Internal Sulfate Attack of Concrete due to Iron Sulfide Minerals in Aggregate

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Internal Sulfate Attack of Concrete due to Iron Sulfide Minerals in Aggregate

Three Major Cases

Reaction Mechanism

Reducing Risk

Oslo Region had been plagued with sulfate attack from the pyrrhotite-containing "alum shales".

SULFATE ATTACK ON CONCRETE IN THE OSLO REGION

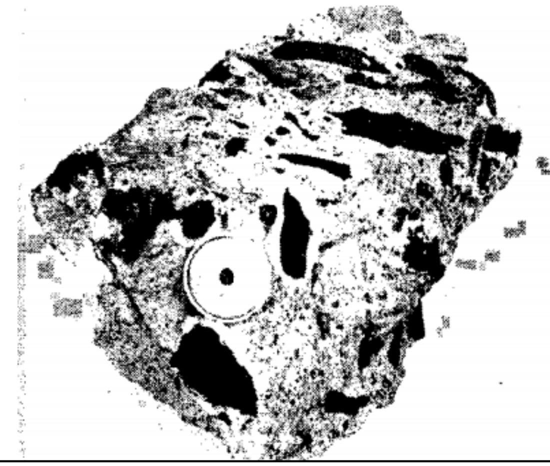
JOHAN MOUM and I. TH. ROSENQVIST

In the Oslo region of Norway, alum shales* containing small amounts of the unstable iron sulfide, pyrrhotite, produce an unusual form of sulfate attack upon concrete placed in or near these deposits, and cause deterioration if they are used as concrete aggregate. The ground water associated with the alum shales carries ferrous sulfate and produces severe sulfate attack and the precipitation of ferric iron compounds in concrete structures made with normal portland cement. Cements of low tricalcium aluminate content resist the sulfate attack but may be subject to attack by acid solutions produced when the ferrous sulfate is oxidized. Air-entrained concrete appears to be pa ularly susceptible.

■ For 40 years the construction industry in the Oslo plagued with problems of concrete deterioration and found related to the presence of slightly metamorphosed shales co usually unstable form of the iron sulfide mineral pyrrhotite. called "alum shales"* or "alum slates," and the expression problem" is familiar to most people engaged in construction work in Norway.

After World War II a semiofficial "Alum Shale Committee" was set up in Oslo, and the Norwegian Geotechnical Institute was requested to take over problems especially connected with the chemical, physical, and mineralogical

Both internal and external sulfate attack were documented.



WEATHERING PRODUCTS

The weathered alum shales are mostly covered by a yellow deposit of jarosite [$KFe_3(OH)_6(SO_4)_2$] and brown-iron ore ($Fe_2O_3 \cdot nH_2O$).

The weathering of the alum shale also yields solutions which very rapidly attack concrete made with normal portland cement. We have seen the concrete walls of an underground bomb shelter built in an alum shale area transformed into mush in about 9 months. In other cases, the attack may proceed more slowly, but generally the attack from the alum shale extracts seem to be much quicker than attack by most other aggressive waters.

Problems reported to originate almost 100 years ago.

Thousands of home foundations deteriorated in Trois Rivières region of Quebec.

Problems reported within 3-5 years of construction.

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Quebec pledges $17M more for pyrrhotite-damaged homes

Government also lowers amount of problematic mineral in foundation concrete required to acce

By Stephen Smith, CBC News Posted: Jan 06, 2017 2:18 PM ET | Last Updated: Jan 06, 2017 7:16 PM ET

This house is one of hundreds that have undergone repairs to fix damage caused by pyrrhotite.

34 shares

Quebec is allocating $17 million more for homeowners in the Mauricie and Central Quebec regions affected by pyrrhotite.

The Liberal government announced the new funds Friday at a news conference in Trois-Rivières, 140 kilometres northeast of Montreal.

Pyrrhotite is a mineral that expands when exposed to humidity and oxygen. Its presence in aggregate can lead to cracks in concrete structures.

That problem has wreaked havoc on the foundations of thousands of homes and commercial buildings in the Mauricie and Central Quebec regions built between 1996 and 2008 with aggregate from a local quarry.

- Homeowners demand $25M from Ottawa for structural damage

Lower threshold

In addition to the new funds, the government also announced Friday that it was lowering the volume of pyrrhotite in concrete that's required to access the funds from 0.3 to 0.23 per cent.

The lower threshold and extra funds will help an estimated 400 homeowners and brings Quebec's total assistance for homeowners coping with pyrrhotite damage to $52 million.

Homeowner Marc Dubord welcomed the decision to lower the pyrrhotite threshold. The concrete in his foundation has a volume of .25 per cent

Related Stories

- What's in the federal budget for Quebec, and what's missing
- Homeowners demand $25M from Ottawa for structural damage

Ottawa to spend $30M helping Quebec homeowners with pyrrhotite problems

Prime Minister Justin Trudeau looks at the foundation of a house, in Trois-Rivieres, Que., on Wednesday, April 6 CANADIAN PRESS/Paul Chiasson)

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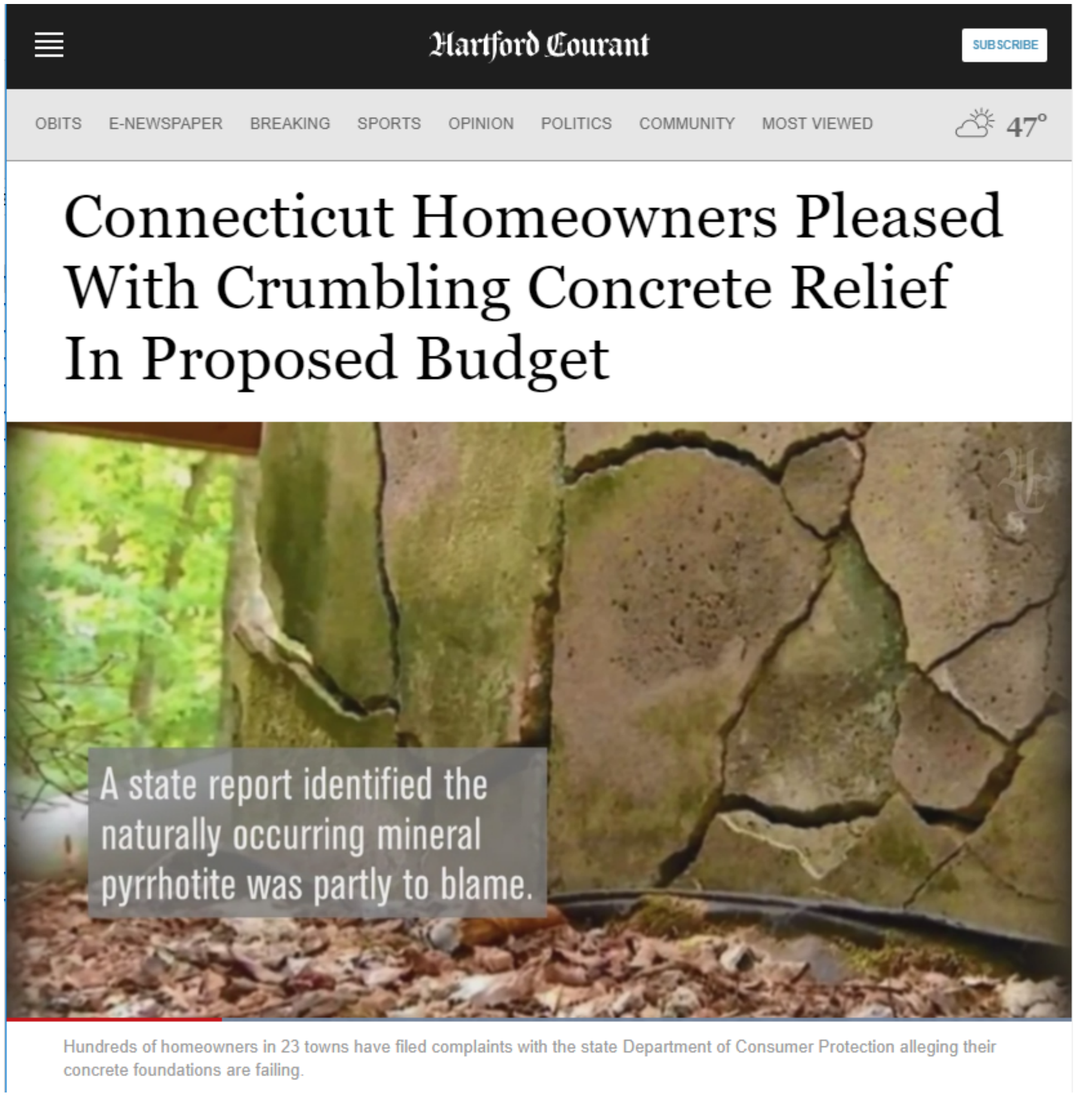
The Canadian Press
Published Wednesday, April 6, 2016 4:10PM EDT
Last Updated Wednesday, April 6, 2016 5:46PM EDT

The latest outbreak of internal sulfate attack was reported recently in Connecticut.



Hartford Courant

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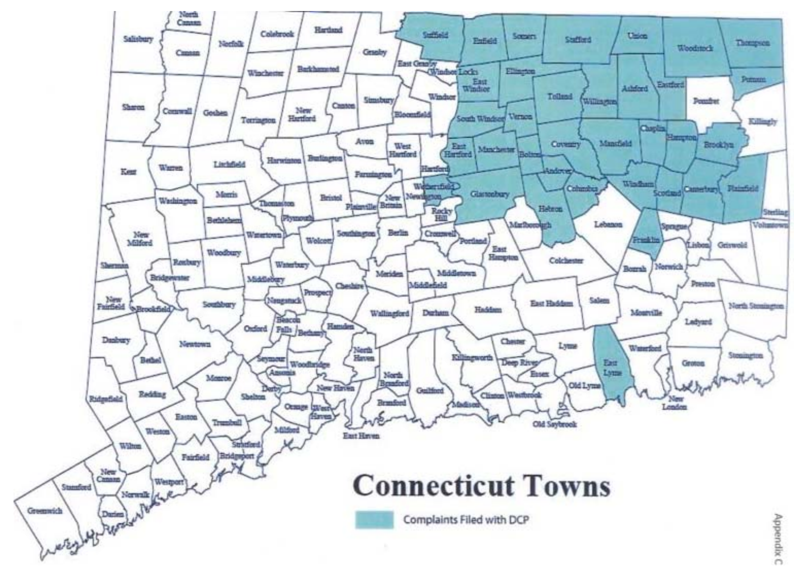
Connecticut Homeowners Pleased With Crumbling Concrete Relief In Proposed Budget

A state report identified the naturally occurring mineral pyrrhotite was partly to blame.

Hundreds of homeowners in 23 towns have filed complaints with the state Department of Consumer Protection alleging their concrete foundations are failing.

Affected structures constructed as early as the 1980's.

Over 600 complaints filed, and up to 34,130 homes are potentially at risk.



Internal Sulfate Attack is initiated by oxidation of iron sulfides.

Pyrite, FeS_2

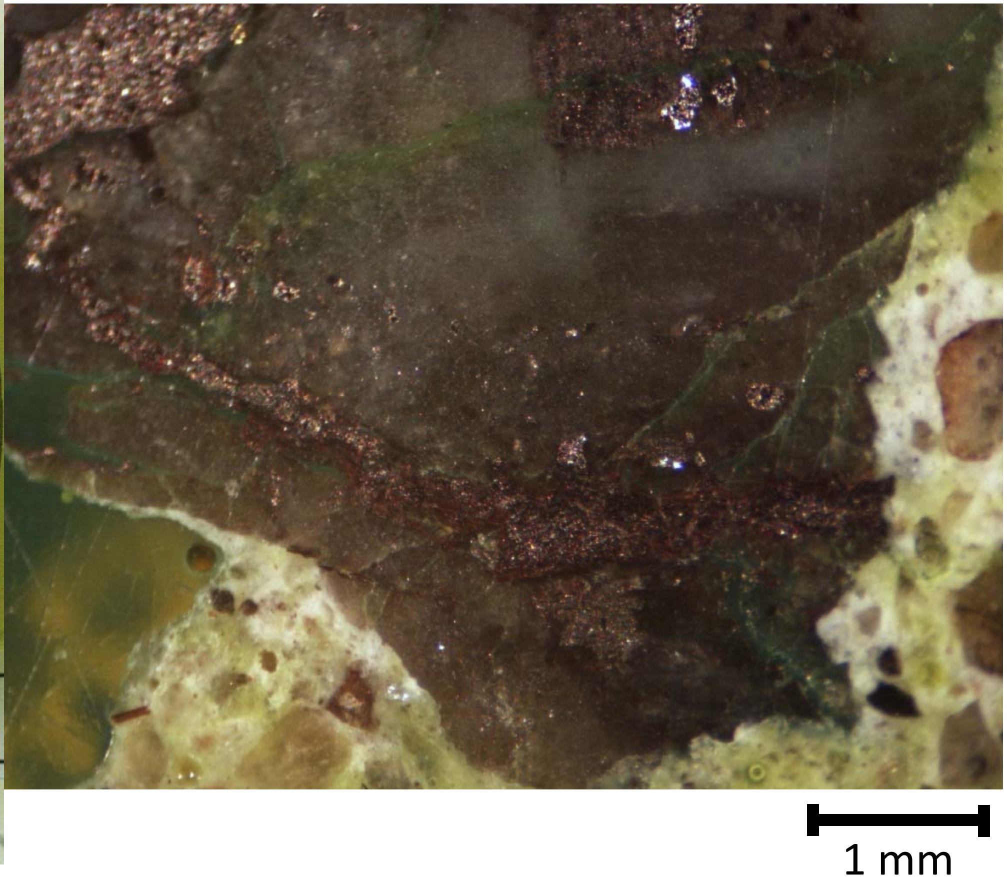
Pyrrhotite, $Fe_{(1-x)}S$, $x \leq 0.125$

$$4FeS_2 + 15\ O_2 + 10\ H_2O \rightarrow 4\ FeOOH\ \text{(goethite)} + 2\ H_2SO_4$$

$$Fe_{(1-x)}S + O_2 + (3-x)H_2O \rightarrow (1-x)\ FeOOH\ \text{(goethite)} + H_2SO_4$$

Pyrrhotite is much more likely to oxidize in concrete than pyrite.

Iron sulfide typically appears as minor inclusions within aggregate.



Sulfuric acid reacts with components of cement paste to form expansive minerals.

$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O$ (gypsum)

$H\hat{S} + CH \rightarrow C\hat{S}H_2$

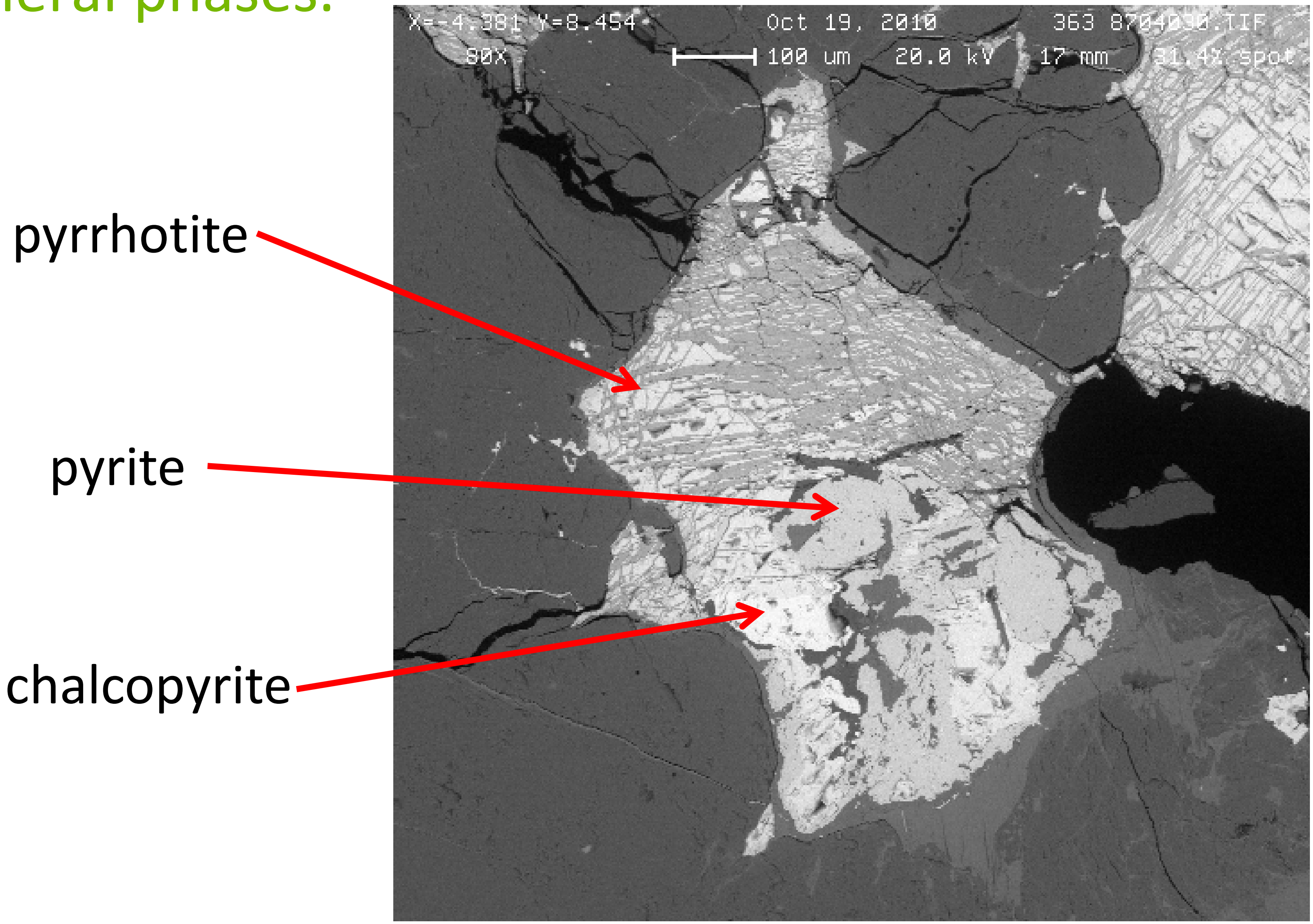
$Ca_3Al_2O_6 + 3\ CaSO_4 \cdot 2H_2O$ (gypsum) $+ 26\ H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ (ettringite)

$C_3A + 3\ C\hat{S}H_2 + 26\ H \rightarrow C_6A\hat{S}_3H_{32}$

$H_2SO_4 + C\text{-}S\text{-}H + Ca(OH)_2 + CO_2 + 12\ H_2O \rightarrow Ca_3Si(OH)_6(CO_3)(SO_4) \cdot 12H_2O$ (thaumasite)

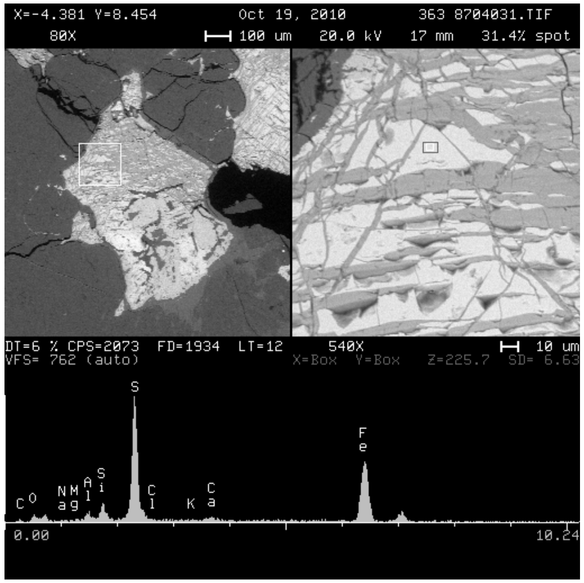
$H\hat{S} + C\text{-}S\text{-}H + CH + \hat{C} + H \rightarrow C_3S\hat{S}\hat{C}H_{15}$

Iron Sulfide deposits often contain multiple mineral phases.

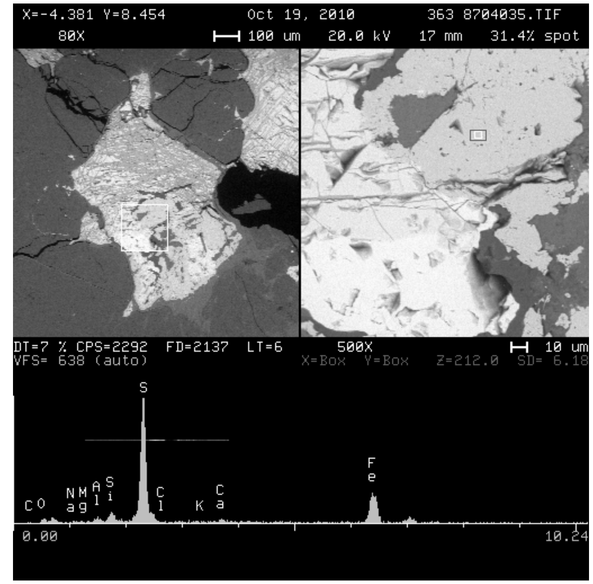


Pyrrhotite is more likely to corrode.

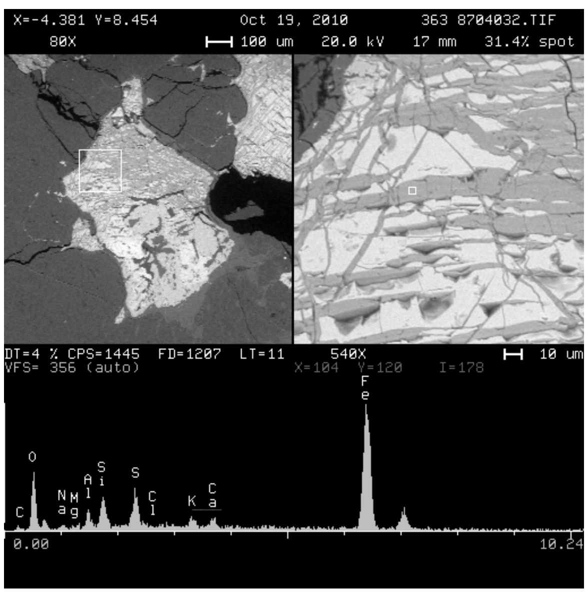
pyrrhotite



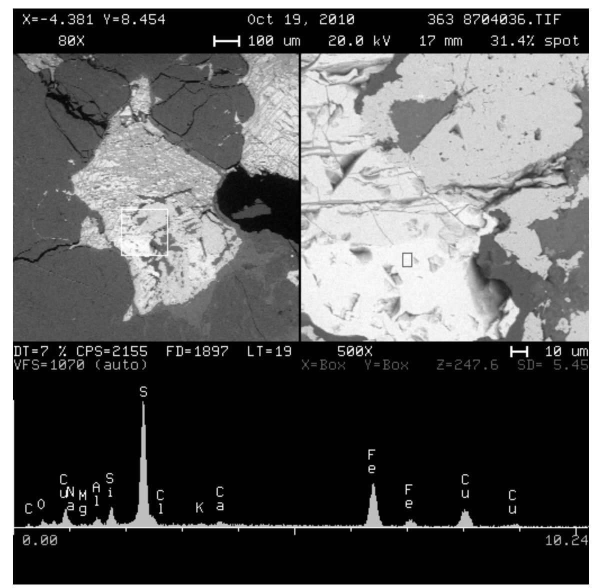
pyrite



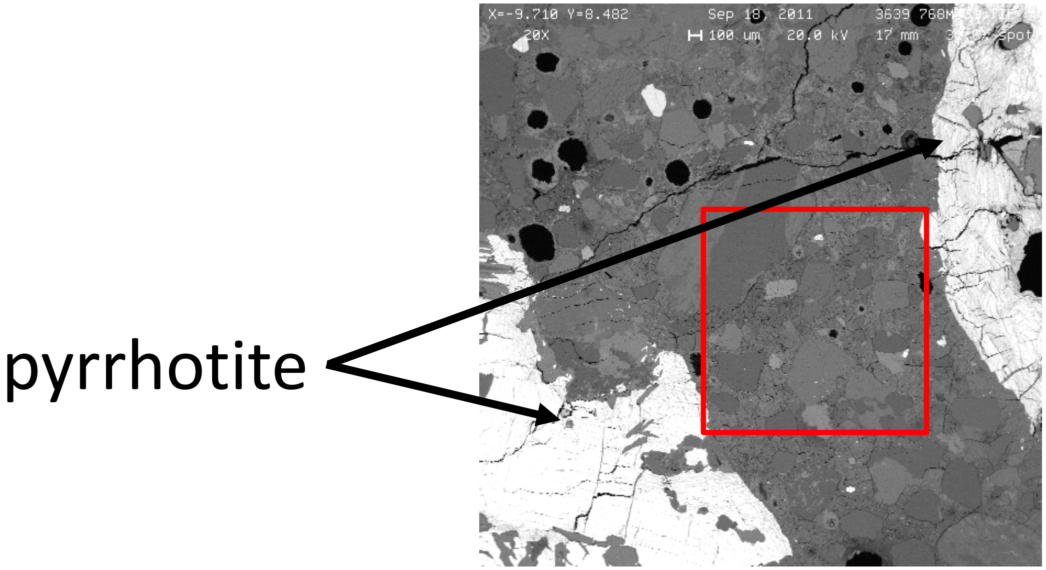
corroded pyrrhotite



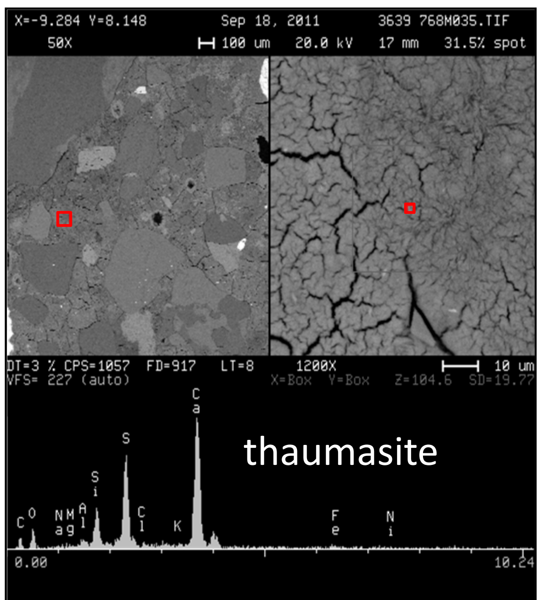
chalcopyrite

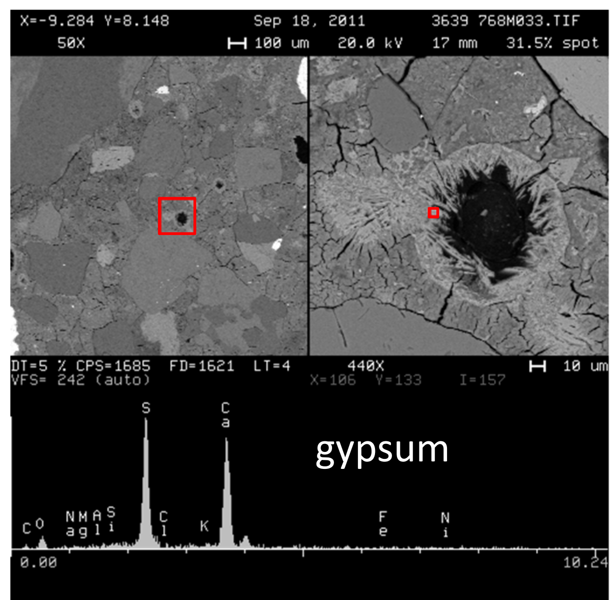


Sulfate attack is evident in the vicinity pyrrhotite inclusions in the aggregate.



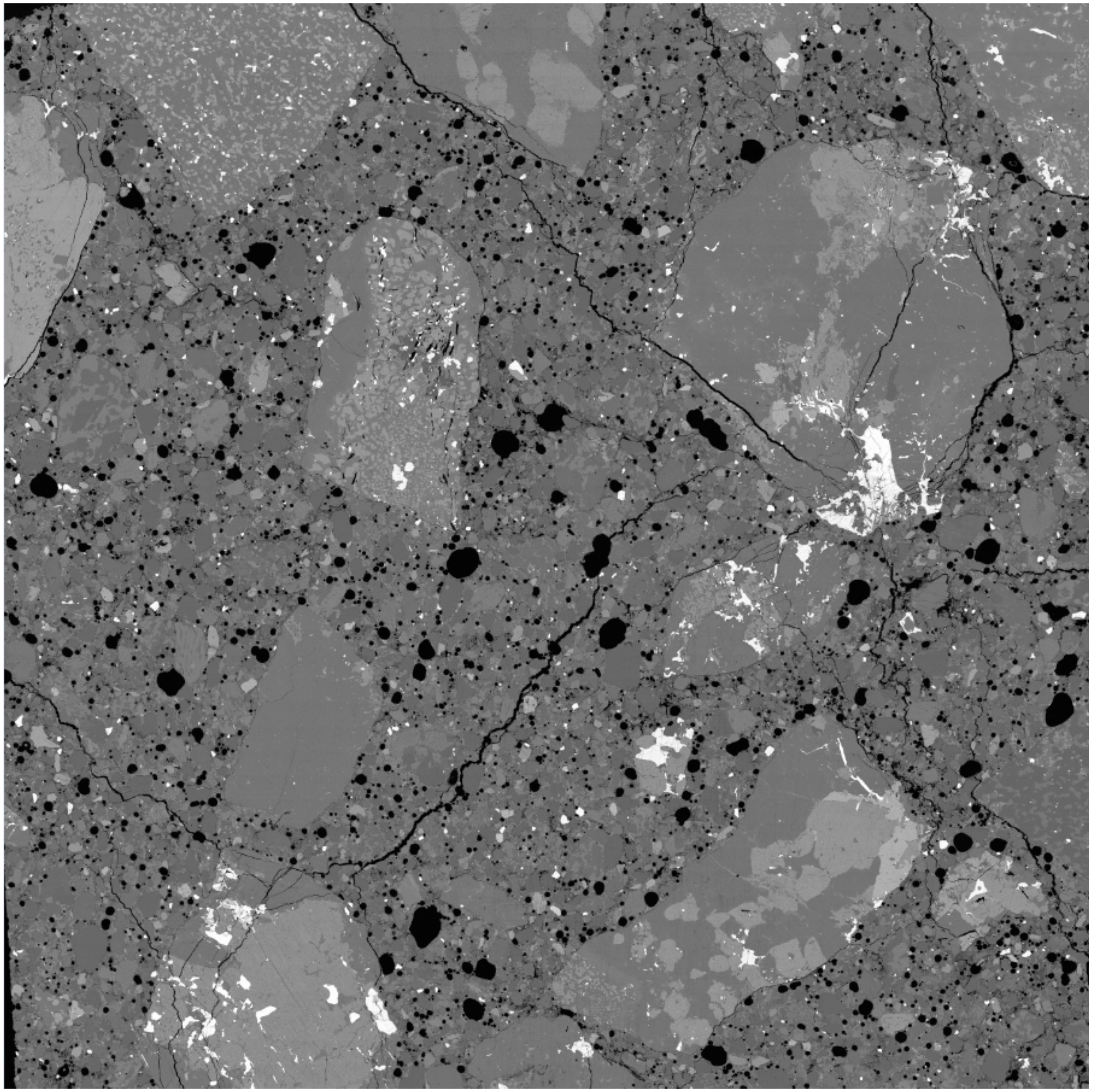
Cement paste replaced by thaumasite.



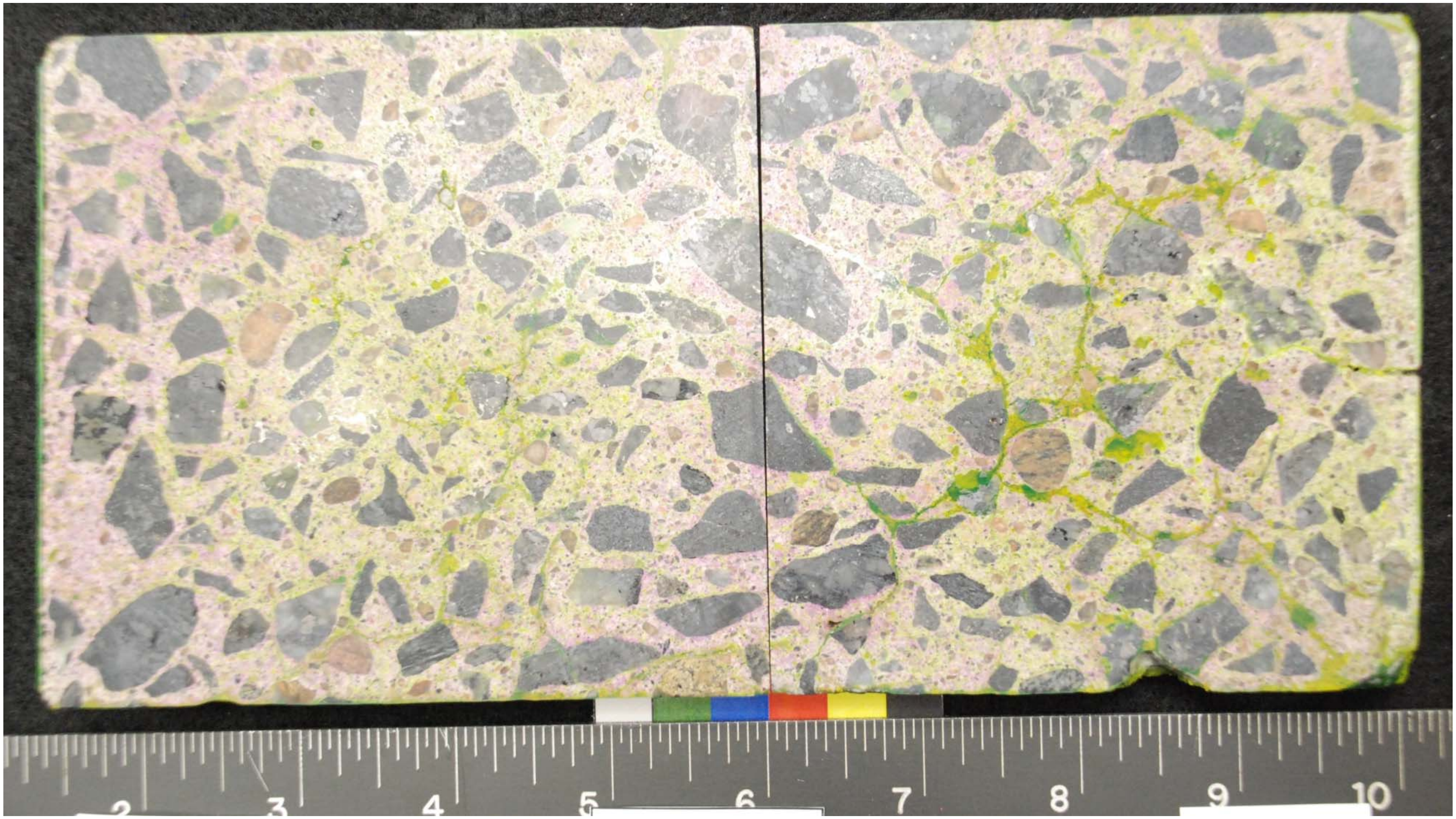


Gypsum in void spaces.

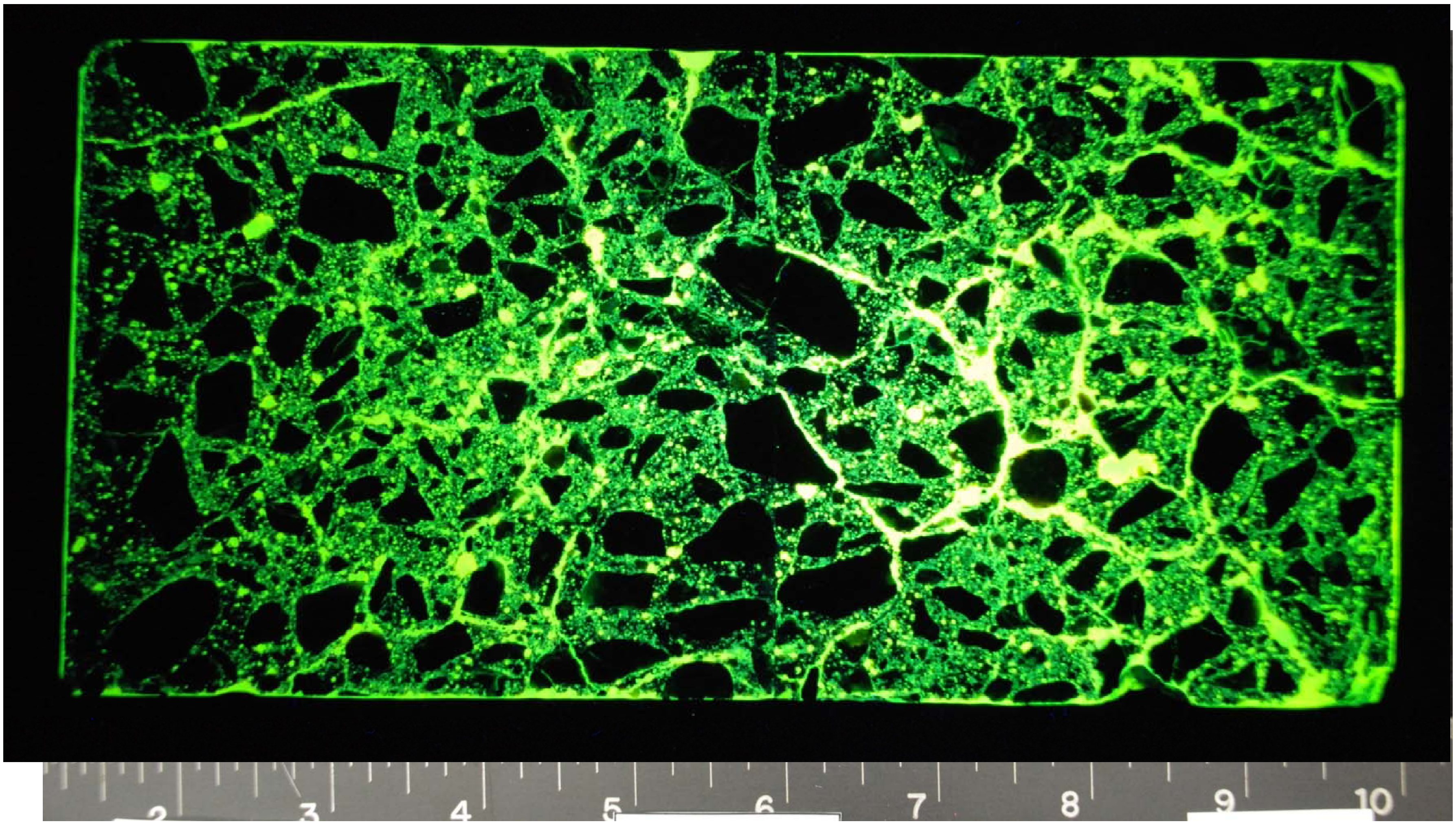
Cracks form between pyrrhotite inclusions.



Extensive cracking shown in fluorescent light images.



Extensive cracking shown in fluorescent light images.



ASTM standards do not address the issue of internal sulfate attack to a significant degree.

This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

ASTM INTERNATIONAL

Designation: C33/C33M – 16$^{\varepsilon 1}$

Standard Specification for Concrete Aggregates[1]

This standard is issued under the fixed designation C33/C33M; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε[1] NOTE—Editorially corrected 3.2.1 and Footnote B of Table 1 in November 2016.

1. Scope*

1.1 This specification defines the requirements for grading and quality of fine and coarse aggregate (other than lightweight or heavyweight aggregate) for use in concrete.[2]

1.2 This specification is for use by a contractor, concrete supplier, or other purchaser as part of the purchase document describing the material to be furnished.

NOTE 1—This specification is regarded as adequate to ensure satisfactory materials for most concrete. It is recognized that, for certain work or in certain regions, it may be either more or less restrictive than needed. For example, where aesthetics are important, more restrictive limits may be considered regarding impurities that would stain the concrete surface. The specifier should ascertain that aggregates specified are or can be made available in the area of the work, with regard to grading, physical, or chemical properties, or combination thereof.

1.3 This specification is also for use in project specifications to define the quality of aggregate, the nominal maximum size of the aggregate, and other specific grading requirements. Those responsible for selecting the proportions for the concrete mixture shall have the responsibility of determining the proportions of fine and coarse aggregate and the addition of blending aggregate sizes if required or approved.

1.4 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system may not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in non-conformance with the standard.

1.5 The text of this standard references notes and footnotes which provide explanatory material. These notes and footnotes (excluding those in tables and figures) shall not be considered

2. Referenced Documents

2.1 *ASTM Standards:*[3]

C29/C29M Test Method for Bulk Density ("Unit Weight") and Voids in Aggregate
C40 Test Method for Organic Impurities in Fine Aggregates for Concrete
C87 Test Method for Effect of Organic Impurities in Fine Aggregate on Strength of Mortar
C88 Test Method for Soundness of Aggregates by Use of Sodium Sulfate or Magnesium Sulfate
C117 Test Method for Materials Finer than 75-μm (No. 200) Sieve in Mineral Aggregates by Washing
C123 Test Method for Lightweight Particles in Aggregate
C125 Terminology Relating to Concrete and Concrete Aggregates
C131 Test Method for Resistance to Degradation of Small-Size Coarse Aggregate by Abrasion and Impact in the Los Angeles Machine
C136 Test Method for Sieve Analysis of Fine and Coarse Aggregates
C142 Test Method for Clay Lumps and Friable Particles in Aggregates
C150 Specification for Portland Cement
C227 Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method)
C289 Test Method for Potential Alkali-Silica Reactivity of Aggregates (Chemical Method) (Withdrawn 2016)[4]
C294 Descriptive Nomenclature for Constituents of Concrete Aggregates
C295 Guide for Petrographic Examination of Aggregates for Concrete
C311 Test Methods for Sampling and Testing Fly Ash or

No mention of iron sulfides in ASTM C33/C33M - 16.

ASTM standards do not address the issue of internal sulfate attack to a significant degree.

This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

INTERNATIONAL

Designation: C294 – 12 (Reapproved 2017)

Standard Descriptive Nomenclature for Constituents of Concrete Aggregates[1]

This standard is issued under the fixed designation C294; the number immediately following the designation in original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 This descriptive nomenclature provides brief descriptions of some of the more commonly occurring, or more important, natural and artificial materials of which mineral aggregates are composed. The descriptions provide a basis for understanding these terms as applied to concrete aggregates. When appropriate, brief observations regarding the potential effects of using the natural and artificial materials in concrete are discussed.

NOTE 1—These descriptions characterize minerals and rocks as they occur in nature and blast-furnace slag or lightweight aggregates that are prepared by the alteration of the structure and composition of natural material. Information about lightweight aggregates is given in Specifications C330, C331, and C332.

1.2 This standard does not include descriptions of constituents of aggregates used in radiation shielding concrete. See Descriptive Nomenclature C638.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C125 Terminology Relating to Concrete and Concrete Aggregates

C227 Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinati

C289 Test Method for Potential Aggregates (Chemical Metho

C330 Specification for Lightwe tural Concrete

C331 Specification for Lightwei Masonry Units

C332 Specification for Lightwe ing Concrete

C638 Descriptive Nomenclature gates for Radiation-Shielding

3. Terminology

3.1 For definitions of terms Terminology C125.

4. Significance and Use

4.1 This descriptive nomenclat terms commonly applied to concre is intended to assist in understandi cance of the terms.

4.2 Many of the materials des particles that do not display all the descriptions, and most of the d varieties meeting one description with all intermediate stages being

4.3 The accurate identification many cases, be made only mineralogist, or petrographer usin dures of these sciences. Reference however, serve to indicate or prevent gross errors in identification. Identification of the constituent materials in an aggregate may assist in characterizing its engineering properties, but

14. Iron Sulfide Minerals

14.1 The sulfides of iron, *pyrite, marcasite*, and *pyrrhotite* are frequently found in natural aggregates. Pyrite is found in igneous, sedimentary, and metamorphic rocks; marcasite is much less common and is found mainly in sedimentary rocks; pyrrhotite is less common but may be found in many types of igneous and metamorphic rocks. Pyrite is brass yellow, and pyrrhotite bronze brown, and both have a metallic luster. Marcasite is also metallic but lighter in color and finely divided iron sulfides are soot black. Pyrite is often found in cubic crystals. Marcasite readily oxidizes with the liberation of sulfuric acid and formation of iron oxides, hydroxides, and, to a much smaller extent, sulfates; pyrite and pyrrhotite do so less readily. Marcasite and certain forms of pyrite and pyrrhotite are reactive in mortar and concrete, producing a brown stain accompanied by a volume increase that has been reported as one source of popouts in concrete. Reactive forms of iron sulfides may be recognized by immersion in saturated lime

ASTM standards do not address the issue of internal sulfate attack to a significant degree.

This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: C295/C295M – 12

Standard Guide for Petrographic Examination of Aggregates for Concrete[1]

This standard is issued under the fixed designation C295/C295M; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This guide outlines procedures for the petrographic examination of samples representative of materials proposed for use as aggregates in cementitious mixtures or as raw materials for use in production of such aggregates. This guide is based on Ref (**1**).[2]

1.2 This guide outlines the extent to which petrographic techniques should be used, the selection of properties that should be looked for, and the manner in which such techniques may be employed in the examination of samples of aggregates for concrete.

1.3 The rock and mineral names given in Descriptive Nomenclature C294 should be used, insofar as they are appropriate, in reports prepared in accordance with this guide.

1.4 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system may not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in non-conformance with the standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

C33 Specification for Concrete Aggregates

C117 Test Meth... Sieve in Min...

C136 Test Met... Aggregates

C294 Descripti... crete Aggreg...

C702 Practice f... Size

D75 Practice fo...

E11 Specificati... Sieves

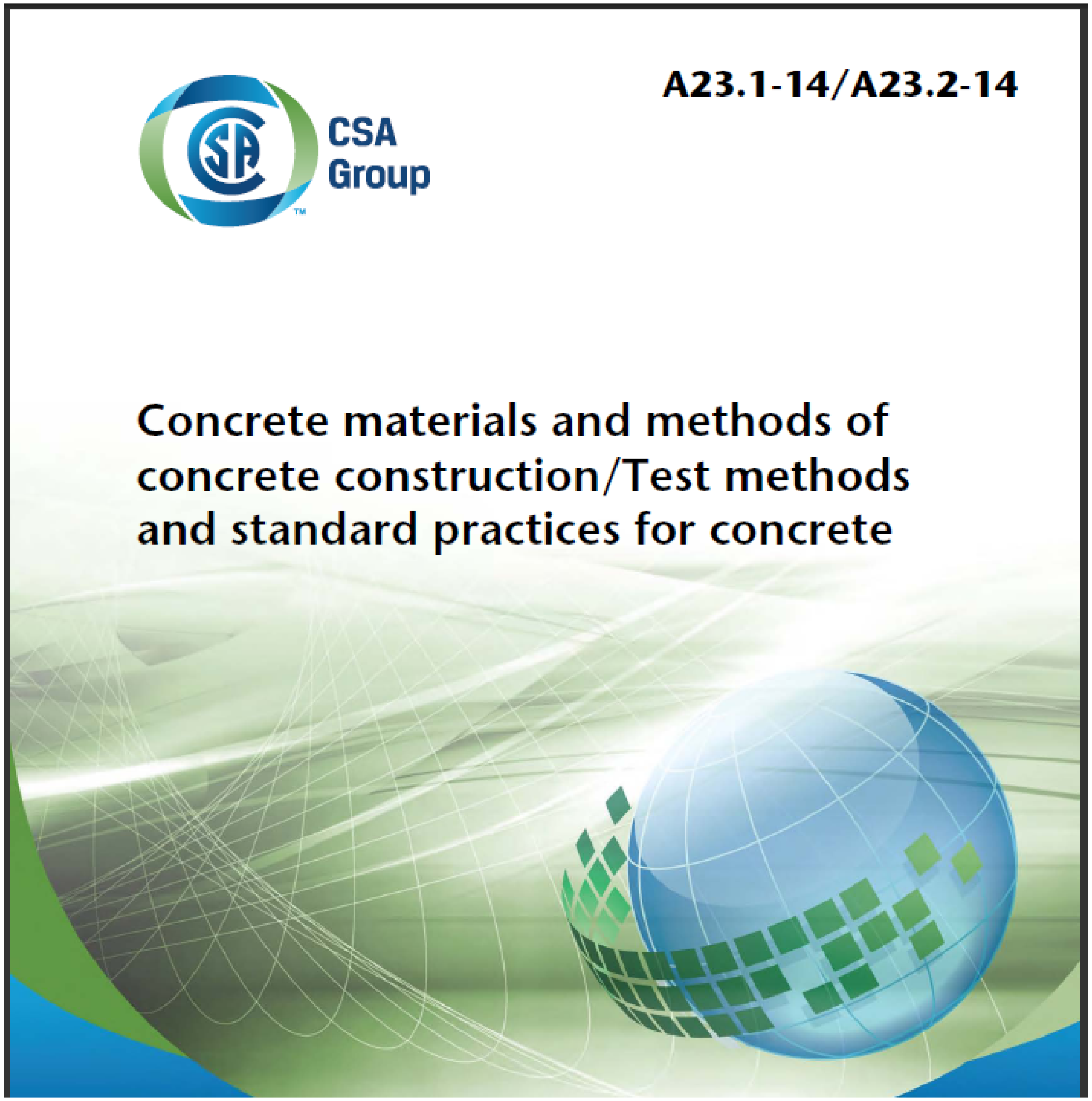
E883 Guide for...

3. Qualifications

3.1 All petrog... concrete as descr... petrographer with... examination of c... petrographer shou... pertaining to ba... optical mineralog... through experien... course work in c... petrographer shou... aggregates on the physical and chemical properties of hardened concrete. Identification of individual minerals in aggregate particles, classification of rock types, and categorizing the physical and chemical properties of rocks and minerals should also be included in the petrographer's experience. The petrographer should have expertise to properly use the equipment and apparatus described in Section 6 and provide detailed interpretations of the petrographic examination. If the petrographer does not meet these qualifications, the individual may perform

5.5 The petrographic examination should establish whether the aggregate contains chemically unstable minerals such as soluble sulfates, unstable sulfides that may form sulfuric acid or create distress in concrete exposed to high temperatures during service, or volumetrically unstable materials such as smectites (formerly known as the montmorillonite-saponite group of minerals or swelling clays). Specifications may limit the quartz content of aggregates for use in concrete that may be subject to high temperature (purposefully or accidentally) because of the conversion to beta-quartz at 573 °C [1063 °F], with accompanying volume increase.

CSA standard addresses the issue without setting limits.



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;"

European Standard specifies a maximum of 1 % total sulfur (0.1% if pyrrhotite is present).

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 12620

September 2002

ICS 91.100.15; 91.100.30

English version

Aggregates for concrete

Granulats pour béton   Gesteinskörnung für Beton

This European Standard was approved by CEN on 2002-08-01.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

The European Standards exist in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

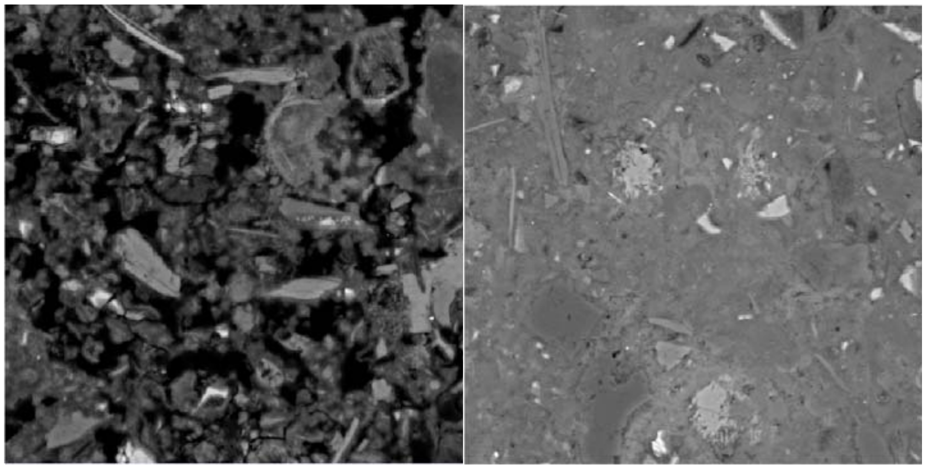
CEN members are the national standards bodies of Austria, Belgium, the Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, the Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom.

b) 1 % S by mass for aggregates other than air-cooled blastfurnace slag.

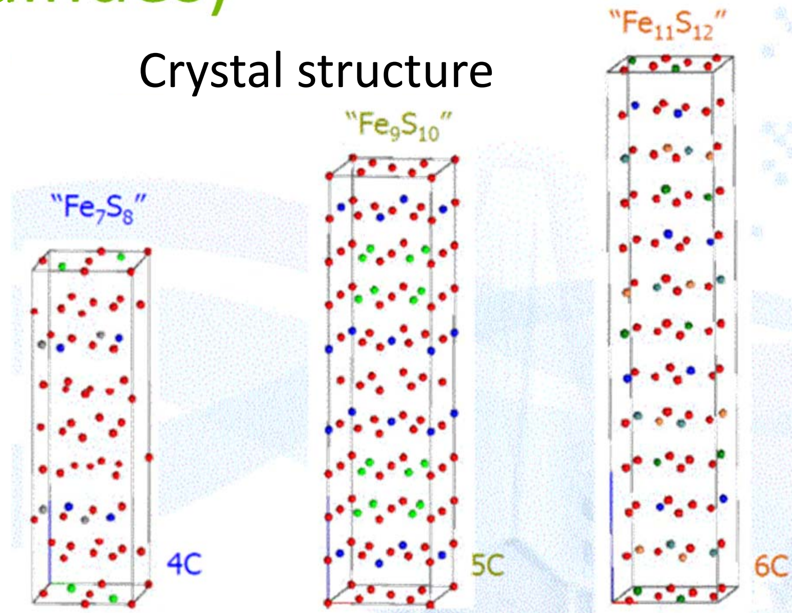
Special precautions are necessary if pyrrhotite, (an unstable form of iron sulfide FeS), is present in the aggregate. If this mineral is known to be present, a maximum total sulfur content of 0,1 % as S shall apply.

Multiple factors determine risk of internal sulfate attack. (not just amount of sulfides)

Concrete Porosity/ Permeability

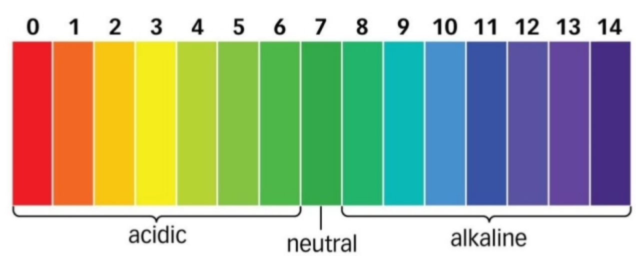


Crystal structure



Environmental conditions

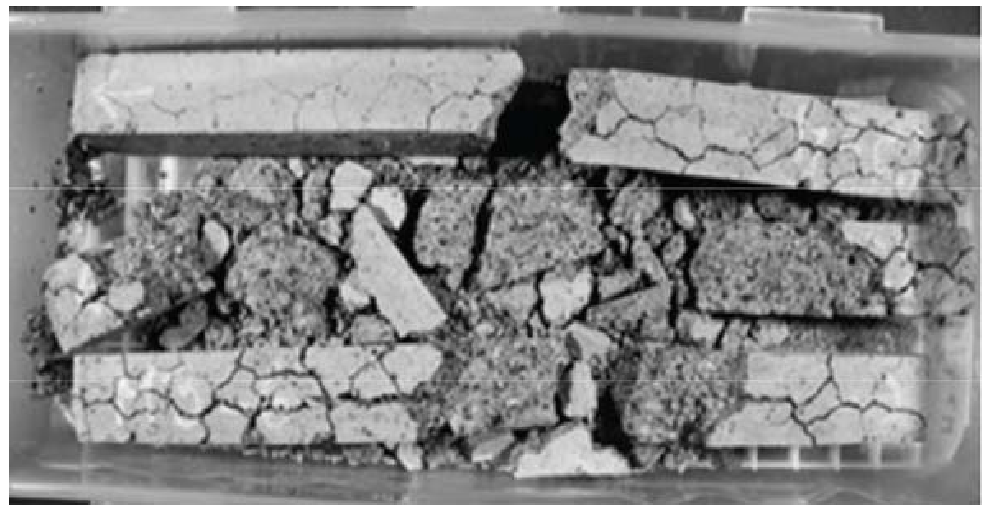
pH



Université Laval group has begun early development of performance-based testing

1 - Total Sulfur Content

3 - Mortar Bar Expansion



From Rodrigues, A., Duchesne, J., Fournier, B., Durand, B., Shehata, M. H., & Rivard, P. (2016) *ACI Materials Journal*, *113*(3).

2 - Oxygen Consumption

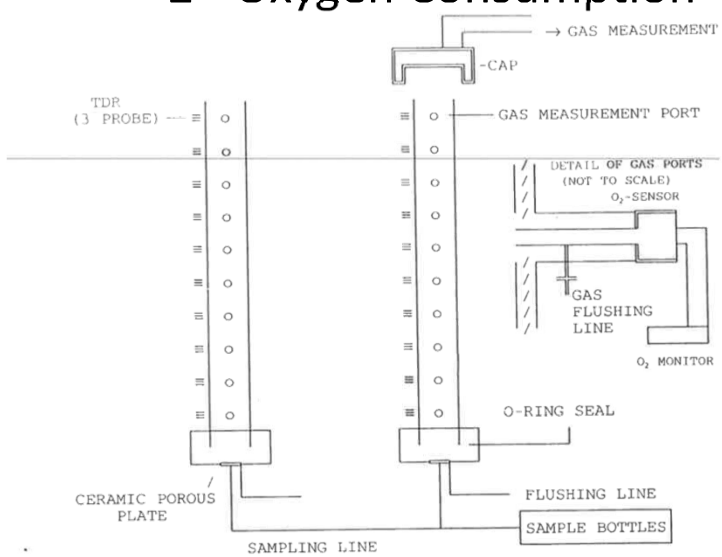


FIG. 3. Schematic configuration of the two columns used in the oxidation-rate experiments.

From Elberling, B., Nicholson, R. V., Reardon, E. J., & Tibble, R. (1994). Canadian Geotechnical Journal, 31(3), 375-383.

Conclusions

Internal sulfate attack occurs very rarely, but the consequences can be quite severe.

Steps have begun to reduce the risk, but more work is required.