P.3 Introduction

P.3.1 General

It has been known since at least the mid-1950s that iron sulphide minerals found in aggregate can cause disruption and deterioration of concrete. A number of papers have been published describing the damaging effects of iron sulphides in aggregate on concrete. The sulphide mineral that is reported to have caused the most damage is pyrrhotite ($Fe_{1-x}S$) with lesser problems being caused by the minerals pyrite (FeS_2) and marcasite (FeS_2). All three minerals are iron sulphides. At present there are no reports of damage to concrete being caused by other common sulphide minerals chalcopyrite ($CuFeS_2$) and sphalerite $(Zn,Fe)S$.

P.3.2 Pyrrhotite

Pyrrhotite is the second most common iron sulphide in nature. Mostly found with pentlandite ($(Fe,Ni)_9S_8$) in basic igneous rocks, as veins in different types of rocks and in metamorphic rocks, pyrrhotite is also found associated with pyrite, marcasite, magnetite and chalcopyrite (Deer *et al*, 1992; Belzile *et al.*, 2004). In hand sample, this mineral has a metallic luster and bronze brown, yellow, or reddish colour.

Pyrrhotite is a monoclinic or pseudohexagonal anisotropic mineral with a pale pink-brown to creamy brown colour with distinct birefringence under the petrographic microscope.

Pyrrhotite has an unbalanced chemical formula ($Fe_{1-x}S$), with x ranging from 0 (FeS) to 0.125 (Fe_7S_8), (Belzile *et al.*, 2004). It is sometimes magnetic depending on the crystal structure.

P.3.3 Pyrite

Pyrite is the most common iron sulphide mineral in nature, as it is present in igneous, metamorphic, and sedimentary rocks. Normally, pyrite can be found in large masses or veins of hydrothermal origin. In hand sample, this mineral has a metallic luster and pale yellow colour. Microscopically, pyrite is a cubic isotropic mineral with a yellowish-white colour in reflected light (Deer *et al.*, 1992).

Pyrite, with the chemical formula FeS_2, is composed by 46.55% Fe and 53.45% S, by mass. It can be crystallized in cubical, octahedron, or dodecahedron form, but is frequently found in the framboidal form in sedimentary rocks such as shale and limestone, or other rocks.

P.4 Iron sulphides oxidation reaction process

P.4.1

It is well known from literature that sulphide minerals are unstable in oxidizing conditions. Upon exposure to water and oxygen, sulphide minerals oxidize to form acidic, iron, and sulphate-rich by-products in accordance with the following equations (Belzile *et al.*, 2004):

$$Fe_{1-x}S + (2 - x/2)O_2 + xH_2O \rightarrow (1-x)Fe^{2+} + SO_4^{2-} + 2xH^+$$

Equation 1

P.4.2

The oxidation of ferrous iron (Fe^{2+}) produces ferric ions (Fe^{3+}) (Equation 2) that can precipitate out of solution to form ferric hydroxide, if pH is not too low. Fe^{2+} is oxidized and precipitated as ferric oxyhydroxides, principally ferrihydrite ($Fe_2O_3 \bullet 0.5(H_2O)$) and goethite ($FeO(OH)_3$) (Equation 3).

$$Fe^{2+} + 1/4O_2 + 2H^+ \rightarrow Fe^{3+} + 1/2H_2O$$

Equation 2

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+$ **Equation 3**

P.4.3

The oxidation reaction of iron sulphides occurs only in the presence of oxygen and water, and it generates various mineralogical phases (Belzile *et al*., 2004; Bérard *et al*., 1975). Steger (1982) has shown that oxidation of pyrrhotite presents two pathways to give goethite and ferric sulphate. According to Grattan-Bellew and Eden (1975) and Shayan (1988), the sulphuric acid generated through this process reacts with the solids of the cement paste, particularly with the Portlandite ($Ca(OH)_2$), to form gypsum ($CaSO_4 \bullet 2H_2O$) in accordance with the Equation 4:

$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 \bullet 2H_2O$ (gypsum) **Equation 4**

P.4.4

The attack of concrete by sulphates resulting from the oxidation of sulphide-bearing aggregates produces the crystallization of secondary ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) following the reaction with the alumina-bearing phases of the hydrated Portland cement paste (e.g., C_3A; Equation 5). If carbonate materials are also present in the concrete in significant amounts, either in the aggregate itself or from limestone fillers/cements, the possibility of a reaction between sulphates, silicates and carbonates to form thaumasite ($Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_2(H_2O)_{22}$) also exists.

$3(CaSO_4 \bullet 2H_2O) + C_3A + 26H_2O \rightarrow C_3A \bullet 3CaSO_4 + H_{32}$(ettringite) **Equation 5**

P.4.5

According to Divet and Davy (1996), high pH conditions, such as those found in concrete, enhance iron sulphide oxidation.

P.4.6

In a general way, secondary products most frequently generated during the oxidation of iron sulphides, are the “rust” under all its forms (ferric oxyhydroxides such as goethite, limonite ($FeO\ (OH) \bullet nH_2O$) and ferrihydrite), sulphates including gypsum, ettringite, and, if carbonate materials are also present, thaumasite.

The degradation of concrete is thus due to the combined mechanisms of oxidation of iron sulphides followed by sulphatation in the cement paste. Both reactions create secondary minerals that can cause expansion. According to Casanova *et al*. (1996), the latter is by far more expansive. In fact, during the formation of gypsum, the volume of the resulting products represents a little more than double of that of the starting solids.

P.5 Case studies of damaging effects in concrete made with aggregates incorporating iron sulphides

The earliest report is from Sweden and concerns the damaging effects of pyrrhotite and pyrite. (Hagerman and Roosaar, 1955):

> *It has for many years been suspected that sulphide minerals in aggregates will cause damages to concrete due to the formation of sulphate ions, which when reacting with the cement aluminates will create voluminous calcium sulphoaluminate crystals. This problem has become a matter of immediate interest in Sweden through power plant constructions in some parts of Norrland where the existence of sulphide minerals is very common.* (From the English summary).

They found that to avoid damage, the content of easily weathered sulphides, in particular pyrrhotite, should be less than about 1% (no mention if this was on a mass or volume basis).

The first Canadian reference to potential problems with iron sulphides in concrete aggregate is found in Swenson and Chaly (1956). They noted that:

> "*Minerals such as pyrites and marcasite may first be oxidized and then hydrated to sulfuric acid and hydrated iron compounds with large increase in volume.*"

Moum and Rosenqvist (1959) described problems caused by the presence of pyrrhotite in shale upon which concrete had been placed near Oslo, Norway. In some cases, the concrete structures were transformed into mush after about 9 months. When the shale had been accidently used in concrete, swelling of the shale aggregate "*…caused cracks and destruction of the concrete.*"

In 1958, Midgley at the Building Research Station in the United Kingdom published a paper in which he noted that some varieties of pyrite were more prone to oxidation than others and proposed a test. The test consisted in placing suspect aggregate in saturated limewater and observing whether or not a blue-green gelatinous stain was produced. Those particles that did not develop the stain within about 30 min were considered to be at low risk of causing staining of the outside surface of concrete if used as an aggregate.

A Canadian example of iron sulphide oxidation causing concrete deterioration is that described by Bérard *et al.* (1975). This paper described the problems brought about by the presence of pyrrhotite in shale that was used in small amounts (less than 5%) in concrete aggregate in the Montreal area of Quebec. They reported on the cracking of basement walls of houses in Montreal-East and damage to bridges in the same area. All affected structures showed map cracking, pop-outs (with fragments of shale in the centre), and, in some cases, iron oxide was seeping out the fractures. Significantly, they also found that concrete of high water-cement ratio or low cement content deteriorated more quickly than concrete of higher cement content or lower water-cement ratio. This indicated that concrete that is more permeable promotes oxidation of iron sulphides. The authors indeed suggested that the deterioration was due to the oxidation of pyrrhotite and the formation of sulphuric acid and rusty secondary minerals (*jarosite* — $KFe_3(SO_4)_2(OH)_6$, although the presence of jarosite was not confirmed by x-ray diffraction analysis). The sulphuric acid would then react with the calcite within the shale or with the Portlandite of the hydrated cement to form gypsum; the latter was believed to be the main cause of the swelling of the shale. Bérard *et al.* (1975) found that concrete that contained as little as 2% shale was damaged. They estimated that the amount of pyrrhotite in the shale was about 4.5% (no mention if this was on a volume or mass basis).

Soles (1982) reported an unusual example of oxidation of iron sulphides in concrete aggregate from the Ottawa area. In this case, pyrite found in a sound dolomite aggregate oxidized when concrete was stored for several months at temperatures of about 150 °C. The concrete expanded and cracked with the formation of gypsum as a result of the oxidation process. The concrete aggregate is perfectly sound in concrete used at normal temperatures.

Oberholster (1984a and b) conducted studies of the cause of serious cracking of house foundations in South Africa. This was caused by the use of slate aggregate containing pyrrhotite that oxidized and was the cause of the damage to both concrete floor slabs and to concrete blocks for the walls. In some cases, the houses started to show signs of deterioration within two years after construction. Examination of the concrete bricks revealed a white powdery material around the black carbonaceous aggregate, which was found to be well-crystallised hexagonal crystals containing calcium, silicon, carbon and sulphur (*thaumasite*).

> *It is difficult to determine … how much pyrrhotite in an aggregate should be regarded as deleterious. However, an analysis for the mineral sulphur gave the pyrrhotite content as only 0.5 per cent by mass.* Oberholster (1984b).

Regourd et al. (1987) describe an unusual concrete from Arctic Canada. This concrete had been made with mine rock that contained pyrite (FeS_2), sphalerite (ZnS), and galena (PbS). They found no damage due to internal sulphate attack which they attributed to the low ambient temperature of the concrete and surroundings.

Shayan (1988) described damage to a concrete floor surface in a 10 year old building in Australia caused by aggregate (shale) containing pyrite. The expansion was sufficient to rupture overlying vinyl tiles. The blistering was found to be caused by the oxidation of the pyrite in the aggregates located near the surface of the slab, thus producing a significant amount of jarosite and smaller amounts of gypsum. In this case, no ettringite was observed.

Extensive studies were carried out on cases of deterioration of concrete structures (public buildings, houses, overpasses, and dams) incorporating pyrite-rich aggregates near Barcelona (Spain) (Chinchon *et al*., 1995). In all cases, the deterioration started with expansion with resulting cracking leading to the structures destruction. The affected concretes contained aggregates consisting of limestones and shale incorporating pyrite and pyrrhotite (Chinchon *et al*., 1990a; Chinchon *et al*., 1995). In all studies, the damage was associated with the oxidation of pyrite and pyrrhotite, resulting in internal sulphate attack, cracking and deterioration of the concrete.

Ayora *et al*. (1998) presented a case of two dams presenting map cracking in some surface areas, color changes and expansion. The aggregates consisted of schists containing minor amounts of pyrrhotite (Fe_7S_8). The total sulphur content of the rock was up to 0.8% S, by mass. The authors concluded that the main cause of concrete expansion was pyrrhotite oxidation that led to the attack of the components of the cement paste, and the formation of iron sulphates. Ettringite halos were found in the interfacial paste/aggregate zone.

Divet (1996) and Divet and Davy (1996) presented comprehensive reviews of the mechanism and control of oxidation of pyrite in concrete. They concluded that the nature of the aggregate and the permeability of the concrete played a major role in the rate of oxidation of iron sulphides and that the high pH (more alkaline) nature of concrete also increased the oxidation rate.

Tagnit-Hamou, *et al.* (2005) published a paper describing laboratory investigations on the cause of deterioration of building foundations and concrete slabs that occurred approximately 2 years after construction. The authors attributed the severe cracking in the concrete to the oxidation of pyrrhotite found in the anorthosite aggregates used to produce the concrete. Deposits of *goethite* were observed around affected aggregate particles, while *ettringite* was found in all samples, generally very close to the altered aggregate particles but also in the cement paste near sound aggregate particles.

Araújo *et al.* (2008) reported on internal sulphate attack of concrete dams in Spain caused by oxidation of iron sulphides in the aggregate. The principal sulphide mineral responsible for the reaction was pyrrhotite. They observed oxidation to iron oxides and hydroxides with ettringite formed due to internal sulphate attack. These reactions led to expansion and upstream displacement of the dams.

Duchesne and Fournier (2011) studied the same occurrence as that of Tagnit-Hamou *et al*. (2005) and reported pyrite, pyrrhotite, pentlandite and chalcopyrite in the anorthositic gabbro. They reported that the amount of sulphides was less than 5 to 10% by volume. They reported that the pyrrhotite was mainly oxidized in contrast to the pyrite that was practically unoxidized. They found iron oxides and hydroxides and gypsum formed as secondary minerals. They concluded that deterioration of the concrete was due to the combined action of oxidation of the iron sulphides and sulphatation reactions in the cement paste.

Schmidt *et al*. (2011) reported the results of a study carried out on a concrete dam, constructed in the early 1970s in Switzerland, that was found to suffer from steady expansion since the early 1980s. The aggregates consisted mainly of biotite-schists incorporating randomly dispersed iron sulphides, for instance pyrite/marcasite (20%) and pyrrhotite (80%), which were found at about 0.3 to 0.4% by volume. The authors concluded that “the formation of iron hydroxides can lead to expansion of particles within the aggregates, which leads to cracking of the aggregate” and that “this alone could account for the expansion observed on a macroscopic scale”. Pyrrhotite was found to react much faster than pyrite in alkaline concrete environments. Also, it was unclear to what extent the formation of secondary ettringite, produced in the concrete from released sulphate, might have contributed to the expansion.

Rodrigues *et al*. (2012) presented the results of the petrographic examination of a number of specimens obtained from concrete house foundations containing sulphide-bearing aggregates in the Trois-Rivières area (Québec, Canada), Figures P.1 to P.6. The authors reported that the coarse aggregate used to produce concrete was a quarried intrusive igneous rock (anorthositic gabbro) with different degrees of metamorphism and varying proportions of sulphide minerals (mainly pyrrhotite and pyrite with smaller amounts of chalcopyrite and pentlandite). In the samples examined, the amount of sulphide minerals was, in general, less than 5 to 10% by volume. In the rock, sulphide minerals were often surrounded by a thin layer of carbonate minerals (siderite). Secondary reaction products identified in the damaged concrete include “rust” mineral forms (e.g., ferric oxyhydroxides such as goethite, limonite ($FeO(OH) nH_2O$) and ferrihydrite), gypsum, ettringite and thaumasite. The authors suggested that, in the presence of water and oxygen, pyrrhotite oxidizes to form iron oxyhydroxides and sulphuric acid. The acid then reacts with the phases of the cement paste/aggregate, thus inducing the formation of expansive sulphate minerals within the concrete.

Tremblay (2013) presented data at a court appearance in Trois Rivières on May 2, 2013. He (and others) had conducted a study of about 223 house basements that had been built with varying amounts of iron sulphides in anorthositic gabbro coarse aggregate. Pyrrhotite made up an average of about 75% of the sulphide minerals with lesser amounts of pyrite and chalcopyrite. Many of the pyrrhotite grains showed signs of oxidation but the pyrite and chalcopyrite were largely unaffected. Damage to the concrete basement was rated from 0 to 3 with 0 representing concrete with little or no damage and 3 the most damage. The basements were between about 3 to 9 years old at the time of the study and it has been shown that the damage is progressive and the rating increases with time. The volumetric pyrrhotite content found in the coarse aggregate and causing damage (rating of 1 or more) was from 0.23% up to 3.69%. All damaged concrete exceeded the European limit (see below) of 0.1% S by mass in the aggregate (when pyrrhotite is present) by 3 times to as much as close to 30 times.

Other cases of deterioration of concrete due to pyrrhotite oxidation of the aggregate have occurred in the state of Connecticut with many hundreds of homes being affected. Currently, much of the information available on this problem is limited to newspaper articles but the cause of deterioration has been confirmed by an investigation conducted by the University of Connecticut (Willie and Zhong, 2016) as oxidation of pyrrhotite present in the aggregate. In contrast to the problems encountered in Québec, manifestation of the damage in Connecticut has taken as much as 10 to 20 years. Typical visual deterioration was in the form of map cracking, causing deformation of the wall, reddish-brown discolouration, and whitish formation in the vicinity of surface cracking. Most of the damage to date has been linked to one quarry operating in Willington, Connecticut. The geology in the vicinity of the quarry is made up of metamorphic rocks predominantly from two to three rock types. The rock types mainly consist of foliated schists and gneissic rock, granofels, and a foliated quartz diorite (USGS map). Iron sulphides from this quarry are found predominantly as pyrrhotite.

P.6 Standards

The Canadian standard alerts users to the risk of using concrete aggregates incorporating iron sulphides in concrete: Clause 4.2.3.6.2 (CSA A23.1):

> *Aggregates that produce excessive expansion in concrete through reaction other than alkali reactivity shall not be used in concrete unless preventive measures acceptable to the owner are applied.*
>
> **Note:** *Although rare, significant expansions can occur due to reasons other than alkali-aggregate reaction. Such expansions might be due to the following:*
>
> a) *The presence of sulphides, such as pyrite, pyrrhotite, and marcasite, in the aggregate that might oxidize and hydrate with volume increase or the release of sulphate that produces sulphate attack upon the cement paste, or both; ...*

NF P18-301 first limited the total sulphur content to 0.4% as SO_3 (0.16% as S) by mass. This threshold was increased a first time in NF P18-541 to 0.4% as S (i.e., 1% as SO_3) by mass, and once again in the context of European standardization. NF EN 12 620 indeed specified the following:

> *the total sulfur content (S) of the aggregates and fillers, when required, shall not exceed the following limits:*
>
> a) *2% S by mass for air-cooled blast-furnace slag; and*
>
> b) *1% S by mass for aggregates other than air-cooled blast-furnace slag.*
>
> **Note:** *Special precautions need to be taken when pyrrhotite, an unstable form of iron sulphide FeS, is present in the aggregate. If the presence of this mineral is proven, a maximum total sulphur content of 0.1% (as S) shall apply.*

P.7 Performance evaluation protocol (PEP) for the determination of the deleterious oxidation potential of sulphide-bearing aggregates

P.7.1 Performance evaluation protocol (PEP)

The potential deleterious character of sulphide-bearing aggregates may be determined in accordance with the performance evaluation protocol (PEP) illustrated in Figure P.7.

When a decision is made to investigate a source of concrete aggregates regarding the above issue, a geological survey of the source shall be performed, with the sampling of representative rock/aggregate specimens in accordance with CSA A23.2-1A (see Clause P.7.2). The potential deleterious character of sulphide-bearing aggregates may also be determined through field performance survey of concrete structures made with aggregates from the same source (see Clause P.7.3).

Alternatively, or in the case of inconclusive results from the field performance survey, the samples collected in the source may be subjected to a laboratory testing program (see Clause P.7.4).

P.7.2 Field evaluation of aggregate source (visual survey and sampling)

P.7.2.1

The geological survey of the source from which the concrete aggregate is produced shall be the first step in the PEP. It should be carried out by a geologist.

Note: *The visit to the source could advantageously be preceded by a survey of regional/local geological and/or testing report(s) that might have been prepared from previous investigations. Historical information of interest could include the mining plans (or location of the extracted areas/zones) over the past years/decades, the rock type(s) present, and its (their) petrographic composition (in particular details on the presence of sulphide mineral (s), its(their) type(s) and proportion(s), the total sulphur content, etc.).*

P.7.2.2

The geological survey shall then be carried out to ascertain the rock type and its distribution/proportion in the current and yearly projected extraction area.

Notes:

1) *The type(s) and proportion of sulphide mineral(s) can indeed change from one location/rock type to another in a source of aggregate, which can affect significantly the deleterious character of the material from one production level to another.*
2) *Since sulphide-bearing aggregates are susceptible to oxidation, traces of rust in the bedrock/production areas and/or in the stockpiles might be valuable observations to include in the report (Figures P.8 and P.9).*

P.7.2.3

Based on the results of the geological survey in the source, sampling should be carried out in accordance with CSA A23.2-1A, with the objective of collecting representative samples

a) from the aggregate production (stockpiles);
b) of the specific rock type(s) present in the current and/or projected exploitation area(s); or
c) both Items a) and b).

Note: *Representative samples will be further subjected to laboratory investigations (see Clause P.7.4).*

P.7.3 Field performance evaluation in concrete structures/elements

When field performance evaluation is proposed for determining the deleterious/innocuous character of sulphide-bearing aggregates proposed for use in new concrete construction, the “appropriate” concrete structure shall meet the following criteria:

a) The concrete examined shall be at least 15 years old.
b) The structure shall contain an aggregate that was produced from the same source as that proposed for use in the new concrete construction (confirmed from construction records, etc.). In the absence of conclusive documentation on the above, petrographic study shall be conducted on cores extracted from the structure to demonstrate that the aggregate in the structure is of the same petrographic/mineralogical composition as that proposed for use in the structure to build.
c) The exposure conditions of the field concrete shall be conducive to the oxidation of sulphide minerals (see Figures P.1 to P.4). It is to be noted that the oxidation of sulphide minerals in concrete aggregates requires access of water and oxygen to the concrete; however, oxidation might not proceed (or might proceed very slowly) in the case of structural elements constantly exposed to moisture, such as submerged portions of structures or parts of concrete elements totally embedded in the ground.
d) In the case of a structure meeting the requirements listed in Items a) to c), and that is not showing any significant signs of deterioration, petrographic examination shall be carried out on specimens prepared from a core (e.g., thin section, polished section, broken pieces) extracted from the

structure to demonstrate the presence (or not) and the type(s) of sulphide mineral(s) (especially pyrrhotite) in the concrete aggregate.

e) In the case of a structure/structural element meeting the requirements listed in Items a) to c), and that is showing signs of deleterious expansion/cracking, a petrographic study shall be conducted on specimens prepared from a core (e.g., thin section, polished section, broken pieces) extracted from the above structure/structural element to confirm that the signs of deterioration are in association with the oxidation of the sulphide minerals present in the concrete aggregate, and resulting internal sulphate attack (see Figure P.6; CSA A23.2-15A; Rodrigues *et al.*, 2012 and 2014; and Tagnit-Hamou *et al.*, 2005 for examples).

Such a field performance review shall be conducted by a professional who is experienced in the assessment of concrete distresses and durability issues in structures.

P.7.4 Laboratory investigations

P.7.4.1

The material(s) collected as part of the geological survey shall be subjected to the laboratory tests included in the performance evaluation protocol (PEP) illustrated in Figure P.7.

Note: *These investigations are meant to provide information that will complement the results of the geological survey of the aggregate source. Deleterious reactions/expansions can occur in concrete due to the presence of very small amounts of pyrrhotite (or other unstable sulphide minerals) in the aggregates, which can often not be easily/readily identified from the macroscopic examination of the rock samples and/or aggregate material in stockpiles in the source.*

P.7.4.2

The laboratory investigations described in Figure P.7 involve a potential of three steps that include a measurement of the total sulfur content in percentage by mass (ST) (Step 1 — see detailed procedure in Clause P.8), and petrographic examination to determine the presence (or not) or iron sulphide minerals, particularly pyrrhotite (see CSA A23.2-15A), oxygen consumption by the aggregate tested in an air-tight container to determine oxidation potential (Step 2 — see detailed procedure in Clause P.9), and finally an accelerated mortar bar expansion test (Step 3 — see detailed procedure in Clause P.10).

Note: *Technical information on the PEP and on the oxygen consumption and mortar bar expansion tests can be found in Rodrigues et al. 2015, 2016a, and 2016b.*

P.8 Determination of sulphide sulphur content of concrete aggregates

See Attachment P1 for the test method for determination of sulphides sulphur content of concrete aggregates.

P.9 Test method for detection of the oxidation potential of sulphide-bearing aggregates by an oxygen consumption test

See Attachment P2 for the test method for detection of the oxidation potential of sulphide-bearing aggregates by an oxygen consumption test.

P.10 Test method for detection of potential reactivity of sulfide-bearing aggregates by accelerated expansion of mortar bars

See Attachment P3 for the test method for detection of potential reactivity of sulphide-bearing aggregates by accelerated expansion of mortar bars.

P.11 Discussion, summary, and interpretation of test results from the PEP

P.11.1 Discussion

Many aggregates contain very small amounts of sulphides; thus, specifying that there be no sulphides present in the aggregate is not a realistic requirement. However, at present, there are insufficient data to provide unequivocal advice as to what amount of sulphide is likely to be harmful or safe to use. It is clear from the literature review that pyrrhotite, even in very small amounts, is potentially deleterious. Pyrite and marcasite can probably be present in small amounts without causing deleterious expansion although objectionable staining can be caused on concrete surfaces by the presence of small amounts of iron sulphide (Figure P.10). In the Trois-Rivières area, no cases of damage were identified when the volumetric pyrrhotite content found in the coarse aggregate was less than about 0.23%; however, this number is still open to debate and is likely applicable only to the aggregate material (containing high pyrrhotite-to-pyrite ratio) produced from the two local quarries identified in this case.

P.11.2 Field performance survey

A PEP has been proposed for evaluating the potential deleterious character of sulphide-bearing aggregates in concrete (Figure P.7). This can be determined through the field performance survey of concrete structures/elements made with aggregates produced from the same quarry as those proposed for the new concrete construction. Normally, concrete suppliers will be aware of reports of objectionable staining or other problems with the use of their concrete/aggregate combinations.

The results of the visual examination of selected concrete structures will be completed by the petrographic examination of concrete cores extracted from structural elements exposed to conditions conducive to the oxidation of sulphide minerals present in the aggregate. A conclusive decision on the deleterious/innocuous character of the aggregate investigated will rely on the capacity to link any signs of visual deterioration (or not) to the presence (or absence) of petrographic signs of oxidation of the aggregate in question and resulting internal sulphate attack.

P.11.3 Geological survey of the source

Alternatively, or in the case of inconclusive results from the field performance survey in concrete structures, a complementary field and laboratory investigation may be carried out.

The investigation shall start with the geological survey of the aggregate source and collection of any historical information on the source investigated (Clause P.7.2). The identification of rock type(s) and its (their) distribution/proportion in the current and yearly projected exploitation area(s) will lead to representative sampling in accordance with CSA A23.2-1A, which, in turn, will be subjected to a series of test methods in the laboratory (Clause P.7.4).

P.11.4 Laboratory investigations — Step 1 (determination of sulphide sulphur content)

Step 1 of the laboratory investigation consists in performing the chemical analysis of the aggregate proposed for use in accordance with the test procedure described in Clause P.8.

Aggregates showing a total sulphur content > 1.00% by mass shall be rejected as concrete aggregate. Aggregates with a total sulphur content less than 0.15% by mass may be used without further investigations. If the total sulphur content of the investigated aggregate is lower than 1.00% and is equal to or greater than 0.15% by mass, the sulphate sulphur content should be determined in accordance with the method provided in Attachment P1. If the sulphide sulphur content (i.e., total sulphur – sulphate sulphur) is less than 0.15%, the aggregate may be used without further investigations. If the sulphide sulphur content is equal to or greater than 0.15%, the nature of the sulphide mineral present should be determined by petrographic examination or other appropriate means (e.g., XRD on concentrates, Mineral Liberation Analyser (MLA)). If pyrrhotite is detected, the aggregate shall be subjected to Step 2 of the laboratory investigation program (Clause P.11.5).

If sulphide minerals other than pyrrhotite are detected and the sulphide sulphur content is no more than 1.00% by mass, the material may be used provided that the sulphide minerals are not susceptible to oxidation (Steps 2 and 3 of the laboratory test program). Midgley (1958), Ramos et al. (2016), and Guirguis and Shehata (2017) proposed staining and other quick screening tests to detect sulphide minerals that can cause objectionable staining or oxidation reactions.

Examples of rocks where the total sulphur content can reach 0.15% by mass and have satisfactory field performance (excluding potential alkali reactivity) include Ordovician limestones and dolostones of the St.Lawrence Lowlands (Québec) and Lake Ontario area that contain significant amounts of minute cubic pyrite, but no pyrrhotite.

P.11.5 Laboratory investigations — Step 2 (determination of oxidation potential — oxygen consumption test)

Step 2 of the laboratory investigation program provides a means of evaluating the oxidation potential of sulphide-bearing aggregates. It is based on the use of an oxygen consumption test developed for mine tailings, where iron sulphides oxidation is the source of acid rock drainage (ARD).

In the test, a compacted layer of aggregate material is exposed to oxygen (O_2) in a hermetic cell, and the O_2 consumption is monitored with an appropriate probe. Optimized parameters included a 100 mm compacted layer of aggregate material (particle size < 160 µm) kept at 40% saturation degree with a 100 mm headspace left at the top of the cell. The consumption of the O_2 present in the headspace is monitored over a 3 h testing period at 22 °C.

Aggregates producing an oxygen consumption of less than 4.0% may be accepted as concrete aggregate; on the other hand, O_2 consumption values greater than 4.0% shall trigger further testing though an accelerated mortar bar test (Step 3).

P.11.6 Laboratory investigations — Step 3 (mortar bar expansion test)

The accelerated mortar bar test includes two phases. Phase I aims at triggering the oxidation reaction of the aggregate investigated, thus producing oxidation products and sulphuric acid that will in turn promote internal sulphate attack and excessive expansion of the test bars. During this phase, the mortar specimens (0–5 mm aggregate particle size; cement-to-aggregate of 1:2.75; water-to-cement ratio of 0.65) are subjected to 90 days of storage at 80 °C/75% relative humidity, with two 3 h wetting cycles per week in a 6% sodium hypochlorite solution. The bars are then transferred for 90 days of storage at 4 °C/100% relative humidity, period over which the specimens are still subjected to two 3 h wetting cycles per week in a 6% sodium hypochlorite solution (Phase II). In the presence of carbonate material in the aggregate, excessive expansion will develop in Phase II through thaumasite attack.

The length change of the mortar bars is monitored regularly over both Phase I and II of testing. Excessive expansion of the mortar bars could also develop during phase I in the case of alkali-silica reactive aggregates; however, mortar bars containing ASR-susceptible aggregates, but that do not contain unstable sulphide mineral, will not expand significantly when exposed to Phase II test conditions.