MICROSCOPIC ANALYSIS FOR THE OXIDATION OF SULPHIDE-BEARING AGGREGATE

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Abstract

Mortar samples were prepared with sulphide-bearing aggregates and tested for the potential of aggregate oxidation and its subsequent sulphate attack. Scanning Electron Microscopy (SEM) was used as a tool to analyze the developed phases in the samples to confirm that the obtained expansion is attributable to sulphate attack. The Energy Dispersive X-Ray analysis (EDS) of the SEM helped to identify sulphide phases in aggregates and the presence of evidence of sulphate attack in mortars exposed to conditions that promote oxidation and sulphate attack. Ettringite and Thaumasite were detected and confirmed by EDS in the mortars with sulphide-bearing aggregates suggesting that the test conditions are suitable for reproducing the damaging mechanism of sulphide oxidation.

Keywords: Durability, scanning electron microscopy, sulphide-bearing aggregate, oxidation mortar bar.

Introduction

Some sulphide-bearing aggregates have been shown to cause deteriorations in concrete due to oxidation and subsequent sulphate attack[1–6]. Common signs of deterioration include map cracking, yellowish colour, and aggregate popout. The iron sulphide minerals Pyrite (FeS_2) and, to a larger extent, Pyrrhotite ($Fe_{1-x}S$ (x = 0 to x = 0.2) are the most prevalent and easily oxidized sulphide minerals. These sulphide minerals can be found in a wide range of rock types[7]. When iron sulphides are oxidized, sulfuric acid is released, which can attack calcium

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hydroxide or calcium silicate hydrate (CSH), releasing calcium ions to form gypsum or to break down the CSH[8,9]. Gypsum formation can cause strength loss[10] and is typically followed by secondary ettringite and Thaumasite formation. Furthermore, oxidation can result in the formation of rust in the form of ferric oxide and ferric oxyhydroxides[4], which can cause expansions and popouts.

Rodrigues et al.[10] and Elmosallamy and Shehata[11] used an oxidation mortar bar test (OMBT) to investigate the detrimental behaviour caused by utilizing sulphide-bearing aggregates in concrete. Furthermore, Elmosallamy and Shehata[14] attempted different exposure conditions that produced expansion and discriminated between aggregates with and without oxidizable sulphide. All exposures consisted of two stages: the first stage promotes the oxidation reaction of iron sulphides in the aggregate, whereas the second stage promotes gypsum, ettringite, and Thaumasite formation.

This paper demonstrates how SEM and EDS were used as tools to investigate the reasons for the obtained expansion in mortars with sulphide-bearing aggregates. This was carried out by analyzing the formed phases at the end of the test. The findings were used to evaluate mortar bar testing and improve its efficacy and applicability.

Experimental Investigation

Materials

The study involves testing two materials with known oxidizable sulphide aggregates. The investigated materials are:

- Maskimo (MSK): Containing Pyrrhotite. This aggregate was derived from Quebec, Canada, with total sulphur ranging between 07-1.0%. MSK was considered responsible for the severe deterioration in the concrete foundation in Trois-Rivières, Quebec, Canada[4,5,12-15].

- Aggregate ONS: Consists of Quartz-biotite schist with oxidizable sulphide minerals. This aggregate is from Ontario and has never been used in concrete. Petrographic examination demonstrated the presence of oxidizable sulphide minerals.

Experimental procedure

Samples Preparation:

Mortar bars were prepared with a water-to-cement ratio (w/c) of 0.65, cement-to-aggregate ratio of 1:2.7, and using the aggregate gradation of the Alkali-Silica Reaction (ASR) accelerated mortar bar test (CSA A23.2-25A)[16] of 5.00 mm to 150 µm. Each tested set comprised three specimens 25 x 25 x 285 mm equipped with a gauge stud in each end for measurements. Titanium studs were used for samples soaked in the oxidizing agent (bleach), while stainless steel studs were used for samples soaked in lime water, as explained in the following sections. Length measurements were taken at room temperature using a length comparator as per ASTM C490[17] every week. Samples were tested in a manner that promotes the oxidation of sulphide-bearing aggregate and subsequent internal sulphate attack by exposing them to two different exposure conditions as follows:

i. Exposure 1

Samples were prepared for this test following the oxidation mortar bar test in the protocol proposed by Rodrigues et al.[10,13]. The exposure condition comprises of two stages:

(a) Stage I (weeks 0 to 13): Soaking the samples in an oxidizing agent (sodium hypochlorite - bleach) for 3 hours followed by placing the samples for 3.5 days in the oven at 80 ℃ and 80% relative humidity (RH); and

(b) Stage II (weeks 13 to 26): Similar to stage I, the samples are immersed in bleach for 3 hours but followed by placing them 3.5 days in a fridge at 4 ℃ and 100% relative humidity.

According to the testing protocol[10,13], samples with expansions > 0.10% in stage II are deemed not suitable for use in concrete.

ii. Exposure 2

This test condition is developed by Elmosallamy and Shehata[12] in which samples were subjected in the oxidation stage to cycles of temperatures and relative humidity, without bleach. A saturated calcium hydroxide solution (lime water) was utilized as a soaking solution to bring the samples to a saturated condition at the start of each cycle. This test, similar to the oxidation mortar bar test, comprises of two stages: (a) Stage I (weeks 0 to 13): Samples are placed in the saturated lime solution for 3 hours followed by placing the samples for 3.5 days at 40ºC and 70% relative humidity. During this stage, it is anticipated that the RH within the sample would range from 100% to 70% during the 3.5 days storge at 40ºC; and (b) Stage II (weeks 13 to 26): Similar to Stage I, the samples are soaked in the saturated lime solution for 3 hours but followed by placing them 3.5 days in a fridge at 4ºC and 100% RH.

Scanning Electron Microscopy (SEM)

Samples from both tests containing aggregates ONS and MSK were prepared for SEM and EDS investigation to analyze the phases produced in the samples under each exposure condition.

The mortar bars were cut and dried by incubation in acetone solution to remove the water gently, without causing specimen shrinkage. After that, the samples were placed under vacuum for five days at 38ºC. The samples were then impregnated with epoxy and polished with a diamond grade of 0.3 µm. The polished specimens were sputtered with carbon using Edwards Vacuum Coating System Model #306A. The polished sections were studied in a JEOL JSM6380 LV - SEM operated at 20 kV in backscattered electron imaging mode (BSE).

Experimental Results and Discussion

An example of using SEM and EDS as a tool in this investigation is illustrated in Figure 1, taken on an aggregate particle within the mortar of the sample containing the aggregate ONS.
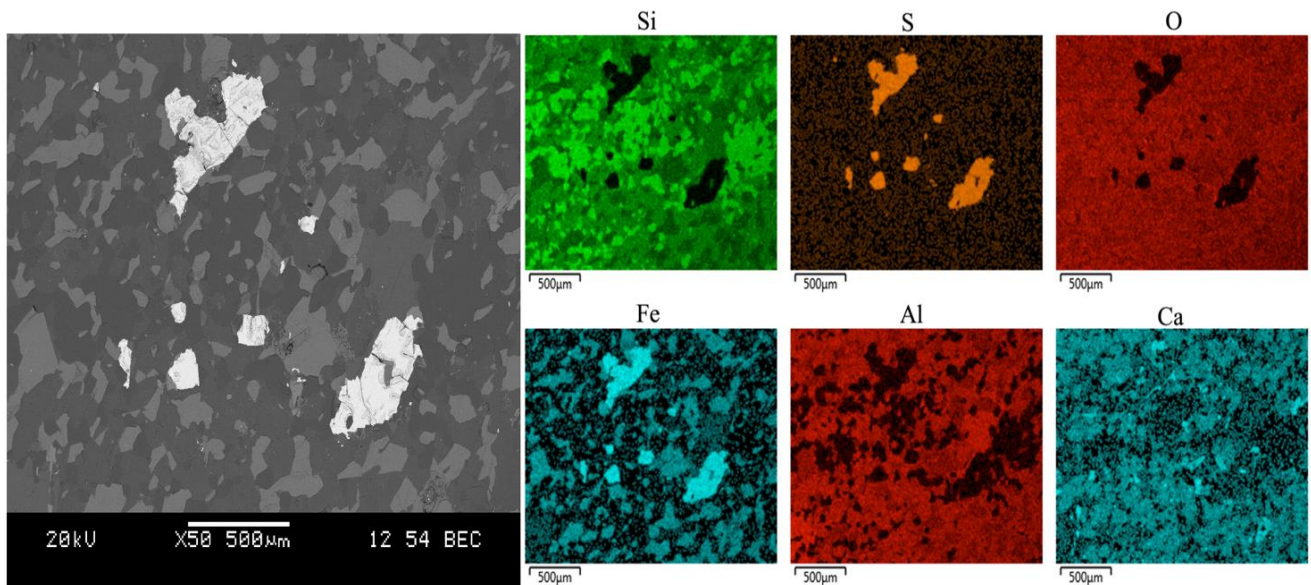
Figure 1. Evidence of unoxidized sulphides in the sulphide bearing aggregate ONS after 26 weeks of testing under Exposure 1.

Figure 1 shows sulphide phases within the particle identified by a very light color reflecting the higher atomic number of the constituents. The x-ray mapping confirms that the two spots are sulphide phases, as reflected in the high concentration of sulphur and iron. The presence of both sulphur and iron suggests that the iron sulphide phase is not oxidized yet, as oxidation would remove the sulphur. The fact that the phase did not oxide at the end of the test suggests that the test procedures do not result in full oxidation of all the sulphide phases. While this is not unexpected, perhaps the test can benefit from more prolonged exposure. Alternatively, the identified sulphide phase in this particle could be of the type that does not readily oxide or oxidize at a slow rate.

The expansions of mortar bars tested under Exposure 2 showed high expansions in the case of sulphide-bearing aggregates compared to aggregates without sulphides [12]. Samples from the tested mortar bars incorporating the MSK aggregate were prepared for SEM and EDS examination for element analysis. Figure 2 shows the SEM-EDS analysis for the mortar bar after 26 weeks of testing.

As shown in Figure 2, ettringite ($C_6A\hat{S}_3H_{32}$) was observed in the sample, indicating the oxidation of sulphide phases and subsequent sulphate attack. The theoretical atomic ratios of Al/Ca, and S/Ca in ettringite are 0.33 and 0.5, respectively [18, 19]. The ratios observed in the spectrum are 0.31 and 0.47 For Al/Ca and S/Ca, respectively which are close to the theoretical values. Since these phases were not detected in samples with non-sulphide aggregates, it is concluded that the expansion is due to the oxidation of sulphide phases and its subsequent sulphate attack.
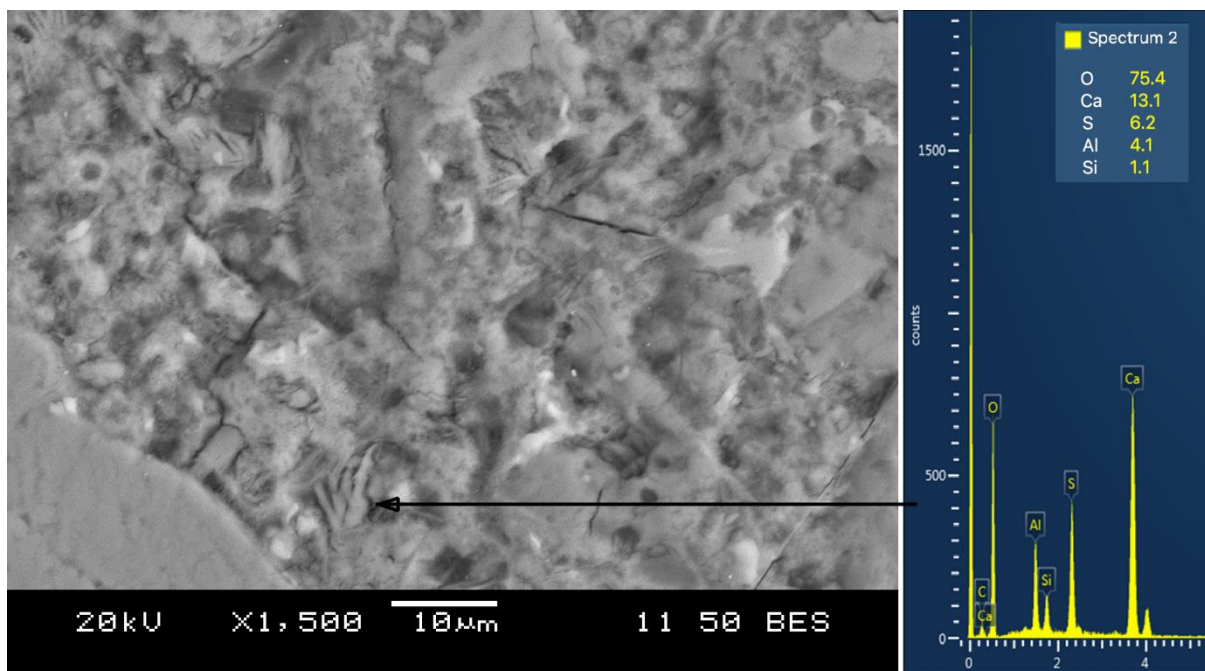

Figure 2. SEM analysis showing the presence of ettringite in mortar bar with MSK tested under Exposure 2

Figure 3 shows the presence of ettringite in location 1 as evidenced by a S/Ca and Al/Ca ratios of 0.42 and 0.33, respectively. The phase found in Location 2, however, is likely to be a monosulphoaluminate ($3C_4A\hat{S}H_{12}$) based on the detected elemental composition. The monosulphoaluminate has lower sulphur content with theoretical values of 0.25 for S/Ca and 0.5 the Al/Ca [18, 19]. The presence of an appreciable amount of silica in location 2 is not due to a substitution of alumina by silica as was reported by Glasser [20] and Elmosallamy and

Shehata[12], as the Al/Ca and S/Ca ratios satisfy the theoretical values for monosulphoaluminate. The detected silica is likely a background from materials surrounding the spot where the EDS was done. With the availability of more sulphur produced from further oxidation of aggregate, the monosulphoaluminate can change to ettringite, causing damaging expansion. The presence of silica and alumina on the same phase with calcium and sulphur may suggest that the phase is a mixture of ettringite and Thaumasite ($C_3S\hat{S}CH_{15}$). However, this is not the case here as the detected calcium and sulphur are not enough for both phases to coexist. Instead, the calcium and sulphur content satisfy the composition of monosulphoaluminate
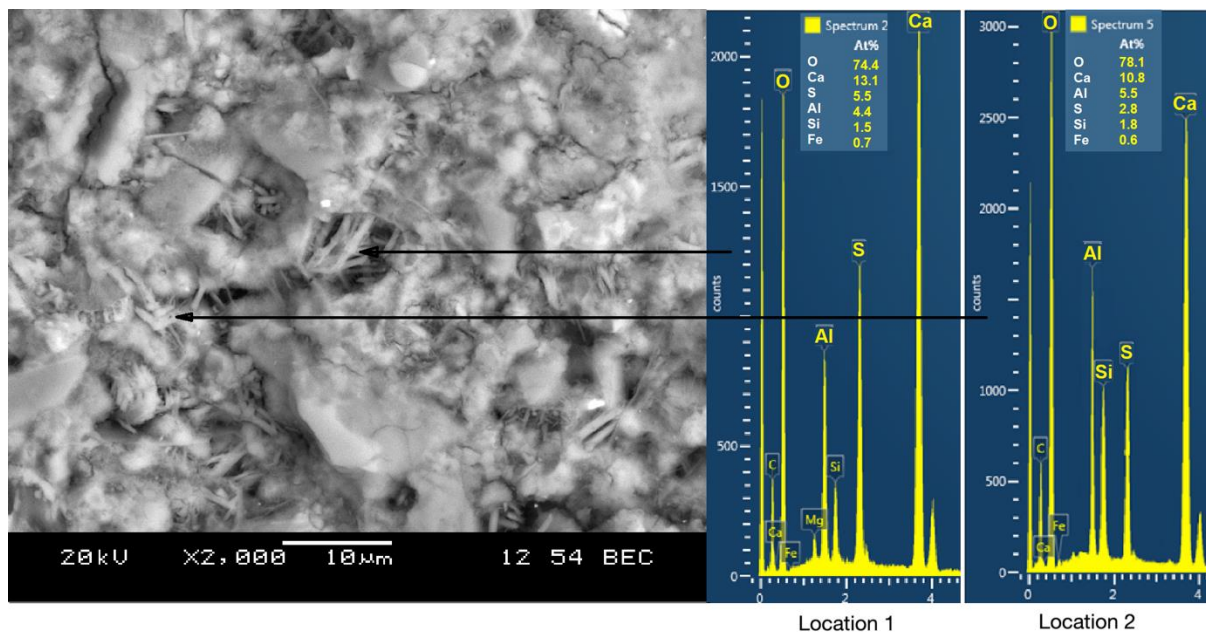

Figure 3. SEM analysis showing the presence of ettringite (location 1) and monosulphoaluminate (location 2) for mortar bar with MSK tested under Exposure 2

Figure 4 shows a BSE image of the mortar bar sample with MSK aggregate. The figure shows the separation between aggregate and the mortar at the interfacial transition zone (ITZ) in addition to mortar cracking. The shown deterioration suggests expansion in the paste, which is a result of the formation of the expansive products of sulphate attack
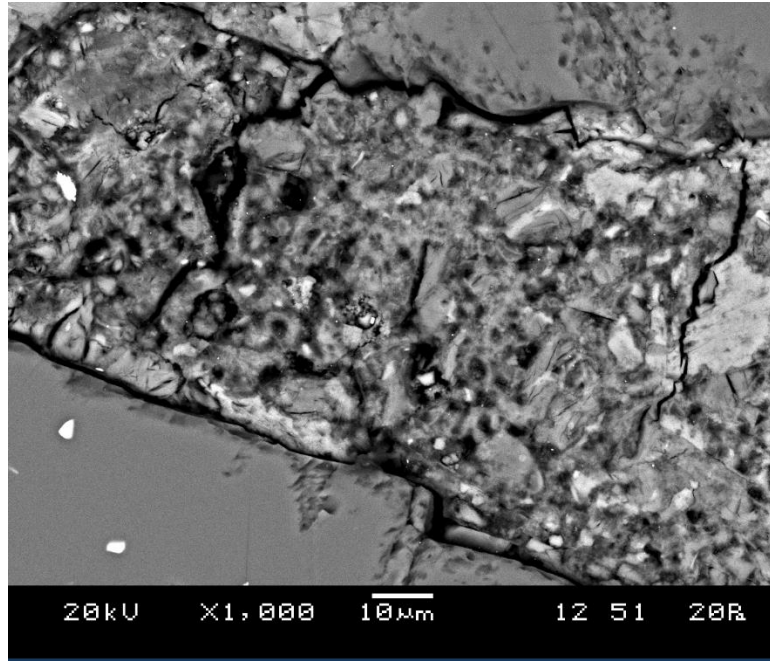
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Figure 4. SEM analysis for mortar bar with MSK showing the separation between the

aggregate and the mortar after 26 weeks of testing under Exposure 2

CONCLUSIONS

For the materials investigated in this study, the following conclusions are drawn:

1. The SEM and EDS analysis is an effective tool in detecting sulphate attack and oxidation of sulphide-bearing aggregates.

2. Using SEM and EDS can help identify iron sulphide phases and determine whether or not they are oxidized.

3. The use of elemental composition helps identify different phases in concrete by comparing the detected elemental ratios to those of the theoretical phase composition. In the current study, this approach was used to differentiate between ettringite and monosulphoaluminte.

4. BSE can help visualize the mode of damage in samples. In the current study, the separation between the aggregate and the mortar shows that a damaging expansion has taken place in the paste.

5. The findings of this study suggested that SEM and EDS are useful tools that can be used in conjunction with other analytical analyses to evaluate the mechanism of damage in cement-based samples.

REFERENCES

1. Belgeri J.J. and Siegel T.C., "Design and Performance of Foundations in Expansive Shale," *Ohio River Valley Soils Seminar XXIV,* Louisville, KY, Vol. 2, No. 6, 1998, pp 2-6.

2. Dougherty M. and Barsotti N., "Structural Damage and Potentially Expansive Sulfide Minerals," *Bulletin of the Association of Engineering Geologists,* Vol. 9, 1972, pp. 105-125.

3. Hawkins A.B. and Pinches G.M., "Understanding Sulphate Generated Heave Resulting from Pyrite Degradation," *Ground Chemistry Implications for Construction*. Rotterdam, Netherlands; 1997, pp. 51-75.

4. Rodrigues A.; Duchesne J. and Fournier B., "Quantitative Assessment of the Oxidation Potential of Sulfide-Bearing Aggregates in Concrete Using an Oxygen Consumption Test," *Cement and Concrete Composite,* Vol. 67, 2016, pp. 93-100.

5. Rodrigues A.; Duchesne J.; Fournier B.; Durand B.; Rivard P. and Shehata M., "Mineralogical and Chemical Assessment of Concrete Damaged by the Oxidation of

Sulfide-Bearing Aggregates: Importance of Thaumasite Formation on Reaction Mechanisms," *Cement and Concrete Res*earch, Vol. 42, No. 10, 2012, pp. 1336-1347.

6. Simonds K. and Epstein I., "Sulfate Attack on Concrete"; 2002.

7. Bryant L., "Geotechnical Problems with Pyritic Rock and Soil," Doctoral dissertation, Virginia Tech 2003.

8. Monteny J.; Vincke E. and Beeldens A., "Chemical, Microbiological, and in Situ Test Methods for Biogenic Sulfuric-Acid Corrosion of Concrete," *Cement and Concrete Res*earch, Vol. 30, No. 4, 2000, pp. 623–634. DOI: 10.1016/S0008-8846(00)00219-2

9. Orndorff Z.W., "Evaluation of Sulfidic Materials in Virginia Highway Corridors," Doctoral dissertation, Virginia Tech 2001.

10. Rodrigues A.; Duchesne J.; Fournier B.; Durand B.; Shehata M.H. and Rivard P., "Evaluation Protocol for Concrete Aggregates Containing Iron Sulfide Minerals," *ACI Material J*ournal Vol.113, No. 3, 2016, pp.349.

11. El-Mosallamy, M., & Shehata, M. H. (2020). Tests for Oxidizable Sulfides in Aggregates:Applicability and Limitations. ACI Materials Journal, 117(2), 229-240.

12. El-Mosallamy, M., & Shehata, M. H. (2020). Sulphide oxidation mortar tests for evaluation of the oxidation potential of sulphide-bearing aggregate. *Construction and Building Materials*, 264, 120627.

13. Rodrigues A.; Duchesne J. and Fournier B., "A New Accelerated Mortar Bar Test to Assess the Potential Deleterious Effect of Sulfide-Bearing Aggregate in Concrete," *Cement and Concrete Research*. Vol. 73, 2015, pp. 96-110.

14. Guirguis B. and Shehata M.H., "A New Screening Test to Evaluate the Presence of Oxidizable Sulphide Minerals in Coarse Aggregates," *Construction and Building Materials*. Vol. 154, 2017, pp.1096-1104.

15. Duchesne J. and Fournier B., "Deterioration of Concrete by the Oxidation of Sulphide Minerals in the Aggregate," *Journal of Civil Engineering and Architecture,* Vol. 7, No. 8, 2013, pp.922.

16. CSA A23.2-25A-14, "Test Method for Detection of Alkali-Silica Reactive Aggregate by Accelerated Expansion of Mortar Bars," 2014.

17. ASTM C490/C490M-11, "Standard Practice for Use of Apparatus for the Determination of Length Change of Hardened Cement Paste, Mortar, and Concrete," 2011.

18. S. Diamond, E.E. Lachowski, Investigation of the composition and morphology of individual particles of portland cement paste: 2. Calcium sulfoaluminates, 13 (1983.) 335–340.

19. Lachowski, E. E., Mohan, K., Taylor, H. F. W., & Moore, A. E. (1980). Analytical electron microscopy of cement pastes: II, pastes of Portland cements and clinkers. Journal of the American Ceramic Society, 63(7-8), 447-452.

20. Glasser, F. P.,"The Stability of Ettringite. International RILEM TC 186-ISA Workshop on Internal Sulfate Attack and Delayed Ettringite Formation," 22. Villars, Switzerland, 2002