

Evaluation of the presence of ettringite in concrete structures affected by alkali-silica reaction

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Abstract

In structures affected by alkali-silica reaction (ASR), it is common to find in the concrete the presence simultaneously of ettringite and alkali silica reaction products, even in concrete not exposed to an external source of sulfates, but in most cases, this does not mean also the existence of an internal sulfate attack.

In this paper, the case of 5 dams affected by ASR in which there was also ettringite have been studied. This research has been completed with other structures in which there was ettringite but not visual evidence of damage.

In a first phase, ASR diagnosis of these dams has been carried out, including tests on concrete (visual inspection and SEM) and aggregates (petrographic study RILEM AAR-1 and expansion measurement ASTM C-1260).

In a second phase, the presence of ettringite has been evaluated, focused on the study of the aggregates and the sulfate content of concrete, including SEM observation. Special attention is paid to the presence of pyrrhotite in the aggregates and its content, checking if an excess of sulfur in concrete could be the cause of an internal sulfate attack.

As a conclusion, the results finally discard the existence of internal sulfate attack as a pathology of the concrete in all the real cases studied.

Keywords: ASR; DEF; ettringite; sulfur; pyrrhotite

1. INTRODUCTION

The initial evaluation of concrete in hydraulic structures usually includes analysis of concrete using Scanning Electron Microscope (SEM). It is common to find the presence simultaneously of ettringite and alkali-silica reaction (ASR) products, even in concretes not exposed to an external source of sulfates.

The detection of ASR gels in concrete with visual evidences of damage is a strong evidence that ASR can be cracking concrete, although a specific study has to be carried out to reach a definitive conclusion. Literature provides different tests to complete this diagnosis [1].

However, ettringite is the reaction product of an expansion process [2], but it is also a normal product of cement hydration. Thus, if ettringite is observed, the presence of an internal sulfate attack (ISA) in field concrete should be evaluated.

Innocuous ettringite is formed during cement hydration (primary ettringite). It is homogeneously distributed in the paste matrix of the hardened concrete and its initial formation in Portland cement concrete does not lead to expansion [3]. Moreover, when concrete is exposed to water for long periods of time, this primary ettringite can slowly dissolve and reform in any available voids or microcracks. Any deterioration of concrete accelerates the rate at which ettringite leaves its original location in the paste to go into solution and recrystallize in larger spaces. This secondary ettringite, which can be observed in the SEM test as acicular crystals, is not detrimental to concrete performance [3–8].

Expansive ettringite (when there is not an external source of sulfates) is formed in concrete because of the presence of sulfates in excess in aggregates or cement, elevated temperatures during curing or the presence of oxidizable sulfides in aggregates [8]. Therefore, one of these causes of internal sulfate attack (ISA) should be proved to diagnose the simultaneous existence of ASR and ISA in concrete.

The next three sections describe each kind of ISA and the tools available to diagnose it in field concrete. This background will allow to decide if ISA is a pathology or not in each case studied below.

1.1 ISA due to excess of sulfates in cement or aggregates

An excess of sulfates in concrete components can produce expansion that occurs rapidly, within about 6 first months. The amount of sulfates needed to induce expansion depends on the composition of the clinker but is generally above 5 or 6% SO_3 by weight of cement [8].

European Standard limits the amount of sulfate in aggregates [UNE-EN 12620:2003], water [UNE-EN 1008:2007] and cement [UNE-EN 197-1:2011] to prevent expansion.

1.2 Delayed ettringite formation

DEF may be defined as the formation of ettringite in a cementitious material by a process that begins after hardening is substantially complete and in which none of the sulfate comes from outside the cement paste. When elevated temperatures appear during curing, substantial fractions of Al_2O_3 and SO_3 enter the C-S-H. Most of the Al is firmly bound, but the sulfate is very loosely bound, and has been described as absorbed. Thus, C-S-H will be a source of SO_3 that can react with aluminates and monosulfate present in cement to form expansive ettringite after hardening of concrete [5].

There are two necessary but not sufficient conditions for expansion to occur from DEF. First, the internal temperature of the material must be above 70°C (or 80°C [9]) for a sufficient length of time [4]; and second, after returning to ordinary temperature, the material must be kept wet or moist, intermittently or permanently [5]. Moreover, the sulfate content of cement is also important. No DEF expansion occurs when cement with total sulfate content up to 2% SO_3 is used and it is recommended SO_3 in cement be lower than 4% SO_3 if curing temperature can be higher than 70°C [10]. Finally, a common factor in some thoroughly studied field concretes affected by DEF is a cement content greater than or equal to 400 kg by m^3 of concrete [11, 12].

The incidence of delayed ettringite formation (DEF) in field cases is low [8]. Despite the relative ease with which researchers can “create” expansion due to DEF in the laboratory, reported occurrences in the field are relatively rare and often surrounded by doubt as to the true role of DEF in the deterioration process [13].

A case of DEF that has been studied in depth is a concrete viaduct in southern U.S.A., which was constructed in the late 1980s [12]. The diagnosis of DEF was carried out creating an expansion test of cores extracted from the structure. ~50-mm core samples were immersed in hot alkaline solution to determine any residual potential expansion due to ASR and in lime-saturated water at normal laboratory temperature to examine the potential for DEF. Cores showed significant expansion (0,3 to 1,3% at 280 days) when immersed in limewater at normal laboratory temperature. Therefore, delayed ettringite formation was confirmed as a cause of damage.

1.3 ISA due to presence of oxidizable sulfides in aggregates

Oxidizable sulfides in aggregates are an important cause of ISA, with structures affected in Australia [14], U.K. [15], Canada [16, 17], Switzerland [18] or Spain [19].

The expansion process has three steps. Firstly, the oxidation reaction of sulfides forms sulfuric acid and iron oxide. Then, sulfuric acid and portlandite present in cement produce gypsum, with volume increase and expansion [20]. Finally, gypsum and aluminates react to form ettringite, increasing the expansion of concrete.

Sulfide oxidation is very slow compared with other common expansive reactions in concrete (e.g. sulfate attack) [20]. Thus, although ISA due to sulfide oxidation produces expansion since first years of service, this process extends over time.

Iron sulfides are common minor constituents in many rock types. Consequently, concrete aggregates may contain a certain amount of iron sulfides, mainly pyrite and pyrrhotite [17]. Pyrrhotite is more reactive than pyrite because pyrrhotite solubility is about four times higher than that of pyrite [18]. Because of that, the European Standard UNE-EN 12620 limits the total sulfur content to 1% S, and this threshold is decreased to 0,1% S when the presence of pyrrhotite is proved.

Moreover, CRIB [21–24] has developed a protocol to evaluate the potential deleterious effects of iron sulfide-bearing aggregates prior to their use in concrete. This protocol is divided into three phases: total sulfur content measurement, oxygen consumption evaluation and an accelerated mortar bar test. In a first phase, aggregates with total sulfur content higher than 1% should be rejected and aggregates with content lower than 0,1% can be accepted without any further testing. For aggregates showing a total

sulfur content between 1% and 0,1% further testing is necessary to identify the sulfide minerals, and the phase 2 should be carried out.

2. OBJECTIVES

This communication shows 4 dams (A to D) and a channel (E) with damage evidences in which ettringite and ASR products have been identified by SEM.

The first objective is to confirm the ASR diagnosis of these structures. For that purpose, the reactivity of aggregates used in each one is evaluated, using the petrography quantification of reactive components and the accelerated mortar bar test.

Afterwards, the diagnosis of a possible simultaneously internal sulfate attack (ISA) has been studied in these structures. For that purpose, aggregate tests (petrography and sulfur content) and concrete tests (sulfur content and SEM) have been carried out. This ISA evaluation is completed with three other old dams (X, Y and Z) in which ettringite was also observed but there was not any signal of deterioration.

3. MATERIALS AND METHODS

3.1 Materials

Eight hydraulic structures have been evaluated. They are between 49 and 87 years old. All of them are dams apart from Structure E which is a channel. Table 3.1 compiles the concrete batching information available.

Table 3.1: Concrete Batching.

Hydraulic Structure	Description
A	Concrete (m ³): 300-350 kg Portland cement. w/c ratio: 0,6
B	Concrete (m ³): 300, 250, 225 y 200 kg Portland cement, depending on the part of the dam
D	Concrete (m ³): 300 kg Portland cement, w/c ratio: 0,6
X	Concrete (m ³): 200 kg Portland cement, w/c ratio: 0,85
Z	Concrete (m ³): 250-300 kg of Portland cement; w/c ratio: 0,55; aggregates: 717 kg 40-120 mm fraction, 515 kg 10-40 mm fraction, 291 kg 4-10 mm fraction and 464 kg of sand
C, E, Y	Batching information is not available

All constructions have low cement content (200-300 kg cement/m³ concrete), except dam A with cement content between 300 and 350 kg/m³. There is not an external source of sulfate (water or soil) in any of them.

3.2 Methods

Firstly, Concrete samples from all these structures have been analysed by SEM-EDX. After that, sulfur content (UNE-EN 1744-1:2010), compression strength (UNE-EN 12504-1:2009) and density are also evaluated in these concrete samples. Sulfur content is measured with high temperature combustion with non-dispersive infrared detection (NDIR). This method is a fast and easy technique to evaluate the sulfur content of concrete.

Secondly, coarse aggregate has been extracted from all field concretes. The mortar attached to the aggregate particles is removed using a small pneumatic drill. Next, each aggregate sample is crushed and washed to obtain a homogeneous sample. It is assumed that sand and coarse aggregate used in each concrete have the same origin and composition, because hydraulic structures are large size constructions in which aggregates (fine and coarse) are taken from the place where the construction is located.

Once aggregates are extracted, their sulfur contents are measured (UNE-EN 1744-1:2010).

Finally, in aggregates with some evidences of ASR (from A to E), the evaluation of aggregate reactivity has also been carried out. Figure 3.1 shows the methodology followed in CEDEX to evaluate it.

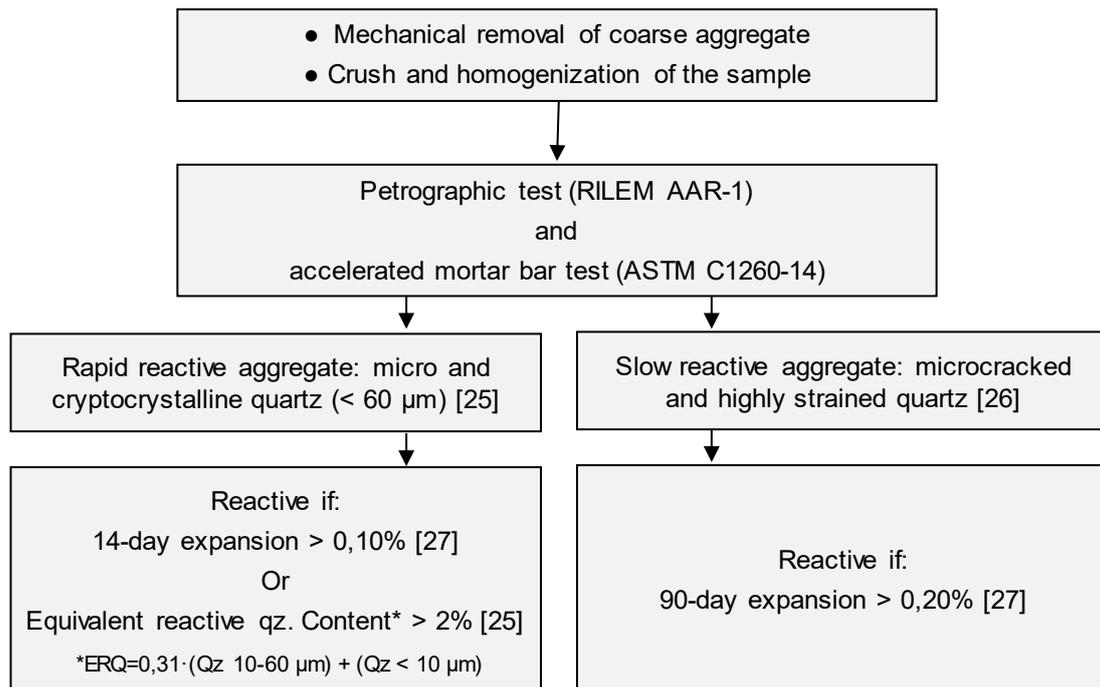


Figure 3.1: Methodology for Alkali silica reaction diagnosis in field concrete based on the study of the aggregates [25–27].

4. RESULTS

4.1 Hydraulic Structures: preliminary evaluation

The inspection of structures has distinguished two groups: structures A, B, C, D and E have shown apparent signs of pathology: expansion, movement and cracking of concrete (Figures 4.1 and 4.2 are shown as examples of the visual damage). However, dams X, Y and Z have not shown any prove of expansion, movement or cracking.

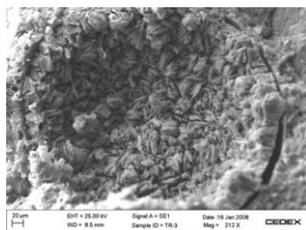


Figure 4.1: Cracking in DAM C

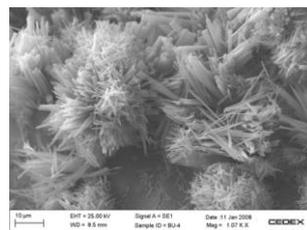


Figure 4.2: Cracking in pillar of Channel E

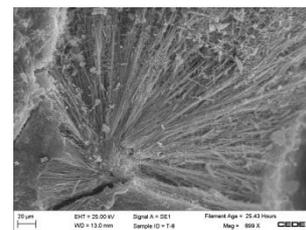
Concrete samples from all these structures have been analysed by SEM-EDX. All of them have shown ettringite, regardless of the presence or not of visual sign of pathology (Figure 4.3 to 4.5). Moreover, concrete from structures A, B, C, D and E have also shown alkali-silica reaction products (Figures 4.6 and 4.7).



Al: 7%; S: 12%; Ca: 41%; O: 40 %

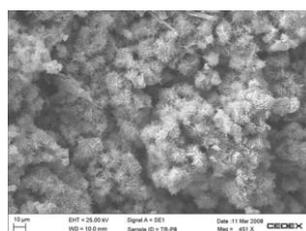


Al: 9%; S: 15%; Ca: 32%; O: 44 %

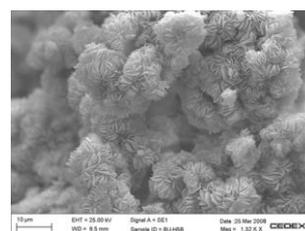


Al: 9%; S: 14%; Ca: 35%; O: 42 %

Figure 4.3: Ettringite in DAM D Figure 4.4: Ettringite in Channel E Figure 4.5: Ettringite in DAM X



Na: 3% - Si: 32% - K: 15% - Ca: 7% - O: 43%



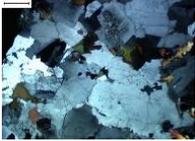
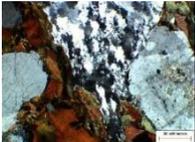
Na: 6% - Si: 31% - K: 12% - Ca: 8% - O: 43%

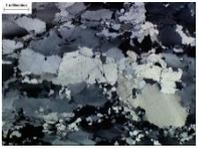
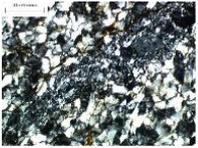
Figure 4.6: Alkali Aggregate reaction products in Dam D Figure 4.7: Alkali Aggregate reaction products in Channel E

4.2 Aggregate properties: petrography, accelerated mortar bar test and Sulfur content

Table 4.1 shows the petrography of aggregates.

Table 4.1: Petrography of aggregates

	Petrography	Characteristics of quartz	Photography.
A	<p>Biotitic porphyritic Monzogranite with medium-coarse grained. Holocrystalline texture, inequigranular, porphyritic texture with 2-3 cm size feldspars phenocrysts.</p> <p>Main minerals: Quartz (25-30%), potassium feldspar (25-30%), plagioclase (25-30%) and biotite (10%).</p> <p>Opagues as a minor component</p>	<p>Quartz: Allotriomorphic crystals with undulose extinction, mosaic texture, microfractured and sutured boundaries. Grain size between micro and medium-grained crystals.</p>	 <p>Monzogranite; quartz with undulose extinction and microfractured</p>
B	<p>Granodiorite: Granodiorite medium grained. Holocrystalline texture, inequigranular, hypidiomorphic with myrmekitic textures.</p> <p>Main minerals: Quartz (28%), potassium feldspar (23%), plagioclase (39%) and biotite (10%).</p> <p>Opagues as a minor component</p>	<p>Quartz: Subhedral crystals with undulose extinction and microfractured.</p>	 <p>Quartz with undulose extinction and microfractured</p>
C	<p>Porfidic biotite granodiorite, quartz rich and fine to medium grain sized. Quartz (41%): The rock shows microcrystalline quartz in the subgrain boundaries formed by recrystallization, Plagioclase feldspar (30%), Potassium-rich feldspar (12%), Biotite (17%).</p> <p>Opagues as a minor component</p>	<p>Quartz: 2,5 vol% of equivalent reactive quartz in fraction 2-4 mm and 2,5 vol% in fraction <2 mm.</p>	 <p>Microcryst. quartz, biotite and plagioclase.</p>

	Petrography	Characteristics of quartz	Photography.
D	Quartzite with homogeneous composition. Heterogeneous fabric: Cataclastic and heterogranular (from cryptocrystalline to millimetric strained quartz). Opaques as a minor component	Quartz: 7,4 vol% of equivalent reactive quartz in fraction 2-4 mm and 5,8 vol% in fraction <2 mm.	 Quartzite with micro and cryptocryst. Qz.
E	Quartzarenite (60%): angular grains. Heterogranular. Ferruginous cement Quartzite (40%): granoblastic and xenomorphic texture. Polygonal Fabric, sutured contact. Opaques as a minor component	Quartz: 10,5 vol% of equivalent reactive quartz in fraction 2-4 mm and 13,8 vol% in fraction <2 mm.	 Vein of micro and cryptocryst. quartz
X	Dolomite rock: 80% dolomite and 20% calcite (DRX). Opaques as a minor component		
Y	60% Quartzite with tourmaline, muscovite, biotite, opaques and iron oxide. 40% Two mica granite, with opaques and apatite.		
Z	Limestone dolomite rock. Homogeneous venulated texture. 95% dolomite, mainly with microcrystalline crystal size, but also with drusy crystals up to 0,4 mm. 5 % sparite filling veins and voids. Opaques as a minor component		

The aggregates are two carbonated rocks, three igneous rocks (granite or granodiorite), two quartzite aggregates, and a mix of quartzite and granite. Opaque minerals have been detected as secondary minerals in all of them.

Table 4.2 shows sulfur content of aggregates and expansion in the accelerated mortar bar test.

Table 4.2: Sulfur content and expansion (AMBT)

Aggregate	Total Sulfur content (% of SO ₃ by weight of agg.)	Expansion in Accelerated mortar bar test
A	0,050	0,06% (14 day) and 0,37% (90 day)
B	0,303	0,06% (14 day) and 0,27% (90 day)
C	0,240	0,10% (14 day)
D	0,027	0,20% (14 day)
E	0,015	0,42% (14 day)
X	0,088	Without evidence of ASR
Y	0,050	
Z	0,138	

4.3 Field concrete: physical properties and sulfur content

Table 4.3 shows sulfur content of concrete, compression strength and density.

Table 4.3: Properties of concrete

Field concrete	Compression Strength MPa	Density Kg/m ³	Total Sulfur content (% of SO ₃ by weight of concrete)
A	37,2	2431	0,394
B	32,7	2350	0,390
C	48,7*	2350	0,310
D	38,2	2339	0,468
E	41,8	2383	0,341
X	22,0	2320	0,200
Y	24,6	2267	0,299
Z	38,3	2397	0,200

* Result obtained only with one core, with aggregate size higher than the diameter of the core.

Compression strength is always greater than 20 MPa. Density is high because of aggregate large size normally used in dams. Except from dam D, sulfur content is always between 0,2-0,4% SO₃.

5. DISCUSSION

ASR and ISA are evaluated in field concretes from the hydraulic structures tested previously.

5.1 Alkali silica reaction in concrete

Figure 3.1 shows the methodology followed to evaluate the reactivity of aggregates with alkalis of concrete.

Aggregates A and B can be slow reactive because of their content of microcracked and highly strained quartz (Table 4.1). Aggregates with these reactive components will be reactive if 90 day expansion in AMBT is higher than 0,2%, although 14 day expansion may be less than 0,1% [27]. Thus, the expansion results obtained (Table 4.2) classify these two aggregates as reactive.

Aggregates C, D and F are fast reactive because of their content of micro and cryptocrystalline quartz (Table 4.1). The AMBT also corroborates their reactivity (Table 4.2).

Therefore, damages and ASR products detected in these hydraulic structures, together with proved reactivity of the aggregates used in them, demonstrates the existence of ASR in those constructions.

5.2 Internal sulfate attack in concrete

Aggregates and concretes have been tested. The results obtained are discussed below.

5.2.1 Aggregate tests

Petrography of aggregates have shown opaque phases in all samples tested (Table 4.1). Many minerals (ilmenite, magnetite, goethite, graphite, cuprite, hematite ...) are observed as opaques in petrography, but also sulfide minerals as pyrite, pyrrhotite, chalcopyrite or marcasite are opaques [28]. Innocuous opaque phases and sulfide bearing minerals cannot be differentiated using only a petrographic microscope (polarized light).

Thereby, the presence of ettringite in concrete and opaques in petrography could be indications of possible internal sulfate attack due to the presence of oxidizable sulfides. Even so, it is necessary to identify and quantify sulfides to prove it. For that purpose, Figure 5.1 shows the total sulfur content of aggregates and the threshold content for sulfur and sulfate in the European Standard UNE-EN 12620:2003.

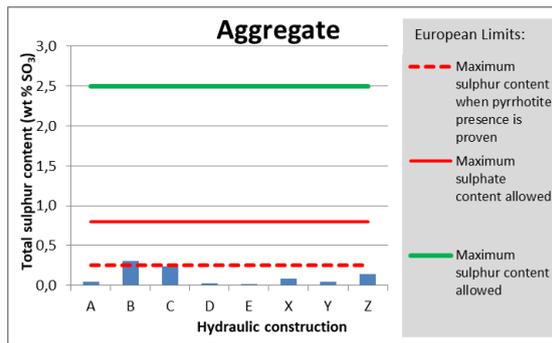


Figure 5.1: Total sulfur content and limits.

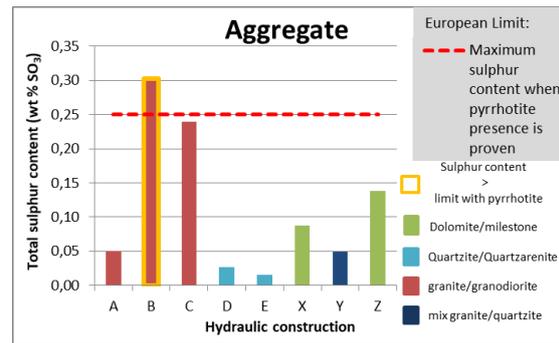


Figure 5.2: Enlargement of the Figure 2, focus in sulfide contents and its maximum content allowed.

Results of quartzites, quartzarenites and carbonated aggregates (belonging to structures A, D, E, S, Y Z) have been far from any limit (Figures 5.1 and 5.2). Therefore, an internal attack coming from the presence of sulfur in these aggregates can be discarded.

Only igneous aggregates B and C have total sulfur content close to the sulfur limit when pyrrhotite presence is proved (0,1% S). Specifically, total sulfur content of aggregate B exceeds this limit, so a deep study is necessary in this case. To do this, Spanish Standard [29] and Rodrigues et al [24] recommend that the sulfate content should be subtracted from the total sulfur content to apply the 0,1% S limit.

The measure of the sulfate content in aggregate B is carried out (0,119% SO₃ [UNE-EN 1744-1:2010]) and the difference between sulfur and sulfate content has provided its sulfide content. The sulfide content of aggregate B is 0,074% S. This value is lower than the maximum allowed (0,1% S), discarding the presence of an internal attack coming from the aggregate also in this case.

As a conclusion, none of the eight hydraulic structures studied has an internal sulfate attack due to an excess of oxidizable sulfides or sulfates in their aggregates.

5.2.2 Concrete tests

It has been proved that aggregates are not the cause of an internal sulfate attack in the structures studied. Now, the presence of ISA due to an excess of sulfates in concrete (coming from the cement or the water) can be evaluated with the chemical tests carried out. It is important to point out that if an excess of sulfates in concrete had produced damages, this process would have happened during the first year of service.

Sulfates are intentionally added to Portland cement to regulate early hydration. The sulfate threshold of Portland cement is 3,5% SO₃ in 32,5 and 42,5N cement, and 4,0% SO₃ in 42,5R and 52,5 cement [UNE-EN 197-1:2011].

When cement content is known, the sulfate content of concrete can be compared with the maximum content admitted in cement. For that purpose, two assumptions have been done. The first one is that all these concretes have 1750 kg aggregate by m³ of concrete. This assumption allows to subtract the sulfur provides by aggregates to the total sulfur content of concrete. The second supposition is that the total sulfur content of concrete, after subtracting aggregate contribution, is equivalent to its sulfate content. In this way, it can be evaluated if sulfates from cement can explain the sulfate content of concrete. These two assumptions simplify chemical work and provide conservative results, with a low level of error.

Figure 5.3 shows the results obtained when sulfate content of concrete is compared with the cement contribution, when the cement content is known.

Red and green lines are the maximum sulfate contribution of each kind of Portland cement to concrete. Blue bars are the sulfate content of field concrete, after subtracting aggregate contribution. The sulfate content of concretes A, B, D, X and Z are in accordance with the cement content used. Thus, in these hydraulic structures there has not been an internal sulfate attack because of an excess of sulfates in concrete.

When cement content is unknown (field concrete C, E, Y), it is calculated the amount of cement that fits the sulfate content measured in each concrete. Although the analysis of results is more accurate when cement content is known, this estimation will allow to evaluate if concrete has an excess of sulfates.

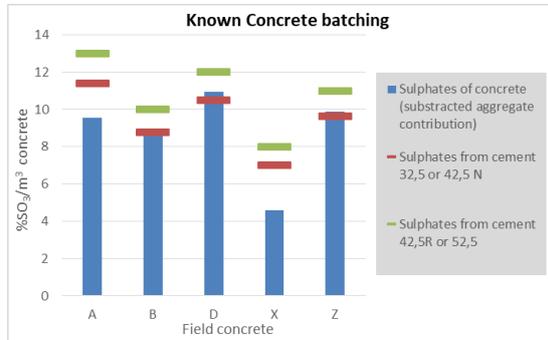


Figure 5.3: Evaluation of sulfate content of concrete when cement content is known.

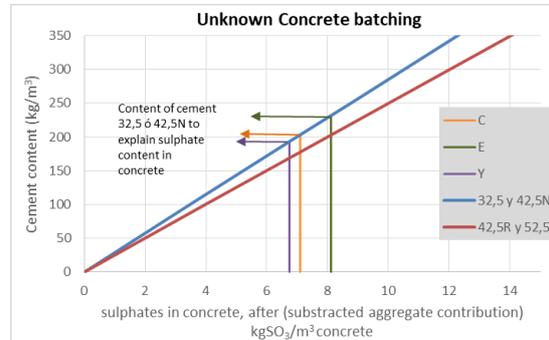


Figure 5.4: Evaluation of sulfate content of concrete when cement content is unknown.

The cement contents obtained in field concrete C, E and Y are between 193 and 232 kg cement 32,5 or 42,5N by m³ of concrete (Figure 5.4). These cement contents are consistent with the other concretes from the dams studied, always with cement content lower than 350 kg/m³. Thus, field concretes C, E and Y have a normal amount of internal sulfates according to the usual cement content in concrete for dams, so an internal sulfate attack due to an excess of sulfates in these structures is discarded.

5.2.3 Delayed ettringite formation

It has been proved in the previous sections that the aggregates used or the sulfate content of concrete are not the cause of an internal sulfate attack in the structures studied. Finally, the possible existence of an ISA due to delayed ettringite formation will be studied in this section.

When cement content is known, it can be estimated the sulfate content of the cements used in these field concretes. Table 5.1 shows these estimations.

Table 5.1: Content of SO₃ of cements used in structures with known batching

Structure	A	B	D	X	Z
% SO ₃ in cement	2,9	3,6	3,6	2,3	3,6

None of these cements exceeds the limit of 4% of SO₃ in cement proposed by Collepardi et al [10] to avoid DEF in concrete.

In addition, DEF expansion is a process substantially completed within 1 or 2 years when it is carried out on laboratory mortar prisms [5]. Although expansion in field concretes may be presumed to occur much more slowly [5], the hydraulic structures evaluated have more than 50 years of service life. Therefore, it is logical to assume that, if an expansive process had existed, it would already have finished.

Even so, it is possible to measure the residual expansion test of field concrete. If the test is negative, this means that, either DEF has not damaged this concrete, or if DEF has damaged it, it is already a completed process that will not continue in the future.

For that purpose, the residual expansion test exposed in Section 1.2 is carried out on cores extracted from dam D. This structure is selected because it has the most favourable properties to have DEF: the highest content of sulfur in concrete (Table 4.3), the highest sulfate content of cement (3,6% SO₃), one of the youngest structures evaluated (51 years old) and the second highest cement content tested (300 kg/m³ of Portland cement).

Figure 5.5 shows the expansion results obtained.

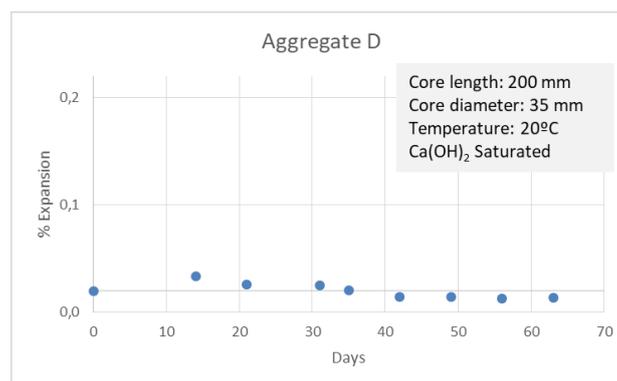


Figure 5.5: Aggregate D. DEF Residual expansion

Although the test is still going on, Concrete from dam D has not expanded during the first 63 days of test. These results indicate that delayed ettringite formation is not expanding concrete nowadays.

To confirm that DEF is not damaging the other hydraulic structures, this test should have been done to the rest of field concretes. Even so, considering that the other structures have less content of sulfur in concrete, and also, or they are older or they have lower cement content, it could be assumed that DEF has not damaged these structures, or this process has finished.

5.3 Origin of the ettringite in concrete

Although ettringite has been observed in all the eight structures evaluated, it has been proved that none of them has an internal sulfate attack, in any of their forms: DEF, oxidizable sulfides in the aggregates or an excess of sulfates in the concrete.

Moreover, three of these dams (X, Y, Z) in which ettringite was observed there was no signal of deterioration after more than 50 years of service life. Thus, the ettringite observed in them should be considered innocuous.

Structures A-E, with clear evidences of damage due to ASR, have also shown ettringite. ISA diagnosis has proved that this ettringite should be innocuous, but this conclusion is also corroborated with the evaluation of dams without damages. The eight structures, damaged or not, have been done with Portland cement, with similar batching and similar sulfate content, and also with aggregates without enough sulfides to produce ISA. Thus, the absence of damages in dams without ASR but same physical properties is another evidence that ettringite observed in hydraulic structures with ASR is also innocuous.

Therefore, after evaluating eight structures, it can be concluded that ettringite is commonly observed in hydraulic constructions because concrete is exposed to water for long periods of time, so the existing primary ettringite can slowly dissolve and reform in any available voids or microcracks. As literature explains, ASR deterioration of concrete can accelerate the rate at which ettringite leaves its original location in the paste to go into solution and recrystallize in larger spaces. In any case, it has been proved that this ettringite is innocuous.

6. CONCLUSIONS

It has been studied four dams (A to D) and a channel (E) with damage evidences in which ettringite and ASR products have been identified by SEM.

- The presence of a pathology due to **alkali silica reaction** has been **confirmed**. The diagnosis includes visual damages observed, ASR products detected by SEM, and the proved reactivity of aggregates, evaluated using the petrography method RILEM AAR-1 and the accelerated mortar bar test ASTM C1260-14. These tests have been carried out on coarse aggregates extracted from these structures.
- The presence of internal sulfate attack due to the content of **oxidizable sulfides** in aggregates has been **discarded**. To do that, total sulfur content of coarse aggregates extracted from field concretes has been carried out.

7 of the 8 aggregates evaluated have shown total sulfur content less than the limit proposed by EN 12620 when the presence of pyrrhotite is proved (total sulfur content < 0,1%S).

On the other hand, total sulfur content of aggregate B exceeds this limit, so its sulfate content has been measured, and this value has been subtracted from the total sulfur content to obtain its sulfide content. Finally, 0,1%S limit has been applied to the sulfide content, as recommended by Spanish Standard and literature. Sulfide content of aggregate B is lower than 0,1% S, discarding the presence of an internal attack coming from the aggregate also in this case.

- The presence of internal sulfate attack due to **excess of sulfates in concrete** has been **discarded**. For that purpose, total sulfur content of field concretes has been measured. When the cement content of concrete is known, the sulfur content of concrete is in accordance with the cement batching used. When the cement content is unknown, these concretes have shown a normal amount of sulfur according to the usual cement content in concrete for dams.
- The presence of internal sulfate attack due to **delayed ettringite formation** has been **discarded**. All the cements used in these hydraulic structures have low SO₃ content, below the limit (4%) proposed to develop this pathology and all the structures have more than 49 years of service life, so the development of DEF should have finished. In any case, residual expansion test has been carried out on cores extracted from dam D, selected because it has the most favourable properties to develop DEF. The result obtained in this dam has shown that delayed ettringite formation is not active at all in the actual moment.
- As a final conclusion, **Ettringite** observed in these five hydraulic structures with ASR is **innocuous** as it also appears in three other old dams with no signal of deterioration. The absence of damages in these three dams without ASR but same physical properties and same results in the ISA evaluation is an evidence that ettringite observed should be innocuous.

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