# DURABILITY OF CONCRETE CONTAINING SULPHIDE-BEARING AGGREGATE: ASSESSMENT OF TEST METHODS

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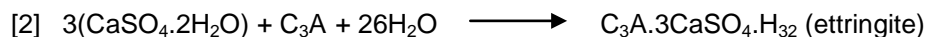Department of Civil Engineering, Ryerson University, Toronto, Ontario, Canada

Abstract: Oxidation of sulphide-bearing aggregates can result in severe damages in concrete structures. The mechanism of damage is believed to consist of two steps: (a) oxidation of the aggregate associated with an increase in volume, and (b) formation of sulphuric acid. Both steps produce damage to concrete. In order to gain an understanding of the oxidation potential of the aggregates, different types of sulphide-rich and non-sulphide bearing aggregates were tested using a simple oxidation test to find out the potential of oxidation in each aggregate. The test involves soaking the aggregate in strong oxidizing agents and exposing it to high temperature. The cycles of heating and soaking are repeated and the disintegration of the aggregates is measured by determining the mass loss after each cycle. The expansions of concrete containing these aggregates are presented which showed a relationship between the potential oxidation of aggregate as determined by mass loss and expansion in concrete. Concrete samples were tested using cycles of wetting in lime water at 23°C or 5°C and heating at 60°C while the expansion was slow, analysis using scanning electron microscopy illustrated that the tested concrete showed the presence of phases associated with sulphide oxidation in concrete.

1. Introduction

Concrete disintegration is a major issue that engineers face. Damage resulting from disintegration mechanisms decreases the serviceability of concrete buildings and leads to major economic loss. Disintegration of concrete can occur due to the effect of external deleterious factors such as de-icing salts, freezing and thawing, and external sulphate attack, or due to internal reactions of one or more of concrete ingredients such as the cases of alkali aggregate reaction and oxidation of sulphide-bearing aggregate. The concrete deterioration resulting from the use of sulphide- rich aggregate in concrete is thought to be due to the oxidation of sulphide minerals, namely pyrite (FeS_2), and pyrrhotite ($Fe_{(1-x)}S$) (Belzile et al. 2004, Chinchon-Paya et al. 2012). Once oxidation of sulphide minerals occurs, it produces sulphuric acid (H_2SO_4) due to the release of sulphur ion, and iron oxide in different forms such as goethite (FeOOH) (Steger 1982). The sulphuric acid in its turn reacts with $Ca(OH)_2$ to form gypsum (Gratten-Bellew and Eden 1975, Shayan 1988) following the equation:

[1] $Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4.2H_2O$ (gypsum)
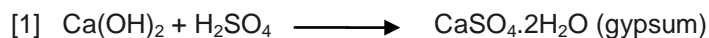
Gypsum can then react with cement paste causing different forms of sulphate attack. If the gypsum resulting from the oxidation of sulphide-bearing aggregate reacts with aluminate phase of the hydration product of cement or monosulphoaluminate, a form of sulphate attack is produced as per the following equations: (Taylor 1997, Ayora et al. 1998, Aguado et al. 2003, Neville 2004, Araújo et al. 2008):

[2] $3(CaSO_4.2H_2O) + C_3A + 26H_2O \longrightarrow C_3A.3CaSO_4.H_{32}$ (ettringite)

[3] $2C\bar{S}H_2$ (gypsum) $+ C_2A\bar{S}H_{12}$ (monosulphoaluminate) $+ 16H_2O \longrightarrow C_6A\bar{S}_3.H_{32}$ (ettringite)

Thaumasite is one of the severe sulphate attack products which can affect the concrete structures, it consists of calcium-silicate-sulphate-carbonate-hydrate, which favorably forms at temperatures under 5°C. The source of sulphate could be ettringite, where thaumasite use the ettringite as a nucleation site to

form, while calcium (CaO) and silica (SiO_2) are usually from calcium silicate hydrate (C-S-H). Source of carbonate might be from air, from carbonate fillers used to produce Portland cement, or from carbonate aggregates.

2. Experimental program

The Scope of work in this paper focuses on: (a) establishing a simple quick and economical test method to evaluate the potential oxidation of aggregate, and (b) developing a concrete test method that mimic the concrete damage due to oxidation of sulphide-bearing aggregate.

2.1 Material properties

Six types of coarse aggregate are used in this study:
(1) CM: a sulphide-bearing aggregate from a quarry in Northern Ontario. The sulphide phases comprise 1-2% of the aggregate.
(2) MW: pyrite and pyrrhotite-rich pieces of mine waste. The mine waste originally came from a nickel mine in Northern Ontario in 1972 or 1973. The collected material was meant to be used in this study to represent high contents of sulphide for test method development and for assessing effects of w/cm. This aggregate has a sulphide content of 56% by mass of the aggregate.
(3) MAS: it is a sulphide-bearing aggregate from Quebec, which consists mainly of pyrrhotite, and noticeable amounts of pyrite, chalcopyrite and pentlandite. The sulphide phases comprise about 2.8% of the aggregate.
(4) Co1: is a crushed quarried dolostone from the Amabel Formation in the Hamilton-Burlington area. The main component is calcium magnesium carbonate $CaMg(CO_3)_2$. In some areas the formation may contain vugs (open spaces); and it is possible to rarely find sulphide minerals especially in these open spaces. The Amabel Formation has an exceptional history of very good field performance as high-quality concrete aggregate in the province of Ontario, with no reported performance issues.
(5) Co2: is traprock which consists of a very fine-grained to aphanitic metabasalt. This aggregate was chosen for a control aggregate because it is an example of an extremely durable, fairly homogeneous, non-carbonate rock type that has almost no sulphide content, although trace disseminated pyrite may be present locally as well as trace amounts on fractures surfaces.
(6) Ore: It is high sulphide aggregate from the Copper Cliff Mine in Sudbury and the approximate grade of the material is: 1.6% Cu & 1.9% Ni & 20% Sulpher & 56% Sulphide.

A general Use (GU) Portland cement, from Ontario (Canada), were used in concrete samples. Three types of coarse aggregate are used, which are (MW & MAS & Co2) and were soaked in limewater solution.

2.2. Aggregate tests

In order to examine oxidation potential of aggregates, the rock cylinder test as described in (ASTM C586) was initially adopted. The rock cylinder is used to evaluate the potential alkali-carbonate reactivity of aggregate by immersing a small sample in the form of a cylinder or prisms of 40 mm length and 10 mm diameter or 10 x 10 mm cross section in 1 N sodium hydroxide solution. In this test, the sample was immersed in an oxidizing agents including sodium hypochlorite (bleach) or lime water. Unlike the rock cylinder test the samples in this test were exposed to cycles of soaking in the oxidizing agent. Initially, the sample was dried in an oven at 100ºC for 24 hours after being prepared in the form of prisms as shown in Figure 1. After that, the samples were subjected to cycles of soaking at room temperature for 7 days followed by drying at 100ºC for other 7 days. The expansion was measured after soaking period while the aggregate was saturated surface dry at room temperature.

(A)   (B)

Figure 1: (A) The standard shape and size, adopted from ASTM C586   (B) Rock cylinder sample prepared in the lab

2.3 Mass loss tests

Based on the obtained results of the rock cylinder test (will be discussed under "Results"), a similar test that is based on mass loss rather than expansion was adopted. The samples were taken from five different aggregates (Ore & CM & MAS & Co2 & Co1) of size larger than 5 mm and were exposed to, three different solutions : (a) bleach = 6% (pH = 11.32), (b) Limewater = 2% (pH = 12.07), or (c) ($KMNO_4$ + Limewater) = 1% + 1% (pH = 12.61). In the testing regime the aggregate was stored in the oven at $100^{\circ}C$ for 24 hours. The samples were then allowed to cool down for 5 hours and the original or zero mass reading was taken. Then, the aggregates were soaked in one of the solution for 5 days at $80^{\circ}C$. After that, the samples were taken out from solutions and were placed in a tray in an oven at $100^{\circ}C$ for 1 day followed by cooling down for 5 hours, the aggregate were sieved over sieve 300 um and the retained mass was determined. The cycles were repeated for 7 cycles where, each cycle runs for a duration of one week. This was the first attempt to run the test and the original mass of aggregate was not kept constant, and hence the aggregate-to-oxidizing agent ratio was not the same for all aggregate. At later stages, the test was carried out using a constant mass-to-oxidixing agent ratio of 1:10 using two sizes of aggregates: (a) 2.36 mm to 5 mm where the mass of aggregate was 25 g and the mass of solution or oxidizing agent was 250 g, and (b) 5 mm to 10 mm where the mass of aggregate was 100 g and the mass of oxidizing agent was 1000 g. For testing the 2.36 to 5.0 mm aggregate, five different aggregates (Ore & CM & MAS & Co2 & Co1) were investigated. The same procedures explained above was followed except that sieve 600 um instead of sieve 300 um was used to screen the aggregate.

2.4 Concrete prism samples

Concrete prisms with standard dimensions of 76 mm x 76 mm x 285 mm were used in this investigation. The samples were prepared and tested under an exposure condition that promote the oxidation of sulphide-bearing aggregate and the formation of gypsum, ettringite and thaumasite, which are different forms of sulphate attack. Three different coarse aggregates (MW, MAS, Co2) were used in the concrete mixtures and subjected to different conditions of temperature, relative humidity (RH), and different periods of wetting and drying cycles in lime water with 2% lime concentration (saturated). Concrete of w/cm of 0.65 was tested. Each concrete sample consisted of a minimum of 3 specimens, cast from the same mixture. All samples were cured for 7 days in a standard moist curing room at RH > 95%. After that, samples were stored in a standard shrinkage room for 7 days at RH of 50% ± 4% prior to exposure to the test conditions. All measurements are taken at room temperature. Samples from concrete prisms were cut, dried under vacuum and impregnated with epoxy in preparation for SEM examination. Backscattered electron images and energy dispersive x-ray analysis were carried out on polished samples coated with carbon.

3. Results and discussion

3.1 Effect of sulphide content of aggregate on oxidation

3.1.1 Rock cylinder test result

Table 1 shows the expansion results of MW aggregate when tested in bleach and lime water. The test was carried out for 4 weeks or two cycles only. The test was stopped because the edges of the rock prisms tested in bleach were broken and expansion measurements could not be taken. Figure 2 shows the samples after two cycles where evidences of oxidation and edge damage are shown. It was also observed that the damage or the disintegration of the aggregate is mainly in the form of materials loss. Hence, it was decided to move from rock cylinder which relies on monitoring expansion to the mass loss test where mass of aggregates particles is monitored after being exposed to cycles that promote oxidation.

Table 1: Rock cylinder test results after 2 cycles

Bleach							Limewater						
Readings (mm)			Expansion %			Expansion %	Readings (mm)			Expansion %			Expansion %
A	B	C	A	B	C	Ave.	A	B	C	A	B	C	Ave.
5.669	5.021	5.354	0	0	0	0	8.852	8.720	8.839	0	0	0	0
5.712	5.074	5.436	0.11	0.14	0.21	0.16	8.854	8.722	8.854	0.01	0.01	0.04	0.02
5.748	5.082	5.486	0.21	0.16	0.35	0.24	8.860	8.735	8.869	0.02	0.04	0.08	0.05

Figure 2: The MW oxidized samples and some iron oxidized precipitated in container

3.1.2 Mass loss test results

Table 2 shows the mass loss % for five types of aggregate tested using three different solutions. The results showed that all aggregates with sulphide content suffered a high mass loss when bleach was used as an oxidizing agent. No mass loss was observed with any aggregate when lime solution was used, and a small loss was observed when (limewater + potassium permanganate) was used. The two types of control aggregates with no sulphide phases did not show any losses with any solution.

Table 2: Mass loss % for five types of aggregates in three different solutions after 7 cycles

Aggregate Type	Mass loss %		
	b	L	L+K
Ore	46.13	0	2.07
CM	10.68	0	1.85
MAS	4.6	0	1.11
Co1	0.67	0	0
Co2	0.44	0	0

Mass loss of aggregate size between 2.36 and 5.00 mm with mass-to-solution ratio of 1:10

Table 3 shows the different results of the same five aggregates soaked in bleach after 4 weeks of testing (4 cycles). This test applied for 4 weeks only due to the small plastic containers were damaged when stored in at $100^{o}C$ after 4 cycles only.

Table 3: Mass Loss % of aggregate size between 2.36 and 5.00 mm

WEEK	Measuring	Ore	MAS	CM	CO2	CO1
0	M0	0	0	0	0	0
1	M1	8.4	6.4	4.8	0	1.2
2	M2	10	8	7.6	0	2
3	M3	12	9.6	8.8	0.8	4
4	M4	19.6	11.6	12	0	4.8

The results after 4 cycles showed aggregates with sulphide, Ore, MAS and CM, to show high mass loss. The control aggregates with no-sulphide did not show significant loss. Figure 3 shows the precipitation of iron oxidized in the bottom of the container used to test Ore aggregate.

Figure 3: Progression of damage in Ore: left image: before testing, middle: after testing, and right: precipitation of iron hydroxides.

Mass loss of aggregate size between 5.00 and 10.0 mm with mass-to-solution ratio of 1:10

Table 4 shows the mass loss of aggregates tested using sizes from 2.3 mm to 5.00 mm after 7 weeks and (7 cycles). For CO2 aggregate, the plastic container was damaged due to high temperature after 4 cycles and no more reading was taken. It is interesting to see that, the smaller the size of aggregate the higher the mass loss. This is likely due to the large surface area of the smaller size of aggregates.

Table 4: Mass loss % of aggregate size between 5.00 and 10.0 mm

WEEK	Measuring	Ore	MAS	CM	CO2	CO1
0	M0	0	0	0	0	0
1	M1	8.7	5.7	3.3	1	0.9
2	M2	10	7.2	4.6	1	1.2
3	M3	15.8	7.4	5.8	1.1	1.2
4	M4	19.3	7.5	7	Container damaged	1.3
5	M5	28.2	8	7.8	-	1.3
6	M6	38.5	11	12.9	-	1.3
7	M7	46	14.7	15.8	-	1.0

3.2 Effect of sulphide content of aggregate on expansion

In this part of the program, the effect of aggregate type is investigated using the concrete prism test (Bassili Guirguis et al. 2014). Three aggregates were used in the concrete mixtures, i.e. MW, MAS, and Co2. The aggregates were listed in the order of their sulphide content – higher to almost none. All samples were soaked in limewater at 23°C or 5°C and had w/cm of 0.65. The bar chart in Figure 4, shows very high expansion in MW, limited expansion with MAS, and approximately no expansion in Co2 after 12 weeks. The mass loss of each aggregate for size 5 and 10 mm is shown at the top of each bar after 6 cycles.
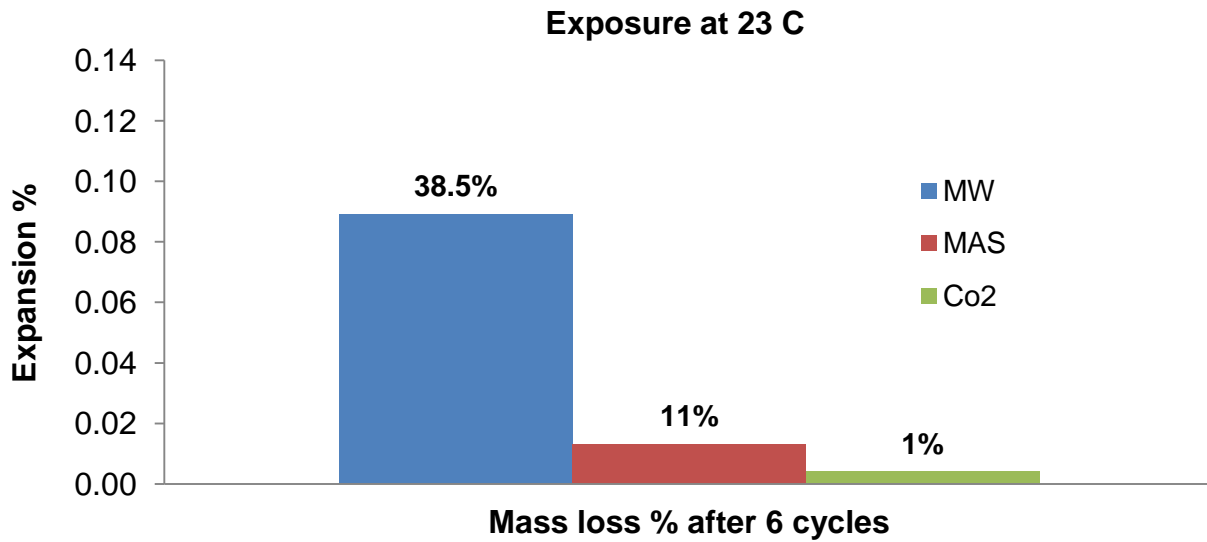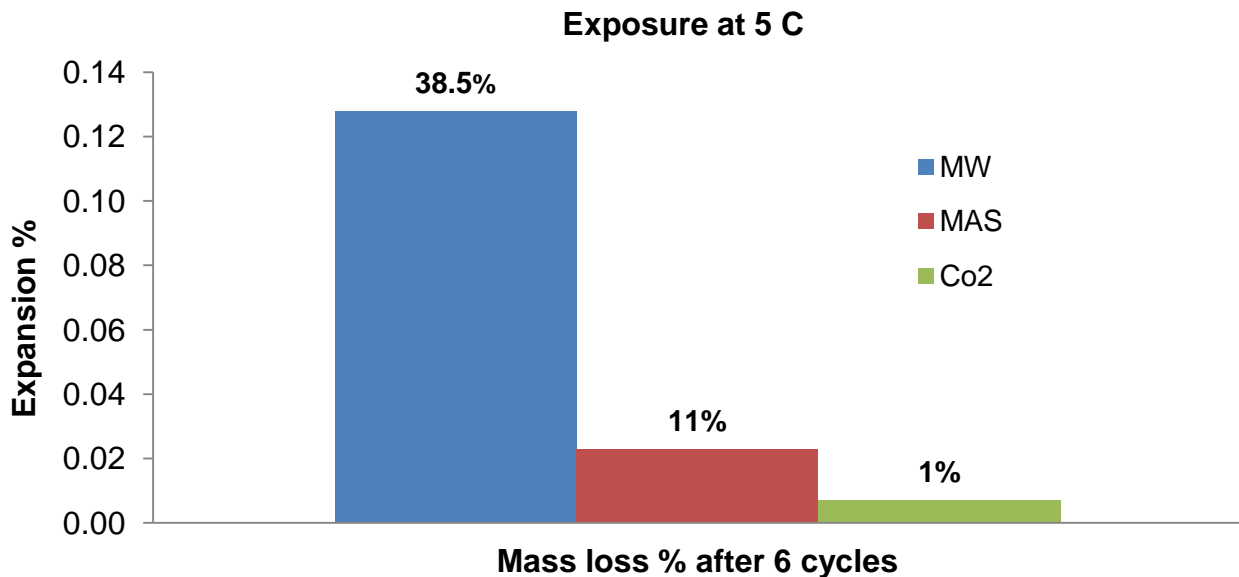
Exposure at 23 C

Figure 4: Expansion of concrete prisms containing MW, MAS and Co2 aggregates tested under repeated cycles of soaking in lime water at 23°C and oven at 60°C.

The expansion of concrete samples containing the same aggregates using the same exposure but soaked at 5°C, instead of 23 °C, is shown in Figure 5. The expansions for all aggregates were slightly higher than those reported in Figure 4 (at 23°C). It should be noticed that the 12 week-testing period reported in Figures 4 and 5 is very short given the nature of the reaction.

Exposure at 5 C

Figure 5: expansion of concrete containing MW, MAS and Co2 aggregates under repeated cycles of soaking in lime water at 5°C and oven at 60°C.

3.3 Scanning electron microscopy (SEM) examination

SEM examination of the concrete samples were carried out to identify the mechanisms that caused the expansion; i.e., ettringite and/or, thaumasite formation. The samples were prepared from the concrete prisms presented in Figures 4 and 5 after being stored at 50% RH and room temperature for 20 weeks and then, moved to 100% RH for other 8 weeks at room temperature. This made the age of the sample to be 40 weeks out of which the samples were tested in cycles of soaking in lime water at 5°C C or 23°C and heating at a temperature of 60°C for the first 12 weeks . There was no change in the expansion when the samples were stored at 50% RH, just a small level of shrinkage. When placed at 100% RH, the sample regain the shrinkage and continue to expand but still at a slow rate. It was found, as shown in Figure 6, that ettringite was formed in concrete samples with MAS soaked in limewater at 23°C and the formation of ettringite and solid solution of ettringite/thaumasite was observed in concrete with the same MAS aggregate at 5°C as shown in Figure 7. This is consistent with literature pertaining to sulphate attack in which it is known that thaumasite is favoured at low temperature 5°C while, ettringite is favoured at higher temperature; i.e., 23°C. However, in many of the cases, ettringite was also found at low temperature and a solid solution of both phases, ettringite and thaumasite, were found at both temperatures.
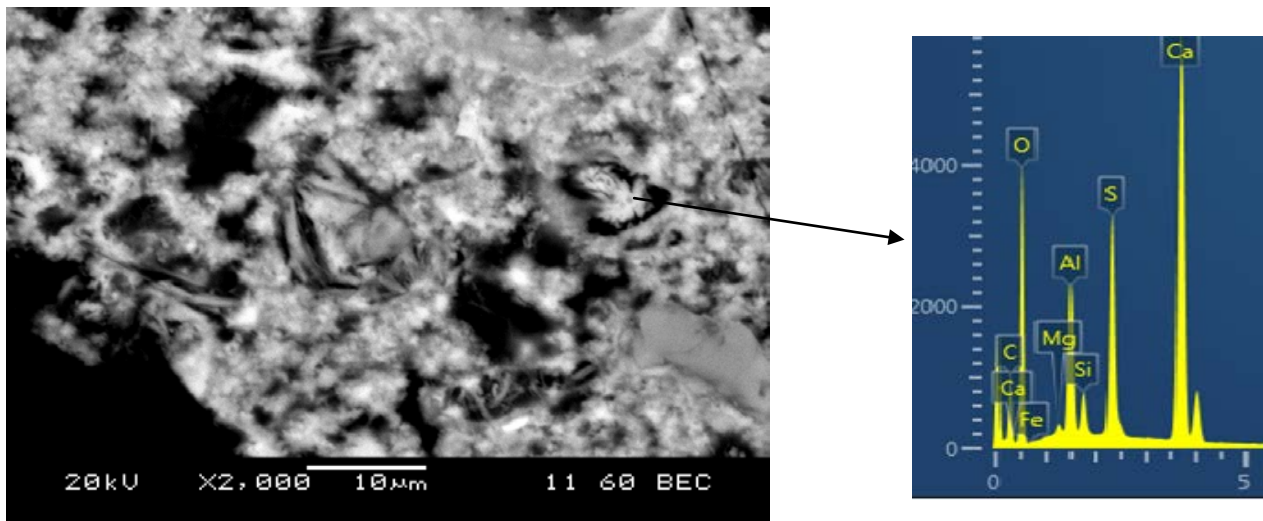

Figure 6: Ettringite formation in concrete samples with MAS aggregate exposed to cycles of soaking in limewater at 23°C and heating at 60°C and the expansion was 0.026% after 40 Weeks.
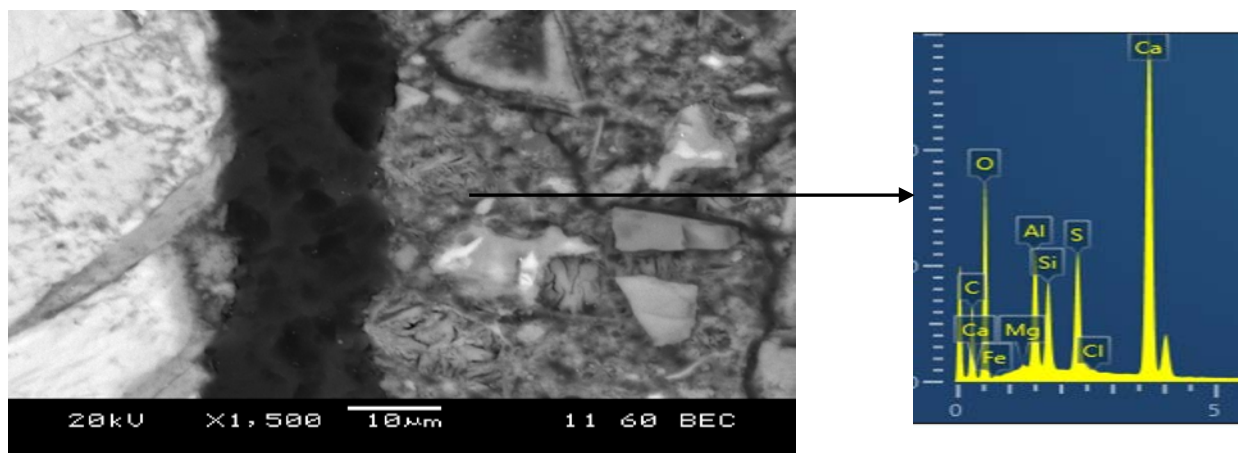

Figure 7: Thaumasite/ettringite formed in concrete samples with MAS aggregate exposed to cycles of heating at 60°C and soaking in lime water at 5°C with expansion was 0.027% after 40 Weeks.

4. Conclusions

1. A simple test is presented to evaluate the presence of oxidizable sulphide phases in aggregate. The method was find to have a good correlation with the expansion of concrete containing such aggregate.
2. Measuring mass loss of aggregates exposed to oxidizing agent provided more realistic results than measuring expansion of rock cylinders made of the same aggregates and exposed to oxidizing agent. This is because the oxidation affect the edges of the rock cylinder making it hard to measure the length. In addition, the oxidation process of aggregates cause more breakdown than swelling or expansion under the test conditions.
3. The expansion of concrete prisms under cycles of wetting in lime solution and heating showed expansion but the rate was very slow, except for one aggregate that contains very high level of sulphide phases.
4. Microscope examination of concrete samples showed the presence of phases that are attributable to internal sulphate attack – likely as a result of oxidation of sulphide phases in aggregates.

5. Acknowledgments

6. References

Aguado, A., Rodrigues-Ferran, A., Casanova, I., Agulló, L., 2003. Modelling time evolution of expansive phenomena in concrete dams as a decision-making tool. Commision Inter - nationale des Grandes Barrages, Montreal. 30 pp.

Araújo, G.S., Chinchón, S., Aguado, A., 2008. Evaluation of the behaviour of concrete gravity dams suffering from internal sulfate attack. Ibracon Structures and Materials Journal 1, 17 – 45.

ASTM C 586 - 05, Standard test method for potential alkali reactivity of carbonate rocks as concrete aggregates (rock-cylinder method). This test method is under the jurisdiction of ASTM committee C09 on concrete and concrete aggregates and is the direct responsibility of subcommittee C 09.26 on chemical reactions.

Ayora, C., Chinchón, S., Aguado, A., Guirado, F., 1998. Weathering of iron sulfides and concrete alteration: thermodynamic model and observation in dams from Central Pyrenees. Spain, Cement and Concrete Research 28, 1223 – 1235.

Bassili Guirguis, Medhat Shehata, Josée Duchesne, Benoit Fournier, Benoit Durand, Patrice Rivard, 2014. Developing of test methods to evaluate the potential damage in concrete containing sulphide bearing aggregate. CSCE 4th international structural speciality. Halifax, NS, CST175.

Belzile, N., Chen, Y.W., Cai, M.F., Li. Y., 2004. A review on pyrrhotite oxidation. Journal of Geochemical Exploration 84, 65 – 76.

Chinchon-Paya, S., Aguado, A., Chinchon, S., 2012. A comparative investigation of the degradation of pyrite and pyrrhotite under simulated laboratory conditions. Engineering Geology, 127: 75 – 80.

Grattan-Bellew, P.E., Eden, W.J., 1975. Concrete deterioration and fl P. heave due to bio- geochemical weathering of underlying shale, Can. Geotech. J. 12, 372 – 378.

Neville, A., 2004. The confused world of sulfate attack on concrete. Cement and Concrete Research 34, 1275 – 1296.

Shayan, A., 1988. Deterioration of a concrete surface due to the oxidation of pyrite con- tained in pyritic aggregates, Cem. Concr. Res. 18, 723 – 730.

Steger, H.F., 1982. Oxidation of sulphide minerals VII. Effect, of temperature and relative humidity on the oxidation of pyrrhotite, Chem. Geol. 35, 281 – 295.

Taylor, H.F.W., 1997. Cement Chemistry, 2nd ed. Thomas Telford Publishing, London.