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Sulphide Oxidation Mortar Tests for Evaluation of the Oxidation Potential of Sulphide-Bearing Aggregate

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Highlights

- Conditions are established to promote oxidation of sulphide-bearing aggregates and subsequent sulphate attack in mortar.
- Two test conditions were found effective in discriminating between aggregates with sulphide and those without.
- One test method involves soaking samples in an oxidizing agent at room temperature.
- The second test method relies on test cycles at certain temperatures and relative humidity.
- The use of slag and low-calcium fly ash reduced the expansion, unlike Metakaolin used at 10%.

ABSTRACT

This paper proposes two new sulphide oxidation mortar bar tests. The two tests involve two exposure conditions: the first one relies on soaking the sample is an oxidizing agent (6% sodium hypochlorite) for three hours at room temperature to promote oxidation while the other test adopts a range of temperature and relative humidity that promote oxidation and sulphate attack. Both tests were effective in discriminating between aggregates with sulphide and those without. Moreover, the effect of supplementary cementing materials (SCM) on the expansion was investigated. Some SCM reduced the expansion but not to the level of bars with non-sulphide aggregates.

Keywords: Sulphide, pyrrhotite, mortar bars, sulphide-bearing aggregate, aggregate oxidation, durability, test methods

1. Introduction

Deteriorations and expansions were reported for concrete elements containing aggregates with small amounts of iron sulphide minerals [1-7]. The deteriorations appeared in the form of whitish deposits, yellowish coloring, stains, pop-outs and map cracking [4,6,7]. In most of the reported cases, the coarse aggregate used to produce the concrete contained various proportions of the iron sulphide mineral, pyrrhotite (Fe_{1-x}S (x=0 to 0.125)). Oxidation of iron sulphide minerals in concrete elements produces sulphuric acid and different forms of rust such as iron hydroxides [4]. Sulphate ions from the produced sulphuric acids can react with the tricalcium aluminate phase of the hydrated cement paste or monosulphoaluminate, and re-crystallize in the form of ettringite [6,8]. These ions can also attack the C-S-H in the cement paste and form Thaumasite [4]. Formation of these materials, results in significant loss of strength, spalling, pop-outs, cracks, and concrete expansion.

In order to evaluate the susceptibility of sulphide-bearing aggregates to oxidation, screening test methods have been suggested to test aggregates for the presence of sulphide [9-11]. Seaton [9] developed a steam test to detect the impurities in cinder aggregates based on visual examination of the stains on filter papers. The test involved exposing crushed aggregate placed in a white filter paper in a cheesecloth bag to steam at 100°C for 16 hours. The filter papers are then thoroughly washed and dried in an oven at 94 to 105°C. The quantity and intensity of the stains on the papers can be then used to evaluate the tendency of the aggregate to develop pop-outs. Guirguis and Shehata [10] proposed a screening test that involves soaking the crushed aggregate in an oxidizing agent (sodium hypochlorite, bleach) and monitor the mass loss after cycles of soaking/drying to determine aggregate susceptibility to oxidation. The color of the soaking solution and its chemical composition after the test were also

used to detect the presence of oxidizable phases [10].

Rodrigues et al. [12] developed a testing protocol for the evaluation of the aggregate susceptibility to oxidation that is adopted as an Annex in the CSA 23.1 [13]. The protocol consists of three sequential steps: (i) the first step is determining the total sulphur content; (ii) the second step is testing aggregates for oxygen consumption [12,14] using the oxygen consumption test (OCT). Aggregates are considered to pass the test if the consumption is $\leq 4\%$ after 3 hours [13]; and (iii) the third step is measuring the expansion using a mortar bar test [12,15], referred to later on as the Oxidation Mortar Bar test (OMBT) [16]. In this test, aggregates are considered suitable for use in concrete if the expansion between 90 and 180 days was $\leq 0.10\%$ [13]. Jana [7] suggested a 5-step aggregate screening test that involves: aggregate petrographic analysis; measurement of sulphur content (SO₃); XRF analysis to determine the types of iron sulphide minerals; monitoring the level of released sulphide by subjecting aggregate to 35-40% hydrogen peroxide solution, and finally aggregates that do not show acceptance from the previous steps should be tested for the OMBT developed by Rodrigues et al. [12]. El-Mosallamy and Shehata [16] studied the applicability of the protocol developed by Rodrigues et al. [12] on aggregates of different compositions and origins. The study suggested some modifications to the OCT test procedures and new expansion criteria for the OMBT. The new criteria for the OMBT were developed to take into consideration the expansion developed in bars containing silicate aggregates regardless of their sulphide content. The obtained expansions in bars with such aggregates were thought to be a result of the long duration of exposing the mortar bars to heat and sodium hypochlorite (bleach) resulting in the dissolution of silica from the aggregates leading to expansion.

This paper aims at developing another test method for mortar bars with conditions that lead to expansion due to oxidation of sulphide phases and its subsequent sulphate attack - with no or minimal expansion due to any other mechanisms. The developed test involves different conditions of temperature and relative humidity with or without the use of an oxidizing agent.

2. Materials and Experimental Methods

2.1. Materials

Cementing materials used in this study are General Use (GU) Portland cement and three types of supplementary cementing materials: (a) Low-calcium fly ash (FA), (b) Granulated blast furnace slag (SG), and (c) Metakaolin (MK). The chemical compositions of these materials are listed in Table 1. In addition, the following aggregates were used in this study:

- Sulphide ore (ORE), a mine waste rock from the Sudbury area, Ontario, Canada, which contains total sulphur of 14%. The main iron sulphide minerals in this rock are pyrite, pyrrhotite, pentlandite, and chalcopyrite. Sulphide ore is used in this study at replacement levels of 10% and 20% by mass of the total aggregate with the remainder being a control limestone aggregate with no sulphides.
- Maskimo (MSK), a sulphide bearing aggregate from Quebec, that contains Pyrrhotite. This aggregate was deemed responsible for the severe deterioration in the concrete foundation in Trois-Rivières, Quebec, Canada [4,12,15,17,18].
- Aggregate # 1052, a sulphide bearing aggregate that is mainly quartz-biotite schist from Ontario with 0.543% total sulphur content. The petrographic examination of this aggregate showed the presence of oxidizable sulphide mineral in the form of discrete isolated particles or nuggets. It should be noted that this aggregate has never been used in concrete.
- Control aggregate C1: Crushed quarried limestone with excellent history as a nonreactive aggregate and is used in concrete in Toronto, Canada.
- Aggregate # 1046: Metabasalt coarse aggregate from Ontario (Traprock).
- Aggregate # 1049: Quartzite with mafic dike from Ontario with 93% silicates. It should be noted that this aggregate failed the OMBT of the original testing protocol [16] which was attributed to its

high silicate content. Table 2 shows the total sulphur and the main chemical properties of the tested aggregates.

Material	PC-GU	FA	SG	MK
LOI (1000°C) (%)	2.8	-	0.91	-
LOI (750°C) (%)		2.78	1.86	1.82
Blain (m ² /kg)	402		639.7	
SiO ₂ (%)	19.4	47.36	35.97	63.1
$Al_2O_3(\%)$	5.0	23.86	8.75	30.69
Fe ₂ O ₃ (%)	3.13	17.40	0.38	1.22
CaO (%)	61.7	3.67	37.34	0.36
MgO (%)	2.4	1.00	11.23	0.5
SO ₃ (%)	3.56	0.40	3.11	0.05
K ₂ O (%)	1.12	1.84	0.57	1.77
Na ₂ O (%)	0.23	0.65	0.17	0.16

Table 1. Chemical composition of the Portland cement (PC) and SCMs (mass %) determined by XRF

Table 2.	Chemical	analyses	of the	tested	aggregates
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Aggre- gate	Rock Type	Iron- Sulphur Minerals	Total Sulphur S _t (%)	SiO2 (%)	CO2 (%)	Fe2O3 (%)	Al2O3 (%)	TiO2 (%)	CaO (%)	MgO (%)	Na ₂ O+ K ₂ O (%)	LOI (%)	Total (%)
ORE	Mine waste	Po, Py, Ccp Pn	14.00	33.1	0.13	39.4	8.53	0.73	4.20	3.05	2.4	5.3	100.0
MSK	Gabbro	Po, Py, Ccp Pn	0.930	50.6	0.71	8.1	19.4	0.53	8.84	6.85	3.8	1.9	100.3
1052	Qz, Fsp	Po, Py	0.543	66.5	0.3	4.3	15.8	0.32	2.61	1.67	6.8	1.2	99.44
C1	Limestone		0.090	1.88	46.1	0.37	0.44	0.02	29.9	20.6	0.22	46.1	100.4
1046	Metabasalt		0.027	49.1	1.3	14.2	13.9	2.12	8.12	4.70	4.42	2.9	100.1
1049	Qz with mafic dike		0.024	93.6	0.36	0.61	3.01	0.18	0.40	0.35	0.84	0.88	99.86
Minerals abbreviations [10]: Po: Pyrrhotite, Py: Pyrite, Ccp: Chalcopyrite, Pn: Pentlandite, Qz: Quartz, Fsp: Feldspar													

2.2. Experimental procedure

2.2.1. Sulphide oxidation mortar bar test

This test incorporates different testing conditions that promote expansion due to the oxidation of sulphide phases in some aggregates. The conditions - as presented here - include the use of oxidizing agent (sodium hypochlorite or bleach) as a soaking solution to promote oxidation or the use of cycles of temperature and relative humidity - without bleach. In the latter case, saturated calcium hydroxide solution (lime water) was used as a soaking solution to bring the samples to a saturated condition at the start of each cycle. The details of the sample preparation and test procedures are presented in the following paragraphs:

2.2.1.1. Sample preparation

The aggregate gradation used to prepare the mortar bars was similar to that used in the accelerated mortar bar test [19] for evaluation of Alkali-Silica Reaction (ASR): 5.00 mm to 150 μ m (Sieve #4 to #100). The water-to-cementing materials ratio (w/c) was raised to 0.65, rather than the 0.47 used in the ASR testing to accelerate the oxidation process and to represent the damaged residential concrete in the

Québec case [4]. Also, the aggregate to cementing materials ratio was kept at one part of cementing materials to 3 parts aggregates. Samples used in this paper consisted of three specimens (25x25x285mm) equipped with gauge stud at each end for measurements. Stainless steel gauge studs were used for mortar bars tested with lime water while titanium studs were used with mortar bars soaked in bleach, as will be explained later. Length measurements were taken weekly using a length comparator as per [20]. Measurements were taken while the samples were in a saturated surface dry condition. After casting, the samples were demolded on the second day and cured for two more days in a standard curing room at a relative humidity (RH) > 95% and a temperature of 21-23°C. This curing duration was chosen to make sure the samples gained some strength before subjecting them to the testing conditions. After the three days of total curing (one day covered in the molds and two days in a standard curing room), the samples were exposed to different testing exposures that aim at promoting oxidation in the aggregate and sulphate attack within the mortar. Mortars with MSK and blend of 50% Ore and 50% C1 aggregate with Supplementary Cementing Materials (SCM) were also tested in this study. The SCM investigated are Low-calcium fly ash (FA), Granulated blast furnace slag (SG), and Metakaolin (MK), with replacement levels of 25%, 30% and 10% respectively.

2.2.1.2. Testing Conditions (Exposures)

Different testing conditions are investigated as listed in Table 3 and presented in the coming paragraphs. The methods used to achieve the investigated environmental conditions are listed in Table 4.

- Exposure BH-S (Bleach-Short Cycle):

This testing regime relied on the use of an oxidizing agent to promote oxidation. The exposure consisted of two stages - 17 weeks each: (i) Stage I, focuses mainly on accelerated oxidation of aggregates within the mortar, and Stage II focuses on promoting sulphate attack. This exposure is a modification of the test developed by Rodrigues et al [12] in light of the findings from El Mosallamy and Shehata [16] when they applied the test to different aggregates. In stage I, the samples are subjected to an oxidizing agent, household bleach (6% sodium hypochlorite), at room temperature (21-23°C) for 3 hours. This is done two times per week followed by storing the samples - after each soaking period - at 21-23°C and 70% RH for 3.5 days. In stage II the samples were soaked in sodium hypochlorite for 3 hours - two times per week - followed by storing at 5° C/100% RH for 3.5 days. Each soaking and storage period in stage I or stage II - is considered a full cycle that is presented schematically in Figure 1a (short cycle). The differences between this exposure and the conditions developed in Rodrigues et al [12] are: (i) the samples were tested at 21-23°C rather than 80°C in stage I. This is adopted as using bleach at 80°C was thought to be a reason for producing high expansion in mortars with silicate aggregates [16], and (ii) the testing duration for each stage was extended to 17 weeks rather than 13 weeks. This longer duration was chosen as it was thought that the oxidation process in stage I is likely to be slower when testing at 21-23°C rather than 80°C.

- Exposures LW-S (Lime Water - Short Cycle):

This group of exposure conditions aimed at promoting the oxidation without using an oxidizing agent, where the samples were soaked in lime water to reach saturation. The short cycle presented in Figure 1a is followed in this group. Using this exposure, different testing exposure subcategories were investigated as follows:

a) <u>LW-S-40°C</u>: This is a One-Stage test where the same conditions were applied throughout the sixmonth testing period. The samples were soaked in lime water at room temperature (21-23°C) for three hours - two times per week - followed by placing them in an environment chamber maintained at 40°C and 70% RH. After the storing period, the samples were allowed to reach room temperature for half an hour before being soaked again for the next cycle. While placed in the environmental chamber - for 3.5 days between each soaking - the relative humidity within the bars is expected to drop from 100% to 70%. It is the assumption that this temperature and range of relative humidity would enable oxidation [21] and perhaps ettringite formation. Length change measurements were taken once per week following the first soaking period when the mortar bars were in a saturated surface dry condition. b) <u>LW-S-5°C</u>: This is a two-stage test in which stage I is similar to exposure LW-S-40°C described above while stage II involves the same short cycle of soaking and storage with the storage being done at °5 C and 100% RH (stored in a fridge above water). Each stage is run for 13 weeks or three months. Compared to LW-S-40°C, stage II was introduced here to provide a longer time (13 weeks) under which the samples are exposed to an environment that is ideal for Thaumasite formation; i.e., 5 °C and 100% RH [15,22,23]. The two-soaking periods at room temperature was applied, mainly, to bring the samples to saturated surface dry and room temperature conditions for length measurements.

c) <u>LW-S-23°C</u>: this is a two-stage test similar to exposure LW-S-5°C above except that the temperature at stage II is set at 23°C rather than 5°C. This is to provide an environment that might be more suitable for ettringite formation compared to 40°C or 5°C.

- Exposures LW-L (Lime Water - Long Cycle):

This exposure group and its exposure subcategories are similar to LW-S except that the cycle here is longer (one week) as presented in Figure 1b. This was designed to study the effect of cycle duration on the expansion.



Figure 1. Testing details of exposure (a) Short cycle (S) and (b) Long Cycle (L)

		Soak	ting Details	Storage Details		
Exposure*	Exposure Subcategory	Host Solution	Soaking Duration - # of cycles/week	Stage I	Stage II	
BH-S		Bleach	3 hrs - two cycles/week	23°C/100-70% RH for 3.5 days for 17 weeks	5°C/100% RH for 3.5 days for 17 weeks	
	<u>LW-S-40°C</u> : 1 stage at 40°C &100-70% RH		3 hrs - two cycles/week	40°C/100-70% RH wee	for 3.5 days for 26 eks	
LW-S	LW-S-23°C: 2 stages with Stage II at 23°C & 100% RH	Saturated	Saturated	3 hrs - two cycles/week	40°C/100-70% RH for 3.5 days for 13 weeks	23°C/100% RH for 3.5 days for 13 weeks
L' wit	LW-S-5°C: 2 stages with Stage II at 5°C & 100% RH			Saturated	Saturated	3hrs - two cycles/week
	<u>LW-L-40°C</u> : 1 stage at 40°C &100-70% RH	solution	2 days - one cycle/week	40°C/100-70% RH we	for five days for 26 eks	
LW-L	LW-L-23°C: 2 stages with Stage II at 23°C & 100% RH		2 days - one cycle/week	40°C/100-70% RH for five days for 13 weeks	23°C/100% RH for five days for 13 weeks	
	LW-L-5°C: 2 stages with Stage II at 5°C & 100% RH		2 days - one cycle/week	40°C/100-70% RH for five days for 13 weeks	5°C/100% RH for five days for 13 weeks	

Table 3. Details of testing exposures for mortar bars

*: 1st letters stand for soaking solution: LW is lime water and BH is bleach, and 2nd letter stands for cycle type: S is Short cycle and L is Long cycle

Table 4.	Methods	used to	achieve	the test	environm	ental	conditions
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Environmental condition	Method				
21-23°C/70% * RH	Mortar bars were stored in a sealed container over a supersaturated solution of NaCl at room temperature				
21-23°C/100% RH	Mortar bars were stored at room temperature above water				
40°C/70%RH	Mortar bars were stored in a controlled humidity chamber at a temperature of 40°C and 70% RH				
5°C/100%	Mortar bars were stored in a conventional refrigerator at a temperature of 5°C above the water				
*: actual measurement showed relative humidity in the range of 71-73%					

2.2.2. Microstructural examination

To investigate the phases developed in the samples under each exposure condition, samples from the tested mortar bars incorporating aggregates MSK and C1+%50%Ore, with and without SCM were prepared for scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) examination for element analysis. For sample preparation, pieces of the mortar bars were cut, dried under vacuum, impregnated with epoxy, and polished with a diamond grade of 0.3 μ m. The polished specimens were sputtered with carbon using the Edwards Vacuum Coating System Model #306A. Polished sections were studied in a JEOL JSM6380 LV (SEM) operated at 20 kV in backscattered electron imaging mode.

3. Results and Analysis

3.1. Expansion under exposure BH-S

This exposure condition was applied to mortar bars that had silicate aggregates with high total sulphur content (MSK and 1052) and silicate aggregates with limited total sulphur (1046 and 1049). The reason for focusing on silicate aggregates using this exposure was to investigate if using a storage temperature of 21-23°C in stage I would reduce the silica dissolution from non-sulphide aggregates observed when running the test at 80°C [16].

Figure 2a shows the level and rate of the expansion of the mortar bars after 34 weeks along with the expansions of the mortar bars stored at 80°C/80% RH in stage I (Figure 4b) from El Mosallamy and Shehata [16]. The results show that when avoiding high storage temperature in stage I, the expansion of all the mortar bars including those with sulphide bearing aggregates was low. However, the rate of expansion for samples with high total sulphur content (i.e., MSK and 1052) increased after moving the samples to $(5^{\circ}C/100\% \text{ RH})$ in stage II of testing (Figure 4a). This expansion behaviour indicates that lower storage temperature in stage I (i.e. room temperature instead of 80°C) reduced the effect of silica dissolution and expansion reported by El Mosallamy and Shehata [16] due to the long exposure to heat and bleach. Applying the t-test - for samples tested using exposure BH-S here - between the expansions of all samples in stage I indicated that they were not significantly different with a confidence level of 95% (t-critical ±2.77 and t-stat between 1.82-2.42) and significantly different in stage II. Applying the t-critical range which indicates they were significantly different. However, in stage II some samples (MSK and 1049 in Figure 2b) were not significantly different, despite their large difference in sulphide content.



Figure 2. Expansion of mortar bars stored soaked for three hours in bleach with exposure (a) BH-S and (b) Samples from [16] stored at 80°C/80% RH in stage I

3.2. Expansions under Exposures LW-S and LW-L

Under these groups of exposures, LW-S involved soaking the samples for three hours in lime water followed by 3.5 days of storage (two cycles/week), while exposure LW-L involved a soaking period of two days followed by five-day storage (one cycle/week). For all of the exposure conditions, the bars were stored in stage I at 40°C/70-100% RH over 13 weeks. Figure 3 shows the change in the moisture content of the bars while under a full cycle of LW-S and LW-L in stage I of the test (soaking followed by storing at 40°C/70-100% RH). The moisture content is expressed as a percentage of the dry mass of the bars (dried at the end of the experiment after the measurements were carried out). As shown in the figure, the mass loss continues throughout both cycles suggesting that the RH within the bars does not reach 70%. However, there is a considerable mass reduction in the first few hours suggesting that the bars do not remain at RH close to 100% for a long time. The graph also shows that for the longer cycle, the sample reaches a higher degree of saturation after soaking and a slightly drier condition by the end of the storage period of each cycle. Expansions under both exposure conditions were investigated.



Figure 3. Moisture content in samples tested under exposures LW-S and LW-L

3.2.1. Effect of Testing Temperature and Relative Humidity during stage II

Under exposures LW-S and LW-L, stage I of the test features the same conditions; i.e., 40°C/100-70% RH. Stage II, however, have different temperature and RH combination as listed in Table 3. The sulphide-bearing aggregates MSK and a blend of C1+50% Ore were tested under the three different

exposure subcategories: LW-S-40°C, LW-S-23°C and LW-S-5°C. Figure 4 shows the rate and level of the expansion of mortar bars tested under each exposure subcategory. The Figure shows that in the case of MSK, the highest expansion was obtained under exposure LW-S-5 °C while for the blend of C1+50% Ore, the highest expansion was obtained under exposure LW-S-40 °C, although the difference between the three exposure subcategory in case of C1+50% Ore was not large. The high value and rate of expansion of samples with a blend of C1+50% Ore are attributed to the high content of oxidizable sulphide. It is likely that testing under 40 °C/100-70% RH can produce the highest expansion for such type of aggregate. These results indicate that the optimum temperature to promote the most damaging form of sulphate attack may not be the same for all aggregate types. It is well-known that Thaumasite formation is promoted by lower temperatures [22-24], so testing at 5°C, might be the optimum condition if carbonate ions are available which is needed for Thaumasite. Hence, it is recommended to test the aggregates under consideration at the three storage conditions in stage II to determine the maximum expansion. For the remainder of the work of this paper, testing at 5 °C in stage II was selected as this the condition that promoted max expansion in MSK and still very high expansion with C1+50% Ore (Exposures LW-S-5 °C and LW-L-5°C).



Figure 4. Expansion of mortar bars tested under exposure LW-S with different conditions in stage II

3.2.2. Testing Different aggregates under Exposure LW-S-5 °C and LW-L-5°C

Figure 5 shows the rate and level of the expansion of the samples with different total sulphur content after 26 weeks (6 months, which is the whole duration of the test) for exposures LW-S-5°C and LW-L-5°C. In both cases, mortar bars with aggregates with high total sulphur content (i.e. MSK, C1+10% Ore, and C1+20% Ore) had high expansions compared to mortar bars with control aggregates (carbonate or silicate); namely, C1, 1046 and 1049. Within the 6-month test duration, exposure LW-S or the short cycle showed higher expansion than the long cycle (LW-L). The expansion in the short cycle is almost double that of the long cycles. This suggests that the long soaking period -2 days instead of 3 hours in case of the short cycle- is not beneficial for the test. This is because no oxidation is taken place during this soaking period as the samples have no access to oxygen. Also, the high level of saturation achieved at the end of this soaking period may not have much effect on increasing the rate of oxidation during the short cycle is almost 7 days while the same in the long cycle is only 5 days. Now that less oxidation occurs in stage I of the long cycle, less sulphate attack is encountered in stage II.



Figure 5. Expansion of mortar bars soaked in under exposure LW-S-5 °C and LW-L-5 °C

To determine the phases produced in the tested mortar bars, SEM-EDS analysis was carried out on bars containing C1+50% Ore and bars with MSK tested under exposure LW-S-5 °C as shown in Figure 6. The analysis showed the presence of ettringite in different locations in both samples. The presence of silica in some of the peaks suggests that the phase is a mixture of Thaumasite and ettringite or the alumina in the ettringite is substituted by silica as reported in [25]. The phases are products of sulphate attack showing that the test can represent the mechanism of damage due to sulphide oxidation.



Figure 6. SEM analysis showing the presence of ettringite or ettringite/Thaumasite mixture for mortar bar tested under exposure LW-S-5°C: (a) 50% Ore +C1, and (b) MSK

3.3. Effect of supplementary cementing materials (SCM)

Exposures LW-S-5°C and LW-L-5°C were used to evaluate the effects of SCM on the expansion of mortars with sulphide aggregates. The aggregate investigated were MSK and blends of limestone aggregate (C1) with the sulphide-bearing aggregate (Ore). The behaviour of mortar bars with general use (GU) Portland cement was compared with that of mortar bars with GU+25% fly ash (FA), GU+30% blast furnace slag (SG), and GU+10% metakaolin (MK).

Figure 7 shows the expansion of mortar bars incorporating C1+50% Ore and MSK aggregates under exposure LW-S-5°C. Fly ash (FA) and slag (SG) reduced the expansion, whereas expansion was higher in bars with metakaolin. The same trend was observed under exposure LW-L-5°C, as shown in Figure 8. These results are in line with the work of [26,27] where low calcium fly ash and slag reduced the expansion due to internal sulphate attack. Under both exposures, the most effective SCM did not reduce the expansion to the level obtained in mortars with no sulphide-bearing aggregates (1049) as shown in the figures. In other words, SCM reduced the expansion but did not mitigate or prevent it.



Figure 7. Effect of SCM on MSK and C1+50% Ore samples tested under exposure LW-S-5°C - Aggregate 1049 is a silicate non-sulphide aggregate



Figure 8. Effect of SCM on MSK and C1+50% Ore samples tested under exposure LW-L-5°C - Aggregate 1049 is a silicate non-sulphide aggregate

To investigate the reason for the higher expansion obtained in samples with 10% metakaolin, mortar bars incorporating MSK with GU+10% MK were tested in the SEM-EDS for microstructural examination. As shown in Figure 9, ettringite and monosulphoaluminate were detected with large amounts in the paste. The monosulphoaluminate is characterized by its lower content of sulphur

compared to ettringite. The theoretical atomic ratios of S/Ca and Al/Ca in the case of ettringite are 0.5 and 0.33 respectively, while in the case of monosulphoaluminate the ratios are 0.25 and 0.5 for S/Ca and Al/Ca respectively [28]. As illustrated in the SEM analysis, the obtained S/Ca and Al/Ca ratio in one location were 0.44 and 0.28, respectively which indicates the presence of ettringite. In the other two locations of the image, the S/Ca ratios were 0.23 and 0.2 and Al/Ca ratios were 0.5 and 0.47, which an indication of the presence of monosulphoaluminate.

The low expansions in the case of samples with SG and FA may be attributed to the dilution effect, where replacing part of PC reduces the amount of C_3A in the system, and lower $Ca(OH)_2$ due to the pozzolanic reaction. This behaviour was similar to that reported in the work of [26,27]. The behaviour of metakaolin (MK) was different where high expansion compared to samples with GU-PC was observed, although MK was reported in [29,31] to reduce the expansion due to delayed ettringite formation (DEF). This may be attributed to the difference in the amount of available sulphate and perhaps the time of its availability. In the case of the DEF, the amount of sulphate is limited (from PC) and available after the termination of high temperature curing which is still early during the reaction of metakaolin. This may result in a low sulphur/alumina ratio in the system leading to the formation of non-expansion monosulphoaluminate rather than expansive ettringite. In the case of mortars with sulphide aggregate, the same case exists at the start where the system has low sulphur/alumina resulting in the formation of an increased amount of monosulphoaluminate. When the iron sulphides in the aggregates oxidize - at a relatively late time - and produce sulphates in the pore solution, the monosulphoaluminate is converted to ettringite leading to expansion. The SEM showed an appreciable amount of monosulphoaluminate in the system with MK - likely not yet converted to expansive ettringite.



Figure 9. SEM for MSK incorporating GU-PC+10% MK tested under exposure LW-L-5°C, showing the presence of monosulphoaluminate and ettringite

4. Discussions

By using an oxidizing agent (Sodium hypochlorite or bleach) at room temperature during stage I, the test was able to discriminate between sulphide-bearing aggregate and aggregate with no sulphide. This was not the case when the same oxidizing agent was used at 80°C in stage I [16] in which case silicate aggregates - namely aggregate1049 and others - showed high expansion regardless of their sulphide content. Following the exposure used here, BH-S, the expansion in stage I was very small for all aggregates unlike the case in [16]; however, stage II - which promotes Thaumasite formation - showed a significant difference in expansions as shown in Table 5. Non-sulphide aggregate showed negligible expansion (close to zero) while sulphide-bearing aggregates showed expansions > 0.04%. A total expansion criterion of 0.03% could be used based on the current results. This limit can discriminate between aggregates with sulphide and those without. It should be noted that more aggregates need to

be tested before finalizing the expansion criterion; however, the obtained results showed this testing condition to be very promising in evaluating the potential oxidation and subsequent sulphate attack.

Aggregato	S (0/)	Expansion %				
Aggregate	St (70)	Stage I	Stage II	Total		
MSK	0.73-1.28	0.014	0.044	0.058		
Sand B +10% Ore	≈1.4*	0.008	0.046	0.054		
1052	0.543	0.011	0.074	0.085		
1046	0.027	0.012	0.006	0.018		
1049	0.024	0.006	0.004	0.010		
*: calculated as 10% of total sulphur content in Ore.						

Table 5. Expansion of stage I and stage II of mortar bars soaked in bleach and tested under exposure BH-S

With the LW-S and LW-L cycles, the focus was to create an environment that promotes both oxidation and sulphate attack. It has been reported that oxidation takes place at relative humidity around 70% to 80% [21]. This was the reason for choosing exposure LW-S-40°C and LW-L-40°C where the relative humidity and temperature can accommodate both oxidation and sulphate attack. With the other two sub-exposures: LW-S or LW-L 23°C and 5°C, the high humidity (100%) and the applied temperatures in stage II were selected to favour the formation of ettringite and Thaumasite, respectively. It was found that sub-exposure LW-S-5°C produces the highest expansion with MSK aggregate although exposure LW-S-40°C produced expansion that is not that far from LW-S-5°C. While LW-S-5°C was selected here to continue the experimental program, it is recommended for future testing to run all sub-exposures as the results may vary from one aggregate to another. The exposure LW-S-5°C was able to distinguish between aggregates with and without sulphide as shown in Figure 10. Mortar bars with aggregates with high silicate content and no sulphides - 1046 and 1049 - produced low expansions when tested here. These aggregates showed significant expansions when exposed to sodium hypochlorite and high heat 80°C in the work of El-Mosallamy and Shehata [16]. Moreover, the microstructural examinations of the mortar bars showed the presence of signs of sulphate attack (i.e., ettringite, Thaumasite or mixtures thereof) in the samples with sulphide aggregates (i.e., MSK and C1+50% Ore). Using an expansion limit of 0.030% - based on the materials tested here - can discriminate between aggregates with oxidizable sulphides and aggregates without.



*calculated based on level of replacement of Ore

Figure 10. Total expansion of mortar bars tested under exposure LW-S-5 °C. The bars indicated the minimum and the maximum expansions of the tested bars

One of the main issues with the presented test methods is that the expansion values are relatively low for MSK and 1052 aggregates (not C1+50% Ore). Extending the period of testing might have produced high expansion but this would be at the expense of the practicality of the test. It is also worth mentioning

that limits on sulphate attack tests, such as ASTM C1012/C1012M-15 [32], are not far from the value suggested here.

Both slag and low-calcium fly ash used at 30% and 25%, respectively reduced the expansion but not to the level of that of bars with non-sulphide bearing aggregates. Possible reasons for the low expansions are the dilution of C_3A due to replacing part of PC with SCM and reduced $Ca(OH)_2$ due to the pozzolanic reaction of the SCM. The availability of calcium is needed to produce ettringite and Thaumasite. The performance of metakaolin is different where its presence at 10% increased the expansion, likely due to increased alumina in the system as explained under results. Perhaps metakaolin can be used at 10% with aggregates to magnify the effect of internal sulphate attack if any. The long-term effects of SCM warrant further investigation.

In light of the above finding and until more testing is carried out on more aggregates, the following two tests - listed in Table 6 - with an expansion criterion of 0.030% at 8 months in case of exposure BH-S and 6 months in case of exposure LW-S are suggested. Applying both tests on aggregates may be beneficial where aggregates that pass both tests are considered safe, aggregates that failed both tests are deemed not suitable for concrete. In the case of aggregates that pass one of the tests and fail the other, further testing including petrographic analysis would be needed.

		Soaking Details		Storage		
Exposure	Exposure Subcategory	Host Solution	Soaking Duration - # of cycles/week	Stage I	Stage II	Evaluation criterion
BH-S		Bleach	3 hrs - two cycles/week	23°C/100-70% RH for 3.5 days for 17 weeks	5°C/100% RH for 3.5 days for 17 weeks	Total maximum expansion <0.03%
	LW-S-40°C		3 hrs - two cycles/week	40°C/100-70% R 26 w	H for 3.5 days for eeks	
LW-S	LW-S-23°C	Saturated lime	3 hrs - two cycles/week	40°C/100-70% RH for 3.5 days for 13 weeks	23°C/100% RH for 3.5 days for 13 weeks	Total maximum expansion
	LW-S-5°C	solution -	3hrs - two cycles/week	40°C/100-70% RH for 3.5 days for 13 weeks	5°C/100% RH for 3.5 days for 13 weeks	<0.05%

Table 6. Expansion	criteria for the	developed new tests
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5. Conclusions

Based on the experimental program and for the materials investigated in this study the following conclusions are drawn:

- 1. Two test methods are suggested for evaluating sulphide-bearing aggregate. These tests are referred to in this paper as exposures BH-S and LW-S. The maximum temperature used in both tests is 40°C. The first test involves an oxidizing agent sodium hypochlorite used at room temperature while the other test relies on adopting temperatures and a range of relative humidity that support oxidation and sulphate attack.
- 2. Both tests were found to differentiate between sulphide-bearing aggregates and aggregates with no sulphide with an expansion limit of 0.03% at 8 and 6 months for the BH-S and LW-S, respectively.
- 3. For test exposure LW-S, it is recommended to test three sets of samples and run each set under the specified exposure subcategory. In these three subcategories, the sets will be tested in stage II at 23°C/100RH, 5°C/100% RH and 40°C/100-70% RH. The maximum expansion should be taken as the test results.

- 4. Using low-calcium fly ash and slag reduced the expansion, but not to the level of that of non-sulphide aggregates. The presence of Metakaolin at 10% produced more expansion.
- 5. The results produced in this research are based on a limited number of aggregates. More testing on aggregates from different locations and of different compositions are recommended to confirm the applicability of the tests and the expansion limit.

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