

The deterioration of concrete in houses and other buildings in Québec due to reaction of iron sulphides (the mineral pyrrhotite) in the concrete aggregate is a significant and well-documented issue. The CSA Technical Committee on Concrete Materials and Construction (CSA A23.1/A23.2) is developing new provisions and information on this issue to be included in the next edition of CSA A23.1/A23.2 in 2019, including a test method intended to measure the sulphide sulphur content of aggregates.

The objective of the research project was to conduct a multi-laboratory study of the proposed test method in order to develop a precision statement and to determine if the test is sufficiently precise to be implemented in the next edition of CSA A23.1/A23.2.

A total of eight laboratories participated in the study. Due to the limited number of laboratories, the results are considered tentative and additional study is recommended. The results of the study provide an estimate of precision of the proposed test method using the high temperature combustion analysis technique.

In addition to the estimate of precision, potential modifications to the test method have been identified for the consideration of the Technical Committee. These potential modifications include studying the powder x-ray fluorescence spectrometry analysis technique further, clarifying when the analysis of insoluble residue is required, and increasing the subsample size for determination of sulphate sulphur.

1. Introduction

In Québec, there has been serious deterioration of concrete in houses and other buildings due to the reaction of iron sulphides (the mineral pyrrhotite) in the concrete aggregate (Tagnit-Hamou et al., 2005; Rodrigues et al., 2012; Duchesne and Fournier, 2011; Rodrigues et al., 2013a; Rodrigues et al., 2013b). The Technical Subcommittee (TSC) on Aggregate Reaction, reporting to the Technical Committee on Concrete Materials and Construction (A23.1/A23.2), has developed a test intended to measure the amount of sulphide sulphur in aggregates. The Technical Committee does not want to publish this test until the multi-laboratory variation of the method is known. It is intended that a limit will apply to the sulphide sulphur content of concrete aggregates in Canada. A test with large variability will cause serious difficulties and have an impact on the supply of concrete aggregates.

A multi-laboratory study was organized, and a number of laboratories across Canada were invited to participate. The objectives of the study were to develop a draft precision statement for the proposed test method, and to determine if the test was sufficiently precise that it could be used with general safety and minimal impact to the supply of concrete aggregates if implemented in the next edition of CSA A23.1/A23.2 in 2019.

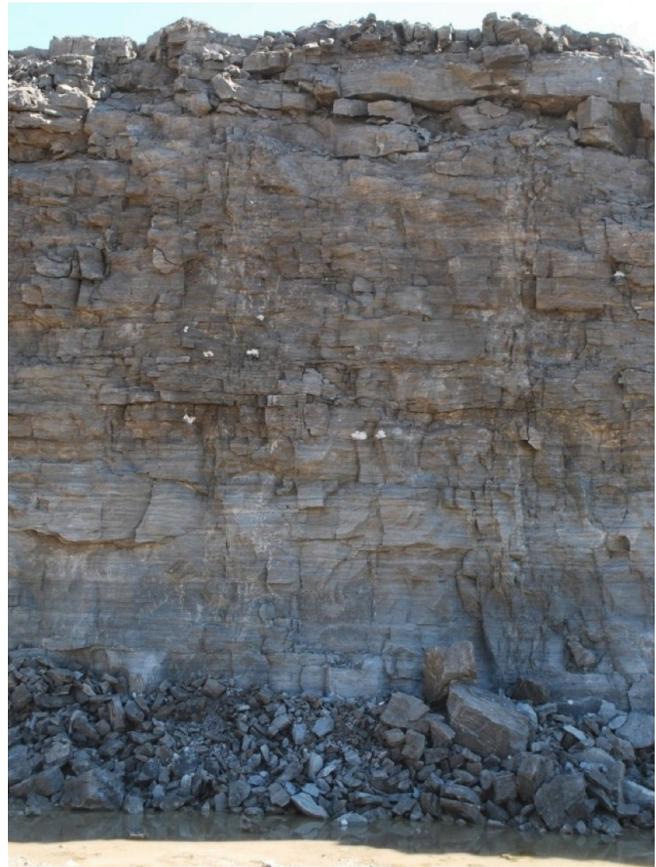
2. Materials and methods

2.1 Sample acquisition

Three samples were acquired for this study. The intent was to represent a likely range of both sulphide and sulphate content that might be encountered in Canadian aggregates.

Sample 1 was from a quarry in the Niagara Peninsula of southern Ontario. It was from an approximately 7 m high quarry face in horizontally-bedded laminated dolomite of the Lockport Formation of Silurian age (Figure 1). The face contained occasional nodules of gypsum up to about 100 mm in diameter. Four 30 kg bags of crusher screenings finer than 4.75 mm from the secondary crusher were sampled. This source has been used successfully for many years as a source of concrete aggregate. The amount of gypsum has not been found to cause deleterious expansion of concrete.

Figure 1: Photograph of the approximately 7 m high quarry face used for Sample 1. Horizontally-bedded laminated dolomite with white gypsum nodules at about mid-face height.



Sample 2 was from a quarry in the Gull River Formation (middle Ordovician age) in the Orillia area of Ontario. The rock was a limestone from the 9 to 10 m high upper bench and has been used as a source of concrete aggregate with no reported issues associated with deleterious expansion (Figure 2). The sample consisted of four 30 kg bags of crusher screenings finer than 4.75 mm from the secondary crusher. Microscopic examination of similar rock from quarries in this area has shown very small amounts of microscopic pyrite. It should be noted that the lowest bench of the quarry had very thin (2 to 5 mm thick) seams of gypsum making up less than 0.1% of the face. That material was not sampled.

Figure 2: Photograph of the 9 to 10 m high quarry face for Sample 2. Medium-bedded limestone.



Sample 3 was from a quarry about 20 km north of Trois-Rivières in Québec, north of the St. Lawrence river. The rock was a gabbroic anorthosite with small (usually < 5% by mass) amounts of pyrite and pyrrhotite. Coarse aggregates from this quarry have caused failure due to expansion and extensive cracking of concrete due to pyrrhotite oxidation. The material was obtained from a freshly-produced 0 to 20 mm aggregate stockpile (Figure 3); 0 to 5 mm material was extracted by hand sieving the material over a 5 mm sieve.

Figure 3: Photograph of the quarry from which Sample 3 was obtained. Extraction zone of the quarry at the time of the visit.



2.2 Sample preparation

The samples were placed in flat-bottomed open steel trays and oven dried at about 105 °C and allowed to cool to room temperature.

To ensure, as far as possible, that all the specimens of each sample were the same, a spinning riffler was used (see Figures 4 and 5). The use of spinning rifflers was found by Allen and Khan (1970) to give the lowest variation of any sampling technique for powders and to be superior to other methods. The device consisted of a spinning turntable about 1 m in diameter and was driven at variable speed with an electric motor to give a rapid speed of rotation. Twenty-four containers were placed at the outside edge of the turntable. A vibrating horizontal feeder, fed by a hopper containing the aggregate to be sampled, discharged aggregate into the containers on the turntable.

The hopper's rate of feed was set so that it took many rotations to fill the sample containers under the flow of material falling off the feeder. Spinning rifflers are capable of removing the effects of segregation in a stream of material by using multiple passes to acquire the sample. The process works best if the turntable rotates relatively quickly and the material flows slowly and homogeneously so as to maximize the number of passes needed to obtain the sample. To make sample specimens of about 1.8 kg, approximately 200 passes under the feeder were required.

For each sample, material was taken in turn from each tray containing the oven dry material using a metal scoop. The material was then placed in the hopper of the riffler. This resulted in a mixture of each of the four subsamples in the hopper of the riffler.

Samples of about 1.6 to 1.8 kg were prepared. A total of 40 samples were prepared from each bulk sample. Twenty samples were randomly selected and designated as Sample 1.1 and the other 20 designated as Sample 1.2. Two more bulk samples were prepared in the same way and designated as Samples 2.1 and 2.2 and 3.1 and 3.2.

2.3 Test program

Each participant was shipped three pairs of samples (1.1 and 1.2, 2.1 and 2.2, and 3.1 and 3.2) for a total of six samples weighing 1600 to 1800 g each. The participant

Figure 4: Spinning riffler sample containers. The table holding the containers is rotated at a speed of about 10 to 15 rpm.



Figure 5: Bottom of a hopper and vibrating horizontal feeder discharging material into spinning sample containers.



was identified as the laboratory that volunteered to take part in the multi-laboratory study. Since the testing involved aggregate processing operations and chemical analyses, participants were permitted to perform both activities or to subcontract the chemical analyses to a commercial chemical laboratory.

Each participant was requested to strictly follow the test procedure provided (see Appendix A for the draft test method), including ensuring that the technical staff in the participant's laboratory and any subcontractor's laboratory involved in the study were well aware of the instructions and procedures described in the test method.

The test method required participants to process separately, in accordance with Clause 7.2, each one of the six samples of aggregate materials in order to obtain the appropriate particle size ($< 160 \mu\text{m}$). The subsamples were then used to determine, in each of the six samples (three pairs) provided, the following:

- A. the total weight percentage of **sulphur** (to the nearest 0.01%), either by high temperature combustion analysis or by powder x-ray fluorescence spectrometry (Clause 8.1);
- B. the weight percentage of the **sulphate sulphur** (to the nearest 0.01%), by digestion in hydrochloric acid (Clause 8.2); and
- C. the weight percentage of the **sulphide sulphur** (obtained by calculating the difference from the above, i.e., $A - B$, to the nearest 0.01%) (Clause 9).

3. Results and discussion

3.1 General

Eight laboratories participated in the study. A total of ten sets of results were compiled since two of the participating laboratories each returned two sets of results for total sulphur content. These results were considered as separate data points for total sulphur and sulphide sulphur content. Of the ten sets of results, the total sulphur was determined using high temperature combustion analysis for eight sets of results and powder x-ray fluorescence spectrometry for two sets of results.

The results are summarized in Table 1 and illustrated in Figure 6. Examination of the chemical analysis sample means shows that there is close correlation between the results of the paired samples, indicating good sample preparation, although it should be noted that Samples 3.1 and 3.2 show larger differences than would normally be expected. Data in the scatter diagrams (Figure 6) tends to fall in the top right and lower left quadrants in an approximately linear fashion, indicating laboratory bias. If results were totally random and without bias, the points would tend to fall relatively equally in each quadrant of the scatter diagram.

3.2 Total sulphur determination by high temperature combustion analysis

For seven of the sixteen results using high temperature combustion analysis for Samples 1.1 and 1.2, the sulphate

sulphur determined in accordance with the test method was higher than the total sulphur. This may be related to testing sensitivity where sulphide sulphur content is low but sulphate sulphur is relatively high.

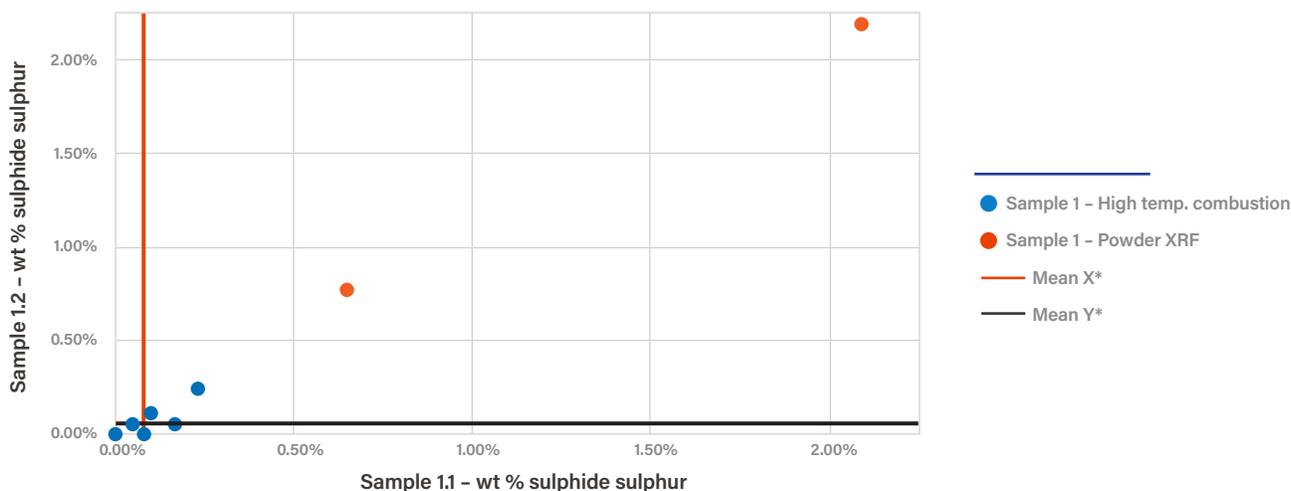
Table 1: Summary of sulphur content test results

| Chemical Analysis Method | Sample | n† | A (wt % total sulphur) | | | | B (wt % sulphate sulphur) | | | | A - B (wt % sulphide sulphur) | | | |
|--|--------|----|------------------------|---------------|---------|---------|---------------------------|---------------|---------|---------|-------------------------------|---------------|---------|---------|
| | | | Mean (%) | Std. dev. (%) | Min (%) | Max (%) | Mean (%) | Std. dev. (%) | Min (%) | Max (%) | Mean (%) | Std. dev. (%) | Min (%) | Max (%) |
| High temperature combustion (Clause 8.1.2 of test method) | 1.1 | 8 | 0.49 | 0.12 | 0.30 | 0.65 | 0.48 | 0.15 | 0.34 | 0.75 | 0.08 | 0.09 | 0.00 | 0.23 |
| | 1.2 | 8 | 0.47 | 0.14 | 0.33 | 0.66 | 0.48 | 0.15 | 0.35 | 0.75 | 0.06 | 0.08 | 0.00 | 0.24 |
| | 2.1 | 8 | 0.13 | 0.07 | 0.03 | 0.22 | 0.03 | 0.02 | 0.01 | 0.05 | 0.10 | 0.07 | 0.01 | 0.21 |
| | 2.2 | 8 | 0.13 | 0.07 | 0.03 | 0.21 | 0.02 | 0.02 | 0.01 | 0.06 | 0.10 | 0.07 | 0.01 | 0.18 |
| | 3.1 | 8 | 1.27 | 0.26 | 0.93 | 1.66 | 0.05 | 0.03 | 0.01 | 0.09 | 1.22 | 0.24 | 0.90 | 1.61 |
| | 3.2 | 8 | 1.35 | 0.32 | 1.10 | 1.99 | 0.05 | 0.02 | 0.03 | 0.08 | 1.29 | 0.32 | 1.06 | 1.94 |
| Powder x-ray fluorescence spectrometry (Clause 8.1.3 of test method)* | 1.1 | 2 | 1.73 | 1.03 | 1.00 | 2.46 | 0.36 | 0.01 | 0.35 | 0.37 | 1.37 | 1.02 | 0.65 | 2.09 |
| | 1.2 | 2 | 1.87 | 1.02 | 1.15 | 2.59 | 0.39 | 0.01 | 0.38 | 0.40 | 1.48 | 1.00 | 0.77 | 2.19 |
| | 2.1 | 2 | 0.17 | 0.10 | 0.10 | 0.24 | 0.04 | 0.01 | 0.03 | 0.05 | 0.13 | 0.11 | 0.05 | 0.21 |
| | 2.2 | 2 | 0.16 | 0.13 | 0.06 | 0.25 | 0.05 | 0.02 | 0.03 | 0.06 | 0.11 | 0.16 | 0.00 | 0.22 |
| | 3.1 | 2 | 2.41 | 2.09 | 0.93 | 3.88 | 0.05 | 0.00 | 0.05 | 0.05 | 2.36 | 2.09 | 0.88 | 3.83 |
| | 3.2 | 2 | 2.28 | 2.19 | 0.73 | 3.83 | 0.05 | 0.01 | 0.04 | 0.06 | 2.23 | 2.18 | 0.69 | 3.77 |

*Due to the variability of results and lack of correlation with values obtained by high temperature combustion, values obtained by powder x-ray fluorescence analysis were excluded from the statistical calculations for Figures 6 and 7.

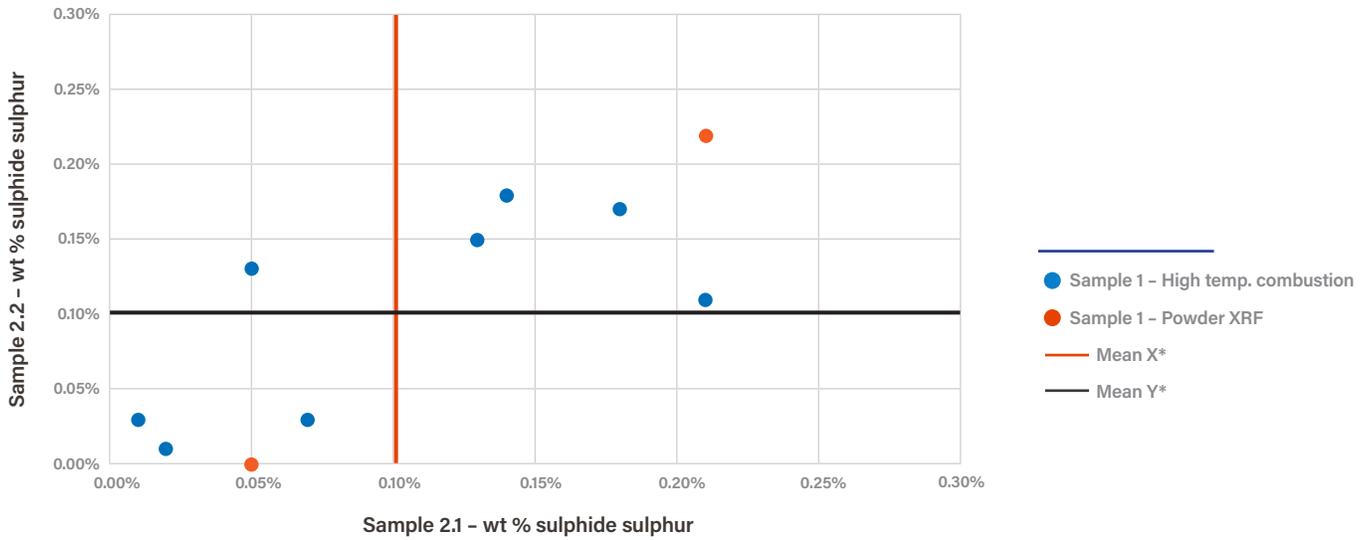
† n = number of supplied results

Figure 6 a) Sulphide sulphur content scatter diagrams: Sample 1



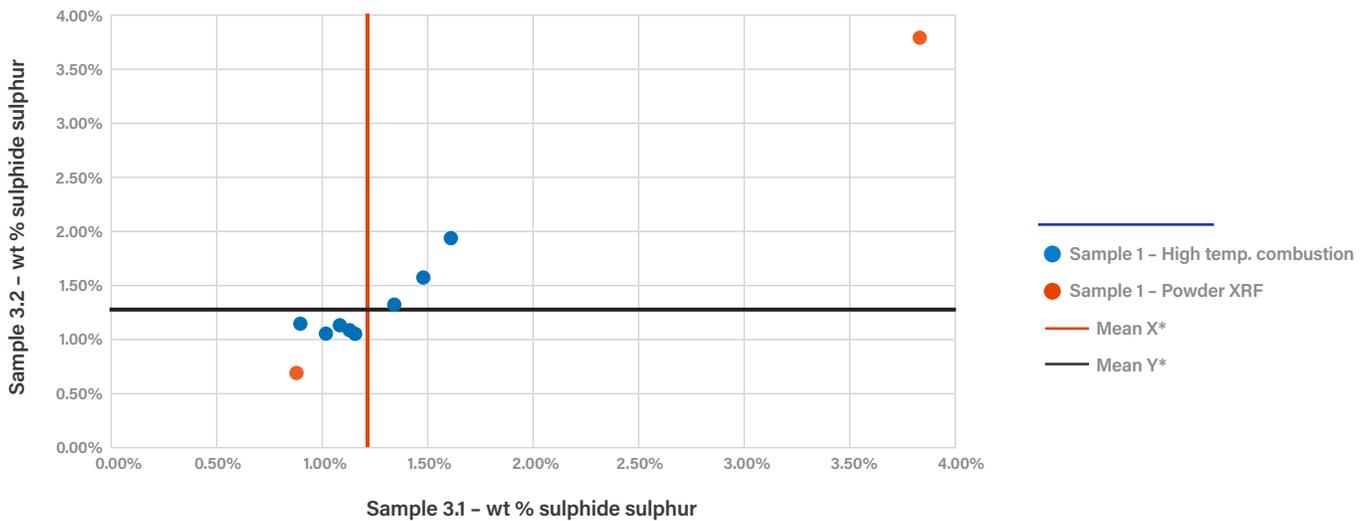
*Mean values in scatter diagrams are based on results obtained using high temperature combustion analysis only. Data points obtained using powder x-ray fluorescence spectrometry analysis are shown for comparison.

Figure 6 b) Sulphide sulphur content scatter diagrams: Sample 2



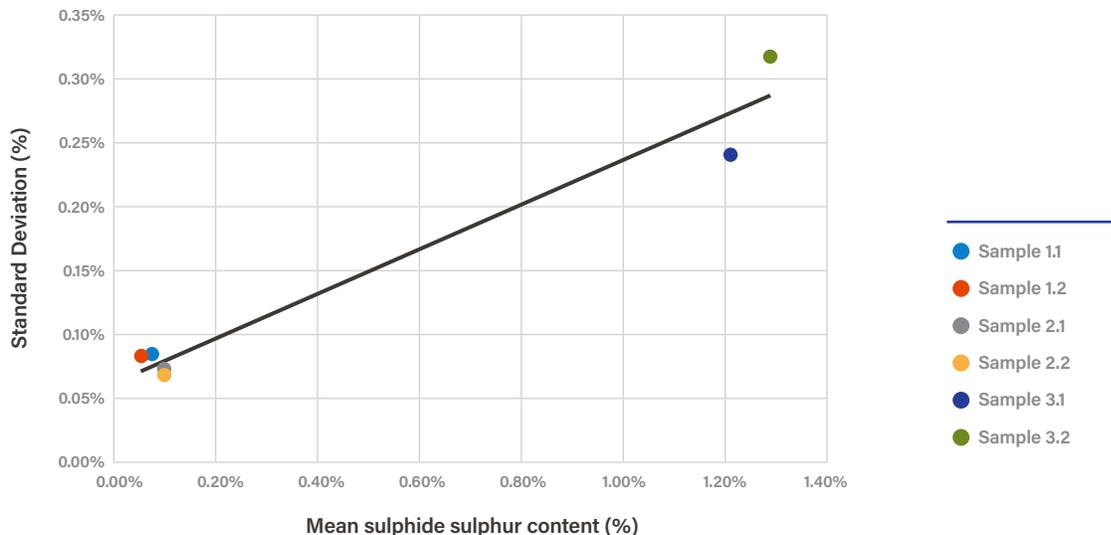
*Mean values in scatter diagrams are based on results obtained using high temperature combustion analysis only. Data points obtained using powder x-ray fluorescence spectrometry analysis are shown for comparison.

Figure 6 c) Sulphide sulphur content scatter diagrams: Sample 3



*Mean values in scatter diagrams are based on results obtained using high temperature combustion analysis only. Data points obtained using powder x-ray fluorescence spectrometry analysis are shown for comparison.

Figure 7 Sulphide sulphur content mean vs. standard deviation (results using high temperature combustion analysis only)



The following additional comment was noted by a participant:

- “Total sulphur results using high combustion analysis with acid base detection are consistently lower when compared to high combustion analysis with infrared absorption. High combustion analysis with infrared absorption does not use acid base detection thus, it will detect any total sulphur that is not soluble or soluble in acid system.”

3.3 Total sulphur determination by powder x-ray fluorescence analysis

This analysis technique was used by two laboratories, one of which also conducted high temperature combustion analysis. The results obtained by powder x-ray fluorescence analysis did not correlate well with the results obtained by high temperature combustion analysis, particularly for Samples 1 and 3.

At this stage, and until more data are available, this technique does not seem to be directly comparable with high temperature combustion. Further study is needed.

3.4 Additional comments on the test method

The proposed procedure for determination of sulphate sulphur (Clause 8.2) includes using a representative aggregate subsample between 2 and 5 g. One laboratory returned sulphate sulphur results using subsamples of both 2 g and 5 g. In all cases, the results obtained for a 5 g sample were slightly higher (0.01 to 0.03% absolute) than for a 2 g sample. In the future, it may be useful to modify the test method to use a subsample between 4 and 5 g. Generally speaking, a larger sample for analysis is always preferred.

A potential error in the test method was identified during the course of the study. In the draft test method, analysis of insoluble residue is referenced in the Note to Clause 8.2.2. However, this analysis should be optional only if the percentage of sulphide sulphur present is less than the critical limit of 0.1%. If the sulphide sulphur is greater than the critical limit, the residue shall be analysed for remaining sulphur in accordance with the procedure described in the Note and calculated in accordance with Equations 3 and 4 of the test method. Participants in the study were not explicitly instructed to conduct or report the analysis of insoluble residue.

The following additional comments were noted by participants:

- “The sulphate procedure is very similar to the original CSA A23.2-3B method, however the proposed method is somewhat shorter and simplified. Digesting the precipitate for 12-24hr can be problematic if the beakers are not covered with a watch glass, otherwise the solution volume may evaporate too low.”
- “Many labs may not have an ICP OES system to measure the sulphate sulphur, or may not have the expensive platinum crucibles for the ignition step. A lower capital cost method we have tried is to use pre-weighed filters (0.45 micron) to filter and weight the barium sulphate precipitate. No burning is required, only the purchase of a vacuum pump and glass filter funnel system (Millipore).”

4. Conclusions

The intent of the test is to provide a relatively rapid and economical means of warning of an aggregate that contains amounts of sulphides that could possibly cause deleterious expansion. European standards indicate that if the amount of total sulphur in an aggregate is not more than 1% and pyrrhotite is not present, the aggregate can safely be used in concrete. Two of the samples used in the study have a long history of successful use in concrete and easily met the 1% total sulphur limit. For those two samples (Samples 1 and 2), that are probably representative of the majority of aggregates found in Canada, the sulphide sulphur content using the high temperature combustion analysis technique met the European standard.

The powder x-ray fluorescence spectrometry analysis results were not satisfactory. The technique gave higher values for the samples (Samples 1 and 3) containing small amounts of gypsum or iron sulphides compared with the combustion analysis technique which is the traditional means of analysis for sulphides. The x-ray fluorescence spectrometry technique requires further study.

For the known deleterious aggregate (Sample 3), 7 of 8 analyses gave values that exceeded 1.0%. In the normal course of events, this material would not meet the European or proposed Canadian standard of a maximum of 1%. Inevitably, when close to any specification limit based on testing, this situation will usually occur. Possible solutions are either to reduce the action limit or to increase the quantity of specimens tested or laboratories used and to establish an agreed reference material for laboratories for qualification purposes. The decision to do this should be based on the perceived risk and consequences of getting a false positive or negative result. Knowledge of the precision or variability of the test will provide guidance in making such judgments when test values are close to the specification or action limit.

The estimate of precision is based on samples of three aggregates that were tested at seven different laboratories. When more laboratories are capable of doing this test, further studies should be undertaken. Due to the limited number of laboratories, these results should be regarded as tentative.

The following statements are based on high temperature combustion analysis of total sulphur:

- For aggregates with sulphide sulphur content of approximately 0.1% or less, the multi-laboratory standard deviation was found to be an average of 0.08%.
- For aggregates with sulphide sulphur content in the approximate range of 1.2%, the multi-laboratory standard deviation was found to be an average of 0.28%.

Acknowledgements

The following organizations whose laboratories participated in the multi-laboratory study are gratefully acknowledged for their contributions to this study:

- **CRH Canada Group Inc.**, Mississauga, ON
- **CTLGroup**, Skokie, IL
- **Davroc Testing Laboratories Inc.**, Brampton, ON
- **Golder Associates Ltd.**, Burnaby, BC
- **Ministère des Transports, de la Mobilité Durable et de l'Électrification des Transports – Direction des Matériaux d'Infrastructures**, Québec, QC
- **Stantec Consulting Ltd.**, Dartmouth, NS
- **Tetra Tech Canada Inc.**, Calgary, AB
- **Votorantim Cimentos – St Marys Cement**, Bowmanville, ON and St. Marys, ON

The Ministry of Transportation Ontario, Materials Engineering and Research Office, is thanked for the use of its equipment and facilities for sample preparation.

The quarries that provided aggregate samples for the study are gratefully acknowledged for their contributions.

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Rodrigues, A., Duchesne, J., Fournier, B., Rivard, P., Durand, B. and Shehata, M. (2013b). Concrete in the 21st Century: Are we still fighting durability issues? Canadian Civil Engineer, Winter 2013.

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Tagnit-Hamou, A., Saric-Coric, M., and Rivard, P. (2005). Internal deterioration of concrete by oxidation of pyrrhotitic aggregates, Cement and Concrete Research, 35, 99–107.

Appendix A

DRAFT TEST METHOD*

Determination of sulphide sulphur content of concrete aggregates

*This draft test method is under development and subject to change; it should not be used for reference purposes.

1. Scope

1.1

This Test Method describes a procedure for testing coarse and fine aggregates to determine the content of sulphur present due to the presence of sulphide minerals.

The test may also be used to characterize the sulphate sulphur content of proposed (i.e., not previously used) sources of aggregate through the testing of exploration samples (e.g., rock drill core, chunk samples, test pit / drill samples from granular deposits).

1.2

Sulphur, when present in iron sulphides such as pyrite, pyrrhotite, chalcopyrite, and in other forms, can oxidize and hydrate with volume increase, or the release of sulphate that produces sulphate attack upon the cement paste, or both.

2. Reference publications

In addition to the references in CSA A23.1, this Test Method refers to the following publications, and where such reference is made it shall be to the editions listed below, including all amendments published thereto:

CSA Group

A23.1-19 [in development]

Concrete materials and methods of concrete construction

A23.2-1A-19 [in development]

Sampling aggregates for use in concrete

A3001-18 [in development]

Cementitious materials for use in concrete

A3005-18 [in development]

Test equipment and materials for cementitious materials for use in concrete and masonry

American Chemical Society (ACS)

Specifications and Procedures for Reagent Chemicals

Other Publications

Bérard, J., Roux, R., and Durand, M. (1975). Performance of concrete containing a variety of black shale. *Canadian Journal of Civil Engineering*, 2:58–65.

Rodrigues, A., J. Duchesne, B. Fournier, P. Rivard, B. Durand, and M. Shehata. (2012). Mineralogical and chemical assessment of concrete damaged by the oxidation of sulphide-bearing aggregates: importance of thaumasite formation on reaction mechanisms. *Cement and Concrete Research*, 42:1336–1347.

3. Summary

The sulphur present in the samples in excess of sulphate sulfur (HCl-soluble) is measured, calculated, and reported as sulphide sulphur, even though total sulfur might also contain some organic sulphur.

4. Significance and use

4.1

Oxidation of iron sulphides in concrete aggregate has led to expansion and cracking of concrete in Canada (Bérard *et al.*, 1975; Rodrigues *et al.*, 2012). Different iron sulphides can oxidize at different rates. Pyrite within an aggregate can be stable in concrete for many years throughout its service life. Pyrrhotite and marcasite can oxidize relatively rapidly. Pyrrhotite has caused significant problems in concrete in Canada and elsewhere.

4.2

This test measures the amount of sulphur present in an aggregate in the form of sulphide. Generally, certain sulphur-bearing minerals, such as pyrite, can be present in an aggregate without causing deleterious expansion or other effects such as staining of the concrete. However, if the sulphide is easily oxidized, usually when present in the form of fine-grained or framboidal pyrite, or as coarse crystalline pyrrhotite, the sulphur can cause adverse chemical reactions leading to expansion and cracking of the concrete. Further information regarding the reactions that can take place and a review of the literature on such reactions are found in Annex P of CSA A23.1.

4.3

Sulphur can be present in the form of sulfate or sulphide minerals. This test quantifies each of these two forms of sulphur.

4.4

Users are cautioned that the size of the sample selected will impact the likelihood of detecting harmful levels of sulphur. The sample sizes given in this test are judged suitable for those aggregates where the sulphides are fairly widely dispersed through the aggregate. In cases where there are very few sulphide-bearing particles, such as nuggets of sulphide in otherwise sulphide-free aggregate, the sample size might be insufficient to consistently detect their presence. Such nuggets can cause popouts or objectionable staining on concrete surfaces, or both but are unlikely to cause bulk expansion of the concrete.

4.5

Samples taken from above the groundwater table are often oxidized, and sulphide minerals might not be present, or might be present in reduced amounts. Samples taken from below the permanent groundwater table will often be unoxidized because water is an effective barrier to the oxidation process. Thus, within both quarries and gravel pits, and even in the same source, consideration should be given to the location and frequency of sampling relative to the groundwater table.

5. Apparatus and supplies

5.1 General

Equipment and materials, including the temperature and humidity of the testing room, dry materials, and mixing water, shall meet the requirements of CSA A3005, unless otherwise specified in this Test Method.

5.2 Apparatus

Depending on the test options chosen, the following equipment shall be used for the procedure:

- a) a small jaw crusher or other suitable equipment capable of crushing aggregate to pass a 2.5 mm sieve;
- b) a pulverizer or other suitable equipment capable of grinding aggregate finer than 2.5 mm to pass a 160 μm sieve;
- c) standard laboratory glassware;
- d) a balance, sensitive to 0.1 mg;
- e) crucibles, made of porcelain, platinum, alumina zirconia, or silica, of 10 to 25 mL capacity;
- f) a hot plate, electric or gas-heated with capability of temperature control;
- g) a furnace, electrically-heated and capable of regulating the temperature at 800 ± 25 °C;
- h) an x-ray fluorescence spectrometer; and
- i) one of the following:
 - i) a high temperature combustion analyzer for sulphur; or
 - ii) an inductively coupled plasma spectrometer (ICP).

5.3 Supplies

5.3.1 Water

Water conforming to the requirements of CSA A3005 shall be used for this testing.

5.3.2 Concentrated reagents

All reagents shall conform to the requirements of ACS *Specifications and Procedures for Reagent Chemicals* where such specifications are available. Where no such specification is given, the best grade obtainable shall be used.

5.3.3 Dilute reagents

Concentrations of reagents, except when standardized, shall be specified as the ratio of the number of volumes of the concentrated reagent to be diluted with the number of volumes of water.

Note: Hydrochloric acid (HCl 2:3) solution, for example, means 2 volumes of hydrochloric acid diluted with 3 volumes of water.

5.3.4 Non-standard solutions

Concentrations of non-standard solutions, prepared by dissolving a given mass of solid reagent in a solvent, shall be specified in grams of the reagent per litre of solution. Water shall be the solvent except if stated differently.

Note: Barium chloride ($BaCl_2 \cdot 2H_2O$, 100 g/L), for example, means 100 g of barium chloride di-hydrate ($BaCl_2 \cdot 2H_2O$) dissolved in water and diluted to 1 L.

5.3.5 Filter paper

Filter paper used shall be Grade 40: 8 μ m (medium speed, ashless) or equivalent.

6. Hazards

This Test Method does not purport to address the safety problems associated with its use. It is the responsibility of the user of this Test Method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

7. Sampling and preparation of test specimens

7.1 Sampling

The procedures outlined in CSA A23.2-1A shall be followed to obtain a representative sample of the aggregate to be tested (Table 1).

The sample, if possible, shall be obtained from a stockpile of aggregate produced in a manner identical to that which will be used in subsequent production.

Note: Some materials to be tested may be exploration samples, such as drill cores or test pit samples, in which case there will be increased doubt as to the applicability of the results.

7.2 Test specimen preparation

The test specimen shall be prepared as follows:

- a) Reduce the sample obtained in accordance with Clause 7.1 for further processing by the use of a sample splitter or by a suitable method of quartering to obtain a representative subsample (Table 1). No attempt shall be made to obtain the required test subsample by adding or subtracting individual pieces. Materials proposed for use as coarse aggregates in concrete shall be processed by crushing the minimum subsample mass given in Table 1, as described in Clause 8.3, to ensure that it is representative of the composition of the coarse aggregate as proposed for use.

| Nominal maximum Aggregate size, mm | Minimum mass of field samples, kg (from CSA A23.2-1A) | Minimum mass of subsample, kg |
|------------------------------------|---|-------------------------------|
| 14 and less | 15 | 3 |
| 20 | 25 | 5 |
| 28 | 50 | 10 |
| 40 | 75 | 15 |
| 56 | 100 | 20 |
| 80 | 150 | 60 |

- b) Crush the minimum mass of subsample (Table 1) to which this Test Method is applied using a small jaw crusher or other suitable means, so that the entire sample passes a 2.5 mm sieve. Take care that the jaw crusher is clean prior to use and that no material is lost.
- c) Mix the crushed test specimen thoroughly, and prepare, using a sample splitter or other suitable means, a representative specimen of 400 ± 10 g. Pulverize the specimen obtained in accordance with Clause 7.2.2 using suitable equipment so that it passes a 160 μ m sieve. Further treat any material retained on the 160 μ m sieve until it is able to pass the sieve. Take care that no material is lost.

Note: An intermediate step in sample reduction may be taken by reducing the 400 g of passing 2.5 mm sample to pass a 630 μ m sieve. 40 ± 1 g of passing 630 μ m, prepared by splitting or other suitable means, may then be reduced to pass 160 μ m. The sequence of sample reduction will depend on the equipment that is used.

- d) Mix thoroughly the material passing the 160 μm sieve. Obtain specimens of a suitable size for chemical analysis.

8. Procedures

Note: The sulphur present in the samples in excess of sulphate sulphur (HCl soluble) is calculated and reported as sulphide sulphur, even though total sulphur might contain some organic sulphur.

8.1 Total sulphur determination

8.1.1 Determination of total sulphur of the base sample

The total sulphur shall be determined by either high temperature combustion analysis or by powder x-ray fluorescence spectrometry.

Notes:

- (1) High temperature sample preparation methods such as fusion for x-ray spectrometry or inductively coupled plasma spectrometry can cause a loss of volatile sulphur.
- (2) Pyrrhotite is soluble in hydrochloric acid (HCl) and its decomposition will result in the formation and release of hydrogen sulfide gas (H_2S). Total oxidative sulphur analysis with aqua-regia therefore should not be used for total sulphur analysis.

8.1.2 High temperature combustion analysis

The total sulphur shall be determined on a separate sample aliquot by combustion at a minimum operating temperature of 1350 $^{\circ}\text{C}$ in a stream of oxygen. The high temperature combustion analyzer shall be equipped with either an acid base detection or infrared absorption detection system. The total sulphur analysis result shall be recorded as S_T . The sulphur, reported as sulphide (S_o), shall be calculated by difference in accordance with Equation 2.

8.1.3 Powder x-ray fluorescence analysis

The total sulphur shall be determined on a separate sample aliquot by preparing a pressed powder disc for analysis on an x-ray fluorescence spectrometer calibrated for sulphur (S) using properly matrix matched

calibration samples. The total sulfur analysis result shall be recorded as S_T . The sulphur, reported as sulphide (S_o), shall be calculated by difference in accordance with Equation 2.

8.2 Determination of sulphate sulphur

8.2.1 Blank determination

A blank determination shall be run, following the same procedure and using the same amounts of reagents as the test specimen.

8.2.2 Sample digestion with hydrochloric acid (HCl insoluble residue)

The procedure shall be as follows:

- a) Weigh a representative subsample of the aggregate of between 2 and 5 g and record the mass as M_1 . Quantitatively transfer it into a 250 Erlenmeyer flask or beaker.
- b) Add 50 mL of HCl (2:3).
- c) Bring the solution to and maintain at a boil for 30 min.
- d) Filter the contents into a 400 mL beaker through a tared glass frit, (mass recorded as M_2) which was previously dried at $105 \pm 5^{\circ}\text{C}$.
- e) Wash the filter paper and contents with a sufficient number of hot water washings to ensure no transferal of the HCl extract to the beaker as shown by a negative chloride reaction.
- f) Reserve the filtrate for the determination of sulphate sulphur (S_s).

Note: If desired, the glass frit with residue may be dried in an oven at $45 \pm 5^{\circ}\text{C}$ to constant mass, M_3 . The HCl insoluble residue may be calculated using Equation 3. The residue (R_s), which might require some pulverizing, may then be analyzed by high temperature combustion methods, for sulphur contained in mineral-sulphides not soluble in hydrochloric acid. Examples: Pyrite (FeS_2) and chalcopyrite (CuFeS_2) are not soluble in hydrochloric acid but are soluble in nitric acid (HNO_3). Residual hydrochloric acid fumes can damage the inner parts of the induction furnace; therefore, care should be taken to ensure the residue is free from chloride.

8.2.3 Determination of Sulphate Sulphur

The procedure shall be as follows:

- Dilute the filtrate obtained in accordance with Clause 8.2.2 to 250 mL and heat to boiling.
- Add slowly, dropwise, 10 mL of hot barium chloride solution ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, 100 g/L) and continue the boiling until the precipitate is well formed.
- Digest the solution for 12 to 24 h at a temperature just below boiling.
- Take care to keep the volume of solution between 225 and 260 mL and add water for this purpose if necessary.
- Filter through a retentive paper, wash the precipitate thoroughly with hot water, and place the paper and contents in a tared platinum crucible, (M_4).
- Slowly dry, char, and consume the paper without inflaming.
- Ignite at 800 to 900 °C, cool in a dissector, and weigh, (M_5).
- Calculate the sulphate sulphur in accordance with Equation 1.

Note: Alternatively, the filtrate obtained in accordance with Clause 8.2.2 may be quantitatively transferred and diluted to volume in a volumetric flask. An aliquot of this dilution may then be analyzed by inductively coupled plasma spectrometry for sulphate sulphur or by x-ray analysis using a suitably equipped and calibrated x-ray fluorescence spectrometer.

9. Calculation

The following equations shall be used to calculate results:

Equation 1: Sulphate sulphur (Clauses 8.2.2 to 8.2.3)

$$S_s = [(S_{M5} - S_{M4}) - (B_{M5} - B_{M4})] / M_1 \times 13.74$$

where: S_s = sulphate sulphur (as %S)

S_{M5} = sample ignited residue plus crucible, g

S_{M4} = sample tared crucible, g

B_{M5} = blank ignited residue plus crucible, g

B_{M4} = blank tared crucible, g

M_1 = sample mass, g

13.74 = molar ratio of S to $\text{BaSO}_4 \times 100$

Equation 2: Sulphide sulphur by difference (total sulphur – sulphate sulphur)

$$S_o = S_T - S_s$$

where: S_o = sulphide sulphur, wt% (Total – Sulphate Sulphur)

S_T = total sulphur, wt% (Clause 8.1 – either method)

S_s = sulphate sulphur, wt% (Clause 8.2 - HCl Soluble)

Equation 3: HCl-insoluble residue (information only if desired)

$$R_s = (M_3 - M_2) * 100 / M_1$$

where: R_s = insoluble residue, wt%

M_1 = sample weight, g

M_2 = glass frit empty weight, g

M_3 = glass frit with residue weight, g

Equation 4: Non-HCl-soluble sulphur in the HCl digestion residue

$$S_N = (S_R \times R_s) / 100$$

where: S_N = sulphide sulphur wt% (Non HCl soluble sulphur corrected to original sample mass)

S_R = sulphur wt% determined on the insoluble residue (see note to Clause 8.2.2)

R_s = insoluble residue, wt% (Equation 3)

100 = dimensionless to convert wt% residue to decimal %

10. Report

10.1 Required information

The report shall include the following:

- sample number or identification marks;
- type and source of aggregate;
- a description of the elevations and location of the quarry face or elevation and location within the gravel or sand pit that was sampled, and the location of the sample with respect to the groundwater table, if known;
- nominal maximum aggregate size and the mass of specimen;
- the weight percentage of the sulphate sulphur to the nearest 0.01%;

- f) the weight percentage of the sulphide sulphur to the nearest 0.01%;
- g) a description of the type of analytical method used;
- h) identification of the certified laboratory performing the test (i.e., name and address);
- i) name and signature of the person responsible for the review and approval of the test report; and
- j) any deviation from the test procedure.

10.2 Optional information

The following information may be included in the test report:

- a) name of the person or organization who sampled the aggregate;
- b) name of the technician performing the test; and
- c) date the sample was taken or received by testing laboratory.

11. Precision and bias

This is a recently developed method and as yet no formal multi-laboratory study has been conducted.

12. Interpretation of results

See Clause P.13.4 of CSA A23.1 for the interpretation of data obtained in this Test Method.

CSA Group Research

In order to encourage the use of consensus-based standards solutions to promote safety and encourage innovation, CSA Group supports and conducts research in areas that address new or emerging industries, as well as topics and issues that impact a broad base of current and potential stakeholders. The output of our research programs will support the development of future standards solutions, provide interim guidance to industries on the development and adoption of new technologies, and help to demonstrate our on-going commitment to building a better, safer, more sustainable world.

