EVALUATION OF THE DELETERIOUS CHARACTER OF SILICEOUS AGGREGATES INCORPORATING SULFIDE MINERALS

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Abstract

Deterioration of concrete structures incorporating sulfide bearing aggregates has been reported in Trois-Rivières area, Québec, Canada. In this case, iron sulfide oxidation and internal sulfate attack were observed leading to excessive cracking of concrete within only a few years after construction.

In order to evaluate the deleterious character of concrete aggregates incorporating sulfide minerals, an accelerated mortar bar test was developed. The manufacture of the mortar specimens is modeled on the ASTM C 1260 test method; however, the storage conditions were modified to maximize the oxidation reaction of sulfide minerals and related expansion. The first phase of the test thus consists in 90 days of storage at 80°C/80% RH, with 2 three-hour wetting cycles per week in a 6 vol % bleach solution.

A number of different rock types were investigated in this study. However, the test was found to induce excessive expansion with alkali-silica reactive aggregates.

Keywords: Sulfide-bearing minerals, performance testing, oxidation reaction, alkali-silica reaction

1 INTRODUCTION

In the Trois-Rivières area (Quebec, Canada), more than 1 000 houses and commercial buildings are showing serious concrete deterioration problems. A large number of those house foundations started to show signs of deterioration 3 to 5 years after construction [1].

Figure 1 shows typical signs of concrete deterioration observed in the foundations, which mainly consist of map-cracking, with some crack openings reaching more than 40 mm. Sometimes, those cracks were filled up with sealer to prevent the moisture to penetrate into the damaged concrete and in an attempt to delay the progress of deterioration. Yellowish and brownish discoloration is often observed surrounding these cracks. Pop-outs can be observed on the walls showing the presence of oxidized and rusted aggregate particles. It is also possible to observe small bumps/blisters that can be easily detached from the surface thus showing oxidized and rusted aggregate particles.

The deterioration problems are related to the coarse aggregate used in the concrete. The coarse aggregate is a gabbro, an intrusive igneous rock, containing various proportions of sulfide minerals, including pyrite (FeS₂), pyrrhotite, pentlandite and chalcopyrite, disseminated or in veins [1]. Iron sulfides have the tendency to be unstable in the presence of oxygen and water. The chain of reactions generated after the iron sulfides oxidation in the concrete can thus lead to a deleterious internal sulfate attack [2]. The problematic concrete has a porous and friable paste and, in many cases, it is possible to observe the breakdown and disintegration of concrete. In some cases, the deterioration is such that the concrete foundation has to be replaced (Figure 2).

An extensive research project was undertaken to develop a global evaluation protocol to predict the deleterious potential of aggregates containing iron sulfides, including a performance test or expansion test that can reproduce, under well controlled and reproducible laboratory conditions, the mechanisms responsible for the concrete deterioration. Different conditions of temperature, humidity, and oxidation solutions were tested in order to find the optimal conditions promoting the oxidation of iron sulfide minerals with resulting acid formation and sulfate attack of the cement paste, including thaumasite formation [3]. Surprisingly, the test was also found to induce excessive expansion with alkali-silica reactive aggregates.

The goal of this research is to present potential testing conditions that allow the generation of a significant expansion of aggregates that present sulfide oxidation and/or alkali-silica potential.

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2 MATERIALS AND METHODS

2.1 General

Based on extensive literature reviews and laboratory investigations, a two-phase accelerated mortar bar test was developed to reproduce, in the laboratory, the deterioration mechanisms observed on site related to the oxidation of sulfide-bearing aggregates followed by internal sulfate attack [3]. To achieve this goal, an accelerated test on mortar was selected because an increase in the specific surface area of the iron sulfides significantly increases the rate of oxidation [4-5].

2.2 Materials

In addition to the aggregate responsible for the concrete deterioration in the Trois-Rivières area (MSK), three sulfide-bearing aggregates and two aggregates with no or only traces of iron sulfides (control) were selected for this study, including the well-known Spratt limestone. Table 1 presents the mineralogy of the aggregates tested along with their ASR potential according to ASTM C 1260 accelerated mortar bar test. Figure 3 shows examples of mineralogy responsible for concrete damage due to sulfide oxidation or alkali silica reaction.

MSK is the problematic aggregate used in the construction of the Trois-Rivières house foundations; it corresponds to a hypersthene gabbro containing various proportions of pyrite [FeS₂], pyrrhotite [Fe_{1-x}S], pentlandite [(Fe,Ni)₉S₈] and chalcopyrite [CuFeS₂] [3]. The percentage of sulfur (% S by mass) obtained from different MSK sub-samples tested varied from 0.73 to 1.28 wt%.

GGP is a gneiss of granitic origin containing pyrrhotite and pyrite but without carbonates.

SBR is a fine-grained hornfels from the greater Montreal area (Canada). This aggregate is not used in concrete; however, it was selected due to its mineralogical composition and the presence of iron sulfide minerals. This aggregate is also alkali-silica reactive.

SW is mica schist aggregate that was used in the construction of a large concrete dam back in the early 1970s and that started to show signs of expansion in the early 1980s. The structure showed signs of concrete elements displacement and deposits of rust in the inspection galleries. This aggregate is also alkali-silica reactive.

SPH is a phyllite containing iron sulfide minerals. This aggregate has been described in the literature as the source of concrete deterioration in public buildings, houses, overpasses and dams due to the iron minerals present. The affected concrete showed extensive cracking, iron sulfide stains, and white rims surrounding the aggregate particles. In some cases, the deterioration led to the destruction of the structures. This aggregate is also alkali-silica reactive.

PKA is a control aggregate, an anorthosite rock, containing only traces or no sulfide mineral. Finally, Spratt is also a control aggregate. It is a siliceous limestone, well-known for its high level of alkali-silica reactivity [6]. Spratt aggregate contains only traces or no sulfide mineral.

2.3 Methods for assessment and analysis

Nature and preparation of the test specimens

With the objective of generating reliable test results in a reasonable time period, the decision was made to work on mortar specimens. Furthermore, in order to minimize the number of parameters involved and for practical reasons, the nature and preparation of aggregate materials and mortar test specimens were modelled in many ways on the commonly-used accelerated mortar bar test (AMBT) for alkali-silica reaction (ASR) (ASTM C 1260, CSA A23.2-25A) [7,8], with necessary adjustments considering the scope of this work.

Mortar bars, $25 \times 25 \times 285$ mm in size, were manufactured, using a General Use high-alkali (0.95 wt% Na₂Oeq) Portland cement, a cement-to-aggregate ratio of 1:2.75, with the proportions of the various aggregate size fractions similar to that used in the accelerated mortar bar test for ASR (ASTM C 1260) [7]. A w/c of 0.65 was selected to simulate the characteristics of concrete used for housing foundations in the Trois-Rivières area.

The mortar bars were prepared by following the various steps described in ASTM C 1260 test procedure. Considering the condition of testing used in this program, titanium studs were used to avoid metal degradation in the presence of oxidizing agents. After casting of the mortar bars, the moulds were placed in a moist curing room at $23 \pm 2^{\circ}$ C, protected with a plastic sheet. Because of the higher water-to-cement ratio selected for this study, the bars were left to cure in their moulds for a period of 72 h. Upon stripping, the bars were weighed, measured longitudinally and then placed into conditions, as will be described hereafter.

Testing conditions

Based on the results obtained previously [3], the experimental conditions that appear to most effectively promote the oxidation of the sulfide-bearing aggregates are high temperature (80°C), a relative humidity of 80% and two wetting cycles of 3 hours per week in a solution of 6 vol% sodium hypochlorite solution (bleach). A period of 90 days of testing under the above conditions seemed to be effective and sufficiently long to reliably separate between deleterious and control (non reactive) aggregate specimens. After 90 days in the above conditions, mortar bars are transferred to conditions favorable to thaumasite formation, i.e. 4°C and relative humidity values of 100%.

The different temperatures and relative humidity values used for the storage of the mortar specimens between the wetting cycles were maintained using environmental (i.e. temperature and humidity controlled) cabinets (Cincinnati Sub-Zero Z16 and Z44), or by using oversaturated salt solutions at the bottom of hermetic storage containers that were then placed in conventional laboratory ovens maintained at 80°C. For example, an oversaturated solution of sodium chloride (NaCl) is used to maintain a relative humidity close to 80% at a temperature of 80°C. At 4°C, water maintains 100% relative humidity.

3 RESULTS AND DISCUSSION

There are a number of factors contributing to the iron sulfides oxidation resulting in the formation of sulfuric acid and internal sulfate attack, but also to thaumasite formation. Although the two types of deterioration mechanisms coexist in the concrete elements of the Trois-Rivières area under study, the approach taken in the development of a new accelerated mortar bar test was to separate them by submitting the test specimens to exposure conditions specifically prone to their development.

The two-part mortar bar test consists of a first part to reproduce the deterioration resulting from the oxidation reaction of the iron sulfides in the aggregates. The oxidation reaction is promoted at high temperature and 80°C was selected for the first part of the expansion test. The oxidation of sulfide minerals with the resulting formation of various rust products occurs in the presence of water and oxygen. In order to promote the oxidation in the test specimens, it is thus necessary for oxygen to diffuse through the porosity of the mortar. Since the diffusion rate of oxygen in water is low, it will be similarly very slow through the pore space of saturated mortar specimens. For that reason, a relative humidity of 80% was selected.

The second part of the mortar bar test consists in promoting thaumasite formation from the sulfate generated in the first part of the test. The conditions that promote thaumasite formation are somewhat different from those contributing to the iron sulfides oxidation, including a low temperature exposure (4°C) and a source of carbonate material. More details of a parametric testing program aiming to evaluate the effect of, for instance, temperature, relative humidity, and use of oxidizing solutions, on the expansion of mortar bars incorporating different control and sulfide-bearing aggregates are presented elsewhere [3].

Figure 4 presents the expansion results for the two-phases accelerated mortar bar test to assess the deleterious effect due to the oxidation of sulfide-bearing aggregates.

As illustrated in Figure 4, different behaviors were observed based on aggregates mineralogy (Table 1). The mortar bars incorporating the control aggregate PKA did not suffer from significant expansion during both phases of the program. This confirms that the somewhat harsh conditions used in the proposed mortar bar method do not in themselves induce excessive expansion in mortars incorporating sulfide-free aggregate materials. Figure 5 shows the condition of the PKA control samples at the end of the experiment. The very low expansion observed for these samples is confirmed by the good condition of the test specimens during the entire test.

In the case of the MSK aggregate, the specimens transferred to low-temperature conditions showed a slowed down of the expansion following 4°C transfer (at 90 days), but then increased dramatically after 150 days to reach about 1.5% ℓ/ℓ at 300 days. At 300 days, one of the bars transferred to 4°C was so deteriorated that it broke in pieces. Figure 6 shows the condition of the MSK aggregate at the end of the test. It is important to note that the MSK aggregate is the problematic aggregate used in the Trois-Rivières area.

Figure 7 presents examples of reaction products observed by scanning electron microscopy (SEM) after the completion of expansion testing. Figures 7A to 7D show typical alkali silica reaction products (mortar bars incorporating GGP aggregate), while Figures 7E and 7F present ettringite/ thaumasite crystals formed at low temperature from sulfate ions generated by sulfide oxidation (mortar bars incorporating MSK aggregate).

As mentioned previously, some of the aggregates selected for this study that contain iron sulfide minerals were also found to be alkali-silica reactive (SBR, SW and SPH). The 14-day expansions obtained in the accelerated mortar bar test (CSA A23.2-25A equivalent to the ASTM C1260) were 0.23, 0.20 and $0.35\% \ell/\ell$ for SBR, SW and SPH aggregates, respectively.

In the present test, the sulfide-bearing and alkali-silica reactive aggregates SBR, SPH and SW, present a different expansion pattern, characterised by a rapid onset of expansion that stopped shortly after the transfer of the bars at 4°C (Figure 4). It is interesting to note that the mortar bars incorporating the highly alkali-silica reactive Spratt limestone also showed a quick onset of expansion in the particular storage conditions used for testing; however, the expansion level reached at 90 days was much lower than that measured for the SBR, SPH and SW aggregates. The rapid onset of expansion is suspected to result from the development of ASR in the above mortar specimens; however, additional testing and the detailed petrographic examination of the mortar bars will be required to confirm this hypothesis. The absence of expansion following transfer of the bars at 4°C, suggests that thaumasite formation did not occur in the above alkali-silica reactive mortar specimens. This result is not surprising in the case of the Spratt aggregate since it contains limited sulfide minerals (some disseminated pyrite grains) capable of forming sulfate ions necessary for the precipitation of thaumasite.

Microstructural analyses suggest that the GGP aggregate is alkali-silica reactive (Figures 7A and 7B). However, mortar bars incorporating that aggregate did not show the rapid onset of expansion but rather a progressive expansion similar to that of mortar bars made with the sulfide-bearing MSK aggregate up to about 130 days. The potential alkali-reactivity of granitic/gneiss aggregates (i.e. GGP rock type) is often not adequately assessed through mortar bar testing [9].

The combined effects of sulfide oxidation and ASR under the storage conditions proposed will require further clarification. Phase I conditions that appear to most effectively promote the oxidation of the sulfide-bearing aggregates are high temperature (80°C), a relative humidity of 80% and two wetting cycles of 3 h per week in a solution of 6 vol% sodium hypochlorite solution (bleach), seem very effective in promoting ASR in an accelerated manner.

4 CONCLUSIONS

The rapid and extensive deterioration of concrete structures involving sulfide bearing aggregates has been observed in the Trois-Rivières area, Québec (Canada). The extent of the issue triggered the development of an extensive study aiming at developing a performance test for evaluating the risk for deleterious oxidation reaction in aggregates prior to their use in concrete.

In the first phase of the test, sets of three mortar bars, 25 by 25 by 285 mm in size, made in accordance with several characteristics used in the accelerated mortar bar test for ASR (ASTM C 1260 or CSA A23.2-25A), are stored for 90 days at 80°C and 80% relative humidity, with two 3-h wetting cycles in a 6 vol% bleach solution at 23°C per week. This phase allows for the evaluation of the oxidation potential of the aggregates. This phase is followed by up to 90 days of storage at 4°C and 100% relative humidity, again with two wetting cycles in a 6 vol% bleach solution, to determine the potential for thaumasite formation that is confirmed by a rapid regain of expansion followed by destruction of the test specimens.

The mortar bars incorporating the control aggregate without sulfide mineral, the PKA anorthosite, did not show any expansion nor showed any signs of deterioration during both phases of the testing program.

The SBR, SW and SPH are sulfide-bearing and alkali-silica reactive aggregates. Those three aggregates showed a rapid onset of expansion that reached levels ranging from 0.58 % ℓ/ℓ (SW) to $\approx 1.31\% \ell/\ell$ (SBR) upon 90 days of testing (Phase I), expansion way above that obtained with the MSK aggregate. The observed expansions are a combination of alkali-silica reaction and the iron sulfides oxidation. Interestingly, none of the above three aggregates has generated significant expansion upon the transfer to 4°C.

However, the combined effects of sulfide oxidation and ASR under the storage conditions proposed will require further clarification. Phase I conditions that appear to most effectively promote the oxidation of the sulfide-bearing aggregates are high temperature (80°C), a relative humidity of 80% and two wetting cycles of 3 h per week in a solution of 6 vol% sodium hypochlorite solution (bleach), seem very effective in promoting ASR in an accelerated manner. More fundamental testing is necessary to better understand the behavior of the alkali-silica reactive aggregates during the first phase of the new accelerated mortar bar presented here to address the oxidation potential of sulfide-bearing aggregates.

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Aggregate		Rock type	Mineralogy		% S	14-day
			Main mineral constituents	Iron sulfide minerals	(by mass)	expansion (AMBT)
Sulfide- bearing aggregates	MSK	Norite or Hypersthene Gabbro	Plagioclase, Biotite, Pyroxenes, Quartz	Pyrrhotite, Pyrite, Chalcopyrite, Pentlandite	0.73 -1.28	0.07%
	SBR	Hornfels	Feldspars, Quartz, Clays, Organic matter	Pyrrhotite, Pyrite, Chalcopyrite, Sphalerite	0.75-0.87	0.23%
	SW	Mica Schist	Quartz, Feldspars, White mica, Amphibole	Pyrrhotite, Pyrite, Chalcopyrite	0.07	0.20%
	SPH	Phyllite	Quartz, Feldspar, White mica, Chlorite	Pyrrhotite, Pyrite, Chalcopyrite	0.29-0.32	0.35%
	GGP	Granitic gneiss	Quartz, Hornblende Pyroxenes, Plagioclase	Pyrrhotite, Pyrite	0.24-0.33	0.05%
Control aggregates	PKA	Anorthosite	Plagioclase, Hornblende, Biotite	_	0.04-0.06	n.a.
	Spratt	Limestone	Carbonates	Pyrite	n.a.	0.39%

TABLE 1: Aggregates tested and their respective mineralogy.



FIGURE 1: Concrete foundations showing map-cracking and yellowish/brownish discoloration. B: Cracks filled with caulking material to prevent moisture ingress. C and D: Yellowish and brownish discoloration surrounding the cracks. E and F: Pop-outs showing the presence of oxidized and rusted aggregate particles, as well as whitish/yellowish secondary reaction products.



FIGURE 2: Replacement of the concrete house foundations walls. A: lifted house with all the brick work removed. B: New foundations being placed.



FIGURE 3: Example of mineralogy responsible for concrete damage. A: Reflected polarized light view of iron sulfide minerals responsible for oxidation (MSK aggregate) (Py = pyrite, Po = pyrrhotite, Pent: pentlandite). B: Potentially reactive silica (microcrystalline and stained quartz) viewed under crossed polarized light (GGP aggregate).



FIGURE 4: Expansion of mortar bars subjected to two 3-hour wetting periods in bleach (6 vol%) per week, and kept at 80°C and 80% RH during 90 days. The bars are transferred after that period to 4°C and 100% RH and exposed to the two 3-hour soaking periods in bleach per week.



FIGURE 5: Mortar bar made with PKA aggregate at 90 days, showing no signs of deterioration for the entire duration of the test. B and C: Deterioration details of mortar bars at 180 days.



FIGURE 6: A: MSK mortar bars kept at 80°C and 80% relative humidity and then transferred at 4°C and 80% relative humidity immediately after rupture at 118 days. B: The same mortar bar series left at 4°C and 80% relative humidity for 7 months; the M3-5 bar illustrated in A is the one in the middle of the container.

А



FIGURE 7: Secondary electron images of reaction products examined under SEM after testing with corresponding EDS spectrum. A and B: Rosette-like crystalline product typical from ASR (mortar bar incorporating GGP aggregate). C and D: ASR gel product (EDS spectrum corresponding to zone 3 on the micrograph) (mortar bar incorporating GGP aggregate). E and F: Ettringite-thaumasite crystals from sulfide oxidation and sulfate attack of cement paste (mortar bar incorporating MSK aggregate).