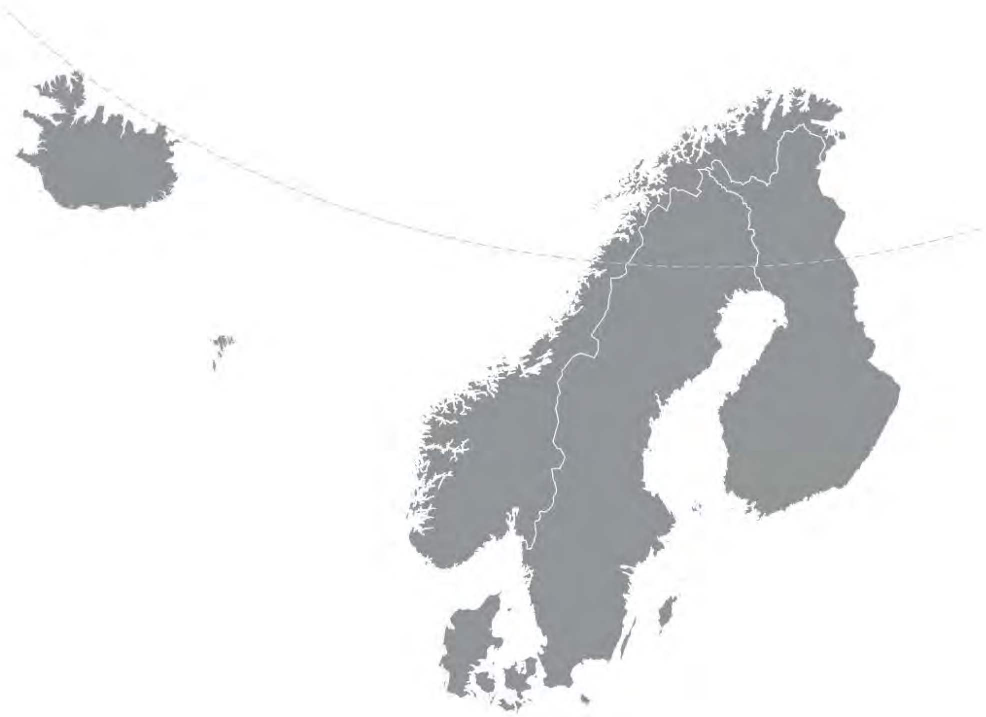
Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour

WORKSHOP PROCEEDINGS FROM A NORDIC WORKSHOP

OSLO - NORWAY, 15. – 16. NOVEMBER 2018



NCF Nordic Concrete Federation

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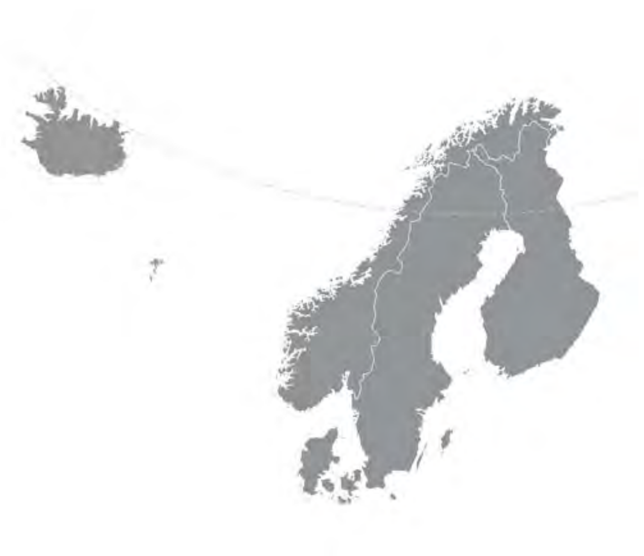

WORKSHOP PROCEEDINGS NO. 14

FROM A

NORDIC WORKSHOP

Oslo, Norway

15.-16. November, 2018

Nordic Concrete Federation

Workshop

15th – 16th November 2018, Oslo, Norway

Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour

Proceedings

Stone from Norwegian tunnelling-project containing sulphide minerals. Photo: Børge J. Wigum.

Preface

This publication contains program, abstracts and presentations given at the Workshop "*Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour*". The workshop took place in Oslo on November 15th and 16th, with 32 participants from academia, industry and infrastructure owners in Norway, Sweden, Finland, Canada, Switzerland and United Kingdom.

The workshop was sponsored by the Norwegian Public Roads Administration, HeidelbergCement Northern Europe and the Norwegian Concrete Association, and was organized by Bård Pedersen (Norwegian Public Roads Administration) and Børge Johannes Wigum (HeidelbergCement Northern Europe).

Background and motivation for the workshop

It has been known since the mid 1950-ties that sulphide bearing aggregates may cause deterioration of concrete structures. A number of damage cases from several countries have been reported, stating that pyrrhotite is the mineral responsible for most of the damages. At present, there are many questions related to quantification of pyrrhotite, assessment of the potential deleterious effect of different forms of pyrrhotite, mitigating effects of SCMs etc. that needs to be addressed.

In Norway, pyrrhotite has recently become a hot topic. One obvious reason for this is the Follo Line Project, a major railway project where local tunnelling mass was supposed to be used as aggregate for production of concrete tunnelling elements. Due to indications of pyrrhotite in 60 % of the samples in combination with relatively high contents of sulphur, it was decided to stop the use of local tunnelling mass for concrete aggregate and to use other commercially available aggregates.

The Norwegian Concrete Association has a series of guidelines for concrete; of these is Publication no. 18 "Aggregates for concrete". During the ongoing revision of this publication, it has become clear that there are two major durability issues related to concrete aggregates. One is Alkali Silica Reactions (ASR), which is a topic with well-established knowledge after 30 year of research in Norway. The other topic is sulphide-bearing aggregates, where there is an obvious lack of knowledge. The revision committee, chaired by Bård Pedersen, therefore took an initiative to collect available information from the research community, and to initiate national research on this topic. This workshop is considered a very important step in this process. The goals of this workshop were to:

- Collect information from Norway and the international research community
- Establish collaboration with international partners
- Activate national partners for a future research project

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Participants, from left; Magnus Gade Skjeggerud, Hannu Pyy, Nikolas Oberhardt, Bård Pedersen, Roland Weiss, Øystein Mortensvik, Silje Gystad Ytterdal, Petter Hemstad, Kurt Aasly, Klaartje De Weerdt, Philip Santo, Paul Glamo, Børge Johannes Wigum, Jan Lindgård, Knut Li, Terje Bjerkgård, Per Hagelia, Ian Sims, Kjersti K Dunham, Magnus Döse, Viggo Jensen, Benoît Fournier, Maarten Broekmans, Marit Haugen, Josée Duchesne, Andreas Leemann, Svein Willy Danielsen, Ian Willoughby, Rolands Cepuritis, Inger Lise Ullnæss

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3	Ian Willoughby	Bane NOR SF
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22	Petter Hemstad	NTNU
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25	Magnus Döse	RISE
26	Ian Sims	RSK Environment Ltd
27	Jan Lindgård	SINTEF
28	Marit Haugen	SINTEF
29	Josée Duchesne	Université Laval
30	Benoît Fournier	Université Laval
31	Hannu Pyy	Vahanen Building Physics Ltd.
32	Roland Weiss	VersuchsStollen Hagerbach AG

Program

DAY 1: Status, Mechanics & Cases		
11:00	*--- Lunch ---*	
12:00	***Introduction / Welcome*** Background of the Norwegian project	**Bård Pedersen** *NPRA*
12:15 13:55	**Topic; Status in Scandinavia – Chair: Bård Pedersen**	
	Lessons learned from the Follo Line Project – Pyrrhotite; a showstopper for reuse of TBM material as concrete aggregates.	**Silje Gystad Ytterdal** *BaneNOR/Multiconsult* *Norway*
	Determination of total sulphur content in aggregates (2004 – 2018) – results from SINTEF.	**Marit Haugen** *SINTEF* *Norway*
	Total S and Pyrrhotite in Norwegian concrete aggregate deposits. Statistical assessment from NBTLs database over projects.	**Viggo Jensen** *NBTL* *Norway*
	Sulphides in aggregates/concrete, cases in Sweden.	**Magnus Döse** *Research Institutes of Sweden RISE* *Sweden*
	Cases in Finland where sulphide minerals in aggregate have caused damages in concrete structures.	**Hannu Pyy** *Vahanen Building Physics Ltd.* *Finland*
13:55 14:30	--- Coffee break ---	
14:30 15:50	**Topic; Mechanics of Deterioration & Cases – Chair: Børge Johannes Wigum**	
	Overview of the Deterioration mechanisms. ***Cases of deterioration in Canada and US.***	**Josée Duchesne** *Université Laval,* *Québec, Canada*
	Mineralogical properties of pyrrhotite, pyrite and associated weathering products.	**Per Hagelia** *NPRA* *Norway*
	Iron sulphides: Formation and conditions for occurrence in bedrock.	**Terje Bjerkgård** *NGU* *Norway*

15:50 16:10	Break	
16:10 17:10	*Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam.*	**Andreas Leemann** *EMPA* *Switzerland*
	Suddenly the aggregates for concrete are a risk for the durability of the structure - experience from material management for the Gottard Basetunnel GBT using AAR as an example	**Roland Weiss** *VersuchsStollen Hagerbach AG* *Switzerland*
	Managing the "Mundic" Problem in South-West England.	**Ian Sims** *RSK Environment Ltd* Philip Santo *RICS* *UK*
	Closure – Day 1	
19:00	--- **Dinner** ---	

DAY 2 Characterisation & the Path Forward		
09:00 10:20	**Topic; Characteristics and test methods – Chair: Silje Ytterdal**	
	The development of the accelerated test method and the content of a new Canadian R&D project.	**Benoit Fournier** *Université Laval* *Québec, Canada*
	Use of advanced mineral characterization techniques to quantify sulfides in rocks and aggregates, and to investigate deterioration of concrete containing sulfide-bearing aggregates.	**Kurt Aasly, Klaartje De Weerdt & Mette Geiker** *NTNU* *Norway*
10:20 10:50	*--- Coffee Break ---*	
10:50 12:00	**Discussions - Conclusions and future initiatives** **End of meeting**	**Børge Johannes Wigum** *HC NE/NTNU* **Svein Willy Danielsen** *Geomaterials Consultant* **Benoit Fournier** *Université Laval*
12:00	*--- Lunch ---*	

Essence of presentations, discussion – uncertainties & possibilities The path forward

The presentations were divided into sessions related to the; *Status in the Scandinavian Countries*, along with presentations related to; *Mechanics of Deterioration & Cases*. Eventually the presentations were summarised and the topic and potential path forward were discussed.

As introduced by Bård Pedersen, and presented further by Silje Gystad Ytterdal, the topic related to sulphide minerals in concrete aggregates and the potentially deleterious effect was actualised in Norway in connection to the railway-tunnel-project at the Follo line, near Oslo. However, no cases of deterioration of concrete due to this type of aggregates have ever been observed in Norway, even though both Marit Haugen and Viggo Jensen, from SINTEF and NBTL respectively, provided results showing that several commercial quarries in Norway, producing crushed rock aggregates, are exhibiting results above the critical limits of sulphur, where it is indications of pyrrhotite. It was discussed that one reason for not observing any deleterious damage so far in Norway could be the fact that up to now mainly natural sand and gravel have been used as concrete aggregates, and consequently sulphide minerals have already been oxidised. With an increased use of freshly crushed concrete aggregates, both as coarse aggregates and as manufactured sand, the situation could be different. It is not known if the sand- or the stone-aggregate size fraction will be the most damaging component.

Cases from Sweden, presented by Magnus Döse, and cases from Finland, presented by Hannu Pyy, exhibited only minor damages in concrete structures, mainly in cases as pop-outs, staining, or other more esthetical effects.

Josée Duchesne presented an overview of the deterioration mechanisms, and the very severe cases of deterioration both in Canada and in the US. Amazingly, the damage expansion creates very wide cracks only after a relatively short time of construction, i.e. 3-5 years. Even though this damage occurred in concrete with high w/c-ratio, and hence low strength, subsequent laboratory experiments have showed that the deleterious reaction happens in a similar degree also for concrete types with a much lower w/c-ratio. During discussions, it was explained that during ongoing court-cases in Canada, it has been juridical decided that the critical lover limit of sulphur should be 0.23% when there are indication of pyrrhotite in the concrete aggregate.

Per Hagelia went through the historical challenges in Norway when the alum-shale caused damage in Norwegian concrete, and the establishment of the Alum-shale Committee. He also mentioned examples from Norway with relatively severe acid rock drainage from deposits of sulphate-bearing rocks. Terje Bjerkgård presented the formation and conditions for occurrence of sulphides in bedrock in Norway, and the many various types of sulphides.

From Switzerland, Andreas Leemann presented a case where simultaneous iron sulphide oxidation and alkali silica reactions (ASR) had occurred in a Swiss dam. Even though the ASR was considered as the main deleterious mechanisms, it was evident that iron sulphide oxidation was leading to crack formation in the concrete. In another case in Switzerland, the Gottard Basetunnel, Roland Weiss presented how to deal with the sudden occurrence of aggregates that are not in accordance with the specification. In this case, they were dealing with alkali silica reactive aggregates.

Ian Sims and Philip Santo presented the very severe cases of the so-called; "Mundic"-problem in concrete in domestic houses in South-West England, and how the problem directly affected the economy of families when the banks stopped lending for the houses due to the damaged and cracked concrete. However, it was shown how it was possible to manage the problem by developing a pragmatic scheme, based on practical concrete petrography, which now has been in place for more than 20 years. See report: www.rics.org/globalassets/rics-website/media/upholding-professional-standards/sector-standards/building-surveying/the-mundic-problem-3rd-edition-rics.pdf

Benoit Fournier presented the development of accelerated test methods in Canada, along with the content of a new Canadian R&D project. It was initially emphasised that there are still lots of issues unresolved, and hence, there is a huge need for further research. However, research efforts from 2010 – 2014 provided a protocol looking into the total sulphur measurement, oxygen consumption evaluation and an accelerated mortar bar test. A new R&D project (2018 – 2022) will focus on the acceptance limits, test development, preventive measurements, development of technical capacity, and eventually implementation into the standards.

Kurt Aasly presented use of advanced mineral characterization techniques to quantify sulphides in rocks and aggregates. The challenge is to detect very low amounts of minerals, sometimes near the detection limit of the equipment. For instance, the detection of pyrrhotite in Norway is based on an old DTA-equipment developed in the 1950-ties, and there is a lack of calibration of the equipment. However, new advanced techniques are developing, such as quantification of amount of minerals by automated mineralogy system and multispectral optical microscopy. Klaartje De Weerdt presented how to investigate deterioration mechanisms of concrete containing sulphide-bearing aggregates, and considerations on the effects of different mitigating measures. The importance of comparing laboratory measurements to what happens in field was emphasised. It was also emphasised that more accurate methods for sulphur and pyrrhotite in aggregates and performance tests for concrete containing sulphide-bearing aggregates based on the fundamental understanding of the degradation mechanisms would have a tremendous impact on the sustainable use of aggregates.

In the general discussions after all the presentations, it was pointed out that future challenges are both related to geology/petrography, but also to concrete technology. First, we need to implement and evaluate the newest and most advanced equipment in mineral characterisation, and see if we could quantify critical limits. However, those critical limits need to be investigated by mortar- and concrete testing. It was asked if we should depend on the DTA to detect pyrrhotite, or do we need to quantity the pyrrhotite at all if we just could depend on performance testing? A reliable performance test needs, however, to be verified by comparing the lab data with relevant and sound field results. Hence, this will take time, and we should start necessary research as soon as possible.

In Norway, we have started planning for a national project (with international cooperation) involving two PhD students. Possible funding sources are NPRA/E39 Coastal highway route, the Norwegian Research Council, NTNU, NGU, HeidelbergCement Northern Europe and possibly other industry partners.

As a curiosity, it was agreed that both the term *sulphide* (British English) and *sulfide* (American English) both were perfectly acceptable. Sulfide may become the accepted British English spelling too. In any case, language is fluid and irrelevant to the chemistry.

BANE NOR

Abstract

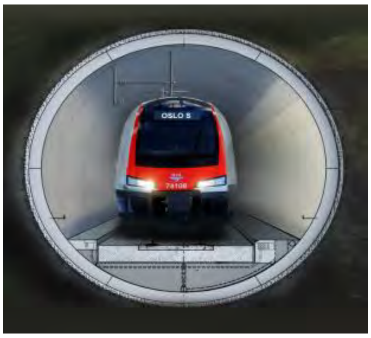
Lessons learned from the Follo Line Project –

Pyrrhotite: a showstopper for reuse of TBM material as concrete aggregate

Silje Gystad Ytterdal, Bane NOR/Multiconsult Oslo, October 2018

Presentation of project – The Follo Line Project

The Follo Line will be the longest railway tunnel in the Nordic region. The tunnel will be 20 km, whereas 18 km is excavated by use of four tunnel boring machines (TBM). The Follo Line will be the longest tunnel in Norway consisting of two separate tunnels, and will secure a direct connection between Oslo and Ski. With the new railway tunnel, the travel distance between Oslo and Ski reduces from 22 minutes to 11 minutes. The construction work started up in the beginning of 2016, and the finalization of the project will be by December 2021.



Reuse of TBM material

Prefabricated concrete segment are covering the TBM- tunnel. The segments are produced in a large factory area at the construction site at Åsland. The segment factory is located at the construction site in order to ease logistical operations and reduce the environmental impact. It also allows reuse of TBM-material in production of aggregates for use in concrete segment production.

The TBM- project involves excavation of 10 – 11 million tons of rock material. A goal for the project is to maximize reuse of rock material from the construction. This involves reuse of material locally as landfills for a new living district at Åsland, and production of concrete aggregates. The project planned to use 10-15% of the TBM-excavated material for concrete aggregate production.

Geology

The rocks in the project area consist predominantly of Precambrian gneisses. The different gneisses and rock types cannot be assigned to specific tunnel sections as the amphibolite and the intrusives appear as elements within the gneisses with varying shape and thickness in alternating sequences. The rock type gneiss formation is therefore defined as one geological unit for the whole project area. The tunnel face will normally contain both gneisses and amphibolite.

Picture 1 - Tunnel face containing both gneisses and amphibolite

Aggregate testing

According to NS-EN 12620+NA total content of Sulphur shall not exceed 0.1% S when it is known that pyrrhotite is present in the aggregate material. Testing of material from the project showed that 30 % of the samples did not fulfill the requirements of NS-EN 12620+NA. Pyrrhotite was identified in 60% of the samples. The performed testing did not reveal any clear correlation between rock type and the presence of pyrrhotite, as shown in Figure 1. As selective production is more or less impossible, aggregate production from TBM material was stopped and commercial aggregates are now used in production of tunnel segments.

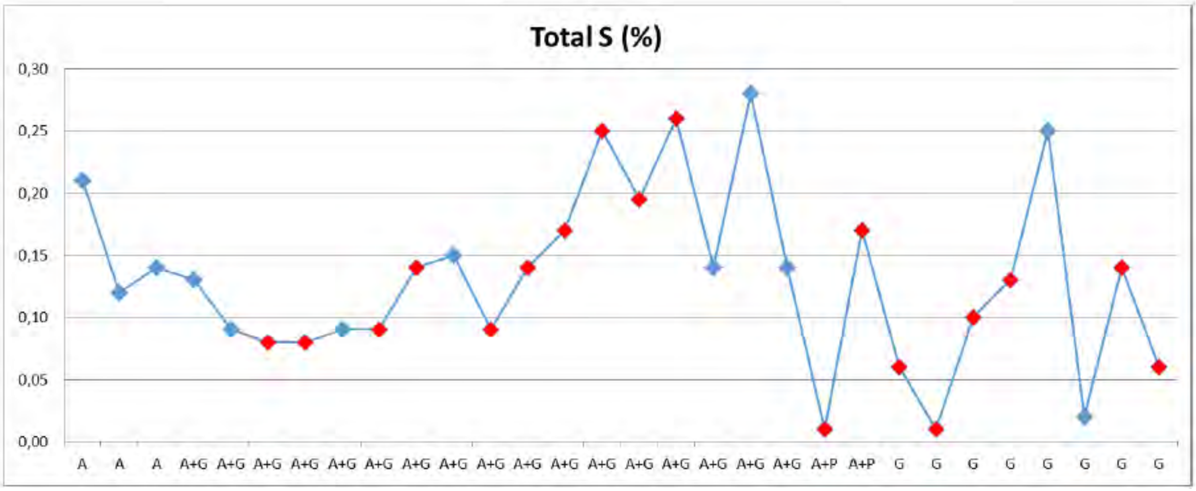


Figure 1 - Variation in pyrrhotite content in terms of geology, red dots are samples with pyrrhotite

Questions that were raised

- ✓ Is the limit of 0.1% S correct?
- ✓ What is the effect of Norwegian cement types, fly ash, GGBFS, silica, low water-cement ratio?
- ✓ Which content of pyrrhotite will cause concrete damage?
- ✓ The geology at the Follo Line is not unique- why is pyrrhotite not a problem for other aggregate producers in Norway?
- ✓ Why have we not seen damages caused by the presence of pyrrhotite in concrete aggregates in Norway?
- ✓ Time between aggregate production and usage in concrete production was short. Can longterm pre-storage of the aggregates improve the quality?

Lessons learned from the Follo Line Project – Pyrrhotite: a showstopper for reuse of TBM material as concrete aggregates

Workshop: Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour
15.11.2018

InterCity-nettet

The Follo Line will ensure a direct connection between Oslo S and Ski – 22 km

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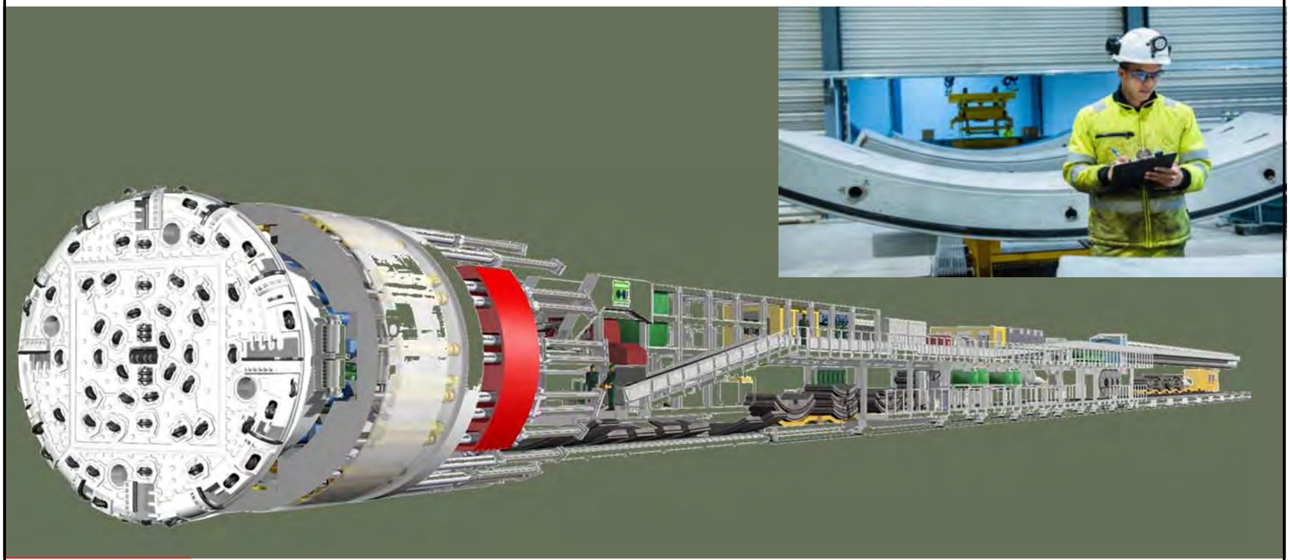

Excavation with 4 custom-made TBM - length 150 m, diameter 9.96 m, 71 cutters
Production of concrete tunnel segments at construction site – 3 segment factories

Concrete segments

Concrete	1000 m^3/d
Aggregate	1900 tonn/d
Cement	390 tonn/d
Steel fibers	21 tonn/d
Reinforcement	40 tonn/d
Total concrete volume	500 000 m^3

(numbers from AGJV)

B55
MF40

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Production of concrete aggregates from TBM-material

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Concrete aggregates - geology

- Mainly Precambrian gneiss, and also amphibolite
- The Follo Line can be regarded as one geological unit throughout the entire project area
- The Follo Line route is fixed and aggregate production cannot be adapted to geological conditions

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Sulphur content and pyrrhotite

- NS-EN 12620+NA section 6.3.2:
  - ✓Total content of Sulphur < 1 mass percent S
  - ✓ ***If it is known that the aggregate contains pyrrhotite, the limit of total Sulphur content is reduced to 0.1 % S***
- Reported extensive damages in Canada, Sweden, South-Africa, Switzerland
- Little experience with the damage type in Norway
- Follo Line: design life time of 100 years…

How «correct» is the limit of 0.1%?

Which contents of pyrrhotite will lead to damage?

Foto: Aftenposten Scanpix

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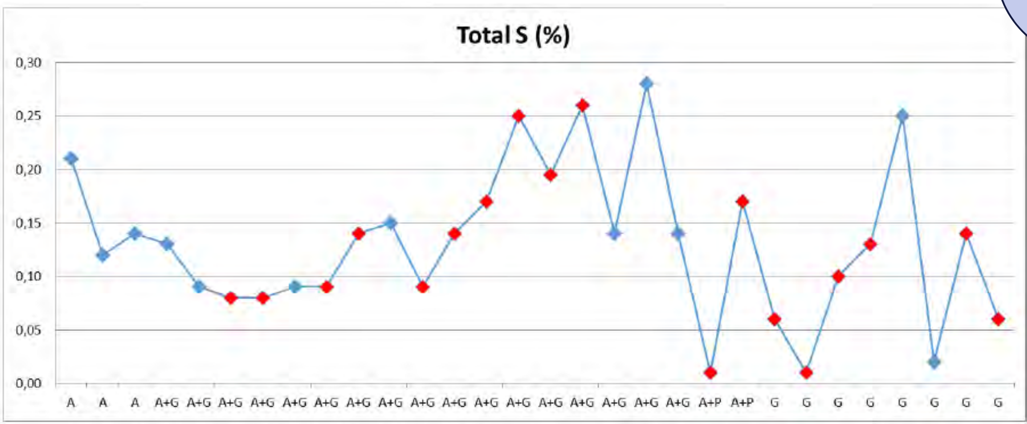
Variation in pyrrhotite content in terms of geology

How to perform quality control? Selective production?



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Lessons learned

Challenges with production of concrete aggregates from TBM-material:

- Production: short time between production and use, production system must allow sufficient quality control
- High humidity in crushed sand due to washing
- Variation of rock quality – selective production is difficult
- NS-EN 12620+NA is not adapted to production of concrete aggregate from tunneling material

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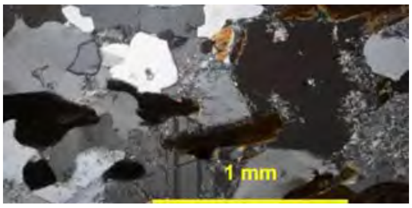
Lessons learned

Questions raised regarding pyrrhotite:

- ✓ How correct is the limit of 0.1 % in the presence of pyrrhotite?
- ✓ Why is there no known damages caused by pyrrhotite in Norway?
- ✓ What is the effect of Norwegian cement, flyash, GGBFS, silica, low w/c?
- ✓ Which content of pyrrhotite will lead to concrete damage?
- ✓ The geology at the Follo Line is not unique- (why) is this not a problem for other aggregate suppliers?



BANE NOR

Determination of total sulphur content in aggregates (2004-2018) - results from SINTEF

Marit Haugen and Jan Lindgård, SINTEF Building and Infrastructure, Box 4760 Torgarden, 7465 Trondheim, Norway

Abstract

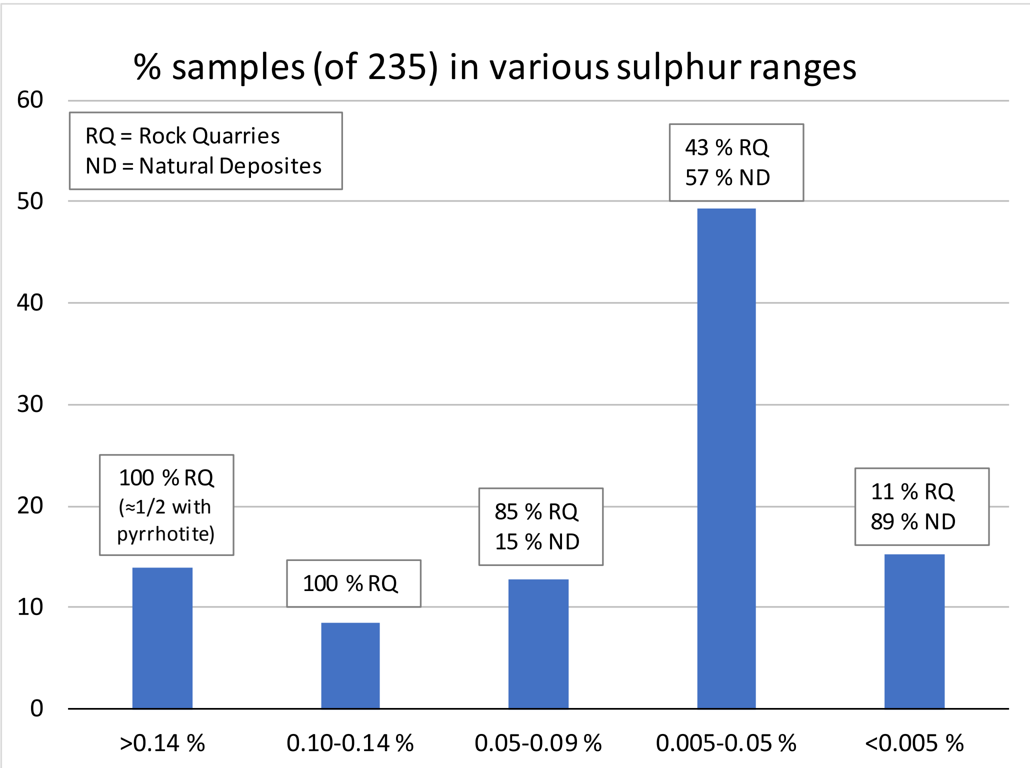
During the period 2004 to 2018, SINTEF has determined total sulphur content in aggregates according to the reference method in the standard NS-EN 1744-1, chapter 11. This reference method is a wet chemical method where the material is treated with hydrogen peroxide, hydrochloric acid and a solution of ammonia, in order to alter the sulphur components to sulphate. Thereafter, barium chloride is added. The sulphates will then precipitate as barium sulphate.

The requirements in the aggregate standard NS-EN 12620 with respect to maximum allowed content of total Sulphur (S) is:

- 1 % S if pyrite is the only ore mineral present (i.e. up to 1.4 % S is acceptable)
- 0.1 % S if pyrrhotite is present (i.e. up to 0.14 % S is acceptable)

In total, SINTEF has examined 264 individual aggregate samples with respect to total sulphur content. 142 of these analyses are performed on crushed rock from rock quarries (RQ), 107 on sand- and gravel samples from natural deposits (ND), and 16 analyses are carried out on other materials (rock cores, rock samples, light weight aggregates, recycled concrete and waste materials). When excluding the 16 latter samples and the 13 samples origin from other countries, 235 samples remain. Only results for these 235 Norwegian aggregate samples, origin from 58 RQ and 62 ND, are included in the summary. From 10 of the rock quarries and 6 of the natural deposits ≥ 4 samples have been analyzed. These have been treated statistically.

The histogram below gives an overview of the total sulphur content in various sulphur ranges.



As shown, 14 % of the 235 samples have a total sulphur content higher than 0.14 %. Of these, 58 % (19 aggregate samples) contain pyrrhotite and are thus not accepted used in concrete according to the requirements in NS-EN 12620. These 19 samples origin from 8 different rock quarries.

Overall for the 235 Norwegian aggregate samples analyzed, 8 % do not satisfy the requirements given in the NS-EN 12620.

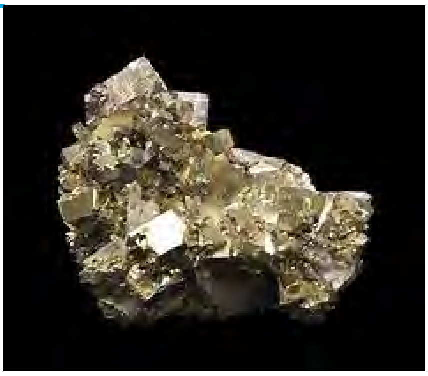
According to the review of the SINTEF results, the rock quarries that show a pyrrhotite content above the critical acceptance limit consist of limestone, dark rocks (i. e gabbro and amphibolite) or a combination of gneiss/granite and dark rocks.

DETERMINATION OF TOTAL SULPHUR CONTENT IN AGGREGATES (2004-2018) - RESULTS FROM SINTEF

Marit Haugen, Jan Lindgård

SINTEF Building and Infrastructure

Sulphides



Pyrite, FeS_2

The acceptance limit 10 x
higher than for pyrrhotite

Pyrrhotite, $Fe_{1-x}S$

2

Sulphur analyses

- Determination of total sulphur content in aggregates:
  - SINTEF uses the reference method in NS-EN 1744-1, chapter 11: Wet chemical method
    - Treating with hydrogen peroxide, hydrocloric acid and a solution of ammonia – altering the sulphur components to sulphate
    - Addition of barium chloride – precipitation of sulphates as barium sulphate
- Aggregate standard NS-EN 12620 – max. allowed content of total sulphur (S):
  - 1 % S if pyrite is the only ore mineral present (up to 1.4 % ok)
  - 0.1 % S if pyrrhotite is present (up to 0.14 % ok)
- Type of sulphide determined by DTA (if > 0.1 % S)

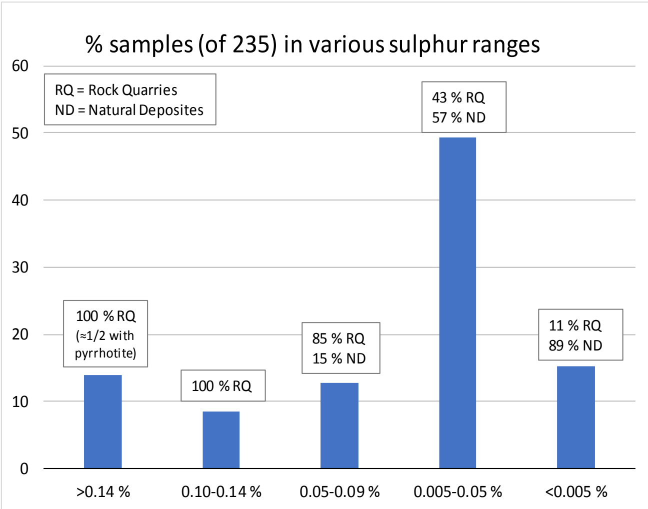
3 SINTEF

Sulphur analyses at SINTEF

- 2004-2018: Totally 264 samples examined
  - Rock quarries (142 samples)
  - Sand - and gravel deposits (107 samples)
  - Other materials (15 samples)
    - Rock cores, rock samples, light weighted aggregates, recycled concrete and waste materials
- Norwegian aggregate samples (235)
  - Rock quarries (RQ): 133 samples (58 locations)
  - Sand - and gravel deposits (ND): 102 samples (62 locations)
- The Norwegian results (235 samples) are handled statistically

4 SINTEF

Results from SINTEF



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Statistics rock quarries

	Location ID	Number of analyses	% S Min.	% S Max.	% S Median	% S **Mean**	% S **STDEV**	c.o.v (%)
One outlier	RQ 1	5	0.02	0.10	0.03	0.04	0.03	71.3
	RQ 2	10	0.05	0.17	0.13	0.12	0.03	29.0
	RQ 3	4	0.03	0.07	0.05	0.05	0.02	36.9
	RQ 4	4	0.10	0.12	0.12	0.11	0.01	9.3
	RQ 5	5	0.02	0.06	0.05	0.04	0.02	37.8
	RQ 6	4	0.08	0.15	0.10	0.11	0.03	29.5
Large scatter	RQ 7	17	0.01	1.13	0.37	0.45	0.30	66.9
	RQ 8	5	0.02	0.15	0.05	0.07	0.05	79.2
	RQ 9	4	0.00	0.03	0.02	0.02	0.01	71.9
	RQ 10	7	0.00	0.04	0.01	0.01	0.01	107.3

6

Statistics natural deposits

Location ID	Number of analyses	% S Min.	Max.	Median	**Mean**	**STDEV**	c.o.v (%)
ND 1	6	0.01	0.03	0.02	0.02	0.01	47.9
ND 2	5	0.00	0.03	0.03	0.02	0.01	59.7
ND 3	5	0.00	0.04	0.02	0.02	0.01	66.0
ND 4	4	0.02	0.04	0.04	0.03	0.01	26.4
ND 5	4	0.00	0.01	0.00	0.00	0.01	200.0
ND 6	4	0.00	0.02	0.02	0.02	0.01	66.7

Summary

- 14 % (33 samples) of 235 Norwegian aggregate samples contain ≥ 0.14 % total S
  - All samples origin from rock quarries
  - About half of the samples (19) contain pyrrhotite and thus do not satisfy the requirements in NS-EN 12620
  - These 19 samples constitute 8 % of all the Norwegian aggregate samples examined at SINTEF
  - These 19 samples origin from 8 different rock quarries

- The rock quarries with pyrrhotite > the acceptance limit consist of
  - Limestone
  - Dark rocks (i.e. gabbro and amphibolite)
  - Combination of gneiss/granite and dark rocks

Abstract for workshop "Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour. 15th – 16th November 2018, Oslo Norway

Total S and Pyrrhotite in Norwegian concrete aggregate deposits. Statistical assessment from NBTLs database over projects

Viggo Jensen

Norwegian Concrete and Aggregate Laboratory LTD

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Norwegian Standard NS-EN 12620 «Concrete Aggregate» require analysis of total S according to an acid solution- and gravimetric method alternatively a combustion method (Leco). In case the aggregate contain pyrrhotite the limit for total S is 0.1 % S.

Testing over years has shown that several Norwegian commercial aggregate quarries do not fulfil the requirement for total S and pyrrhotite in the standard. Recently focus on this problem has been actual in Norway by the Follobane tunnel project where excavated tunnel material was planned to be used as concrete aggregate. However, the aggregate contained varying high total S as well as pyrrhotite. Because of a potential risk for concrete deterioration the tunnel mass was not approved to be used in concrete. The extent of the "pyrrhotite problem" and type of aggregates with high sulfur and pyrrhotite is not known today. Moreover, according to the author's knowledge, cases of concrete deterioration due to pyrrhotite, has not yet been reported in Norway today.

The aim of the investigation is to reveal how many Norwegian aggregate quarries and rock types, which not fulfil the requirement in the standard. This has been done by statistical analyses based on data from NBTls database of commercial testing including analyse result from both the leco method and acid solution – gravimetric method as well as petrographic analyses

Analyse results from 300 total sulfur analyses and DTA analyses carried out by NBTL in the period Marts 2016 to October 2018 has been assessed. The correlation between leco analyses and acid solution – gravimetric analyses has been calculated to be R^2 0.802. About 12 % of the analyses is higher than 0.15 % S and 19-23 % is higher than 0.10 % S.

35 commercial quarries (inclusive tunnel mass project) containing pyrrhotite do not fulfil the requirement for total sulfur less than 0.10 %. Most of the quarries are crushed rock but two quarries are natural aggregates (glaciofluvial). Rock types containing pyrrhotite with total S more than 0.10 % S is: mafic rock (gabbro, amphibolite, greenstone); gneiss, granite; greywacke, sandstone, silt-claystone; limestone; feldspatic rock (rhomb porphyry) and volcanic rock (rhyolite)

NBTL´ *Workshop "Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour. 15th – 16th November 2018, Oslo Norway*

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NBTL´ *Workshop "Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour. 15th – 16th November 2018, Oslo Norway*

Norwegian Concrete and Aggregate Laboratory LTD (NBTL)

NBTL is certified class HI testing laboratory (no. U19) by the Norwegian Control Council (class PI, PII2, PIII, AI, AII, BI, NI, NII)

Established July 2002 by Viggo Jensen (Owner and managing Director)

Employes: 3 geologist (1 more from January 2019) and 2 technichians

New owners from Mai 2018 (Alnus Holding AS (Pro Invenia))

Aims and methods

The aim of the investigation is to reveal how many Norwegian aggregate quarries and rock types, which not fulfil the requirement in the standard. This has been done by statistical analyses based on data from NBTls database of commercial testing including analyse result from both the leco method and acid solution – gravimetric method as well as petrographic analyses. Correlation by the two methods has been established as well as the distribution of total sulfur.

Synopsis

Analyses results from 300 total sulfur analyses and DTA analyses carried out by NBTL in the period Marts 2016 to October 2018 has been assessed. The correlation between leco analyses and acid solution – gravimetric analyses has been calculated to be $R^2 = 0.802$. About 12 % of the analyses is higher than 0.15 % S and 19-23 % is higher than 0.10 % S.

35 commercial quarries (inclusive tunnel mass project) containing pyrrhotite do not fulfil the requirement for total sulfur less than 0.10 %. Most of the quarries are crushed rock but two quarries are natural aggregates (glaciofluvial).

Rock types containing pyrrhotite with total S more than 0.10 % S is: mafic rock (gabbro, amphibolite, greenstone); gneiss, granite; greywacke, sandstone, silt-claystone; limestone; feldspatic rock (rhomb porphyry) and volcanic rock (rhyolite)

NBTL´ Workshop "Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour. 15th - 16th November 2018, Oslo Norway

Background for the project

Testing over years has shown that several Norwegian commercial aggregate quarries do not fulfil the requirement for total sulfur and pyrrhotite in the standard. Recently focus on this problem has been actual in Norway by the Follobane tunnel project where excavated tunnel material was planned to be used as concrete aggregate. However, the tunnel material contained varying high total sulfur as well as pyrrhotite. Because of a potential risk for concrete deterioration the tunnel mass was not approved to be used in concrete.

The extent of the "pyrrhotite problem" and type of aggregates with high sulfur and pyrrhotite in Norway is not known today. With aim to assess this problem in Norway an "ad hoc" group (Magnetkisgruppen) with participants from the public and the industri was established in 2017. This presentation is from an investigation commissioned by the "magnetkisgruppen" where data from NBTLs database over commercial testing by NBTL has been processed and analysed.

According to the author's knowledge, cases of concrete deterioration due to pyrrhotite, has not yet been reported in Norway today.

Standardisation and requirements

Norwegian Standard NS-EN 12620:2002 +A1:2008+NA:2016 «Concrete Aggregate» require analysis of total sulfur according to the test method NS-EN 1744-1 clause 11. In case the aggregate contain pyrrhotite the limit for total S is 0.1 % S, else 1 % total S.
Note the standard does not recommend any method for analyzing pyrrhotit.

NS-EN 1744-1 clause 11. gives two methods for analyzing total sulfur.

- *Clause 11.1 (reference method) is an acid solution and gravimetric method*
- *Clause 11.2 (alternative method) is a combustion method (e.g. Leco)*

NBTL has over several years used both methods simultaneous for commercial testing of total sulfur and results are presented here.

National appendix to NS-EN 1260 NA:2016 clause NA.10 gives a brief description of a differential thermic method (DTA) for detection of pyrrotite but not as a requirement.

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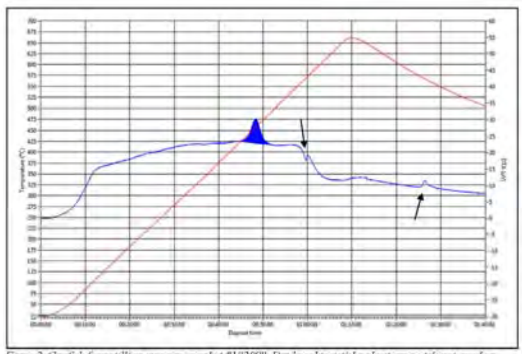
DTA analyse

DTA gives two types of results:

- «indication of pyrite» when one peak is detected or
- «indication of Pyrrhotite or a combination of different types of sulphides when two peaks is detected»



Figur 2. Grafisk fremstilling av prøve merket "18209". Det karakteristiske eksoterme utslaget, med en markant topp ved 460 °C, er markert. Det endoterme (ved oppvarming) og eksoterme (ved avkjøling) reaksjonene for kvarts ved 574 °C er indikert med piler. Den røde linjen viser temperaturforløpet (oppvarming/avkjøling) ved analysen av prøvemateriale.

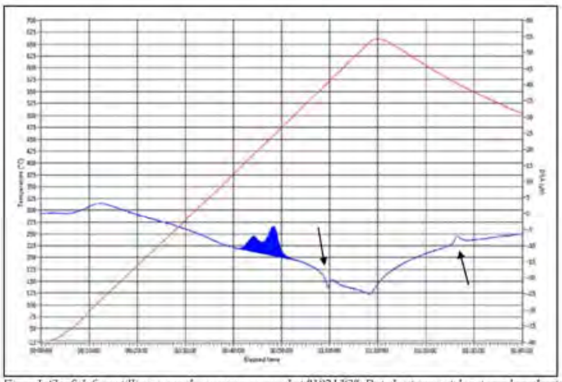
Result: indication of Pyrite

Crushed rock with 70 % gneiss, 25 % mafic rock and 5 % feldspatic rock

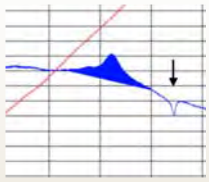
Total sulfur = 0.098 %

18209	18	0,21	Analysen av prøvematerialet viser et karakteristisk eksotermt utslag med en enkeltstående markant topp ved 460° C. Dette indikerer at prøven inneholder svovelkis. (se fig.2).

DTA analyse



Figur 1. Grafisk fremstilling av analysen av prøve merket "18213C". Det eksoterme utslaget, med markante topper ved 458 °C og 417 °C er markert. Det endoterme (ved oppvarming) og eksoterme (ved avkjøling) reaksjonene for kvarts ved 574 °C er indikert med piler. Den røde linjen viser temperaturforløpet (oppvarming/avkjøling) ved analysen av prøvematerialet.



Result: indication of Pyrrhotite or a combination of different types of sulphides

DTA from sandstone

Total sulfur = 0.192 %

Prøvemerking	Kvarts [vekt %]	Kis [vekt %]	*Merknader:*
18213	22	0,43	Analysen av prøvematerialet viser et sammenhengende eksotermt utslag med markante topper ved 458° C og 417° C. Dette indikerer at prøven inneholder magnetkis eller en kombinasjon av ulike kistyper. (se fig.1).

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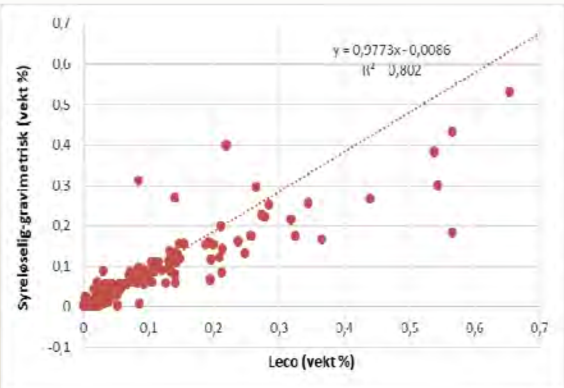
Correlation between acid-gravimetric method and combustion method (leco)



Graph with 300 analyses total sulfur by acid solution -gravimetric method and leco method analysed by NBTL in the period 7. Marts 2016 to 10. October 2018

The graph is excluded results from rhomb porfyry (with pyrrhotite) where leco gived 1.25 % S and acid-gravimetric method gived 1.89 % S

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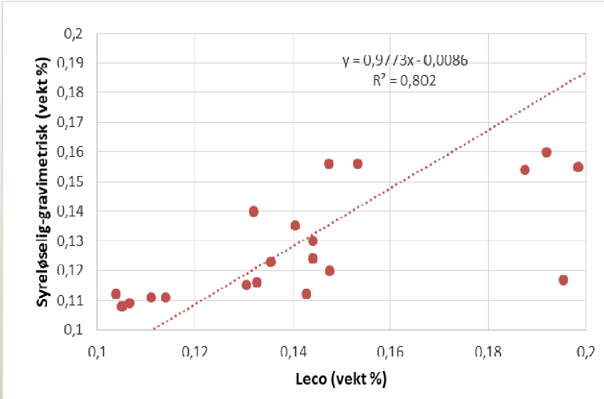

Same results as previous fig. shown in the intervall 0.10 % S to 0.20 % S.

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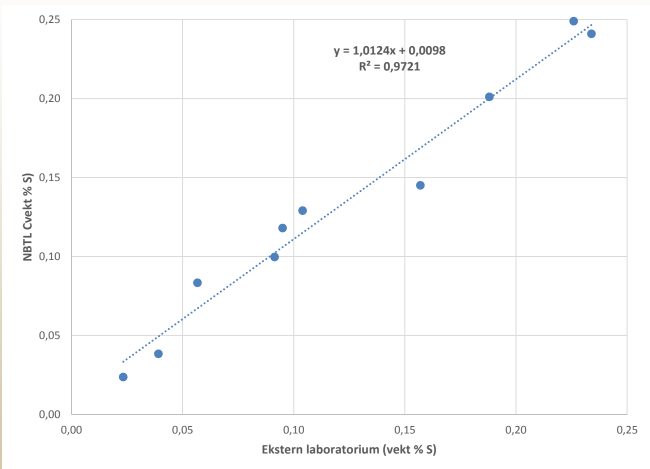
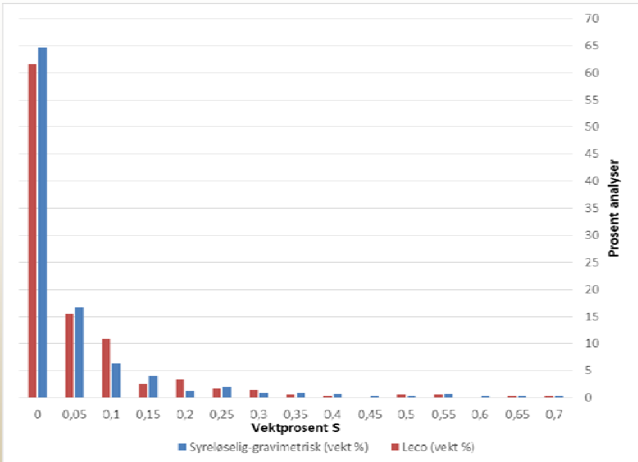
Total sulfur analysed by NBTL and external laboratory (leco)



Leco analysis

Distribution of total sulfur



The graph shows the distribution of total sulfur (percentage) by the two methods

About 12 % of the analyses is higher than 0.15 % S and 19-23 % is higher than 0.10 % S.

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NBTLs database with criteria maks total sulfur > 0.08 % S and DTA

Processing and sorting results from seperate quarries in NBTLs database with criteria maks total sulfur > 0.08 % S and DTA has been performed and revealed 54 quarries of crushed rock (inclusive projects) and 3 natural gravel deposits.

35 commercial quarries (inclusive tunnel mass project) containing pyrrhotite do not fulfil the requirement for total sulfur less than 0.10 %. Most of the quarries are crushed rock but two quarries are natural aggregates (glaciofluvial).

Rock types containing pyrrhotite with total S more than 0.10 % S is: mafic rock (gabbro, amphibolite, greenstone); gneiss, granite; greywacke, sandstone, silt-claystone; limestone; feldspatic rock (rhomb porphyry) and volcanic rock (rhyolite)

Classification of rock types is from simplified petrographic analyses (NS-EN 932-3) and/or from thin section analysis for alkalireactivity (NB21/NB32). For some rock types general names as «mafic rock» or «felspatic rock» has been used. Names in bracket is when more spesific name were avaible)

NBTLs database with criteria maks total sulfur > 0.08 % S and DTA

Excerpt from 57 deposits

Norske tilslagsforekomster med total svovel maks. > 0,08 % og med utført DTA analyse

Nr.	Type	Rock types	N	Median	Maks	Min	St. Av.	Pyrrhotite*
29	k	mafisk (gabbro)	18	0,12	0,37	0,01	0,074	ja
57	k	gråvakke, sandstein	1	0,57				ja
48	k	kalkstein	1	0,71				ja
55	p	kalkstein, mafisk	1	0,55				ja
8	k	mafisk (gabbro)	3	0,21	0,24	0,15	0,045	ja
13	k	mafisk (gabbro)	4	0,18	0,24	0,06	0,079	ja
34	k	feltspatisk bergart	2	0,10	0,11	0,09	0,008	ja
6	n	granitt?	1	0,22				ja
19	k	gneis, granitt, mafisk	7	0,15	0,33	0,06	0,091	ja/nei
16	k	mafisk (amfibolitt)	2	0,17	0,21	0,13	0,057	ja/nei
4	p	feltspatisk, (Rompe porfyr)	2	0,76	1,25	0,27	0,697	ja/nei
7	k	gneis, granitt, mafisk	2	0,22	0,35	0,09	0,183	ja/nei
5	k/n	mafisk (grønnsten),gråvakke, gneis	3	0,23	0,25	0,21	0,122	ja/nei
27	p	mafisk (amfibolitt), gneis	31	0,13	0,28	0,00	0,070	ja/nei
17	k	gneis, granitt, mafisk	7	0,16	0,37	0,13	0,083	ja/nei
36	k	gneis	1	0,09				nei
30	k	eklogitt	1	0,12				nei
44	k	gneis, granitt, mafisk	7	0,08	0,19	0,05	0,058	nei
39	k	gneis, granitt, mafisk	1	0,09				nei
47	k	gneis, granitt, mafisk	2	0,07	0,09	0,04	0,032	nei

* indikasjon

Abbrivations: Type: K = crushed rock, P = projects e.g. tunnel material or unknown origin, n = natural aggregate. **N** is number of leco analysis, **Pyrrhotite** is indikation Yes, Yes/No or No

Conclusion

The correlation between leco analyses and acid solution – gravimetric analyses has been calculated to be R^2 0.802.

About 12 % of the analyses is higher than 0.15 % S and 19-23 % is higher than 0.10 % S

35 commercial quarries (inclusive tunnel mass project) containing pyrrhotite do not fulfil the requirement for total sulfur less than 0.10 %.

Most of the quarries are crushed rock but two quarries are natural aggregates (glaciofluvial).

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After note

Concrete deterioration due to pyrrhotite in aggregates has not yet been reported in Norway. This even several quarries and projects contain pyrrhotite and total sulfur significant higher than the limit value. Several of the quarries have produced concrete aggregates over many years without complains.

Why do we not have durability concrete problem due to pyrrhotite in Norway ????
because the DTA analysis not detect or quantify pyrrhotite correct??
because w/c-ratio is lower in Norwegian concretes comparet to e.g. Canada ??
Because incorrect total sulfur limit value ???

It seems that pyrrhotite in aggregates not is a concrete durability problem in Norway - but caused by the requirements in the standard.

- and it affect several Norwegian produser negatively.

Therefore it is recommented to focus on research of methods replacing or overrule the DTA analysis

NBTL´ Workshop "Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour. 15th – 16th November 2018, Oslo Norway

Thanks

Cases in Sweden were sulphides minerals may contribute to damages in concrete

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Introduction

It is well described in literature that sulphide minerals in aggregates may lead to excess of sulphur in the finalized concrete product and consequent sulfate attack under different conditions. The short information below is a summary of geological bedrock, climate, regulations and a few damages and cases occurring in Sweden during the last decade.

Composition of aggregates and geological background of bedrock in Sweden.

Today, most Swedish aggregates constitute of crushed rock. Approximately 85 % of the Swedish bedrock is generated by crushing bedrock by initial blasting. Glaciofluvial sediments (natural gravel) contribute with approximately 15 %. The bedrock in Sweden mainly consists of Precambrian plutonic (magmatic, crystalline) and metamorphic rocks. Large areas are composed of gneisses and granites. Sedimentary rocks of younger origin (Cambrian) occur in the central parts of Sweden as schists (alunskiffer), sandstones, and calcite carbonate rocks (Hunneberg, Kinnekulle). In the southern parts of Sweden (Skåne region) most rocks are of sedimentary origin with a minor metamorphic imprint. In summary, most aggregates in Sweden consist of granites and gneisses.

Climate

Sweden has semi continental climate with moderate to high humidity, warm summers and cold winters. Due to the nature of the country (skinny but long), the climate can be very different in the northern parts compared to the southern parts.

Regulations and damages in concrete caused by aggregates.

Guidelines concerning the threshold for total sulphur in aggregates (0,1 % weight for pyrrothite) is given in EN 12620:2008. The national standard, SS137003:2015 (EN 2016-1) recommends a maximum of 0.8 % weight (total sulphur) for aggregates in concrete.

The most common features concerning damages in concrete structures in Sweden relate to **frost** and **alkalisilicareactive (ASR)** aggregates. These are the prominent features of concrete damages in Sweden. Very few cases in Sweden are reported that relate to sulphide minerals causing degradation of and reduced durability of the concrete. No cases are known in relation to tunneling (sprayed concrete) or concrete roads. In some cases concrete paving's/facades may pose issues with discoloration. The causes to the discoloration can often be traced to specific aggregate quarries. It is known that the younger sediments in the south of Sweden, may occasionally contain higher concentrations of sulphide phases in the aggregates. These issues are however also of concern in the northern parts of Sweden (region of iron ores and sulphide zones) were local quarries may be used for larger contracts (Kiruna railroad) when constructing. However, no cases have been reported were implications of sulphide minerals have been shown in the finalized concrete product.

PYRROTHITE IN CONCRETE

Oslo – 15th-16th - Workshop

Magnus Döse/RISE CBI

Nov 2018

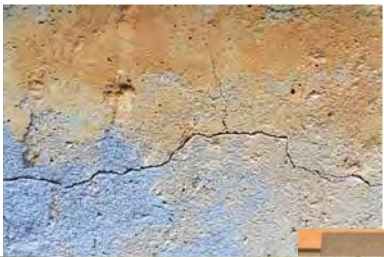
A swedish outlook..

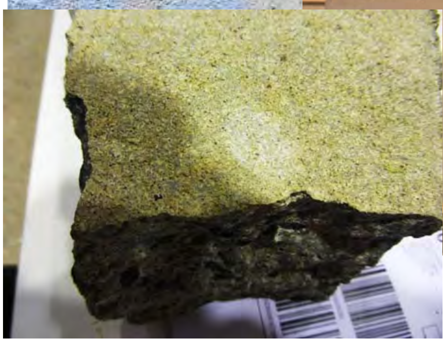
RISE Research Institutes of Sweden

Aggregates with sulphides – issue?

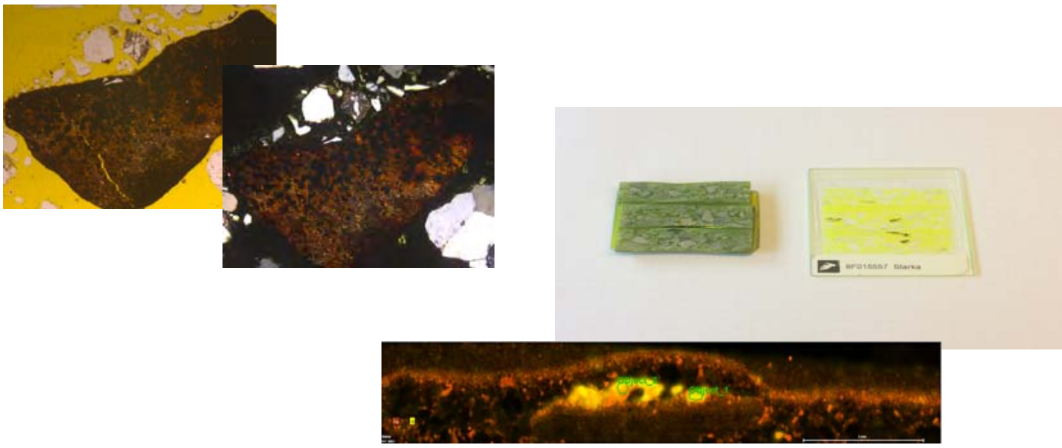
Precast and cast in place?

Sulphides-reactions?



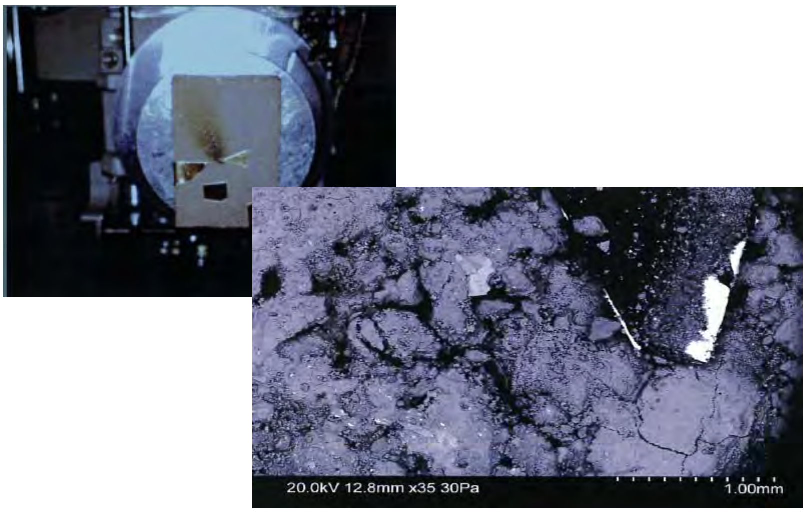


Case I – Discoloration – paving stones/tiles



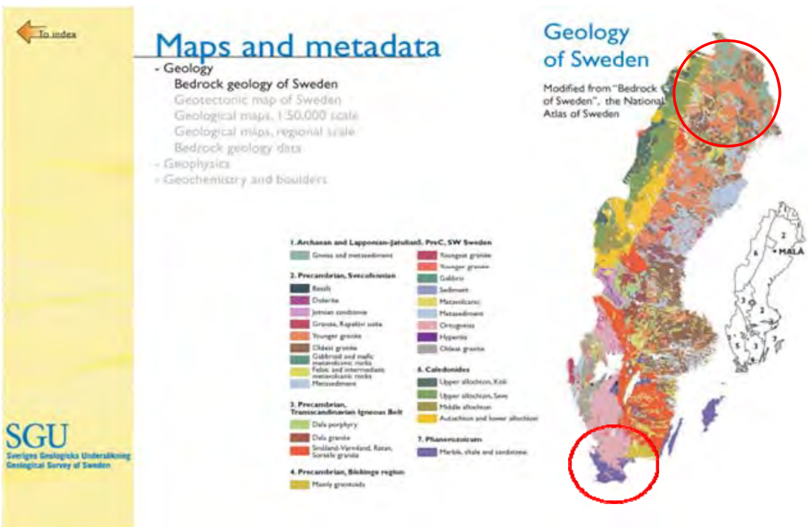
	Mg	Al	Si	S	Mn	Fe	Cu
Object_1	1,03	1,04	29,81	22,51	0,04	42,21	0,00
Object_2	0,76	1,09	25,04	27,32	0,02	39,07	0,00

Case study II – discoloration



ASR a ”bigger” issue in Sweden…

Some areas of interest..



Concluding remarks

- Discoloration on some precast elements
- Discoloration by sulphides – most investigations in relation to tiles/paving stones
- Minor areas of sedimentary rocks contain larger volumes of sulphides
- Northern parts of Sweden – under investigation in larger projects, local quarries could be a potential source of concern
- Sprayed concrete in ores – used under limited time...hence not an issue..
- ”Entreprenadmassor” may cause issue? if used in concrete

RI.
SE

Workshop Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behavior,
Oslo 15th – 16th November 2018

Cases in Finland where sulphide minerals in aggregate have caused damages in Concrete structures

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Geological background of Finnish aggregates

In Finland the bedrock is manly made of Precambrian plutonic and metamorphic rocks. The occurrence of sedimentary rocks is marginal and these rocks are also of Precambrian age. The metamorphic rocks are different metavulcanites, gneisses, schists and quartzites and they are often highly metamorphosed and folded.

The very old bedrock is covered by soil from the latest ice age, about 10000 years ago, so there is a wide time gap between these two. The soil represents well the composition of the underlying bedrock. Granites and granodiorites are the most common rock types in the bedrock and soil. These rock types cover about 60 – 70 % of the average composition of a sporadic aggregate. The rest is mainly made of gneisses and schists. In Eastern Finland quartzites play a more significant role. So, Finland is known as a country having very durable granitic aggregate that is used in a wide range of construction applications.

The geology of Finnish bedrock and soil is well studied and therefore there is a good general view of the composition of aggregates in different parts of the country.
From a geological point of view, there is in general very much in common with Finland and its neighbour Sweden.

EN 12620 specifies the properties of aggregates for use in concrete in conformity with EN 206-1. Guidelines are in the national code By 43 Aggregates for Concrete.

Damages in concrete

Finland has a humid and cool semi continental climate, characterized by warm summers and freezing winters. For this reason damages caused by frost action (freezing and thawing) are the most popular and the Finnish Concrete Code (By 65) gives requirements for the frost resistant concrete; requirements for air-entraining in different exposure classes.

Because of cold winter also de-icing salt is widely used, causing a risk to steel corrosion in structures, especially on bridges. These damages are for the second after frost damages.

Damages are also by alkali aggregate reactions, chemical attack, fire, loads, impacts etc.

Damages caused by sulphide minerals

Damages caused by sulphide minerals in aggregate are quite rare. This is because of the nature of Finnish aggregates; they are mainly granitic and granodioritic gravel sieved from eskers and they are (in general) free from sulphide minerals.

Vahanen Building Physics Ltd is a consulting firm specialized in conditions evaluations of bridges, buildings, water towers, docks etc. and in studying aggregates and doing moisture and other measurements on sites. In the research work done in 2012 – 2018 we have found in three cases concrete damages in façade elements caused by sulphide minerals in aggregate.

In every case the visible signs were rusty surfaces and pop outs. The first thought was that it is question about rusty steel bars in the elements. But in every case the bars were of stainless steel and the bars were in excellent condition. By studying the cored samples with thin section and SEM we found that it is question about damages caused by sulphide minerals (Fig. 1.). The damages were not structural but mainly esthetic.

There was one common nominator in all these three cases. The elements were made in factories in Eastern Finland.

Fig. 1. Damages caused by sulphide minerals on the surface of a concrete panel.

Why this type of damages? There are several explanations:

- Those who analyse aggregates in laboratories are geologists, who knows geology but not that much concrete technology and chemical conditions in concrete.
- When doing a simplified petrographic analysis, you just study the aggregate with your naked eye and under stereomicroscope. If it is a question about a gravel from an esker and the grains are contaminated with fine dust or precipitate from groundwater, can you really detect possible sulphide minerals. And very much that type of aggregate is used in Finland.
- When studying crushed aggregate and / or using petrographic thin section study, it is more probable, that sulphide minerals will be detected on a broken surface.
- Then there is always the speculation, that some “not that well known” aggregate / waste has been used for some (economic) reasons.

CASES IN FINLAND WHERE SULPHIDE MINERALS IN AGGREGATE HAVE CAUSED DAMAGES IN CONCRETE STRUCTURES

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Workshop Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behavior - Oslo 15th – 16th November 2018

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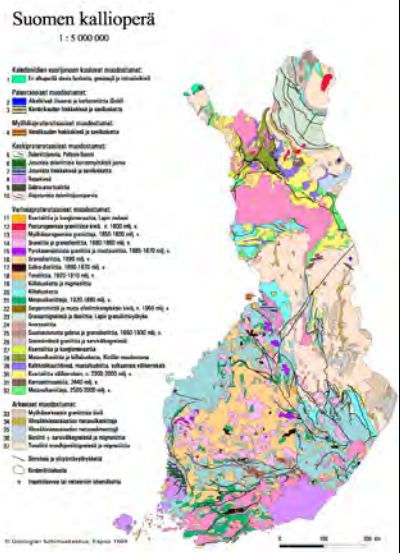
Geological background of Finnish aggregates

In Finland the bedrock is manly made of Precambrian plutonic and metamorphic rocks.

The occurrence of sedimentary rocks is marginal and these rocks are also of Precambrian age.

The plutonic rocks are mainly granites and grano-diorites

The metamorphic rocks are different metavulcanites, gneisses, schists and quartzites and they are often highly metamorphosed and folded.



CASES IN FINLAND WHERE SULPHIDE MINERALS IN AGGREGATE HAVE CAUSED DAMAGES IN CONCRETE STRUCTURES
HANNU PYY

Geological background of Finnish aggregates

- The very old bedrock is covered by soil from the latest ice age, about 10.000 years ago, so there is a wide time gap between these two.
- The glaciofluvial sediments represent well the composition of the underlying bedrock. Granites and granodiorites are the most common rock types and they cover about 60 – 70 % of the average composition of a sporadic aggregate.
- The rest is mainly made of gneisses and schists. In Eastern Finland quartzites play a more significant role.

3

VAHANEN

CASES IN FINLAND WHERE SULPHIDE MINERALS IN AGGREGATE HAVE CAUSED DAMAGES IN CONCRETE STRUCTURES
HANNU PYY

Geological background of Finnish aggregates

- From the geological point of view, there is in general very much in common with Finland and its neighboring country Sweden.

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CASES IN FINLAND WHERE SULPHIDE MINERALS IN AGGREGATE HAVE CAUSED DAMAGES IN CONCRETE STRUCTURES
HANNU PYY

Geological background of Finnish aggregates

- The geology of Finnish bedrock and soil is well studied and therefore there is a good general view of the composition of aggregates in different parts of the country.
- Finland is known as a country having very durable granitic aggregate that is used in a wide range of construction applications.

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CASES IN FINLAND WHERE SULPHIDE MINERALS IN AGGREGATE HAVE CAUSED DAMAGES IN CONCRETE STRUCTURES
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Geological background of Finnish aggregates

- EN 12620 specifies the properties of aggregates for use in concrete.
- Guidelines are in the national code published by the Concrete Association of Finland **By 43 Concrete Aggregates** (in Finnish).

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Damages in concrete

- Finland has a humid and cool semi continental climate, characterized by warm summers and freezing winters.
- For this reason damages caused by frost action (freezing and thawing) are the most common
- Finnish Concrete Code (By 65) gives requirements for the frost resistant concrete
  - requirements for air-entraining in different exposure (XF) classes

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CASES IN FINLAND WHERE SULPHIDE MINERALS IN AGGREGATE HAVE CAUSED DAMAGES IN CONCRETE STRUCTURES
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Damages in concrete

- Because of cold winters also de-icing salt is widely used, causing a risk to steel corrosion in structures, especially on bridges. These damages are the second common after frost damages.

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Damages in concrete

- Damages are also caused by alkali aggregate reactions, chemical attack, fire, loads, impacts etc.

CASES IN FINLAND WHERE SULPHIDE MINERALS IN AGGREGATE HAVE CAUSED DAMAGES IN CONCRETE STRUCTURES
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Damages caused by sulphide minerals

- Damages caused by sulphide minerals in aggregate are quite rare.

- Vahanen Building Physics Ltd is a consulting firm specialized in conditions evaluations of bridges, buildings, water towers, docks etc. and studying concrete and aggregates in laboratory.
- In the research work done in 2012 – 2018 we have found in three cases concrete damages in façade elements caused by sulphide minerals in aggregate.

Damages caused by sulphide minerals

- In every case the visible signs were rusty surfaces and pop outs.
- The first thought was that it is question about rusty steel bars in the elements.
- But in every case the bars were of stainless steel and the bars were in excellent condition.
- The damages were caused by sulphide minerals in aggregate

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CASES IN FINLAND WHERE SULPHIDE MINERALS IN AGGREGATE HAVE CAUSED DAMAGES IN CONCRETE STRUCTURES
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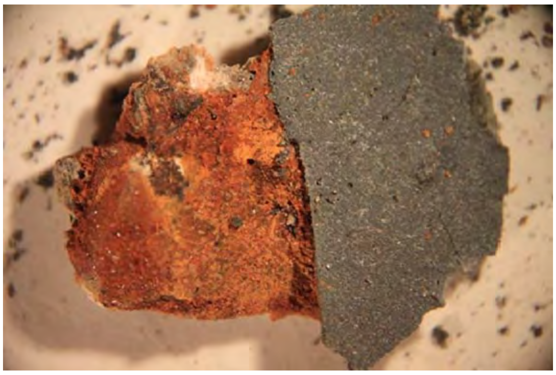
Damages caused by sulphide minerals

- Case N:o 1 apartment house in Vantaa

EN

Damages caused by sulphide minerals

- Case N:o 1 apartment house in Vantaa



CASES IN FINLAND WHERE SULPHIDE MINERALS IN AGGREGATE HAVE CAUSED DAMAGES IN CONCRETE STRUCTURES
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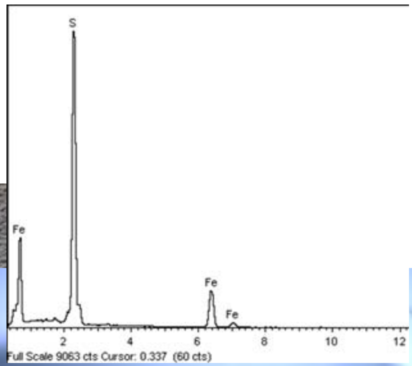
Damages caused by sulphide minerals

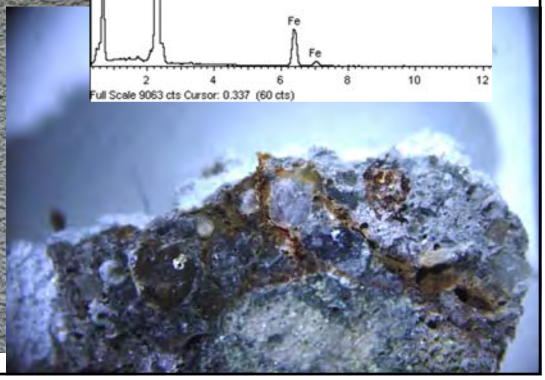
- Case N:o 2 apartment house in Espoo

CASES IN FINLAND WHERE SULPHIDE MINERALS IN AGGREGATE HAVE CAUSED DAMAGES IN CONCRETE STRUCTURES
HANNU PYY

Damages caused by sulphide minerals

- Case N:o 3 apartment house in Espoo





CASES IN FINLAND WHERE SULPHIDE MINERALS IN AGGREGATE HAVE CAUSED DAMAGES IN CONCRETE STRUCTURES
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Damages caused by sulphide minerals

Why these type of damages are possible?

- Those who analyze aggregates in laboratories are geologists, who knows geology but not that much concrete technology and chemical conditions in concrete.
- When doing a petrographic analysis (EN932-3, EN12407), it is common that you just study the aggregate with your naked eye and under a stereomicroscope.
  - If it is a question about a gravel from a glaciofluvial deposit and the grains are contaminated with fine dust or precipitate from groundwater, can you really detect possible sulphide minerals. And very much that type of aggregate is used in Finland.

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Damages caused by sulphide minerals

Why these type of damages are possible?

- When studying crushed aggregate and / or when using petrographic thin section study, it is more probable, that sulphide minerals will be detected on a broken surface / polished section / thin section.
- Then there is always the speculation, that some “not that well known” aggregate / waste has been used for some (economic) reasons.

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CASES IN FINLAND WHERE SULPHIDE MINERALS IN AGGREGATE HAVE CAUSED DAMAGES IN CONCRETE STRUCTURES
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Damages caused by sulphide minerals

What did we learn

- “Finland is known as a country having very durable granitic aggregate that is used in a wide range of construction applications”
  - Yes, in general, but there can be surprises, as we learned also when we found AAR
- More accuracy is needed in analyses
- More information to branch

VAHANEN

THANK YOU

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Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour

November 15-16, 2018, Oslo, Norway

Overview of the Deterioration mechanisms: Cases of deterioration in Canada and US.

by J.Duchesne and B. Fournier, Université Laval, Québec, Canada

Abstract:

Damages in concrete containing sulphide-bearing aggregates were observed in the Trois-Rivières area (Québec, Canada) and more recently in Northeastern Connecticut (USA). The deterioration problems are related to the oxidation of sulphide-bearing aggregates used for concrete manufacturing. In both cases, the aggregates used to produce concrete contained pyrrhotite, an iron sulphide mineral of composition $Fe_{1-x}S$.

In both cases, petrographic examination of concrete core samples was carried out using a combination of tools including: stereomicroscopic evaluation, polarized light microscopy, scanning electron microscopy, X-ray diffraction and electron microprobe analysis. Secondary reaction products observed 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. In 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 and provokes the formation of sulphate minerals. Understanding both mechanisms, oxidation and internal sulphate attack, is important to be able to duplicate the damaging reaction in laboratory conditions, thus allowing the development of a performance test for evaluating the potential for deleterious expansion in concrete associated with sulphide-bearing aggregates.

Keywords: Petrography; Degradation; Sulphate Attack; Thaumasite; Ettringite; Sulphide-bearing aggregate, Pyrrhotite.

Centre de recherche sur les infrastructures en béton

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CRIB

Overview of the Deterioration Mechanisms: Cases of deterioration in Canada and US

J. Duchesne and B. Fournier
CRIB – Laval
Université Laval, Québec, Qc, CANADA

Situation

- More than 2 000 residential owners in the Trois-Rivières area (Quebec, Canada) are facing serious issues related to their concrete deterioration
  - Foundation walls (residential and commercial)
  - Slabs on grade

Trois-Rivières Case Study

Observations

- Rapid Deterioration
- Oxidation on iron sulfide-bearing aggregates
- Presence of rust (iron oxyhydroxide)
- Signs of Sulfatation
- No External Source of Sulfate
- Presence of gypsum

Characterisation Methods

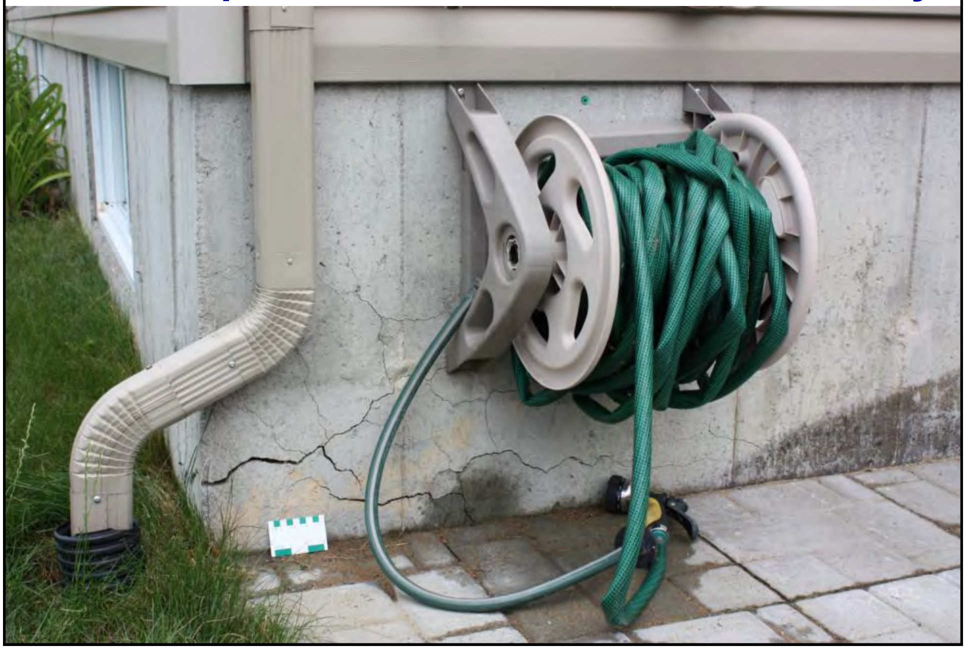
Visual Inspection of Concrete Foundation

- Identify any signs of deterioration
  - deformation
  - cracking (pattern and intensity)
  - exposure conditions, …
- Concrete samples (100-mm diameter cores)
  - cut with diamond blade
  - polished for stereomicroscope observations
  - impregnated under vacuum (low viscosity resin)
  - polished ·SiC and loose alumina abrasive powders
    ·lubricant – isopropyl alcohol

Visual Inspection - Trois-Rivières Case Study

Visual Inspection - Trois-Rivières Case Study

Visual Inspection - Trois-Rivières Case Study



Visual Inspection - Trois-Rivières Case Study

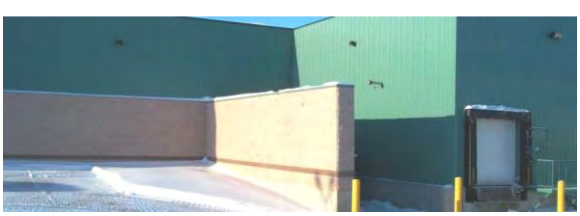
Visual Inspection - Trois-Rivières Case Study

Visual Inspection - Trois-Rivières Case Study

Visual inspection of deteriorated houses




Visual Inspection - Trois-Rivières Case Study


Visual Inspection - Trois-Rivières Case Study

Visual Inspection - Trois-Rivières Case Study

Oxidation Reactions

Oxidation of pyrite

$$FeS_2 + 15/4\ O_2 + 5/2H_2O \rightarrow FeOOH + 2\ H_2SO_4$$

pyrite | goethite | Sulfuric acid

Oxydation of pyrrhotite

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

pyrrhotite

Oxidation Reactions

Oxidation of ferrous iron (Fe^{2+})

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

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

Fe^{2+} is oxidized and precipitated as ferric oxyhydroxides (ferrihydrite and goethite)

Oxidation Reactions

Reaction with portlandite

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

Sulfuric acid + portlandite → gypsum

Secondary Ettringite Formation

$3(CaSO_4 \cdot 2H_2O) + C_3A + 26\ H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot H_{32}$

gypsum + C_3A + water → ettringite

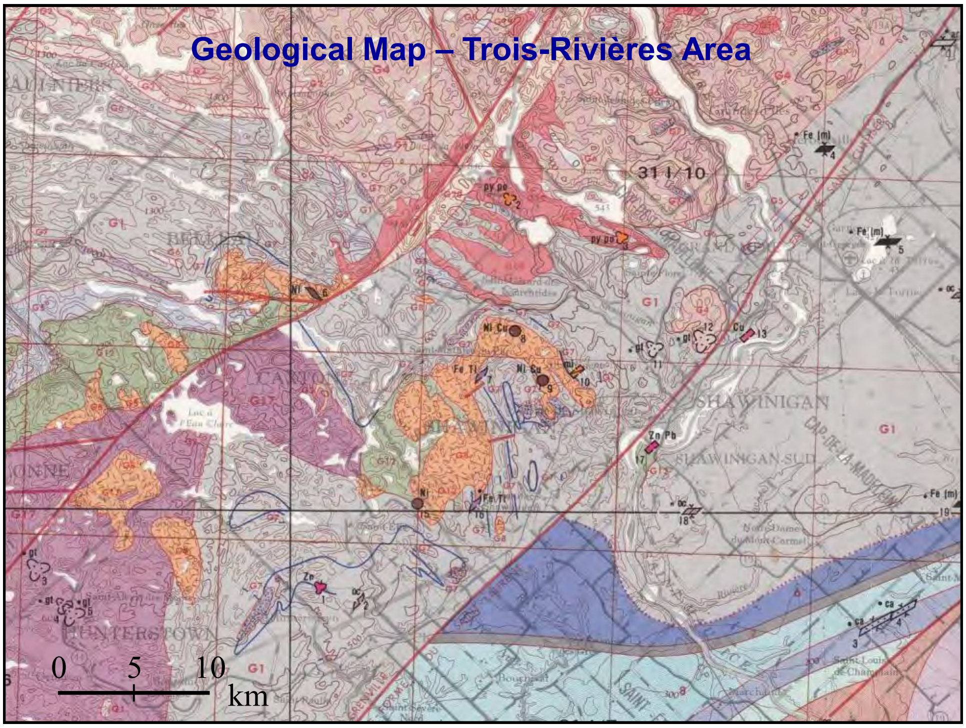
Oxidation Reactions

Most Common Secondary Products

- "Rust"
  - goethite (FeOOH)
  - limonite ($FeO(OH)_nH_2O$)
  - ferrihydrate ($Fe_2O_3 \cdot 0.5\ H_2O$)
  - …
- Gypsum ($CaSO_4 \cdot 2H_2O$)
- Ettringite ($C_3A \cdot 3CaSO_4 \cdot H_{32}$)

Replacement of Concrete Foundation Walls

Replacement of Concrete Foundation Walls



Characterisation Methods

Petrographic Examination → **Aggregate**, **Concrete**

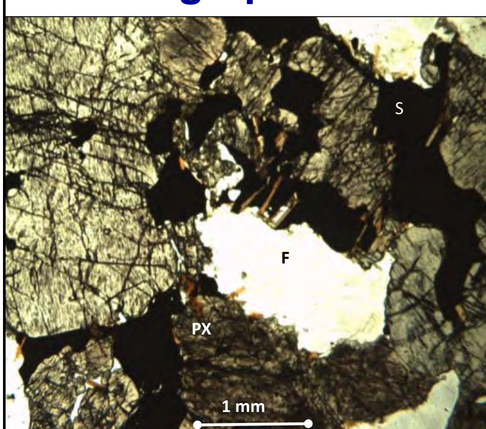
- Macroscopic examination
- Microscopic observation
    - Polarized light microscopy
        - transmitted light
        - reflected light
- Scanning Electron Microscopy (SEM/EDS)
- Electron Probe Microanalysis (EPMA)

St-Boniface Quarry - Lithology

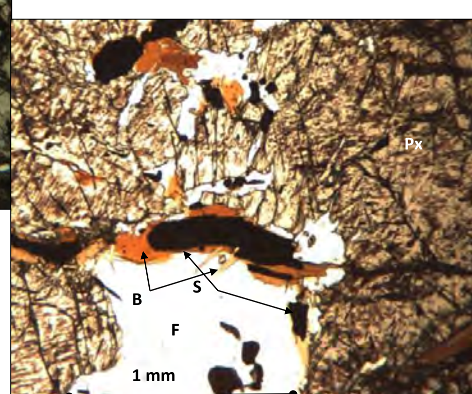
St-Boniface Quarry - Lithology

Petrography & chemistry of rocks

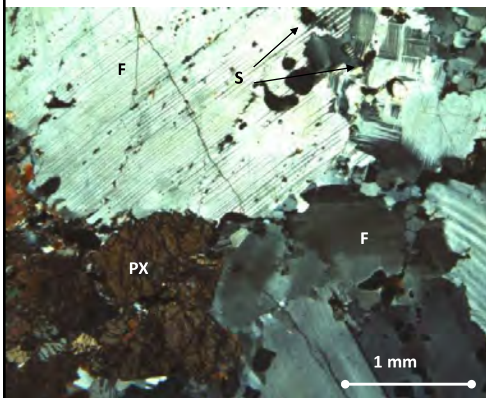
Petrographic Examination of Aggregates



Plane polarized light

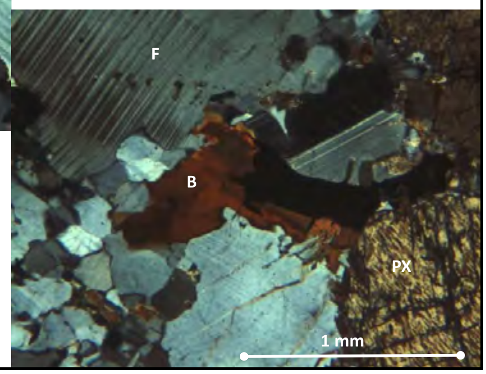


Petrographic Examination of Aggregates

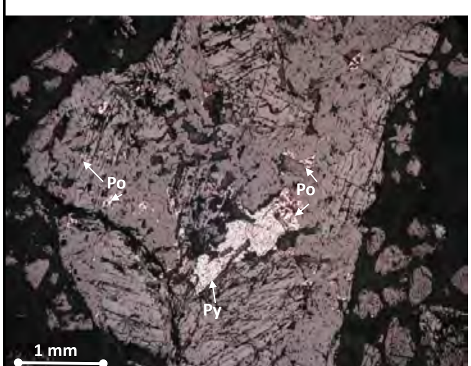


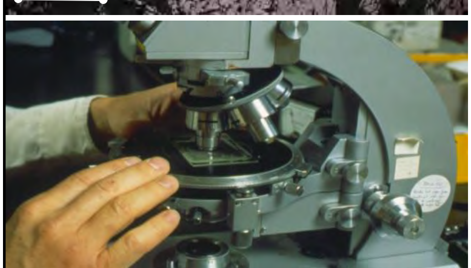
Crossed polarized light

Intrusive mafic rock:
Gabbro - norite
with hypersthene

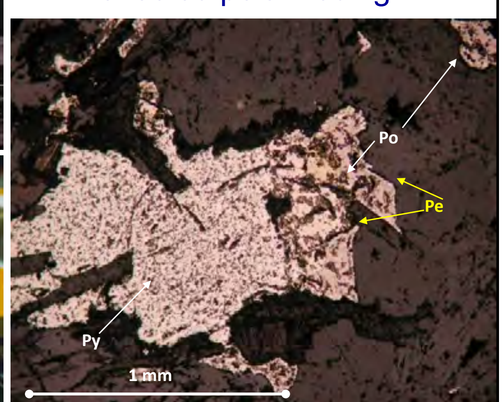


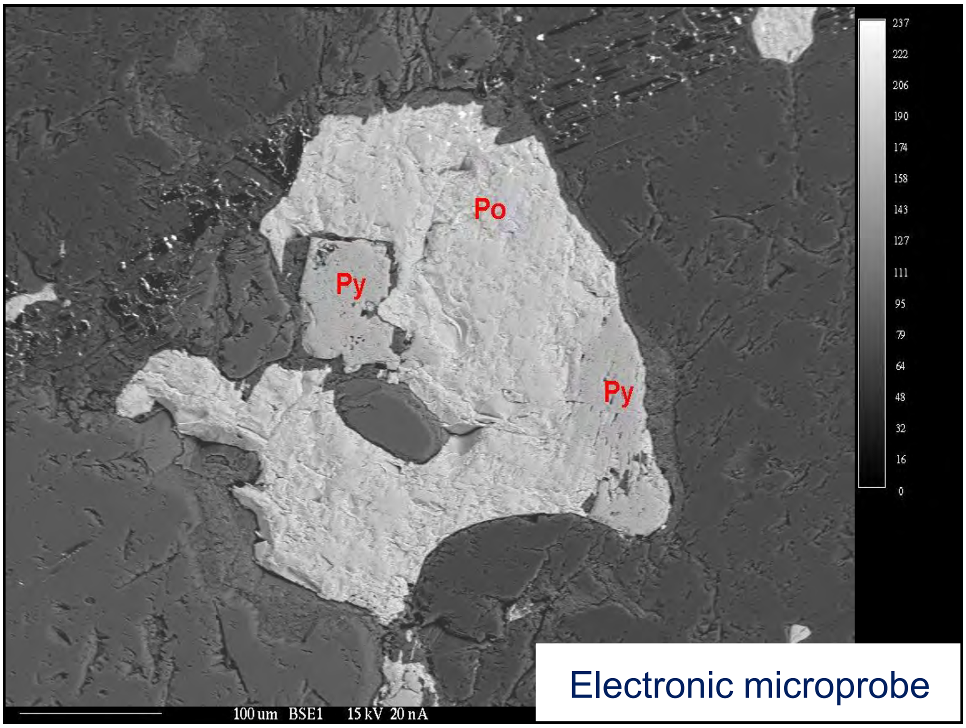
Petrographic Examination of Aggregates

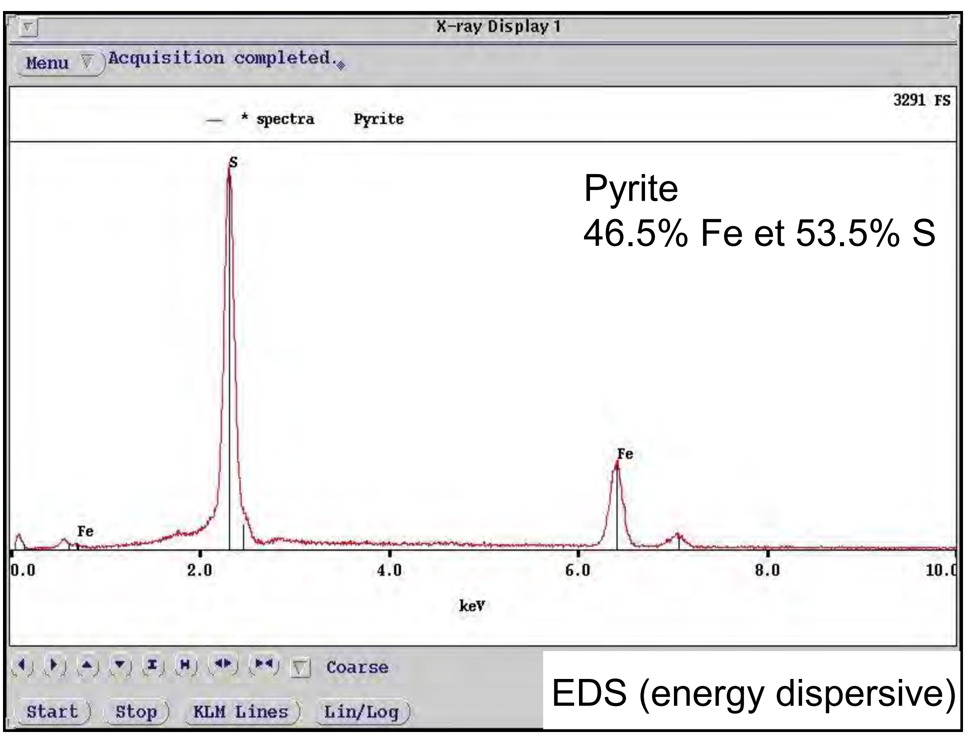


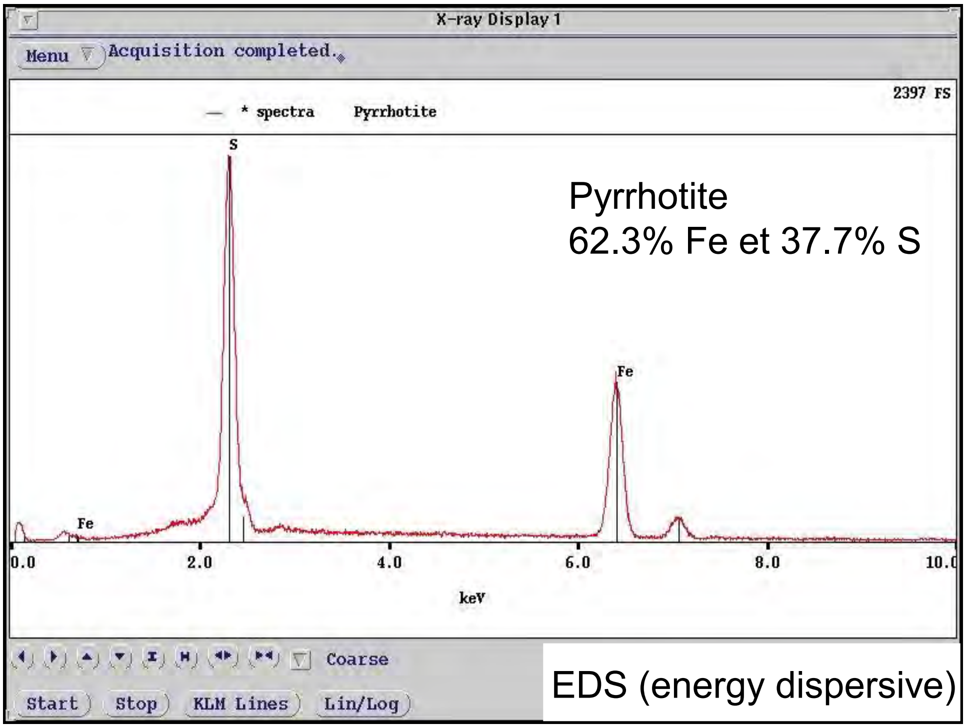


Reflected polarized light

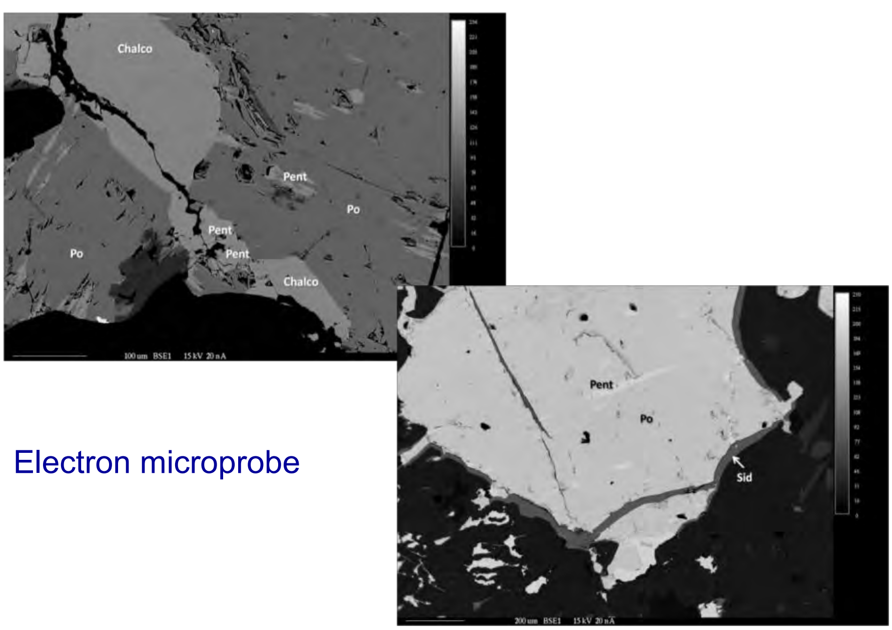



Po
Py
Py
100 um BSE1 15 kV 20 nA
Electronic microprobe


X-ray Display 1
Menu
Acquisition completed.
3291 FS
* spectra Pyrite
S
Fe
Fe
Pyrite
46.5% Fe et 53.5% S
keV
Coarse
Start
Stop
KLM Lines
Lin/Log
EDS (energy dispersive)

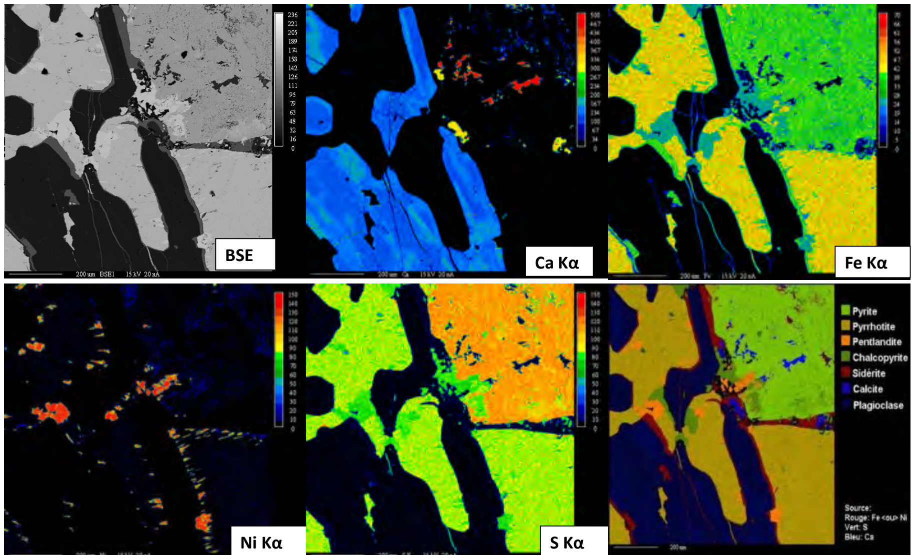


Petrographic examination of rocks



Electron microprobe

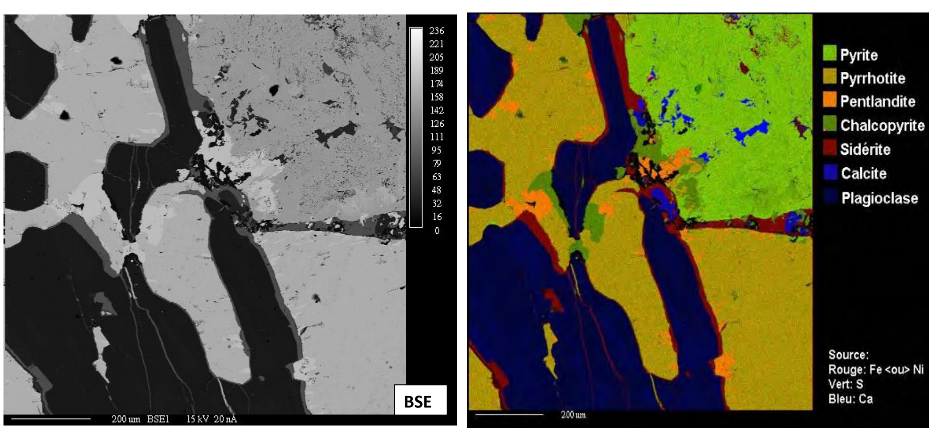
Chemical mapping (microprobe)



False color reconstruction image :

Red : Fe < or > Ni Green: S Blue: Ca

Chemical mapping (microprobe)



False color reconstruction image :

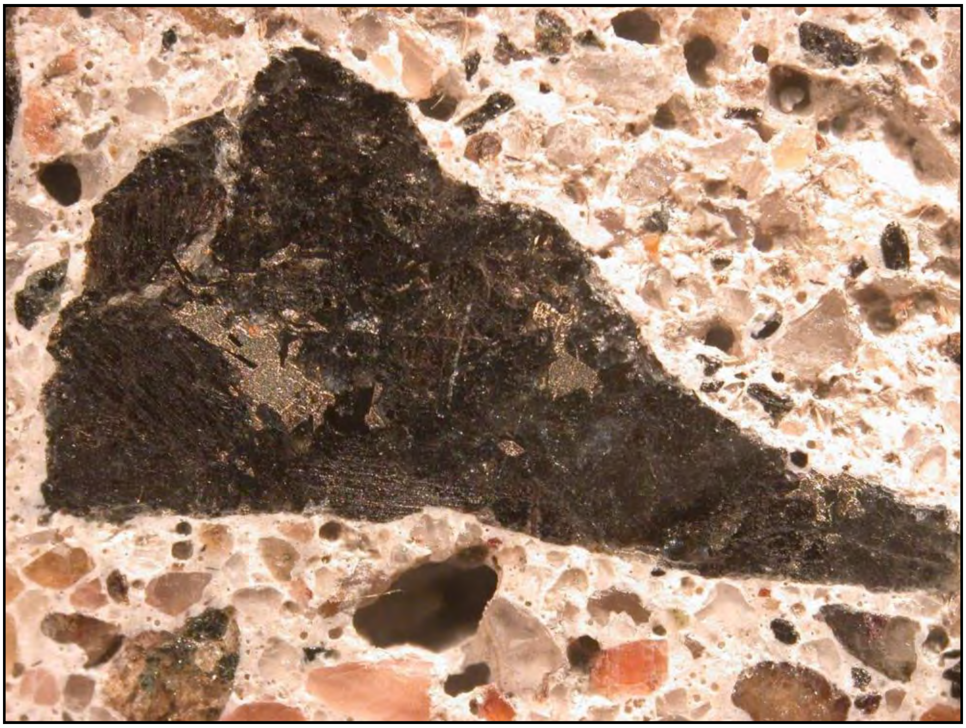
Red : Fe < or > Ni Green: S Blue: Ca

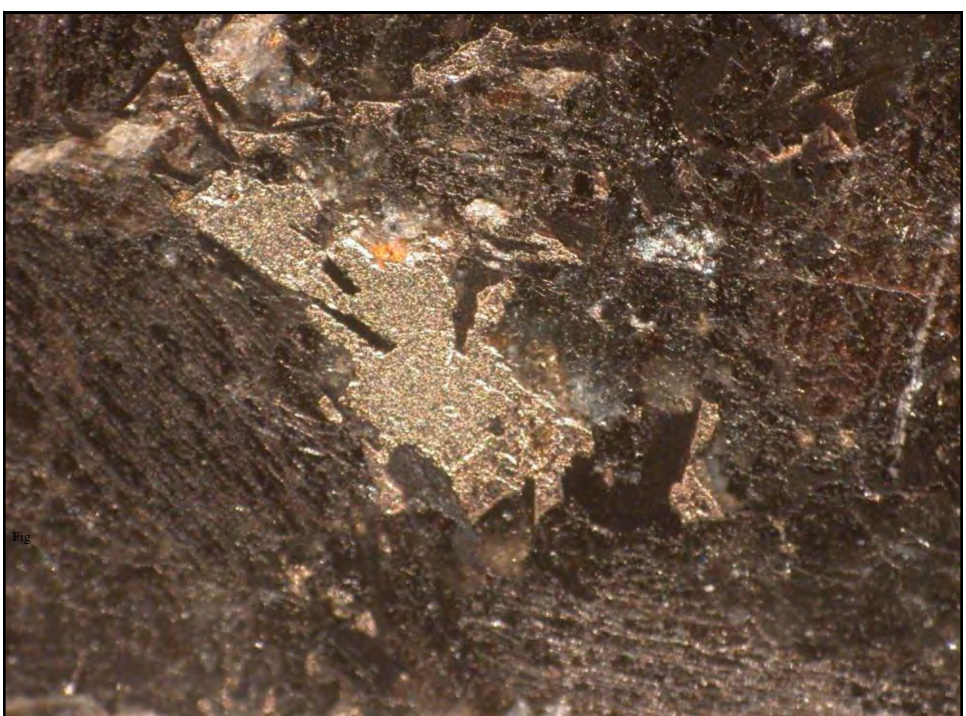
In-Situ Chemical Analysis (EPMA)

	S	Cu	Ni	Fe	Co	As	Total
Po-1	38.456	0.004	0.588	59.717	0.180	0.000	98.945
Po-2	38.693	0.000	0.503	59.020	0.255	0.011	98.482
Po-3	37.957	0.029	0.681	59.368	0.104	0.000	98.139
Po-4	38.052	0.021	0.674	59.225	0.303	0.000	98.275
Po-5	38.008	0.039	0.688	59.365	0.000	0.051	98.151
Po-6	38.644	0.008	0.363	59.631	0.000	0.015	98.661
Moyenne- Po	**38.302**	**0.017**	**0.583**	**59.388**	**0.140**	**0.013**	**98.442**
Py-1	52.708	0.002	0.015	47.565	0.000	0.029	100.319
Py-2	52.821	0.000	0.000	47.720	0.000	0.021	100.562
Py-3	52.685	0.000	0.000	47.129	0.000	0.032	99.846
Py-4	52.554	0.023	0.000	47.993	0.000	0.013	100.583
Py-5	52.570	0.000	0.000	47.338	0.029	0.030	99.967
Py-6	52.580	0.000	0.000	47.082	0.134	0.051	99.847
Moyenne - Py	**52.653**	**0.004**	**0.003**	**47.471**	**0.027**	**0.029**	**100.187**
Pe- 1	32.750	0.000	35.139	28.968	3.548	0.007	100.412
Pe -2	32.646	0.000	35.394	28.700	3.400	0.040	100.180
Moyenne - Pe	**32.698**	**0.000**	**35.267**	**28.834**	**3.474**	**0.024**	**100.296**
Pyrrhotite $Fe_{1-x}S$ où x = 0.099							

Note Po = pyrrhotite Py = pyrite Pe = pentlandite

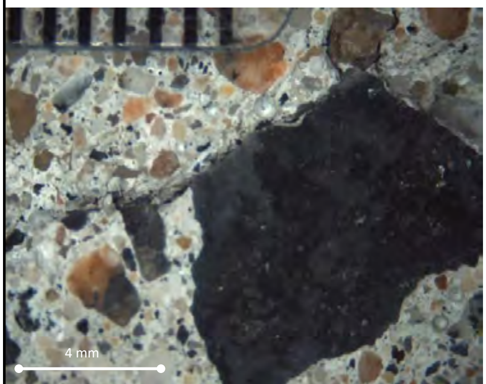
Petrographic Examination of Concrete Samples

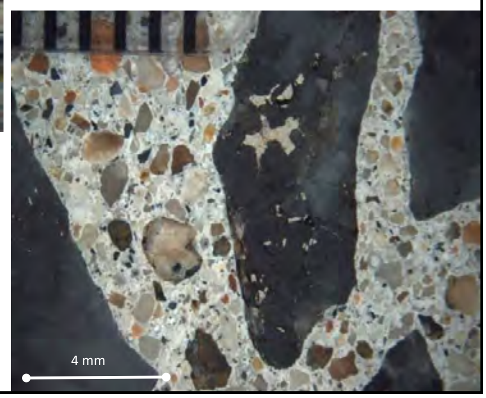




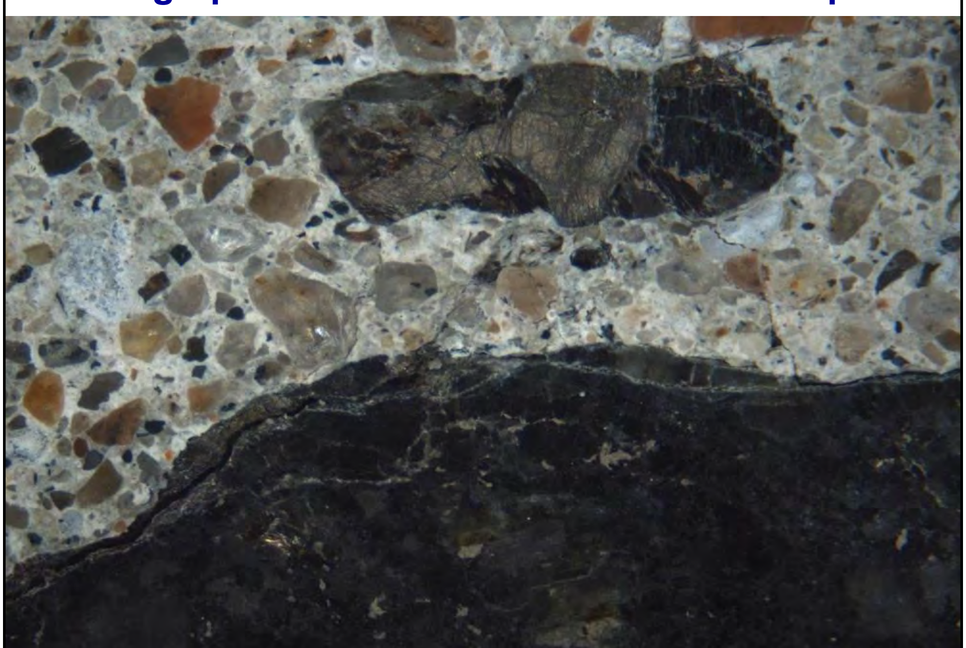
Fig

Petrographic Examination of Concrete Samples

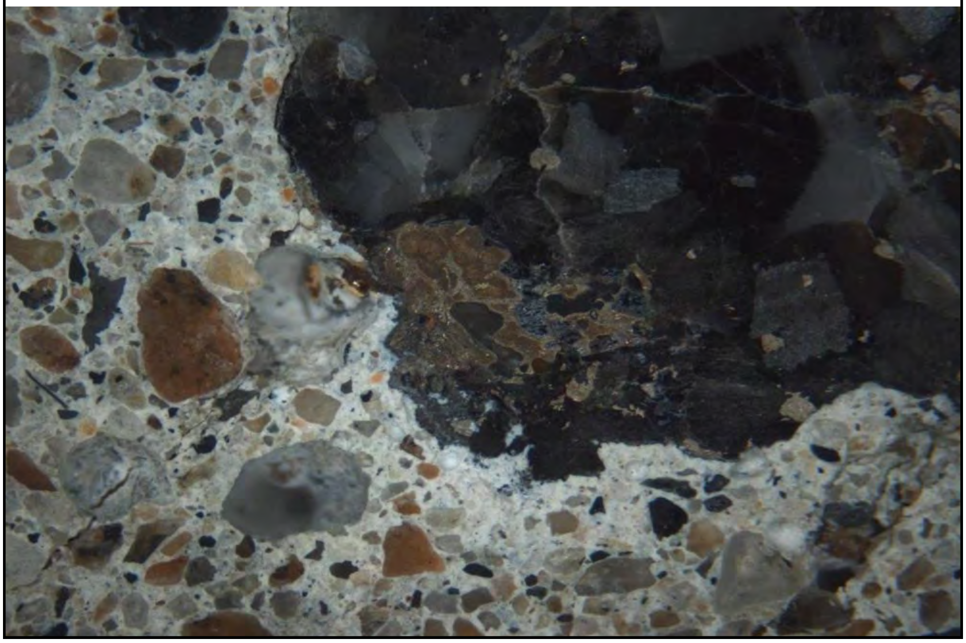




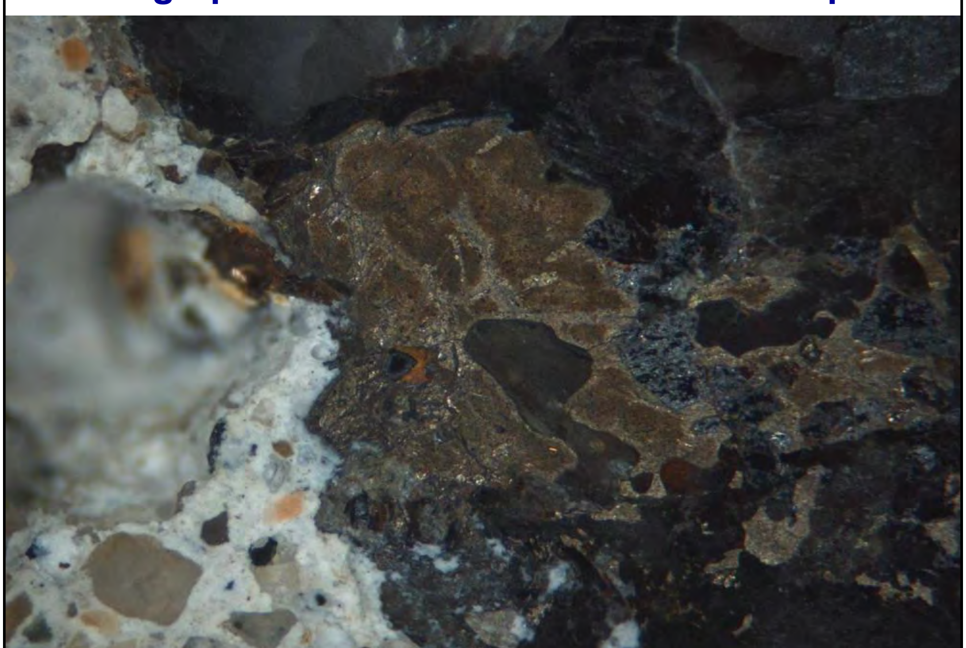
Petrographic Examination of Concrete Samples



Petrographic Examination of Concrete Samples



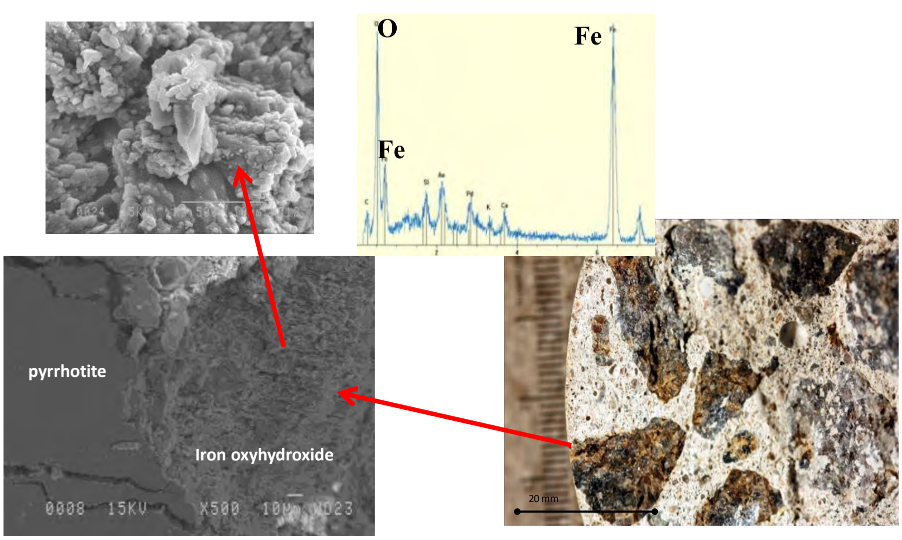
Petrographic Examination of Concrete Samples



Petrographic Examination of Concrete Samples

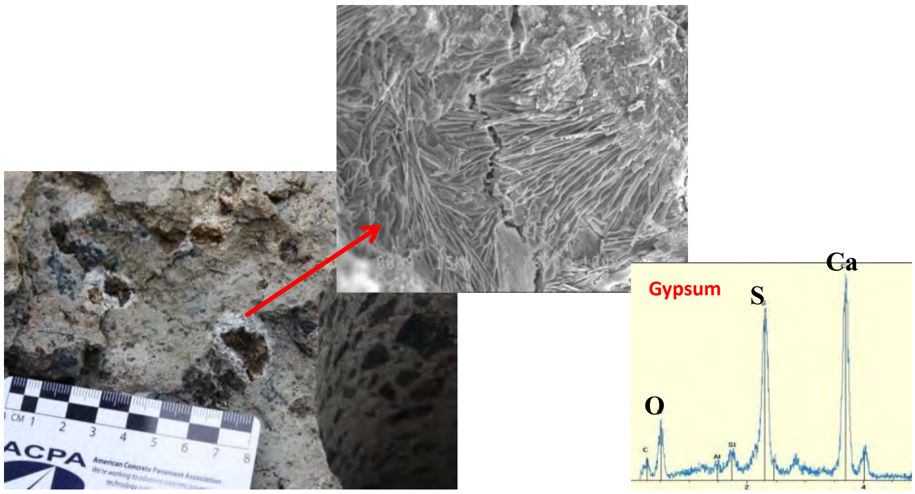
SEM examination of concrete samples

Pyrrhotite + oxygen + water → goethite + sulfuric acid



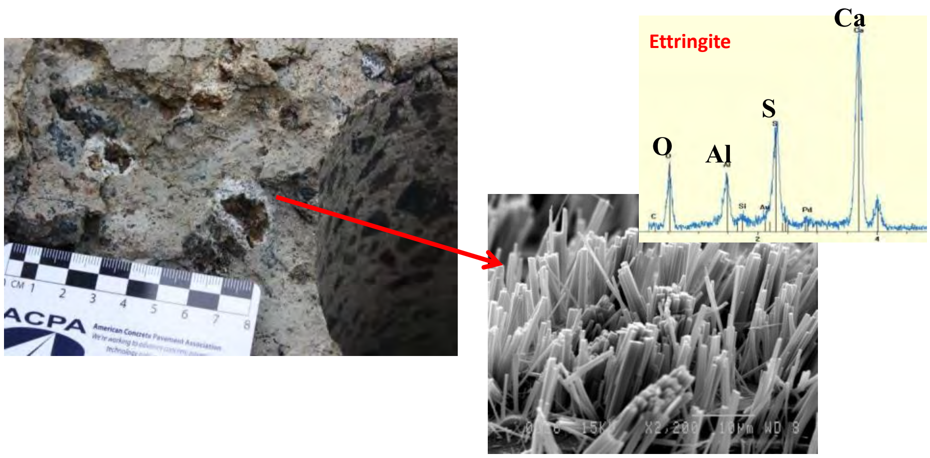
SEM examination of concrete samples

- Pyrrhotite + oxygen + water → goethite + sulfuric acid
- **Sulfuric acid + portlandite (cement) → gypsum**



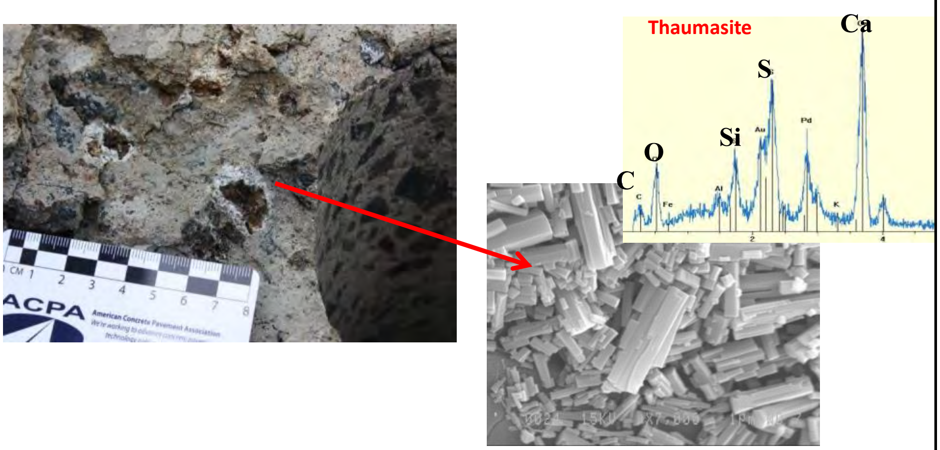
SEM examination of concrete samples

- Pyrrhotite + oxygen + water → goethite + sulfuric acid
- Sulfuric acid + portlandite → gypsum
- **C_3A (cement) + gypsum "sulfates" + water → ettringite**

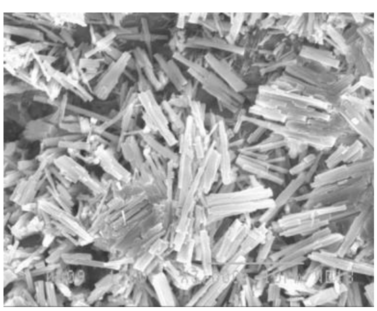


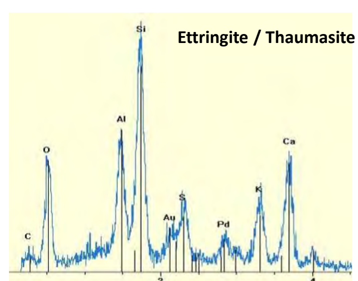
SEM examination of concrete samples

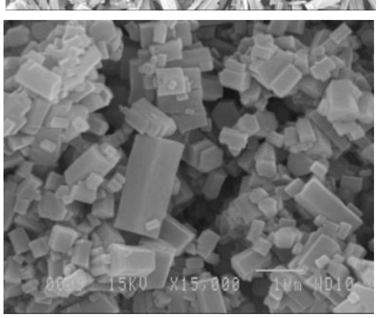
- Pyrrhotite + oxygen + water → goethite + sulfuric acid
- Sulfuric acid + portlandite → gypsum
- "Sulfates" + carbonates + "CSH" + water → **thaumasite**

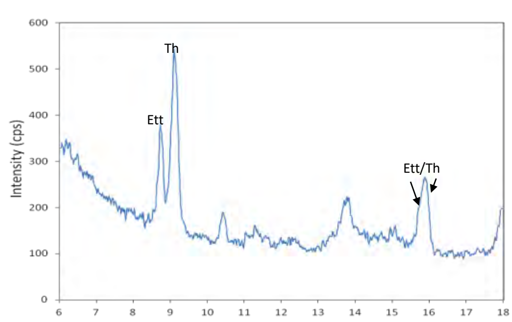


SEM Examination of Concrete Samples





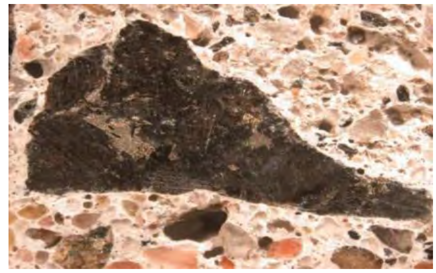


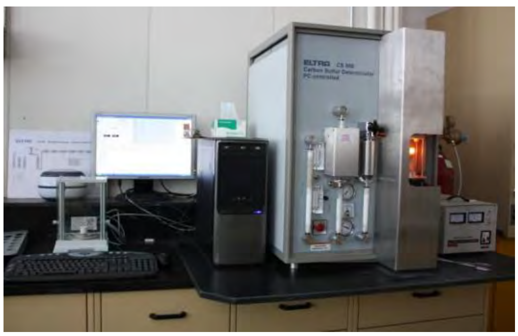


Global evaluation program of concrete aggregate

Chemical approach

Total sulfur content





Chemical approach (S_{total})

Rapid detection of the presence of iron sulfide minerals

? - Use to estimate the sulfide content (based on mineral stoichiometry)

- pyrite (FeS_2) contains 53.45% S
- pyrrhotite ($Fe_{1-x}S$) contains 37.67% S

- Assumptions
  - sulfide minerals?
  - stoichiometry?

Chemical approach (S_{total})

Method

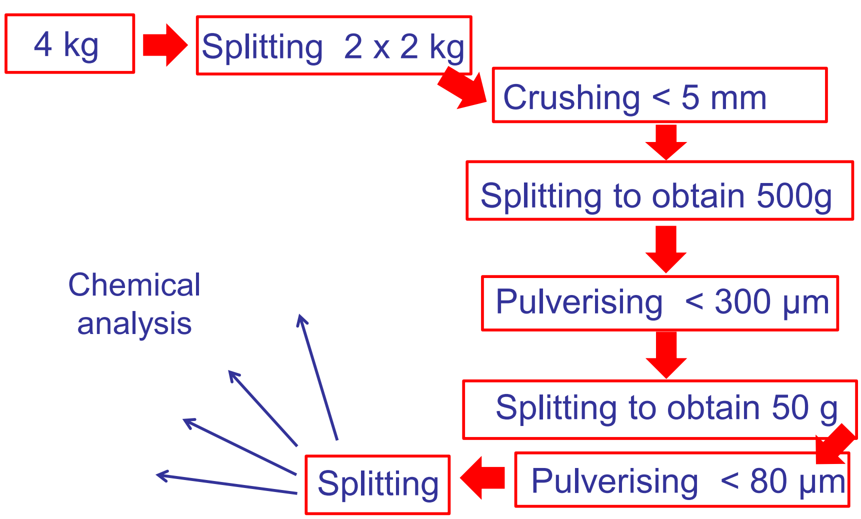
- infrared absorption method
- carbon/sulfur analyser
- sample combustion in an induction furnace
- measurement of SO_2 in the flue gas

Sub-sample

- 0.3 to 1g (important - representative of the initial sample

Chemical approach (S_{total})

Sample preparation method



Chemical approach (S_{total})

Results - interlaboratory variability

Sample	Lab 1 S (%)	Lab 2 S (%)	Lab 3 S (%)	Mean	SD	Coef. de variation (%)
GC24	0,008	0,01	<0.02	**0,009**	**0,001**	**14,9**
GC44	0,024	0,016	<0.02	**0,020**	**0,005**	**27,1**
GC50	0,003	0,002	<0.02	**0,002**	**0,000**	**17,7**
GC55	0,004	0,005	<0.02	**0,004**	**0,000**	**8,1**
GC30	0,045	0,043	0,04	**0,043**	**0,002**	**5,8**
GC46	0,048	0,038	0,04	**0,042**	**0,005**	**12**
GC61	0,058	0,052	0,05	**0,053**	**0,004**	**7,8**
GC31	0,450	0,490	0,540	**0,490**	**0,045**	**9,1**
GC27	0,102	0,088	0,1	**0,097**	**0,007**	**7,7**
GC39	0,105	0,091	0,1	**0,099**	**0,007**	**7,2**
GC34	0,151	0,16	0,16	**0,157**	**0,005**	**3,4**
GC16	0,253	0,23	0,26	**0,248**	**0,016**	**6,3**
GC19	0,228	0,24	0,26	**0,243**	**0,016**	**6,6**
GC38	0,311	0,29	0,3	**0,300**	**0,01**	**3,4**
GC36	0,336	0,33	0,34	**0,335**	**0,005**	**1,5**
GC22	0,351	0,37	0,4	**0,374**	**0,025**	**6,6**
GC5	0,377	0,4	0,44	**0,406**	**0,032**	**7,8**
GC14	0,447	0,49	0,54	**0,492**	**0,046**	**9,4**

Conclusions

In both cases:

- Pyrrhotite – main oxidized sulfide mineral
- Presence of pyrite
- Concrete elements show:
    - Map cracking
    - Deformation
    - Rust
    - Ettringite / Thaumasite (gypsum)

Unresolved Important Issues

- Role of biotite (mica) – Humidity?
- Galvanic interaction between sulfide minerals
- Presence of a siderite rim (TR) on the formation of thaumasite?

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Mineralogical properties of pyrrhotite, pyrite and associated weathering products

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Worldwide experience shows that iron-sulfides in concrete aggregates may lead to internal sulfate attack. In Norway, the problem of pyrrhotite has been revisited due to challenges regarding use of rock mass for concrete aggregate at the new Follobanen railway. The Norwegian limit value for S-total is 0.1 wt. % when pyrrhotite is present. There is no requirement for further detailed petrographic documentation. This contribution aims at shedding some light on the complexity of sulfide minerals and weathering products as a background for further research.

In Norway, the Alum Shale Committee (1947-1973) discovered that a small amount of poorly crystalline monoclinic pyrrhotite (> 0.01 %) caused catalytic oxidation of more abundant pyrite (ca 6-7 modal %) in an electro-chemical process. Severe and fast concrete degradation was due to ettringite attack (later proven to be thaumasite sulfate attack in combination with leaching and internal carbonation) and sulfuric acid. The committee concluded that acidification was related to formation of weathering minerals, such as ferrous sulfate hydrates. In general, sulfide reactivity in concrete aggregates is greatly dependent on:

- the specific surface area and reactivity of each sulfide mineral
- grain sizes and morphologies
- the number and amount of sulfides present
- the degree of weathering and presence of acid-producing soluble sulfates
- the degree to which alkaline pore water in the cement paste matrix can access reactive sulfides in aggregate particles, and hence:
  - the aggregate's resistance to microcracking
  - the presence of soluble minerals, such as microcrystalline quartz

Sulfides in black shales are very fine-grained and more reactive than their coarser grained counter parts. Research during the last two decades has established that pyrrhotite (notably Fe-deficient monoclinic species) represent anodes, whilst the reactive site in the pyrite crystal lattice is a cathode. Hence, electrochemical oxidation is intuitively also governed by pyrrhotite and pyrite connectivity. However, other textural properties are also important. The weathering products melanterite, rozenite, schwerdtmannite, copiapite and some non-stoichiometric forms of jarosite represent acid producing soluble sulfates. They sometimes form fine networks, which is not easily detected by ordinary thin section studies, and can easily be mistakenly identified as iron hydroxides (rust).

Research on acid rock drainage (ARD) represents a good source for further investigations. Results from Norwegian Public Roads Administration show that the relationship between acid producing capacity, sulfide contents and total S is not very clear. Moreover, certain weathering minerals have caused much lower pH-values than some pyrrhotites. Generally, several forms of pyrrhotite: hexagonal, monoclinic, orthorhombic and sub groups, must be considered. ARD research is presently taking advantage of textural classification as well as the acid producing and neutralisation (buffer) capacities. Although iron sulfide oxidation is mostly due to oxygen and ferric iron, nitrate and chlorine are also oxidisers.

Iron sulfide oxidation in presence of high-pH water show that precipitation of ferric iron oxide and iron-hydroxide on sulfide surfaces commonly lead to blocking for further oxidation. This mechanism may be important in presence of high oxygen levels, but might perhaps not be very relevant for the situation within concrete. There is a need for further look into the reaction mechanisms in connection with internal sulfate attack.

It is suggested that research aiming at establishing safer limiting values for sulfide contents for concrete aggregates involves: a) extensive petrographic work on a variety of relevant rock types (texture, mineralogy XRD, chemistry by SEM or EMPA, etc.), b) accelerated concrete testing under variable conditions, c) evaluation of the structural effects and d) detailed documentation of secondary minerals formed, both within aggregates and cement paste. Economic and environmentally friendly use of local aggregate may not be achieved unless a future test method includes a minimum of "strategic" petrographic information, and likely more than one single total S limiting value.

Mineralogical properties of pyrrhotite, pyrite and associated weathering products

Per Hagelia
Tunnel and Concrete Division
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Isochemical sulfate reactions are related to sulfate availability rather than amount
F. P. Glasser 1998

Introduction

- Modern concretes are **designed for service-life of 100 years**
- Challenges regarding use of sulfide-bearing aggregates, and especially the use of limiting values.
- The Norwegian limit values:
  - S-total = 1% in absence of pyrrhotite
  - S-total = 0.1 % if pyrrhotite is present
- Other countries use somewhat different limit values and approaches, likely due to «local» experience with «local» aggregates

Objectives:

- **Some fundamental properties of sulfide minerals & their weathering products**
- **The role of sulfides and secondary sulfates in internal sulfate attack**
- **Bach ground for further research into the complexity of aggregate classification/potential for sulfate attack**
- **However, not exhaustive!**

Illustrated by examples from:

- Sulfate attacks triggered by sulfides and sulfates in Norway (mainly external)
- The Norwegian Alum Shale Committee (ca 1947-1974) – an early fundamental study on the role of sulfides, weathering and severe concrete attack
- The variable reactivity of sulfides (pyrrhotite and pyrite), high-lighted by experience from acid rock drainage and other studies
- Potential role of secondary soluble minerals formed at expense of Fe-sulfides (formed by weathering or hydrothermal activity)
- Significance of geological variation: petrography/textures etc
- Aggregate – cement paste interactions: how well do we understand the processes?
- Further research towards a safe classification of aggregates

***The release mechanisms* of acid, sulfate and carbonate from sulfur bearing aggregates to the cement paste matrix *are complex*:**

***Test methods* for concrete aggregate should be established on the basis of "Enlightened reductionism"**

Norwegian Public Roads Administration

Impact of sulfide minerals (pyrrhotite) in Concrete Aggregate on Concrete Behaviour
Workshop 15th – 16th November – Oslo 2018

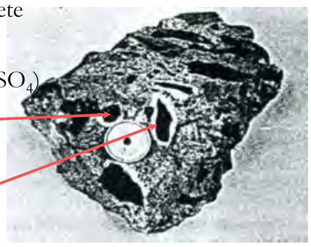
Norwegian experience with severe attack related to Alum Shale in mid (much correctly diagnosed as TSA-PCD)

- Internal swelling in shale when exposed to air (gypsum involved)
- **Severe cement paste deterioration involving mush formation after a few months or years (attributed to sulfate attack by ettringite)**
- Acid attack on steel pipes, reinforcement & concrete

Non-oxidised ground water: pH = 5-6 ($FeSO_{4(aq)}$)
Oxidised water (Vadose): pH = <3-4 ($Fe(OH)_2 + H_2SO_4$)

Alum Shale:
Carbon + Qz + Fsp + Chl + clay
+ *calcite* + *minor monoclinic pyrrhotite:* causing catalytic **oxidation of abundant pyrite**

White "ettringite" halos
Mush at more advanced stage



Internal sulfate attack related to alum shale particles
(Portland cement with 11-12 wt % C_3A)

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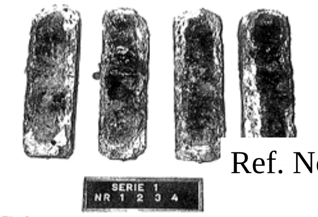
Tests performed by the Alum Shale Committee (1947-1973)



Ref. Nor PC

Silica fume

Limestone filler

Samples exposed at the «Blindtarmen» test site for 20 years

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Impact of sulfide minerals (pyrrhotite) in Concrete Aggregate on Concrete Behaviour
Workshop 15th – 16th November – Oslo 2018

Modern sprayed concrete was attacked by thaumasite! Ettringite was unimportant (NPRA-BRE work)

Thaumasite ($CaSiO_2$. $CaSO_4$. $CaCO_3$. $15H_2O$)
not ettringite ($3CaO.Al_2O_3.CaSO_4.31H_2O$)

Spalling along layer severely influenced by TSA and internal carbonation in the form of PCD: steel fibres completely destroyed

Mush zone

Åkebergveien in 2000
Thaumasite has replaced C-S-H in SRPC and SF based steel fibre reinforced sprayed concrete.
13 years old.

Thaumasite

Intact cement paste (C-S-H)

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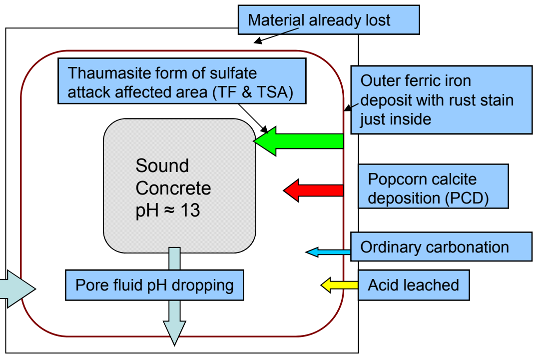
Impact of sulfide minerals (pyrrhotite) in Concrete Aggregate on Concrete Behaviour
Workshop 15th – 16th November – Oslo 2018

Petrography of old test prisms confirmed TSA-carbonation and acid attack (NPRA-BRE)

Stages 1 to 6 (outward)
- Reflect adoption to ground water chemistry
- Increasing porosity and decreasing pH.
- Reaction zones moved inward as material was lost

Groundwater; pH = (2-3) 5-6; & sulfate, bicarbonate, carbonic acid



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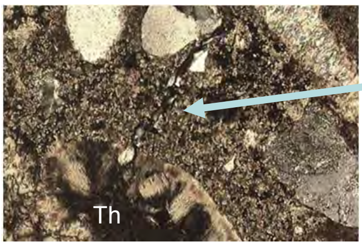
TSA-PCD in Alum shale environment

(Hagelia & Sibbick, 2009)



Full scale TSA most efficient at expense of PCD (internal carbonation) and strongly depleted CSH!
Fast degradation due to thaumasite is clearly linked to Ca-leaching!
Typical of mixes without pozzolana

Local TSA at direct expense of CSH; NOT EFFICIENT. Typical of mixes with pozzolana

This shows the importance of concrete mix design (cement type, w/b, pozzolane etc)

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Impact of sulfide minerals (pyrrhotite) in Concrete Aggregate on Concrete Behaviour

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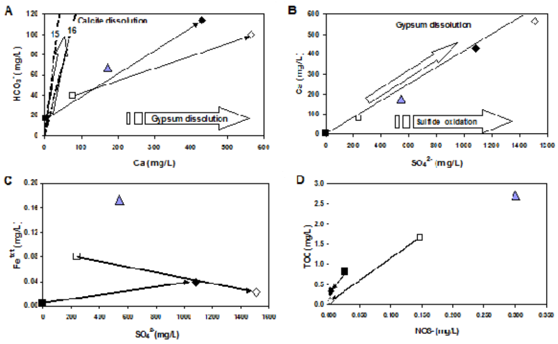
Anhydrite/gypsum may also represent source of sulfate



Alum shale may contain primary anhydrite which hydrates to gypsum
A case where ca 20 % sulfate was derived from iron sulfides
And ca 80 % sulfate derived from anhydrite (much soluble)
(Hagelia 2011)

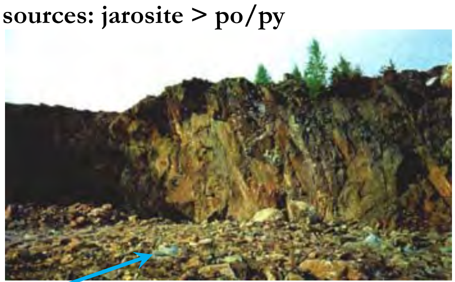
Norwegian Public Roads Administration

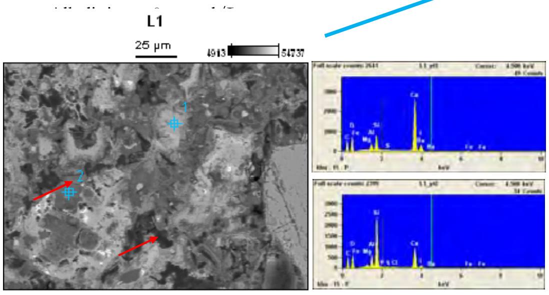
Impact of sulfide minerals (pyrrhotite) in Concrete Aggregate on Concrete Behaviour

Workshop 15th – 16th November – Oslo 2018

Old concrete lumps affected by acid rock drainage
Sulfate/acid sources: jarosite > po/py

- Rusty pyrrhotite-bearing gneiss with much old weathering FeOOH, jarosite; $(H_3O^+, K^+)Fe_3(SO_4)_2(OH)_6$ ± pyrite (**no carbonate!**)
- Total S_{rock} = 0.6-1.3 wt. %
- pH_{aq} = 3.9– 4.9
- $SO_4^{2-}{}_{aq}$ = 50-200mg/L





- Carbonated paste (1: light grey), with S = 0.02 wt.%
- Strongly Ca-depleted and carbonated paste with S = 0.02 wt.% (2: dark grey)
- Paste dissolution due to sulfuric acid (**arrows**)

“Pyrrhotite” does not imply “one single property”

$Fe_{1-x}S$,
where x varies between 0 to 0.125

Potential reactivity increases with increasing x;
reflecting decreasing disorder in the crystal lattice

- Orthorhombic
- Hexagonal
- Monoclinic

Monoclinic pyrrhotite in Oslo Alum Shale a very disordered
$FeS_{1.14}$ (many vacancies)

Pyrite(s) has more uniform properties

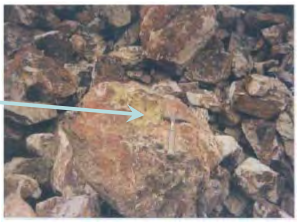
Pure **FeS_2** is least reactive
Substituted varieties with Ni, As, Cd etc are more reactive

Pyrrhotite varieties (University of Pretoria)

PYRRHOTITE SAMPLE		Ideal comp.	xC	No.	At. Metal %		At. Metal / S %		Wt Nickel %	
					Ave	2σ	Ave	2σ	Ave	2σ
2 PHASE										
Troilite and Non-magnetic Po										
Merensky: Impala (*IMP-2*)	Troilite	FeS	2C - Hex	21	49.4	*(0.67)*	0.976	*(0.026)*	0.12	(0.18)
Merensky: Impala (*IMP-2*)	Non-mag Po	$Fe_{11}S_{12}$	6C - ?	101	47.9	*(0.46)*	0.918	*(0.017)*	0.22	(0.07)
1 PHASE										
1 Phase: Non-magnetic Pyrrhotite										
Sudbury: CCN	Non-mag Po	Fe_9S_{10}	5C - Ortho	201	47.2	*(0.38)*	0.894	*(0.014)*	0.75	(0.19)
1 PHASE										
Magnetic Pyrrhotite										
Sudbury: Gertrude	Magnetic Po	Fe_7S_8	4C - Mon	194	46.4	*(0.32)*	0.867	*(0.011)*	0.82	(0.19)
Sudbury: Gertrude West	Magnetic Po	Fe_7S_8	4C - Mon	68	46.4	*(0.37)*	0.865	*(0.013)*	0.78	(0.12)
Merensky: Impala *(IMP-1)*	Magnetic Po	Fe_7S_8	4C - Mon	103	46.5	*(0.40)*	0.870	*(0.014)*	0.67	(0.27)
Nkomati: MMZ (*MMZ-4*)	Magnetic Po	Fe_7S_8	4C - Mon	42	46.5	*(0.32)*	0.870	*(0.011)*	1.10	(0.18)
Tati: Phoenix	Magnetic Po	Fe_7S_8	4C - Mon	203	46.5	*(0.33)*	0.869	*(0.011)*	1.06	(0.67)
2 PHASE										
Non-magnetic and Mag Po										
Nkomati: MSB & *MMZ-1*	Non-mag Po	Fe_9S_{10}	5C - Ortho	115	47.2	*(0.33)*	0.895	*(0.012)*	0.75	(0.10)
Nkomati: MSB & *MMZ-1*	Magnetic Po	Fe_7S_8	4C - Mon	72	46.6	*(0.35)*	0.873	*(0.012)*	0.43	(0.18)
Non-magnetic pyrrhotite		$Fe_{11}S_{12}$	6C	101	47.9	*(0.46)*	0.918	*(0.017)*	0.22	(0.07)
Non-magnetic pyrrhotite		Fe_9S_{10}	5C	316	47.2	*(0.36)*	0.895	*(0.013)*	0.75	(0.16)
Magnetic pyrrhotite		Fe_7S_8	4C	699	46.5	*(0.36)*	0.869	*(0.013)*	0.84	(0.57)

Secondary sulfates may also contribute

Mineral	Idealized formula
Melanterite	$Fe^{II}SO_4{\cdot}7H_2O$
Rozenite	$Fe^{II}SO_4{\cdot}4H_2O$
Szomolnokite	$Fe^{II}SO_4{\cdot}H_2O$
Copiapite	$Fe^{II}Fe_4^{III}(SO_4)_6(OH)_2{\cdot}20H_2O$
Römerite	$Fe^{II}Fe_2^{III}(SO_4)_4{\cdot}14H_2O$
Coquimbite	$Fe_2^{III}(SO_4)_3{\cdot}9H_2O$
Kornelite	$Fe_2^{III}(SO_4)_3{\cdot}7H_2O$
Rhomboclase	$(H_3O)Fe^{III}(SO_4)_2{\cdot}3H_2O$
Voltaite	$K_2Fe_5^{II}Fe_4^{III}(SO_4)_{12}{\cdot}18H_2O$
Halotrichite–bilinite	$Fe^{II}(Al,Fe^{III})_2(SO_4)_4{\cdot}22H_2O$
Gypsum	$CaSO_4{\cdot}2H_2O$
Chalcanthite	$CuSO_4{\cdot}5H_2O$
Schwerdtmannite	$Fe^{II}{}_{16}O_{16}(SO_4)_2(OH)_{12} \cdot nH_2O$



These are highly soluble and may therefore have a great impact on concrete even in rather small amounts

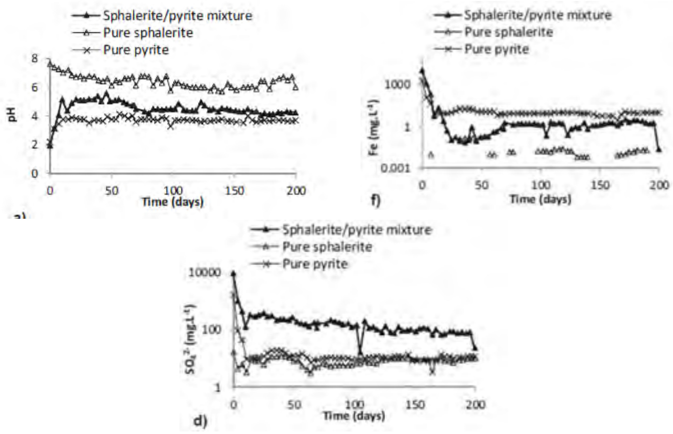
NB! May be mistaken for iron red rust in thin section

Electrochemical oxidation of pyrrhotite & pyrite

- Ever since before first World War it has been established that two or more sulfides in contact oxidise faster than separate sulfides (Gottschalk & Buehler 1912)
- The Alum Shale Committee (Bastiansen et al. 1957) tested $FeS_{1.14}$ and FeS_2 using several electrolytes*:
  - Strong galvanic interaction and fast weathering
  - Pyrite represented the positive pole with both acidic and alkaline (NaOH) electrolytes
  - Oxidation was **fastest at high pH** (comparable to cement paste)
- This is in keeping with modern research results, showing that:
  - The rate limiting step in pyrite oxidation is related to the catodic reaction (Rimstidt & Vaughan 2003)
  - Pyrrhotite behaves anodically due to its non-stoichiometry (Natarjan et al. 1983, Bhatti 1993)

) Bastiansen et al. (1957), therefore, realized that a small amount of higly disordered monoclinic pyrrhotite (ca 0.5 %) caused catalytic oxidation of more abundant pyrite

Electrochemical oxidation of pyrite & sphalerite (ZnS)



Pure and mixed powders show different behaviour
Sphalerite had some Fe. De-ionized water (Chopard et al. 2017)

Reactions – pyrrhotite (po)

Po a lot more reactive than pyrite due to much higher specific surface area (cf. MEND 1995). However, not straight forward.

$Fe_{1-x}S + (2-0.5x)\ O_2 + xH_2O \rightarrow (1-x)\ Fe^{2+} + 2xH^+ + xSO_4^{2-}$ (x = 0: no acid)

$Fe_{1-x}S + 2H^+ \rightarrow (1-3x)\ Fe^{2+} + 2xFe^{3+} + H_2S$ (non-oxidative consumes acid)

or by reaction with oxygen (oxidative);

$2Fe_{1-x}S + O_2 + 4\ H^+ \rightarrow (2-6x)\ Fe^{2+} + 4xFe^{3+} + \mathbf{2S^0}$ (protective layer) + $2H_2O$

Acidithiobacillus ferrooxidans and *Acidithiobacillus thiooxidans* can greatly facilitate pyrrhotite oxidation by *breaking the protecting layer* (Bhatti et al. 1993; Schippers and Sand 1999; Janzen et al. 2000):

$S^0 + 1.5\ O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+$ (bacterially assisted)

Then → oxidation and rust formation – more acid

Yet more possible reactions, including

$FeS_2 + 9/2O_2 + 2H_2O + 4CaCO_3 \rightarrow Fe(OH)_3 + 4Ca^{2+} + 4HCO_3^- + 2SO_4^{2-}$,

Thaumasite can form from this or other carbonate – sulfate sources

Reactions – pyrite and formation of melanterite

Oxidation of pyrite takes place where O_2 is abundant, or by ferric iron, but also NO_3^- and Cl_2 are oxidisers (cf. Appelo and Postma 2005):

$FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$ (then to ferric Fe-compounds/rust)

$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$
(Fe^{3+} ions remain if pH <3,5-4: no $Fe(OH)_3$)

$FeS_2 + 3.5\ O_2 + 8H_2O \rightarrow FeSO_4 * 7H_2O + 2H^+ + SO_4^{2-}$ (soluble melanterite)

$FeSO_4 * 7H_2O + ¼\ O_2 \rightarrow Fe(OH)_3 + 2H^+ + SO_4^{2-} + 4.5H_2O$ (ox. of melanterite)
(role of ferrous iron also stated by the Alum Shale Committee)

Rozenite behaves similarly

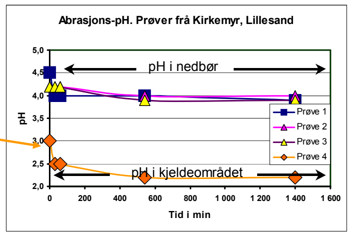
Copiapite may form: Dissolution → very high Fe^{II} & very low pH + sulfate

ARD example (no buffer)

Jarosite–FeOOH crust
no sulfide (Prøve 4)

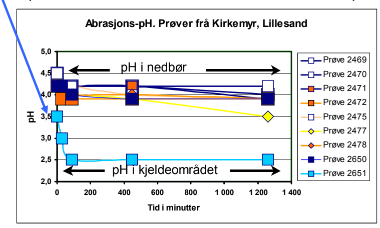
Other samples with py and po
Reached pH = 4

Selected field samples:



- **Fresh pyrrhotite: pH = 4.2**
- **Degraded pyrrhotite pH = 4-3.8**
- **Fresh pyrite from joints pH ca. 2.5**
- **Oxidised pyrite from joints, pH ca. 4**

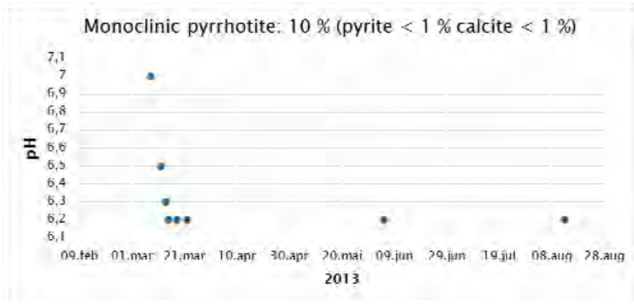
Sulfide separates:
(mortar crush of 125-250 micron):



10 wt. % pyrrhotite – yet no real acidification!



% pyrrhotite from XRD (Rietveld refinement)

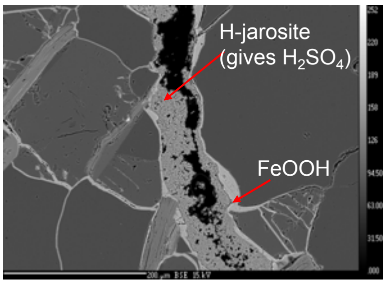


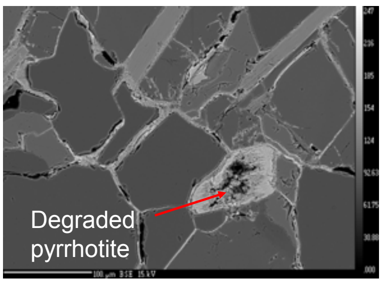
Hornfels
Very hard rock!

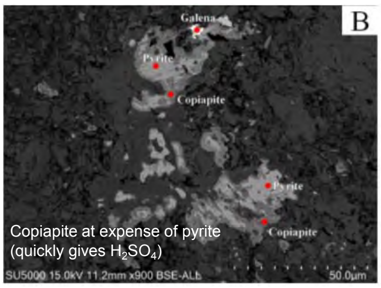
Tested: 0 to 10-20 mm fragments

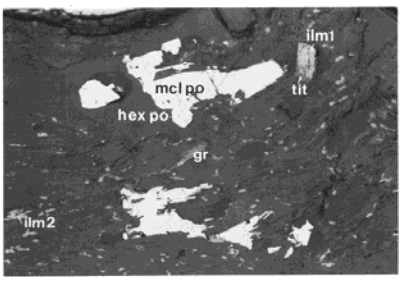
pH still remains at 6.2!
(after 5,5 years),
but all fragments have broken down to fines

Examples of natural microstructures in sulfide-bearing rocks









Reactivity of sulfide-bearing natural rocks (not just pure pyrrhotite or pyrite)

In general, sulfide reactivity in concrete aggregates is greatly dependent on:

- the specific surface area and reactivity of each sulfide mineral
- grain sizes and morphologies
- the number, amount and type of sulfides present (connectivity etc)
- the degree of weathering and presence of acid-producing soluble sulfates
- the degree to which alkaline pore water in the cement paste matrix can access reactive sulfides in aggregate particles, and hence:
  - the aggregate's resistance to microcracking
  - the presence of soluble minerals, such as microcrystalline quartz

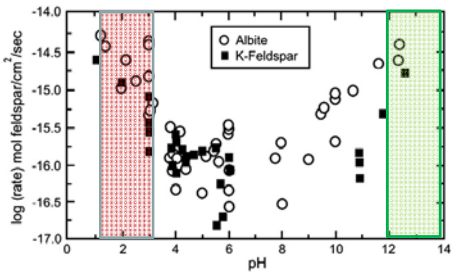
Characterisation by petrographic and other techniques is mandatory for realistic understanding!

Accessibility of cement paste fluids for interaction with aggregate sulfides

- Microcracks in aggregates represent primary fluid conduits
- Los Angeles results seem relevant (lower range LA should be safer)
- w/b-ratio
- Solubility properties of aggregate minerals: secondary conduits:

  - microcrystalline quartz etc. dissolve at high pH: also feldspars, micas

  - once sulfide oxidation (± sulfate acidifiers): very low pH at micro-scale leading to further dissolution of common rock forming minerals



pH in fresh concrete

pH from sulfide-bearing rocks

Norwegian Public Roads Administration

Impact of sulfide minerals (pyrrhotite) in Concrete Aggregate on Concrete Behaviour
Workshop 15th – 16th November – Oslo 2018

ARD classification by detailed petrography gives better prediction

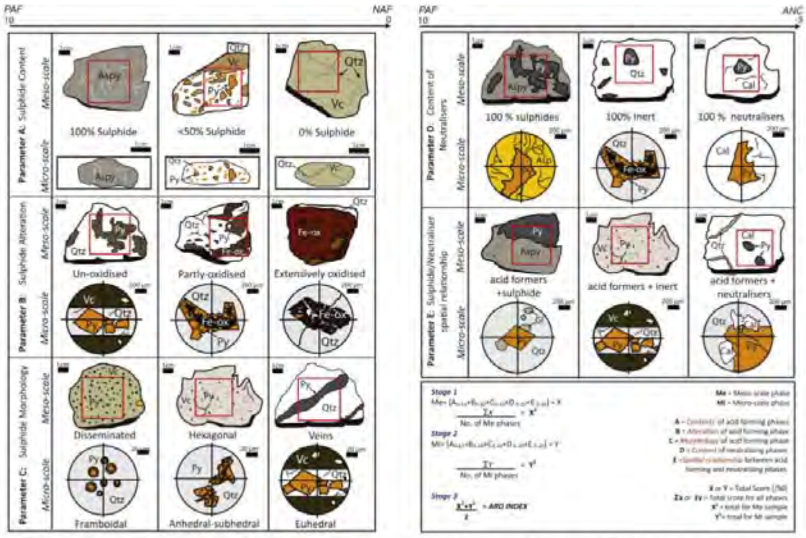


Figure 72 - Cartoon examples of ARD Index method for classification of a rocks ARD potential (Parbhakar-Fox et al., 2011)

Norwegian Public Roads Administration

Impact of sulfide minerals (pyrrhotite) in Concrete Aggregate on Concrete Behaviour
Workshop 15th – 16th November – Oslo 2018

Some recommendations for further research

Research aiming at establishing safer limiting values for sulfide contents in concrete aggregates should involve:

- extensive petrographic work on a variety of relevant rock types (texture, mineralogy XRD, chemistry by SEM or EMPA, etc.)
- accelerated concrete testing under variable conditions (if T = 80 °C: what's in it for us?, primary ettringite dissolves!)
- evaluation of the structural effects on test concrete, and
- detailed documentation of secondary minerals formed in test concrete, both within aggregates and cement paste.

Economic and environmentally friendly use of local aggregate may not be achieved unless a future test method includes a minimum of "strategic" petrographic information, and likely more than one single total S limiting value.

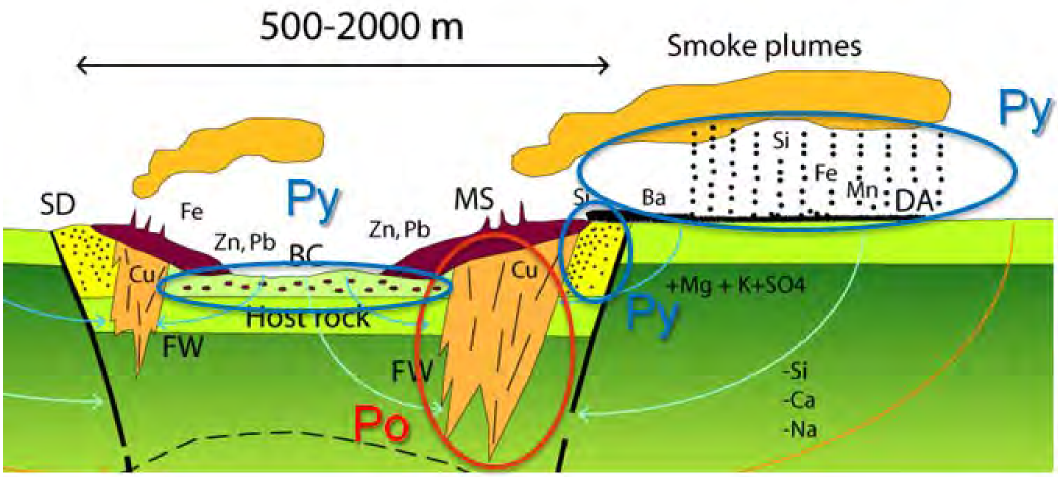
Iron sulphides: Formation and conditions for occurrence in bedrock

Terje Bjerkgård, NGU

Iron sulphides and their weathering products are the major minerals causing acid rock drainage. Other sulphides containing copper, zinc, lead, arsenic, cadmium, etc are rare, but may locally (i.e. in ore districts) be important.

Pyrite is by far the most common sulphide and is a common accessory in felsic igneous rocks and sedimentary rocks, especially carboniferous (organic-rich) sediments. It is abundant in hydrothermal mineralisations and deposits, and in various zones of wallrock alteration, related to hydrothermal activity.

Pyrrhotite is the other common sulphide (albeit less common than pyrite), occurring in mafic to ultramafic igneous rocks, in metasedimentary rocks (schists and paragneiss), in ore deposits (esp. Cu-Ni magmatic deposits) and in certain zones of wallrock alteration, related to hydrothermal activity. Pyrrhotite also forms from pyrite during metamorphism, excess sulphur reacting with iron released from Fe-Mg minerals.

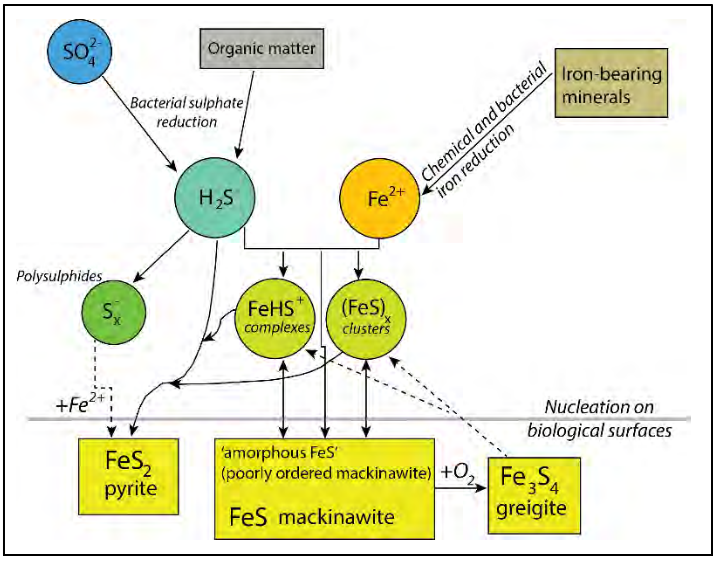


Schematic model of massive sulphide deposit (VMS), showing the main deposits of pyrite (Py) and pyrrhotite (Po) (Modified from Franklin et al. 2005).

In massive sulphide deposits, pyrrhotite is mainly found in the unconformable feeder zone beneath the massive sulphide, whereas pyrite occurs in the massive deposit, in disseminations beside the deposit and in extensive zones and layers distal to the deposit.

Marcasite is formed as a primary phase under low-T acidic conditions. It occurs in sedimentary rocks (shales, limestone and low-grade coals) and in low-T hydrothermal veins. In black shale (e.g. alum shale) it often forms concretions. It forms secondary from pyrrhotite, pyrite or chalcopyrite.

Mackinawite and *Greigite* are mainly products from sulphate-reducing bacteria and occur in clay- and organic rich shales. The minerals transform to pyrite during diagenesis, often forming fine-grained aggregates known as framboids.



Pathways leading to the formation of pyrite and other iron sulphides in the sedimentary environment (modified from Berner, 1984)

Pyrrhotite is generally much more susceptible to oxidation than pyrite, but especially sedimentary (framboidal) pyrite is readily attacked by oxidising solutions. Marcasite, mackinawite and greigite are rare, but may locally contribute to acid drainage.

Acidity because of dissolution of sulphides attacks silicates (e.g. feldspar) leading to formation of sulphates like jarosite, which are sinks for metals like Cu, Zn, Pb, Cd. Under low pH conditions (<3.5), jarosite is unstable and the toxic metals are released.

Lithologies which most likely are enriched in iron sulphides include felsic and mafic metavolcanics (i.e. quartz-feldspatic rocks/schists and amphibolites, respectively), shales (e.g. alum shale) and schists (esp. black schists) and gneisses of sedimentary origin.

Berner, R.A., 1984: Sedimentary pyrite formation: An update. Geochimica et Cosmochimica Acta, vol. 48, p.605-615.

Franklin, J. M., Gibson, H. L., Jonasson, I. R., Galley, A. G., 2005. Volcanogenic Massive Sulfide Deposits. Economic Geology 100th anniversary Volume, p. 523-560.

Iron sulphides:

Formation and conditions for occurrence in bedrock

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Iron Sulphides:

Pyrite – FeS_2 (cubic)

Pyrrhotite – $Fe_{1-x}S$ (x: 0-0.125)

Marcasite – FeS_2 (orthorhombic)

Mackinawite – $(Fe,Ni)_{1+x}S$ (x: 0-0.1)

Greigite – Fe_3S_4

Other important sulphides:

Pentlandite – $(Fe,Ni)_9S_8$ (Fe:Ni ~1:1)

Chalcopyrite – $CuFeS_2$

Sphalerite – (Zn,Fe)S

Arsenopyrite – FeAsS

Galena – PbS

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Pyrrite FeS_2:

Most common iron sulphide.

Common accessory in felsic intrusive and extrusive rocks, less common in mafic to ultramafic rocks.

Common accessory in sedimentary rocks, especially black (carbonaceous, organic-rich) sediments.

In iron-rich sediments where additional sulphur has reacted with iron-rich minerals (e.g. iron oxides).

Hydrothermal mineralisations and deposits, and various zones of wall rock alteration related to hydrothermal activity.

Regarded as the most stable iron sulphide, but 'sedimentary pyrite' esp. framboidal, is very unstable to weathering.

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Pyrrhotite $Fe_{1-x}S$ (x: 0-0.125):

Less common iron sulphide than pyrite.

Common accessory in mafic to ultramafic rocks, often with some chalcopyrite. Pyrrhotite is less common in felsic rocks.

Common accessory in metamorphosed sedimentary rocks, especially black (carbonaceous) schists.

Accessory in metamorphic rocks/schists, in which sulphur has been released or introduced and reacted with iron-bearing minerals.

Hydrothermal mineralisations and deposits, and certain zones of wall rock alteration related to hydrothermal activity (pyrite more common).

Generally more unstable to weathering than pyrite.

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Pyrrhotite $Fe_{1-x}S$ (x: 0-0.125):

Most common polytypes (stoichiometry approximate):

Fe_7S_8 – 4C (monoclinic) - magnetic

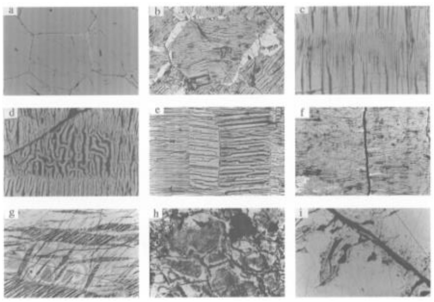
Fe_9S_{10} – 5C (monoclinic)

$Fe_{10}S_{11}$ – 11C (orthorhombic)

$Fe_{11}S_{12}$ – 11H (hexagonal) - nonmagnetic

Monoclinic polytypes are stable at lower temperatures.

Hexagonal varieties more prone to weathering than monoclinic (?)



Very often intergrowth of the monoclinic and hexagonal polytypes

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Marcasite FeS_2:

Marcasite is formed as a primary mineral under low-temperature highly acidic conditions (generally pH<5).

It occurs in sedimentary rocks (shales, limestones and low grade coals) as well as in low temperature hydrothermal veins.

In black shale (e.g. alum shale) often forms concretions with radiating structures.

It forms secondary from pyrrhotite, pyrite or even chalcopyrite.

Marcasite is much less stable in humid conditions than pyrite.

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Mackinawite $(Fe,Ni)_{1+x}S$ (x: 0-0.1):

Formed by sulphate-reducing bacteria. ($SO_4^{2-} \rightarrow H_2S$).
It occurs in clay- and organic-rich shales. "Zwischen-product" which transforms to greigite and pyrite in sedimentary environments.

Occurs in serpentinites (altered ultramafic rocks)
and in certain sulphide deposits (with Cu, Ni).

Unstable phase.

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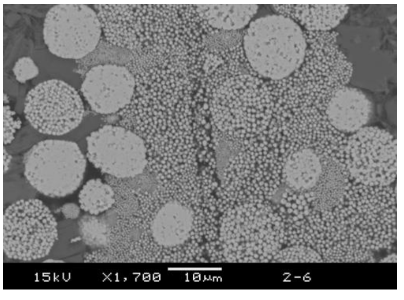
Greigite Fe_3S_4 :

Sulphide-analogue to magnetite (same structure).
Formed by sulphate-reducing bacteria. ($SO_4^{2-} \rightarrow H_2S$).
Sulphide reacts with detrital iron-bearing minerals, forming framboids. By diagenesis changes into pyrite.

It occurs in clay- and organic-rich shales. Rare in low temperature hydrothermal veins.



Unstable phase, more common than anticipated?

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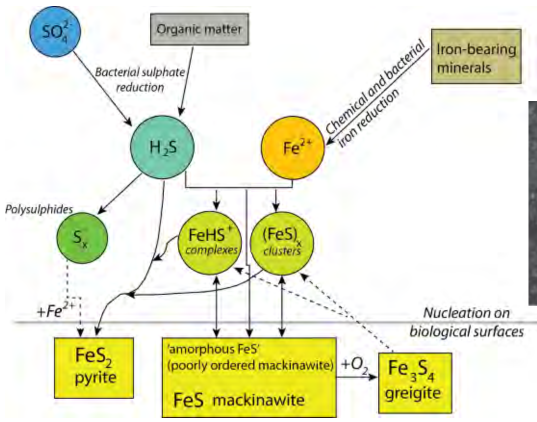
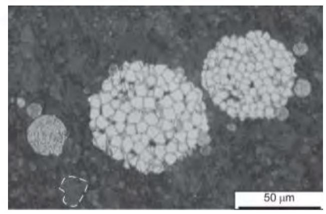
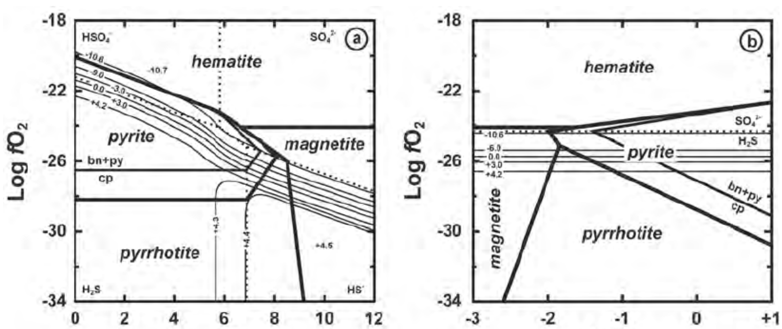
Formation of mackinawite, greigite and pyrite in sedimentary environments:





Mackinawite and greigite, amorphous or as framboids, transform into pyrite.

Pyrrhotite and pyrite stabilities:



Diagrams for 400 °C, 4.0 Kbar

Pyrrhotite more stable in reducing conditions and with lower activities of sulphur.

Pyrrhotite more stable with increasing T and P.

Pyrite forming pyrrhotite during metamorphism:

During release of metamorphic water (above 450 °C):

$FeS_2 + H_2O \rightarrow FeS + H_2S + 0.5O_2$

In carbonaceous schists (250-300 °C):

$2FeS_2 + 2H_2O + C \rightarrow 2FeS + 2H_2S + CO_2$

Excess sulphur reacts with available iron:

$FeS_2 + Fe^{2+} + H_2O + 0.5C \rightarrow 2FeS + 2H^+ + 0.5CO_2$

Iron comes from iron-rich minerals, e.g. iron-oxides, biotite, pyroxene, amphibole, chlorite, etc.

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Relative susceptibility to oxidation:

Pyrrhotite > Sphalerite/Galena > Pyrite/Arsenopyrite > Chalcopyrite > Magnetite

Since pyrite and pyrrhotite are much more abundant than any other sulphides, they are the main cause of acid rock drainage, except in mining areas.

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Dissolution of iron sulphides:

Pyrite breakdown reaction (general):

$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3^- + 16H^+ + 8SO_4^{2-}$

includes:

$4Fe^+ + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$ (ferrous to ferric iron)

$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 16H^+ + 2SO_4^{2-}$ (ferric iron oxidises pyrite)

Pyrrhotite breakdown reaction:

$FeS + O_2 + 5H_2O \rightarrow Fe(OH)_3^- + 10H^+ + SO_4^{2-}$

Acidity will attack other phases, including
Cu, Zn, Pb, As and Ni-bearing sulphides.

Sulphate may react with Ca if available, forming gypsum

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Iron sulphides to sulphates:

Decomposition of silicates, e.g. feldspar under the acidic conditions result in formation of jarosite minerals:
$(K,Na,H_3O)Fe_3(SO_4)_2(OH)_6$

K-, Na-jarosite is generally quite stable at pH>3.5, H_3O-jarosite more unstable

Jarosites are sinks for metals like Cu, Zn, Pb, Cd, which may later be released under dissolution.

Oxidised sulfides forming goethite and jarosite

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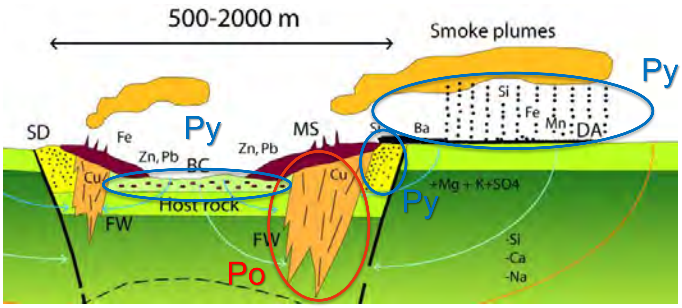
Iron sulphides related to VMS deposits



SD = Disseminated sulfide
MS = Massive sulfides
DA = Distal products
BC = Breccia, talus deposits
FW = Footwall alteration zone

Pyrite most common in massive sulphide, distal products, breccias and outer alteration halo.

Pyrrhotite abundant in the central footwall alteration zone and lower part of massive sulphide.

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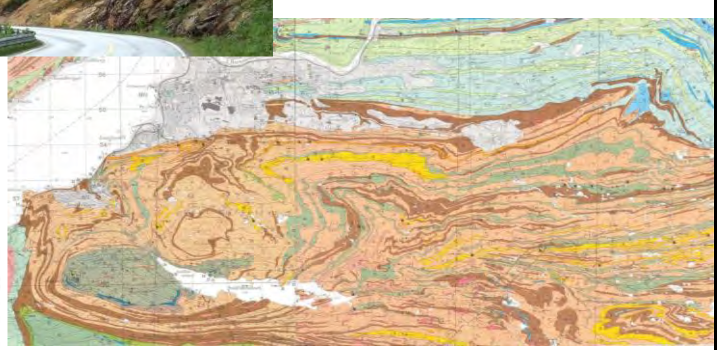
Iron sulphides related to VMS deposits

Pyrite-rich schists east of Mo i Rana.

10s of km in length and
10s of meter in thickness



- Grey gneiss
- Keratophyre/rhyodacite
- Amphibolite
- Pyritiferous biotite(-muscovite) schist
- Pyritiferous muscovite schist
- Pyritiferous amphibole-mica schist

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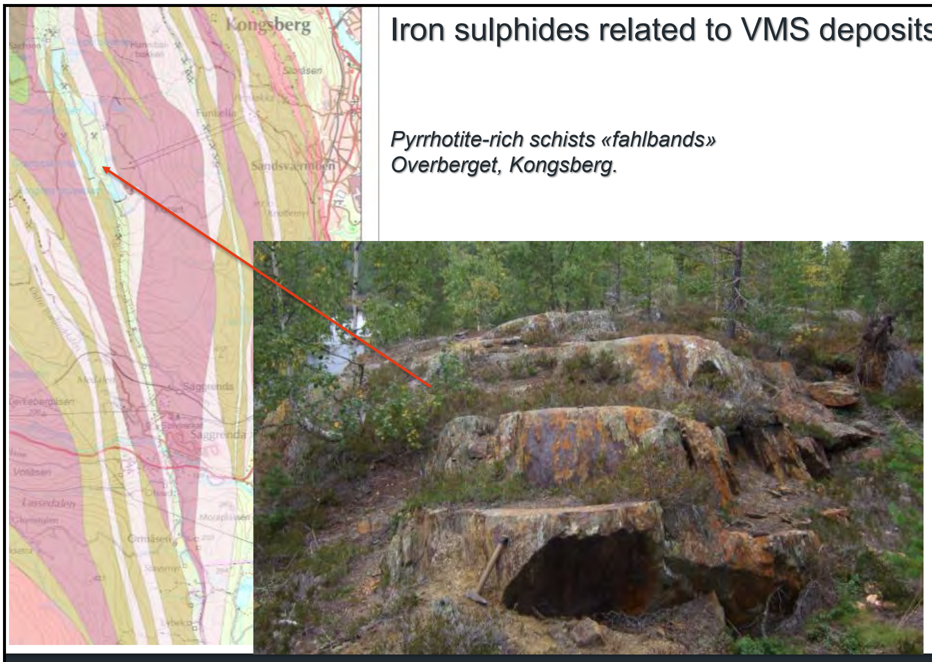

Iron sulphides related to VMS deposits

Pyrrhotite-rich schists «fahlbands»
Overberget, Kongsberg.

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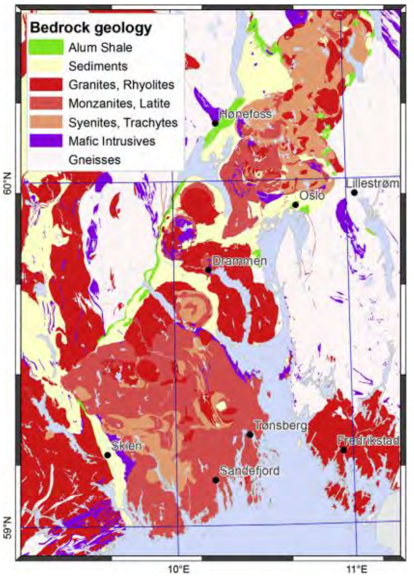
Iron sulphides in sedimentary sequences/units

Alum shale – pyrite and marcasite-bearing



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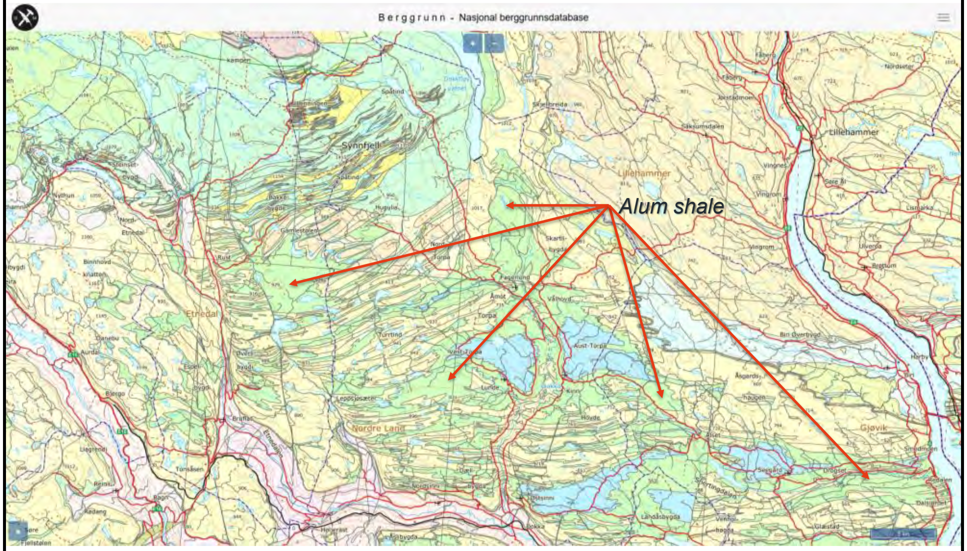
Iron sulphides in sedimentary sequences/units



Pyritiferous schists in the parautochthonous below the Caledonian Nappes

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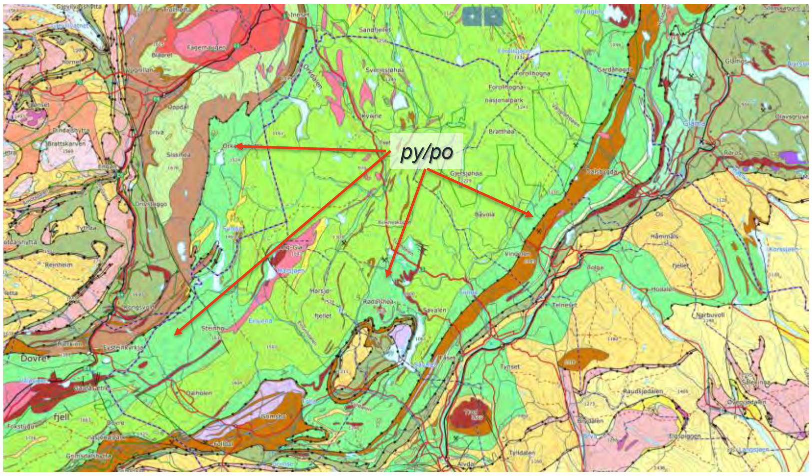
Iron sulphides in black schists



Pyrite/pyrrhotite-bearing black schists in the Caledonian Nappes in Hedmark and Trøndelag. (py/po)

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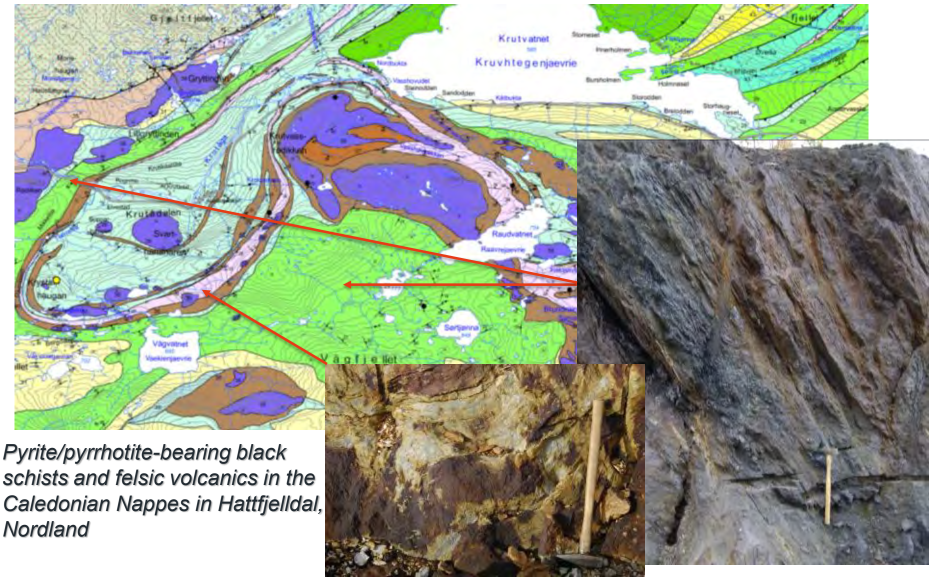
Iron sulphides in black schists



Pyrite/pyrrhotite-bearing black schists and felsic volcanics in the Caledonian Nappes in Hattfjelldal, Nordland

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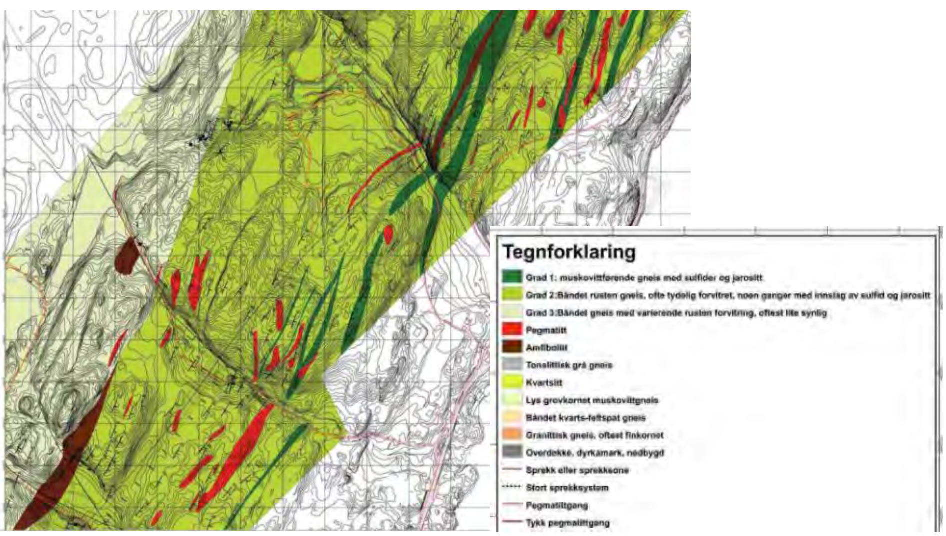
Iron sulphides and sulphates in gneissic units (paragneisses)



Rusty (pyrrhotite/jarosite) gneisses in the Lillesand district.

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Summary

Sulphide-bearing lithologies include:

- Felsic and mafic metavolcanics and intrusives
- Low-grade sediments (shales, esp. carbonaceous)
- Metasediments – esp. black schists
- Gneisses of sedimentary origin (paragneiss): **py → po**
- Lithologies subjected or related to hydrothermal activity

Pyrrhotite is more unstable than pyrite, but is much less common, thus pyrite, esp. "sedimentary pyrite", is also a major concern. Locally marcasite and greigite could be a problem.

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Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

Andreas Leemann, Empa, Switzerland

A 50 year old Swiss dam with a length of 290 m and a maximum height of 36 m is showing a steady expansion since 30 years. As 20-25 % of the Swiss dams are affected by alkali silica reaction (ASR), it was assumed at first that this is the cause for the observed behaviour. However, iron hydroxide formation and a “sulphurous smell” in the gallery of the dam suggest that iron sulphide oxidation is present as well and as such could lead to concrete expansion.

Oxidation of iron sulphides in concrete aggregates has been reported in various studies. The kinetics of iron sulphide oxidation increases with increasing pH, if sufficient moisture and O_2 are available. Additionally, a faster reaction occurs with decreasing grain size. Generally, pyrrothite ($Fe_{(1-X)}S$) reacts faster than pyrite (FeS_2). In order to clarify the cause for expansion in the dam, a microstructural investigation was performed.

After a coring campaign, samples were prepared for optical and scanning electron microscopy. Chemical analysis was performed by energy dispersive X-ray spectroscopy (EDS).

The aggregates consist mainly of biotite schist (80 %) with a minor amount of muscovite schist (15%) and traces of granite (~ 2%) and dolomite (~ 2%). The average iron sulphide content in the aggregates is 0.3-0.4 volume-%.

Fully or partly oxidized iron sulphide particles are present in the aggregates. Moreover, oxidation products present in the cement paste clearly indicate that at least part of the oxidation in the aggregates occurred after concrete production. Some of the oxidized ores are connected with crack formation, others show no connection to concrete cracking. Pyrrhotite shows a higher degree of oxidation compared to pyrite. The presence of ettringite in the typical pockets of former tricalcium aluminate clinker particles usually occupied by monocarbonate/monosulfate indicates a reaction of the sulfur released by iron sulphide oxidation with the cement paste.

However, the dominating degradation process in the concrete is ASR. There is extended cracking starting in aggregates containing ASR products. Most of the cracks in the aggregates are only partly filled with ASR products, whereas the cracks in the cement paste are usually filled with extruded products. The majority of iron hydroxides originating from iron sulphide oxidation that are present in the cement paste is bound into ASR products.

The microstructural analysis reveals that iron sulphide oxidation leading to crack formation occurs in the concrete. Additionally, the released sulfur leads to ettringite formation in the cement paste. But the main cause of crack formation and likely dam expansion is nevertheless ASR.

Data of this case study have been published in [1]. Additional samples have been studied after the publication of the paper.

[1] Schmidt T, Leemann A, Gallucci E, Scrivener K. Physical and microstructural aspects of iron sulfide degradation in concrete. Cement and Concrete Research. 2011 Mar 1;41(3):263-9.

Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

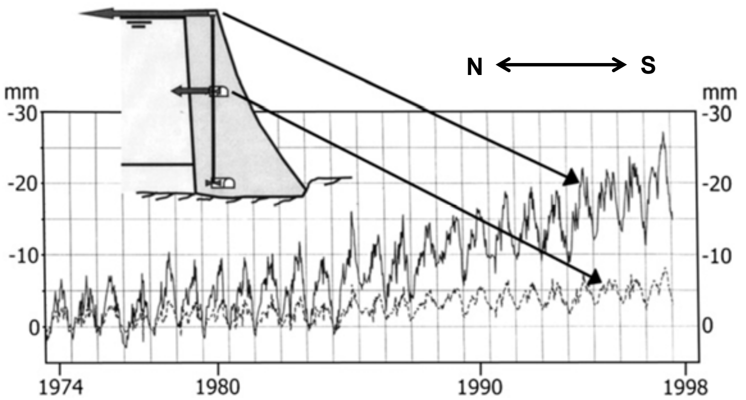
Content

Original data published in Schmidt et al., CCR, 2011
Additional samples analysed after paper publication

Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

Introduction

- Gravity dam (length: 290 m, maximum height: 36 m
- Continuous expansion starting in mid eighties



Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

Introduction

- Displacement at top (upstream): 20 mm
- Displacement at level of gallery: 5 mm
- ASR? (20-25% of Swiss dams affected)
- But:
  - sulfurous smell in gallery
  - iron hydroxides in drainage channels of gallery
  - possible iron sulfide oxidation

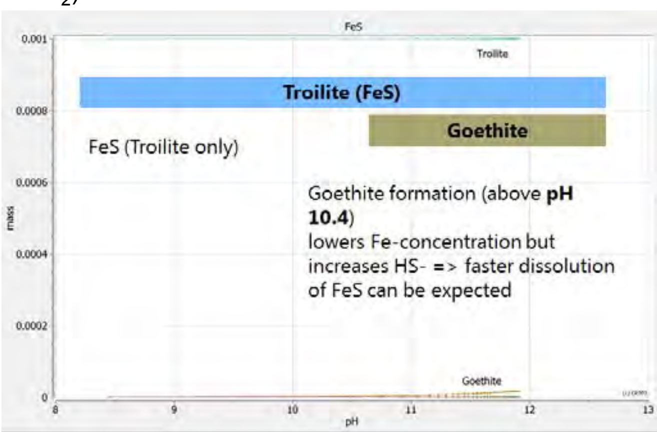
Pyrrhotite (troilite): $2FeS + 2H_2O + 4.5O_2 \rightarrow Fe_2O_3 + 2H_2SO_4$

Pyrite/marcasite: $2FeS_2 + 4H_2O + 7.5O_2 \rightarrow Fe_2O_3 + 4H_2SO_4$

Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

Thermodynamics

- FeS increasingly destabilised to goethite as pH increases (in absence of O_2)

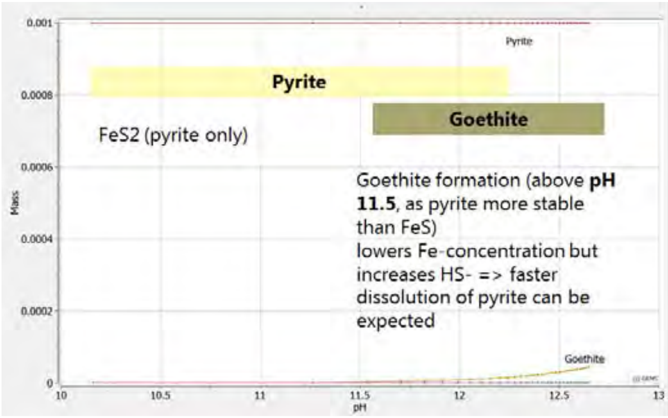


B. Lothenbach

Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

Introduction

- FeS_2 increasingly destabilised to goethite as pH increases (in absence of O_2)



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Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

Materials

- Various cores (Ø 100 mm) of dam (produced with CEM I)
- Prisms (7 x 7 x 28 cm^3, 350 kg/m^3 CEM I, w/z 0.50)

Methods

- Lab samples: storage in water at 60°C for five years
- Optical microscopy
- Scanning electron microscopy with energy-dispersive X-ray spectroscopy

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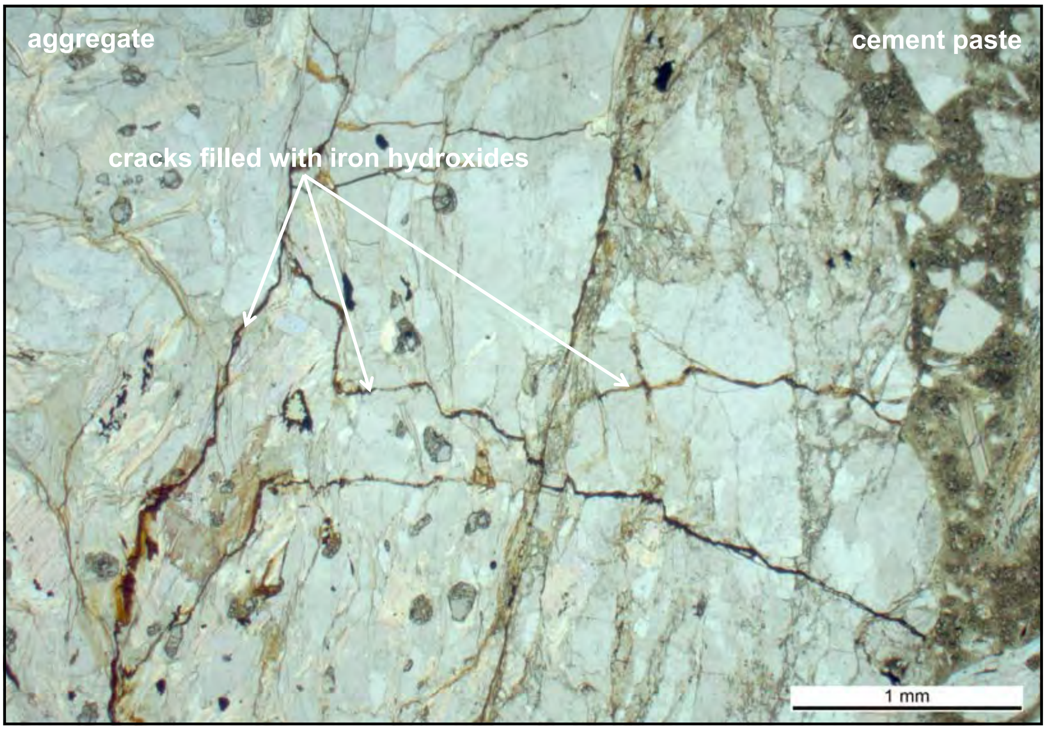
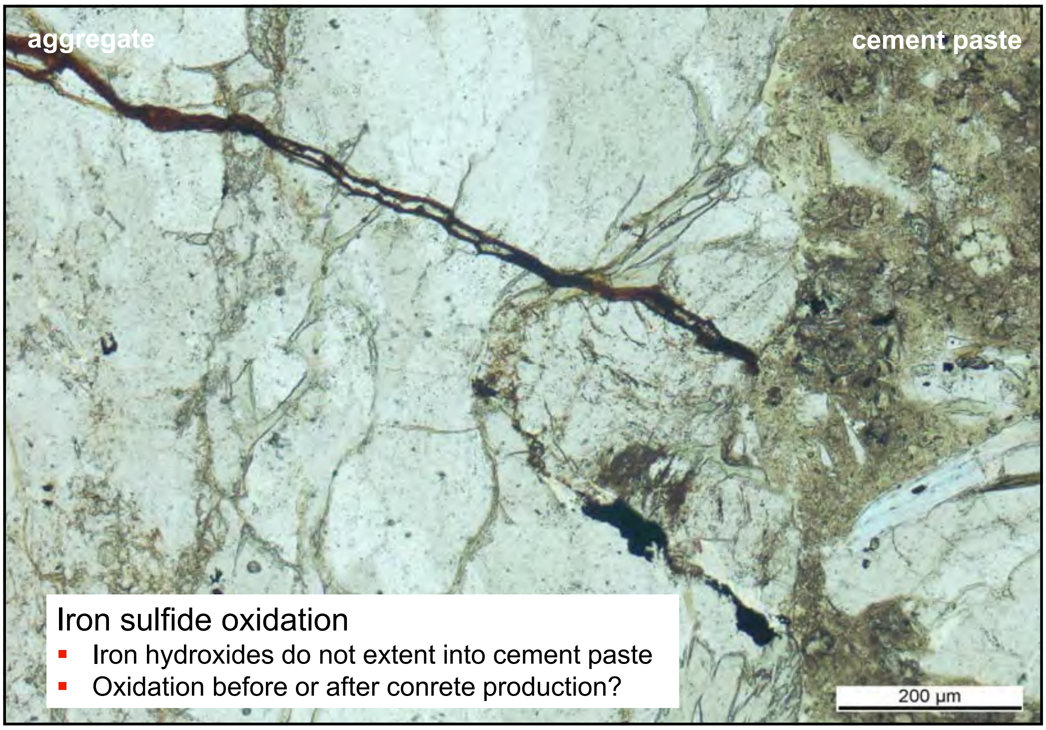
Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

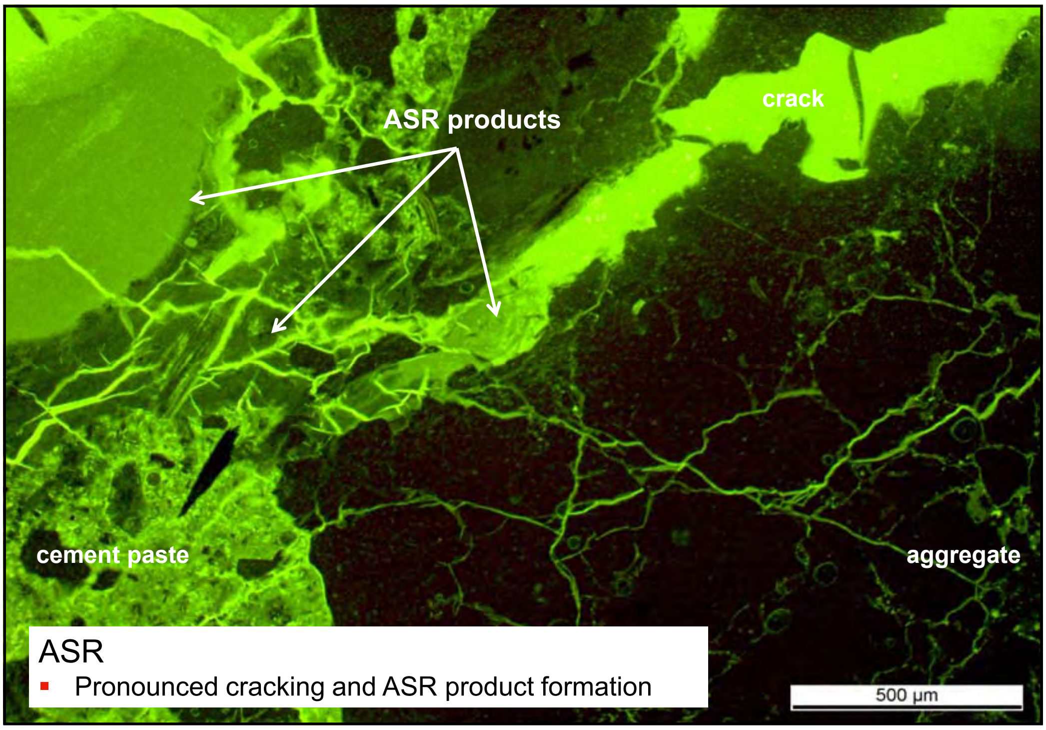
Aggregates

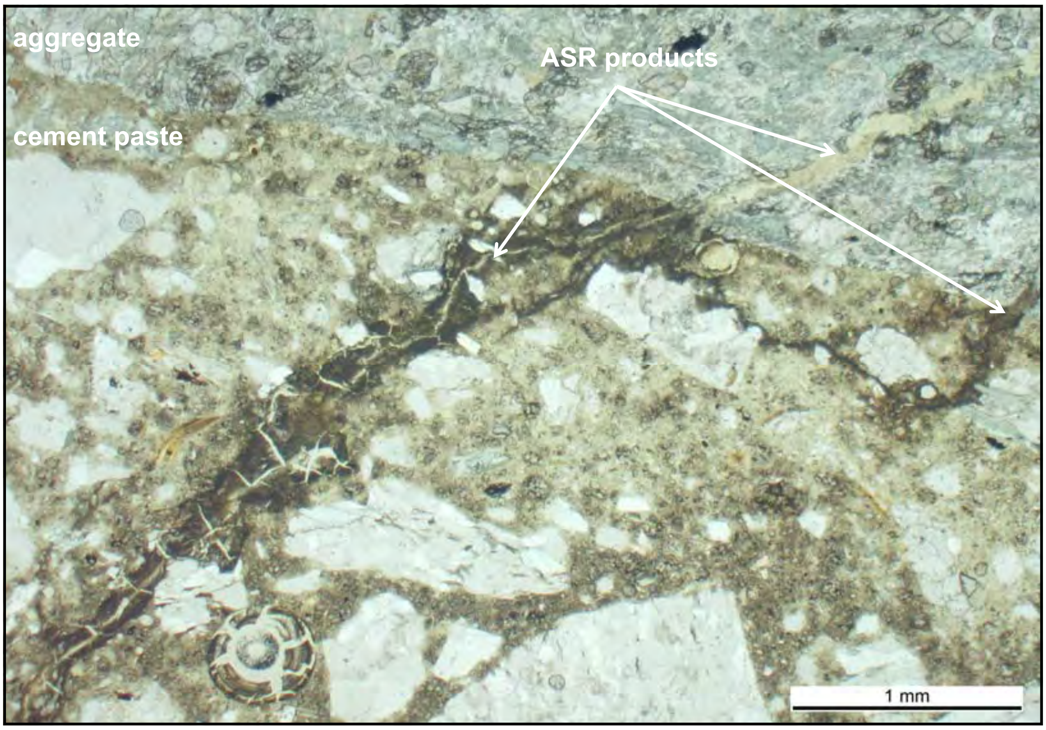
- biotite schist (80 %)
- muscovite schist (15%)
- granite (~ 2%)
- dolomite (~ 2%)

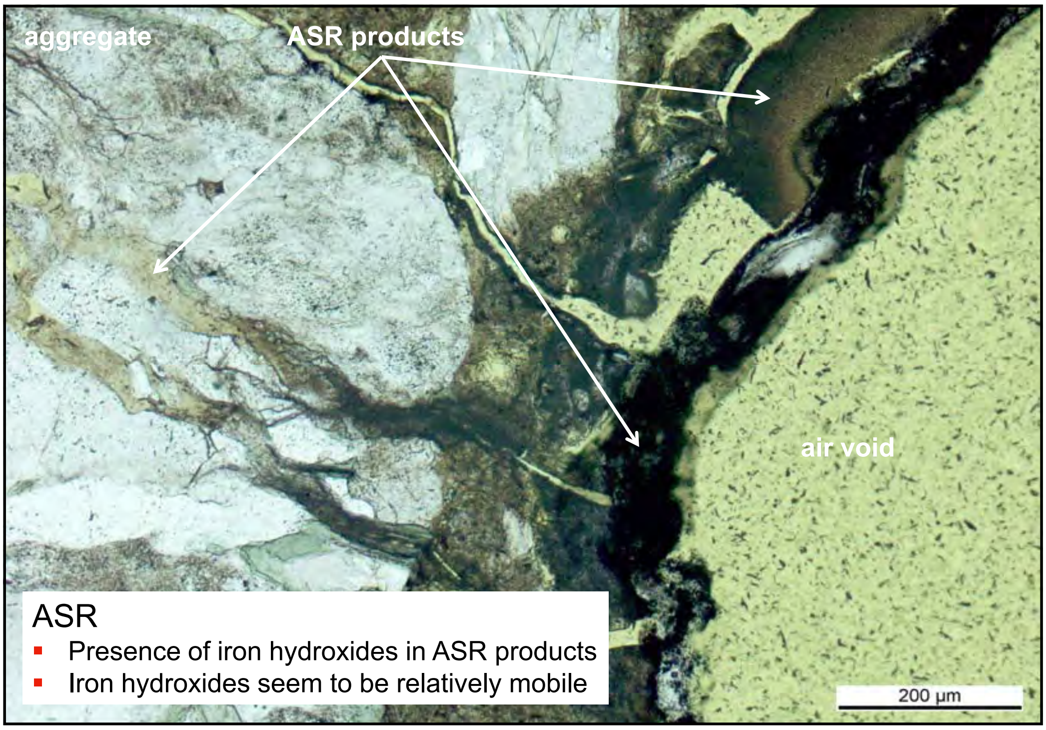
- total iron sulphide content: 0.3-0.4 volume-%




aggregate
cement paste
Iron sulfide oxidation
Iron hydroxides do not extent into cement paste
Oxidation before or after conrete production?
200 µm


ASR products
crack
cement paste
aggregate
ASR
Pronounced cracking and ASR product formation
500 µm

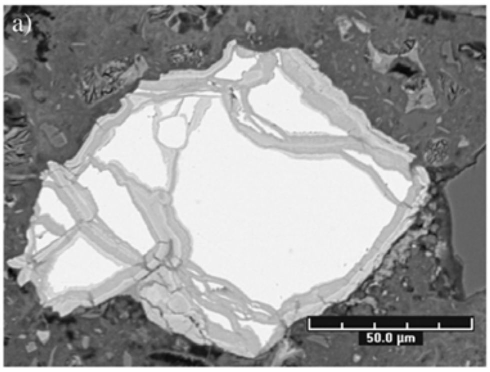


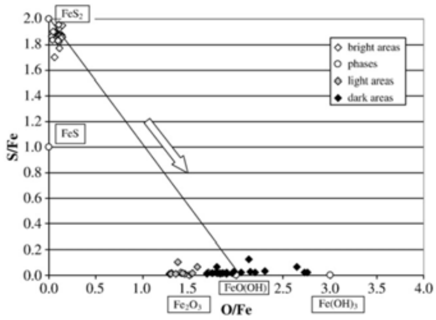


ASR
- Presence of iron hydroxides in ASR products
- Iron hydroxides seem to be relatively mobile

Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

Oxidating iron sulfides

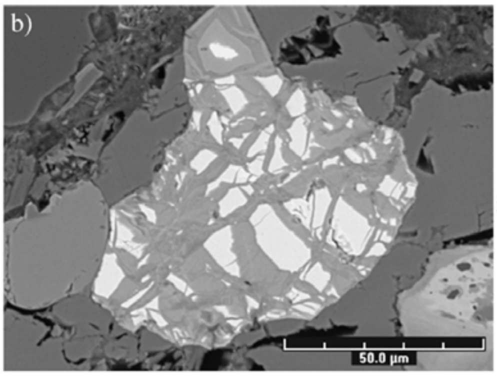


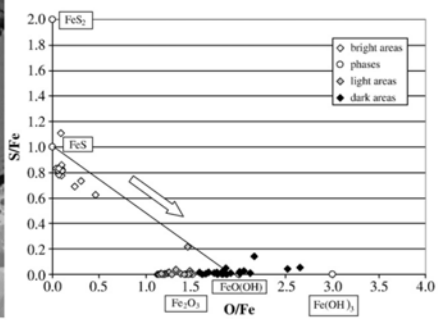


- Pyrite/marcasite (FeS_2) mostly with little oxidation products
- Oxidation still possible

Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

Oxidating iron sulfides



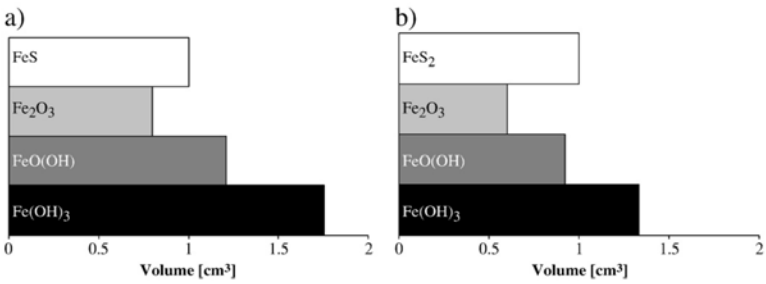


- Pyrrhotite (Fe(1-x)S often with oxidation products
- Less stable than pyrite

Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

Oxidating iron sulfides

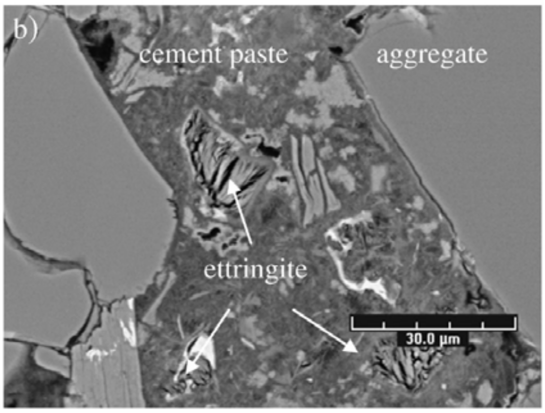
- Substantial (theoretical) volume increase due to oxidation



- Degree of iron sulfide oxidation about 60% in dam concrete
- Degree of iron sulfide oxidation lower in lab samples

Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

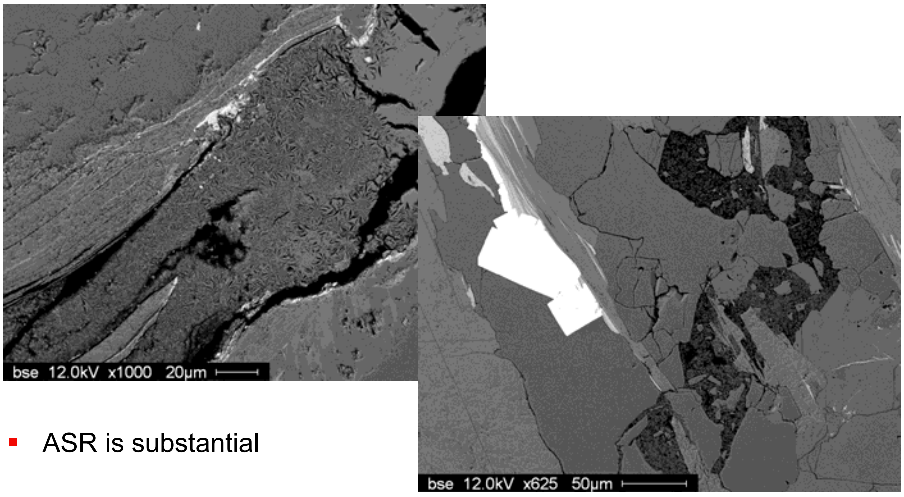
Oxidating iron sulfides



- Sulfur release by iron sulfide oxidation: AFm → ettringite
- Maximum possible SO_3 release of 1.6 mass-% (in relation to cement)

Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

ASR



- ASR is substantial

Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

Summary

- Dam concrete exhibits iron sulfide oxidation and ASR
- Iron sulfide oxidation
  - Pyrrhotite less stable than pyrite
  - Cracking of aggregates possible
  - Iron sulfide concentration in aggregates is low (0.3-0.4 vol-%) and average degree of oxidation is about 60% (30-40% in lab samples)
  - Released sulfur reacts with AFm phases and forms ettringite (with higher amount of oxydated iron sulfides acid attack and thaumasite formation likely possible)
  - No distinction about time of oxidation possible (before or after concrete production)
  - Sufficient supply of oxygen seems to be given
- Extended concrete cracking due to ASR
- Dam expansion mainly attributable to ASR

Suddenly the aggregates for concrete are a risk for the durability of the structure - experiences from the material management project for the Gottard Basetunnel using AAR as an example

Alkali aggregate reaction (AAR) is not pyrrhotite in concrete. The Gotthard Base Tunnel (GBT) is not the Follo Line Project. But there are similarities.

At GBT, the unexpected AAR issue questioned the concept of materials management and with it the whole project.

The GBT started operation in 2016 as a 52 km long railway tunnel. Project planning and construction essentially took place between 1994 and 2016. Beforehand, however, work has started in 1971 with the contract with the Swiss Federal Railways (SBB) and in 1991 with the decision of the Federal Assembly on the project.

The AAR is primarily a chemical reaction between reactive aggregate particles and free alkalis in the pore water in concrete. The reaction product is an expansive gel which leads to cracks and in the worst case to the destruction of the concrete. The affected structures are usually between 20 and 40 years old.

AAR was not an issue generally discussed in Switzerland before 1996. At the beginning of the GBT project it was planned to eliminate reactive aggregates. During the project planning it was found that this would not be possible without violating relevant aspects of the approval procedure of the project. Based on various test campaigns on rock material from the area of the GBT, inspections in various existing underground structures, investigations and a risk analysis, an AAR action plan was developed under the lead of Alp Transit Gotthard Ltd (constructor of the Gotthard axis of the New Rail Link through the Alps) from 2000 to 2003. This AAR action plan had to take into account the existing material management plan and the already existing concrete testing system. The AAR action plan was composed of the following items:

- Regular monitoring of the potential reactivity of the raw material and the aggregates processed from it. Rejection of the highly reactive raw material from processing.
- Determination of the AAR requirements for specific building components.
- Verification of the AAR resistance of the concrete formulation primarily by analysis of the material and secondarily through performance tests.
- Constructive measures to protect the concrete from water contact.

In the presentation, the temporal development of the topic and the increase in uncertainties as well as the procedure and aspects of the AAR action plan are shown.

The following points are passed on as hints and recommendations from the project:

- Clarity about the objective (work project-oriented or generally valid as a basis for a standard)
- Exchange between the parties involved
- Project-related risk management

Suddenly the aggregates for concrete are a risk for the durability of the structure – experiences form material management project for the Gotthard Base Tunnel (GBT) using AAR as example

Roland WEISS
Hagerbach Testing Gallery Ltd.
Flums, Switzerland
Novembre 15th, 2018

V-S-H-

Topics

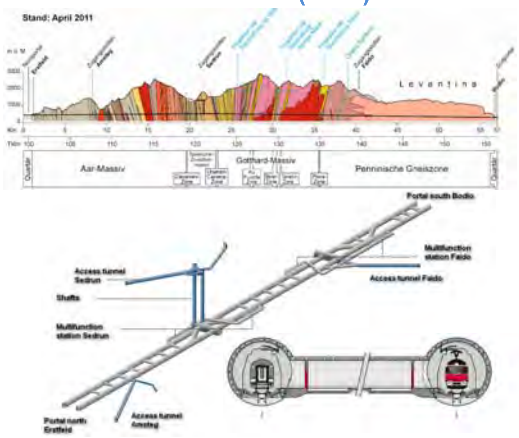
- Short Introduction
- AAR action plan
- recommendations

2

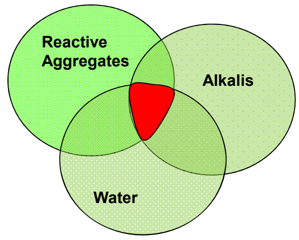
V-S-H-

Introduction

Gotthard Base Tunnel (GBT)



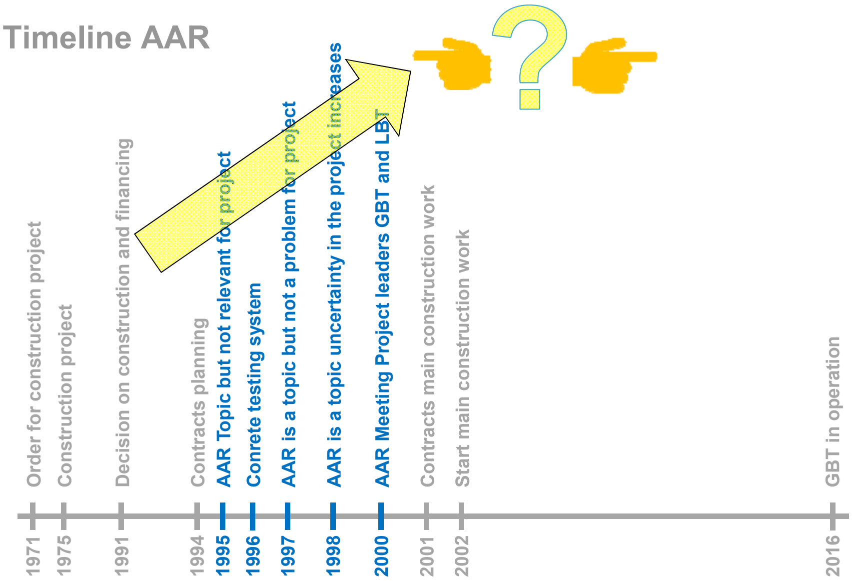
Alcali aggregate Reaction (AAR)



Timeline GBT

- 1971 Order for construction project
- 1975 Construction project
- 1991 Decision on construction and financing
- 1994 Contracts planning
- 2001 Contracts main construction work
- 2002 Start main construction work
- 2016 GBT in operation

Timeline AAR



AAR action plan for the GBT

- Overview of previous literature studies (standards, tests)
- Applicable for the project GBT?
- Open questions risks for the project GBT?

Literature studies

Inspections of existing underground structures

Test campaigns on rock material from GBT and investigations

Risk analysis

Test campaigns on rock material from GBT and investigations

- Examination of rock material/aggregates from GBT
- Testing of concrete mixtures GBT
- AAR investigations of sprayed concrete
- Monitoring concrete first building objects of GBT

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Investigation of existing underground structures

- Investigation of 12 underground structures (road / railway tunnels, tunnels for hydropower plants, underground military complex). All over 1 km long and over 20 years old
- Additional drill core sampling and laboratory tests on 5 selected objects
- The investigations showed that aar occurred in all objects, but in the underground structures no relevant damage was caused.

Gotthard-Strassentunnel, Spritzbeton (s. Kapitel 3.1.4.)

V-S-H-

Risk analysis

Separately considered building components:

- Shotcrete first lining (temporary protection)
- Shotcrete for permanent protection
- Arch concrete
- Bottom concrete

View of place and time (construction/operation)

Gesamtbeurteilung der Gefährdungen			
Mittlere Gefährdung (gewichtete Summe Gefährdungs-pkte)	inkl. Berücksichtigung der Einzelgefährdungen		
	Alle Parameter in der mittleren Gefährdungsklasse	Min. ein Parameter 1 Gefährdungsklasse höher	Min. ein Parameter 2 Gefährdungsklassen höher
Klein	Klein	Klein bis mässig E / A: Gew. Betrieb W	Klein bis erheblich E: SB Betrieb [1] S: Gew. Betrieb W [2]
Mässig	Mässig A: SB Betrieb E / A: Gew. Betrieb O [3]	Mässig bis erheblich S: SB Betrieb S: Gew. Betrieb O E / A / S: Sohle Betrieb [4] E / A: SB Bau [5]	
Erheblich	Erheblich S: SB Bau A / S: Sohle Bau		

1) punktuell "erheblich" auf Grund Km 7-8 (Wasser)
2) punktuell "erheblich" auf Grund Bauteildicke
3) Erstfeld = Grenzfall: mittl. Gefährdung = 52 Pkte
4) "erheblich" in E / A partiell, in S verbreitet
5) "erheblich" infolge 90% Luftfeuchtigkeit

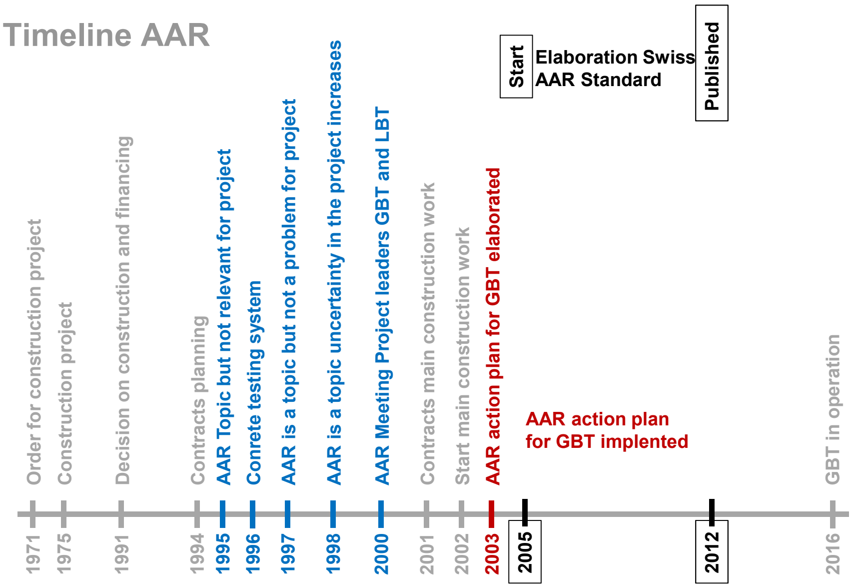
V-S-H-

AAR action plan for the GBT

- Regular monitoring of the potential reactivity of the raw material and the aggregates processed from it. Rejection of the highly reactive raw material from processing.
- Determination of the AAR requirements for specific building components.
- Verification of the AAR resistance of the concrete formulation primarily by analysis of the material and secondarily through performance tests.
- Constructive measures to protect the concrete from water contact.
- Accepted risks

V-S-H-

Timeline AAR



Conclusion and recommendations

- Clarity about the objective (work project-oriented or generally valid as a basis for a standard)
- Exchange between the parties involved
- Project-related risk management

DRAFT: ABSTRACT/SYNOPSIS

Managing the 'Mundic' Problem in South-West England

Ian Sims (RSK) & Philip Santo (RICS)

The so-called 'Mundic' problem relates largely to aggregates derived from mining and processing wastes associated with historic tin and related mining in South-West England (mainly the County of Cornwall). This short presentation will start with a brief description of the background, whereby sulphide-rich waste materials were widely used as aggregates in a 'cottage industry' of low-grade concrete block making, with the blocks being used for building during the first half of the 20th Century. Gradually, especially as the protective effect of the traditional render finish diminished or was breached, many of these blocks disintegrated, causing structural distress, occasional collapse and resultant concern amongst mortgage lenders. It will be explained that this disintegration was caused by a complex variety of decay mechanisms associated with the variable range of sulphide minerals ('mundic' is broadly the Cornish word for pyrite) present within these waste products.

A great deal of more conventional and unaffected concrete was available in the region, but the Council of Mortgage Lenders decided to stop lending on any potentially affected properties until Surveyors could distinguish between the 'mundic' and less problematic concrete varieties. Accordingly, the RICS established a working group that devised a scheme for distinguishing mundic concrete from more conventional concrete and indeed for classifying the various forms of mundic concrete. The resulting guidance was published by RICS in 1994, with substantive updates in 1997 and most recently in 2015. It will be shown that the scheme is based upon sampling of the concrete(s) by Surveyors, then petrographic examinations (and sometimes chemical analyses) by a specialist laboratory, leading to classification of the concrete in question. In 2002 (revised in 2005) a test method was also devised for direct determination of the soundness of concrete varieties that could not be reliably assessed on the basis of composition and condition alone.

This pragmatic and gradually evolving RICS scheme, based on practical concrete petrography, has now been successfully operated in Cornwall (and proximal parts of neighbouring Devon) for more than 20 years. The short presentation will conclude with thoughts on how this experience might assist with other worldwide occurrences of potentially deleterious sulphide constituents within aggregates used, or being considered for use, within concrete.

362 words

IS/23 October 2018

Workshop: Impact of Sulphide Minerals (Pyrrhotite) in Concrete Aggregate on Concrete Behaviour

Mr Philip Santo & Dr Ian Sims

Oslo, Norway – 15 & 16 November, 2018

Managing the 'Mundic' Problem in South-West England

Philip Santo FRICS
Director, Philip Santo & Co
Representing RICS (Royal Institution of Chartered Surveyors)

Background

Background

Background

Background

Background

Background

Managing the 'Mundic' Problem in South-West England

Dr Ian Sims
RSK Environment Limited, UK
www.rsk.co.uk

Concrete Surface Rust Staining from Pyrite

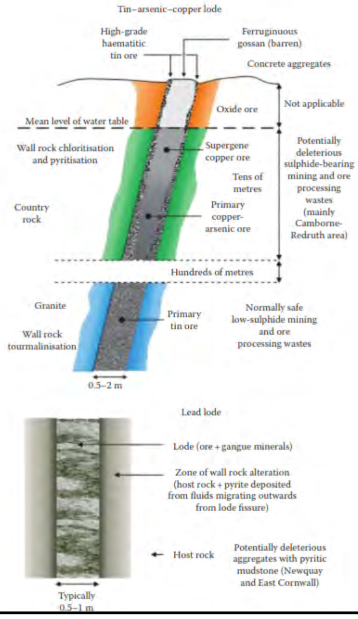
Typical Examples of Mundic Cracking

Typical examples of 'mundic' cracking evident on the rendered exterior of dwellings and building in Cornwall

Typical Examples of Mundic Cracking

Figure 3: Photographs of two different properties exhibiting characteristic mundic damage

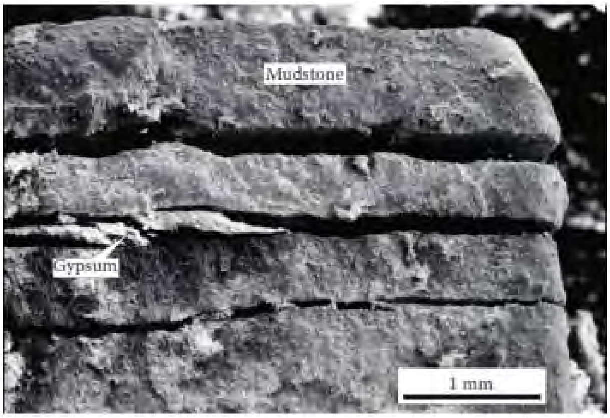
Geological Source of the Sulfides



Diagrams showing typical lodes of tin-arsenic-copper and lead and locations of pyrite and other sulphides

Courtesy of the late Dr Alan Bromley

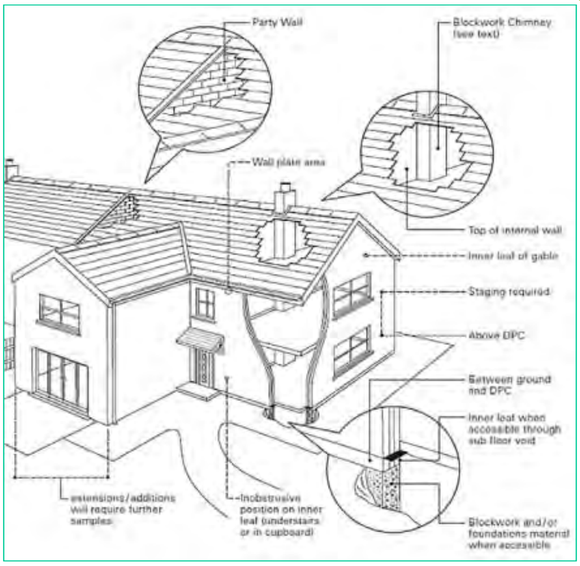
Gypsum-induced expansion of mudstone



Scanning electron microscope image (secondary electron image), showing spalling and expansion of a small mudstone aggregate fragment following growth of secondary gypsum in lenses along cleavage planes. Concrete block from a house in Liskeard, East Cornwall, UK. *Image courtesy of Alan Bromley.*

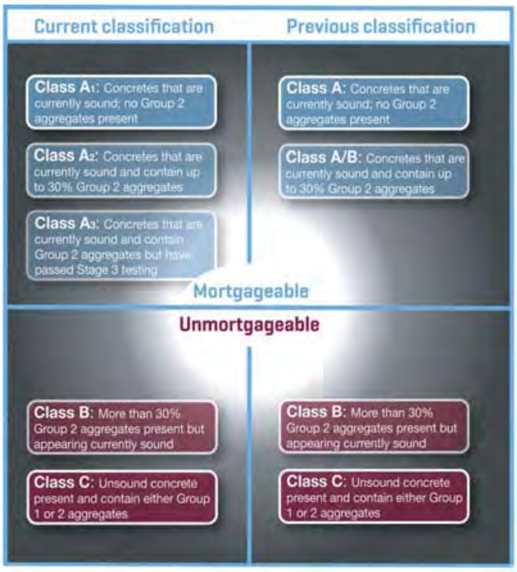
Representative Sampling by Surveyor

Third Edition Diagram: Typical Sampling Locations



The new classifications (Guidance 3rd edn)

RICS RSK



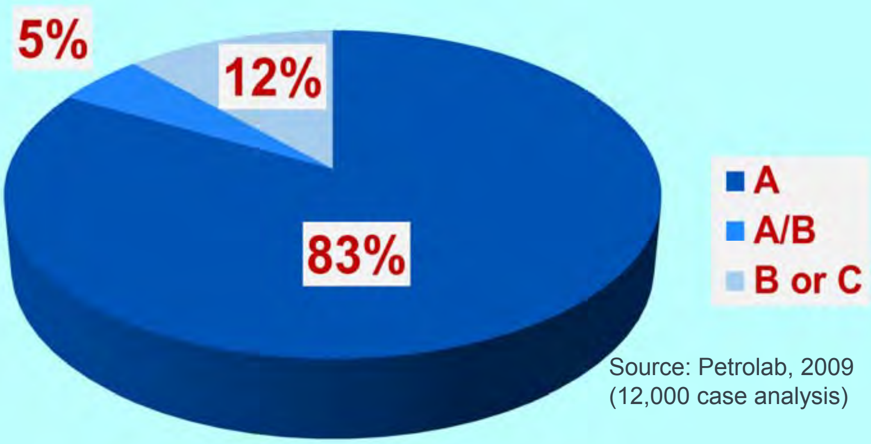
How many properties affected?

RICS RSK

Estimated 30,000 properties tested to date

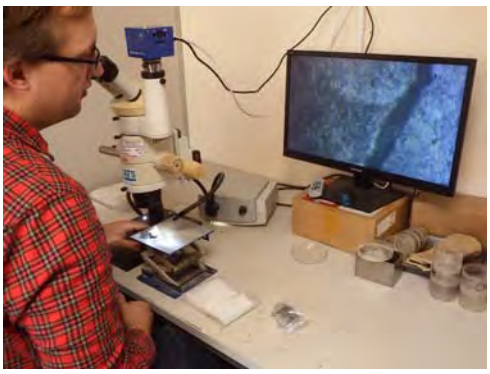
Source: Petrolab, 2009 (12,000 case analysis)

How many properties affected?

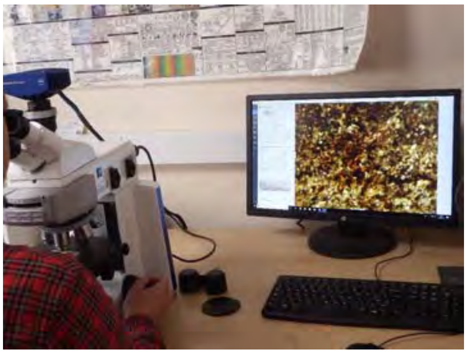


Source: Petrolab, 2009
(12,000 case analysis)

Low- & High-power Microscopy



Low- & High-power Microscopy



Classification Flow Chart

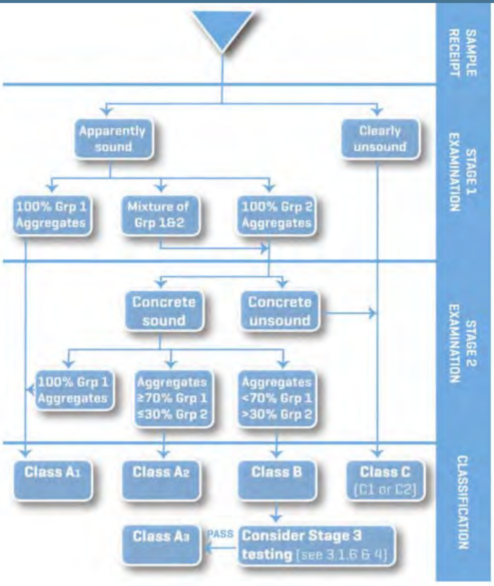


Figure 4: Examination and classification procedure

Note: The flow chart is simplified and reference should be made to the full text.

Concrete Examination - Stage 1

- Visual & low-power microscopy
- Coarse & fine aggregates – petrography
- Evidence of any sulfide minerals – type(s) & reactions
- Cementitious matrix
- Distribution, compaction & voidage
- Assessment of concrete condition

Concrete Examination – Stage 1

Table 1 – Aggregate groups (see also the table notes overleaf)

Group 1:	1–1	China clay waste
	1–2	Crushed granite and related igneous rocks (e.g. elvan)
	1–3	Crushed basic and metabasic igneous rocks (e.g. epidiorite, serpentinite) [1,2]
	1–4	Furnace clinker or coking breeze [3]
	1–5	Beach or river sands and gravels
	1–6	Others (e.g. Group 2, reclassified as a result of current knowledge and/or further investigation) [5]
Group 2:	2–1	Crushed sedimentary or meta-sedimentary rocks ('killas') [2,4,5]
Considered potentially deleterious	2–2	Most metalliferous mining and/or processing wastes [6,7]
	2–3	Slags (largely non-ferrous) and incinerator waste [8]

Scheme for Assessing Concrete Condition

Table 4

Tick the various boxes as appropriate for the sample in question, then trace the column bearing the tick appearing nearest to the right of the table to the bottom of the table, where the assessed concrete condition is given.

	Occurrence*			
Observed feature	***None***	***Rare***	***Common***	***Abundant***
1 Sulphide decay and associated staining of surrounding matrix				
2 Concrete matrix degradation, inc. weakening, alteration & recrystallisation				
3 Secondary sulphate mineral development				
4 Evidence of moisture susceptibility in fine-grained meta-sediment				
5 Physical incoherence				
6 Cracking (other than externally induced)				
Condition assessment:	**Sound**		**Unsound**	

Classification Flow Chart

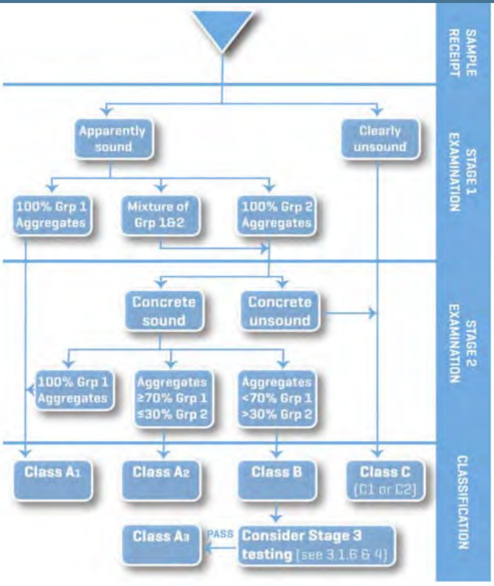


Figure 4: Examination and classification procedure

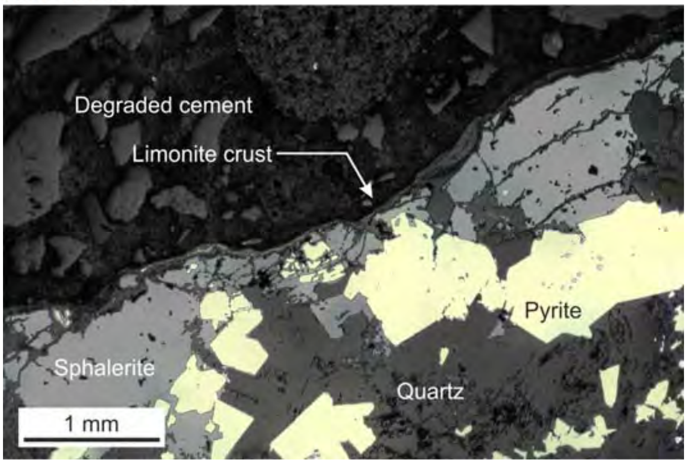
Note: The flow chart is simplified and reference should be made to the full text.

Concrete Examination – Stage 2 (if needed)

- High-power thin-section microscopy
- Reflected light microscopy of polished surfaces
- Chemical analysis – total sulfur & sulfates
- Cement content analysis (mass concrete footings only)
- Coarse & fine aggregates
- Cementitious binder - its condition & voidage
- Sulfides, sulfates & any evidence of reaction
- Cracking of or around aggregates, and/or matrix & concrete

Concrete Examination – Stage 2

7(a) **Coarse sulphide minerals**



Chemical Analysis – Stage 2

- Group 1-3 aggregate (basic & metabasic igneous):
  - 1.5% max pyrite equivalent by mass of concrete
  - 0.5% max acid-soluble sulfate by mass of concrete
- Group 1-6 aggregate (mining and/or processing waste):
  - 1.0% max pyrite equivalent by mass of concrete
  - 0.5% max acid-soluble sulfate by mass of concrete
- Up to 30% Group 2 aggregate (sedimentary or meta-sedimentary)*:
  - 1.0% max pyrite equivalent by mass of concrete
  - 0.5% max acid-soluble sulfate by mass of concrete
- More than 30% Group 2 aggregate:
  - no chemical criteria suggested (Stage 3 possible)

* otherwise appears in sound condition.

Classification Flow Chart

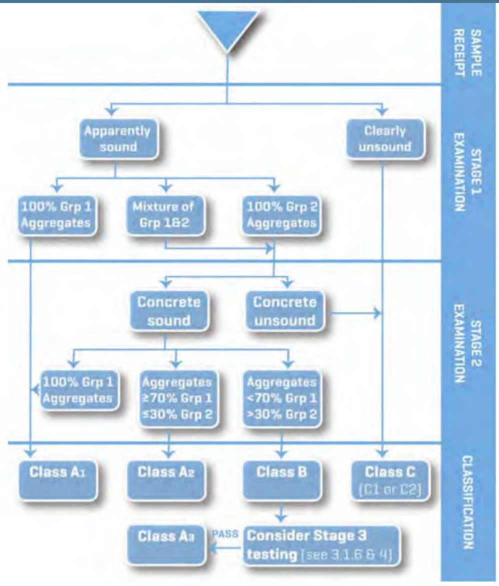


Figure 4: Examination and classification procedure

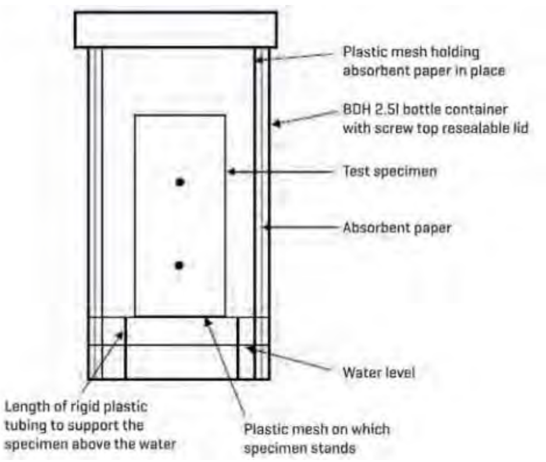
Note: The flow chart is simplified and reference should be made to the full text.

Stage 3 - Moisture Sensitivity Test

- Concrete containing >30% Type 2 aggregate, assigned to Class B, but nevertheless visibly sound
- If recommended by both Surveyor & Petrographer
- Stage 3: unconstrained linear expansion of concrete cores, exposed to water-saturated atmosphere at 38 degrees C
- Re-classify as Class A3, if expansion is <0.025% after at least 250 days (following an initial 7-day conditioning period when the wetting expansion is not >0.075%, and the core remains intact at the end of the test)

Stage 3 – Moisture Sensitivity Test

Figure 10: Cross-section of test specimen within a suitable test container



Classification Flow Chart – After Stage 3

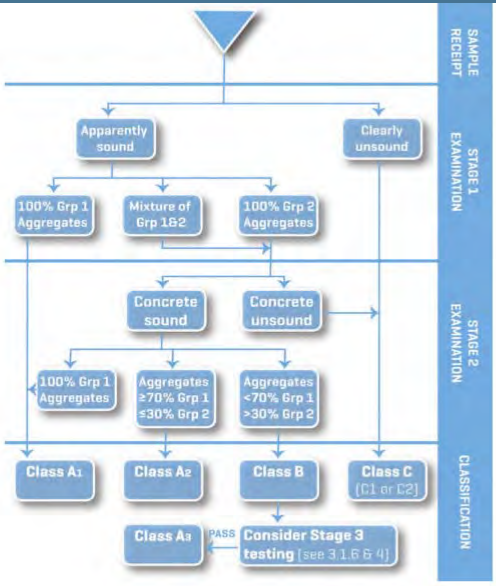
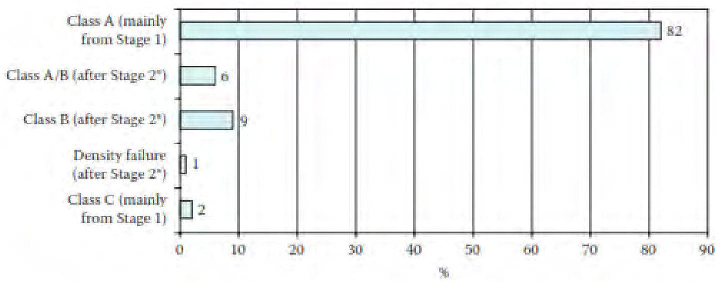


Figure 4: Examination and classification procedure

Note: The flow chart is simplified and reference should be made to the full text.

Proportions of Concrete Classes Found



* Based on proportions returned by Stage 2 testing on about 44% of the 18.5% of the samples subjected to Stage 1 testing and recommended for Stage 2 testing (Stage 2 testing of the other 56% was not commissioned, so that the samples remained unclassified).

Statistical chart, showing frequency of Classes A, A/B (now A2), B & C (based upon data for about 12000 samples over 15 years, courtesy of Petrolab Limited).

Conclusions

- Pragmatic local management of troublesome concrete infrastructure
- Reliable differentiation of ‘mundic’ from other types of concrete
- Co-operation between Building Surveyors and Petrographers
- Representative sampling by Surveyors
- Examination and classification by Petrographers
- Concrete classes A1 & A2, or A3 after Stage 3, accepted as mortgageable
- Concrete classes B & C, considered unmortgageable

Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour

November 15-16, 2018, Oslo, Norway

The development of accelerated test methods and the content of a new Canadian R&D project

by B. Fournier and J. Duchesne, Université Laval, Québec, Canada

Abstract:

Several cases of concrete deterioration involving sulphide-bearing aggregates have been reported over the years. However, limited guidelines are currently available for the quality control of aggregates containing iron sulphide minerals. Research carried out in Canada during the period 2010-2015 resulted in the development of an novel assessment protocol to evaluate the potential deleterious effects of iron-sulphide-bearing aggregates prior to their use in concrete. The protocol is divided into three major phases: 1) total sulphur content measurement; 2) oxygen consumption evaluation; and 3) an accelerated mortar bar expansion test. Tentative limits are proposed for each phase of the protocol, which still need to be validated through the testing of a wider range of aggregates.

In order to ensure the safety of Canadians and minimize the economic impact of restrictions on aggregate sulphide content, NRC proposes to work with Université Laval to lead a new Canada wide research, development and technology transfer project to resolve the outstanding issues associated with sulphide attack on concrete. This project aims to provide the following results : 1) Determination of acceptable limits for the content of different sulphides in Canadian concretes; 2) Rapid, inexpensive and reliable tests for detection of deleterious sulphide contents in Canadian concrete aggregates; 3) Development of preventive measures for the safe use of sulphide-bearing aggregates in concrete applications in order to mitigate the economic impact of sulphide content restrictions; 4) Development of the technical capacity to carry out tests developed for results 1-3 in locations across Canada; and 5) Adoption of appropriate revisions to CSA A23.1/.2, based on the results of the project.

Keywords: Sulphide-bearing aggregate, accelerated testing, oxidation reaction, total sulphur content, mortar bar expansion test.

The development of accelerated test methods and the content of a new Canadian R&D project

B. Fournier and J. Duchesne
Université Laval

CRIB

Workshop on the Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour
November 15th -16th 2018, Oslo, Norway

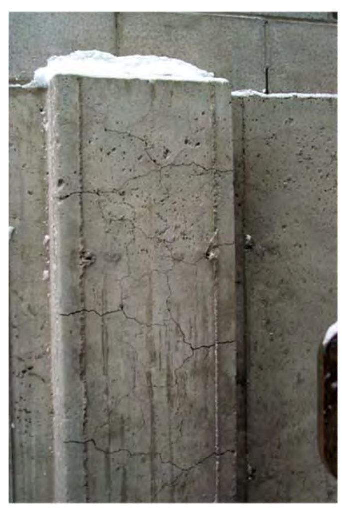
Statens vegvesen
Norwegian Public Roads Administration

norsk betongforening

HEIDELBERGCEMENT
Northern Europe

Background – Trois-Rivières area

Rapid (< 3-4 years) deterioration of concrete elements in the Trois-Rivières area (Quebec, Canada)



Research Project (2010-2014) - Funding structure

Partnership: University – Industry - Gouvernment

Collaborative Research and Development Grant (CRD)

CRSNG NSERC Conseil de recherches en sciences naturelles et en génie du Canada Natural Sciences and Engineering Research Council of Canada

Researchers	**J. Duchesne, B. Fournier (U. Laval); P. Rivard (U. Sherbrooke); M. Shehata (Ryerson U.); B. Durand (HQ)**
Graduate Students	**I. Medfouni (USh), B. Maguire (RU), B. Guirguis (RU), A. Rodrigues (UL), J. Francoeur (UL)**
Research Prof.	**S. Tremblay (UL)**
Post-Doc	**V. Ramos**

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Project overview

Visual inspection of concrete structures

↓

In-situ testing and sampling (blocks and cores)

↓

Outdoor exposure testing (blocks)
- In-situ monitoring
- Non-destructive testing
- Sampling (cores)

↓

Overall analysis and recommendations (standards)

Inspection of local quarries
- Identification/ sampling of rock facies

↓

Laboratory testing
- Damage of concrete
  - Mechanical properties
  - Petrography
  - Non-destructive
- Residual expansion testing

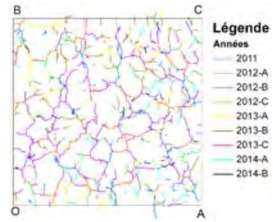
- Characterization of the aggregates (chemistry, mineralogy)
- Development of performance test
  - Chemical
  - Expansion (mortar, concrete)
- Validation with other rock types
- Effect of concrete mix characteristics on expansion

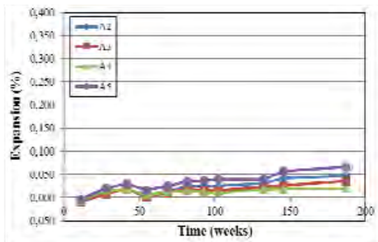
Outdoor exposure testing

5 blocks per house foundation

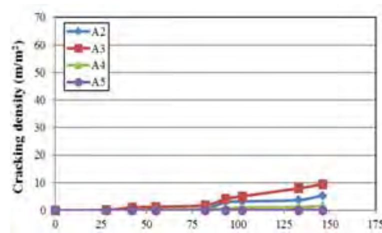
- **Non destructive testing (Sh. U,)**
- **Expansion (Nov. 2011-Aug. 2014)**
- **Monitoring of cracking**
- **Sampling of blocks**

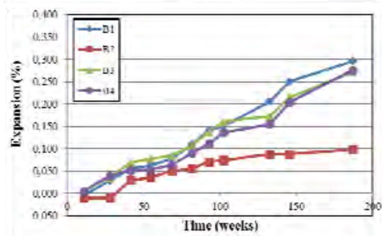
Francoeur (2016)





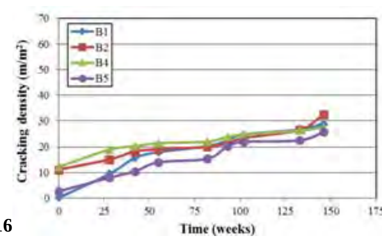
Set A (rating 0)





Set B (rating 2)

Francoeur (2016



Testing & sampling for laboratory investigations

- **Relative humidity measurements**
- **Chemical composition (sulphur content in the aggregate)**
- **Damage assessment of the concrete (physical, mechanical, microstructure)**

Two aggregate sources in Saint-Boniface

Development of new exposure site (IREQ-HQ)

- « Reactive aggregate » & various concrete mix designs
- Monitoring of cracking and expansion development

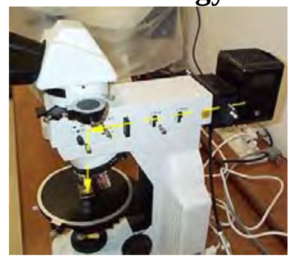
(Durand 2013)

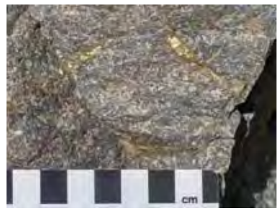
2018

Laboratory testing program

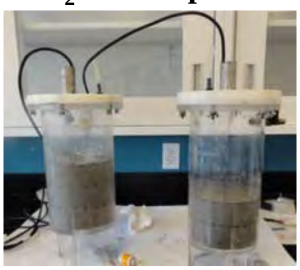
S_T determination

Mineralogy





O_2 consumption



Expansion

1

Standardization process (2012-2018)

Annex P (informative)
Impact of sulphides in concrete aggregate on concrete behaviour

2014

A23.1-14/A23.2-14

CSA Group

Concrete materials and methods of concrete construction/Test methods and standard practices for concrete

CSA A23.1-2014 - Annex P (Informative)

Impact of sulphides in concrete aggregates on concrete behaviour

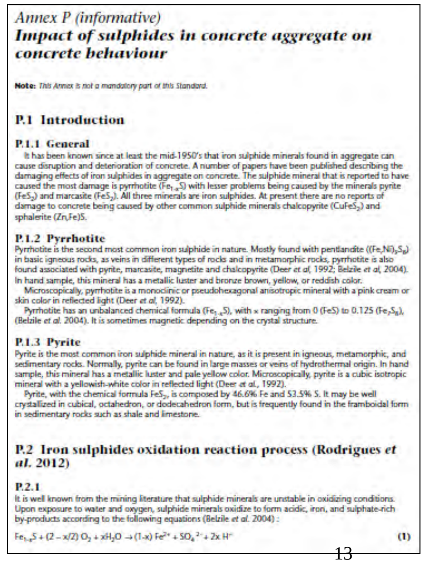
P.1 Introduction
- **General**
- **Pyrrhotite → Fe (1-x) S**
- **Pyrite → FeS_2**

P.2 Iron sulphides oxidation process

P.3 Case studies of damaging effects in concrete made with aggregates incorporating iron sulphides

P.4 Standards

P.5 Discussion



Annex P (informative)

Impact of sulphides in concrete aggregate on concrete behaviour

Note: *This Annex is not a mandatory part of this Standard.*

P.1 Introduction

P.1.1 General

It has been known since at least the mid-1950's 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.1.2 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 color.

Microscopically, pyrrhotite is a monoclinic or pseudohexagonal anisotropic mineral with a pink cream or skin color in reflected light (Deer *et al*, 1992).

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.1.3 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 color. Microscopically, pyrite is a cubic isotropic mineral with a yellowish-white color in reflected light (Deer *et al.*, 1992).

Pyrite, with the chemical formula FeS_2, is composed by 46.6% Fe and 53.5% S. It may be well crystallized in cubical, octahedron, or dodecahedron form, but is frequently found in the framboidal form in sedimentary rocks such as shale and limestone.

P.2 Iron sulphides oxidation reaction process (Rodrigues *et al.* 2012)

P.2.1

It is well known from the mining 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 according to the following equations (Belzile *et al.* 2004) :

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

CSA A23.1-2019 - Annex P (Informative)

(conducive to final accceptance by CSA A23 committee members)

P.1 Scope

P.2 Reference publications

P.3 Definitions

P.4 Significance and use

P.5 Introduction
- **General**
- **Pyrrhotite → Fe (1-x) S**
- **Pyrite → FeS_2**

P.6 Iron sulphides oxidation process

P.7 Case studies of damaging effects in concrete made with aggregates incorporating iron sulphides

P.8 Standards

CSA A23.1-2019 - Annex P (Informative)

(conducive to final accceptance by CSA A23 committee members)

P.9 Performance evaluation protocol (PEP) for the determination of the deleterious oxidation potential of sulphide-bearing aggregates } **Protocol**

P.10 Chemical method (S from iron sulphides)

P.11 Oxygen consumption test

P.12 Accelerated mortar bar expansion test

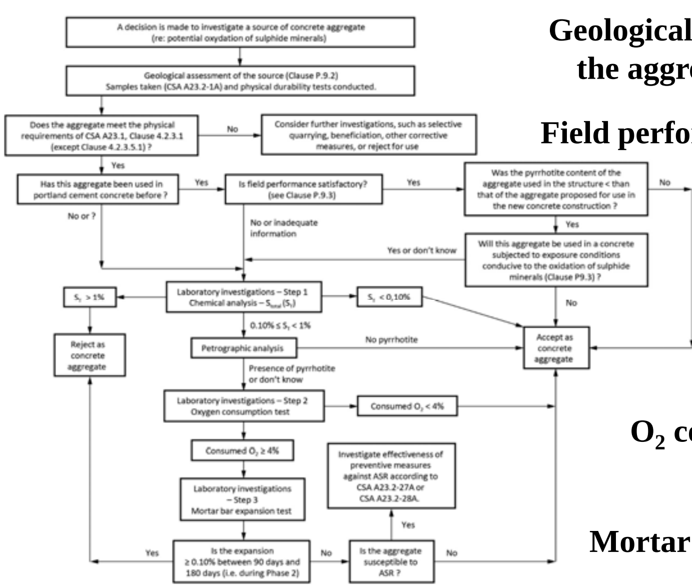
} **New test methods**

P.13 Discussion, summary and interpretation of PEP

P.14 Conclusion

15

Protocol for testing sulphide-bearing aggregates



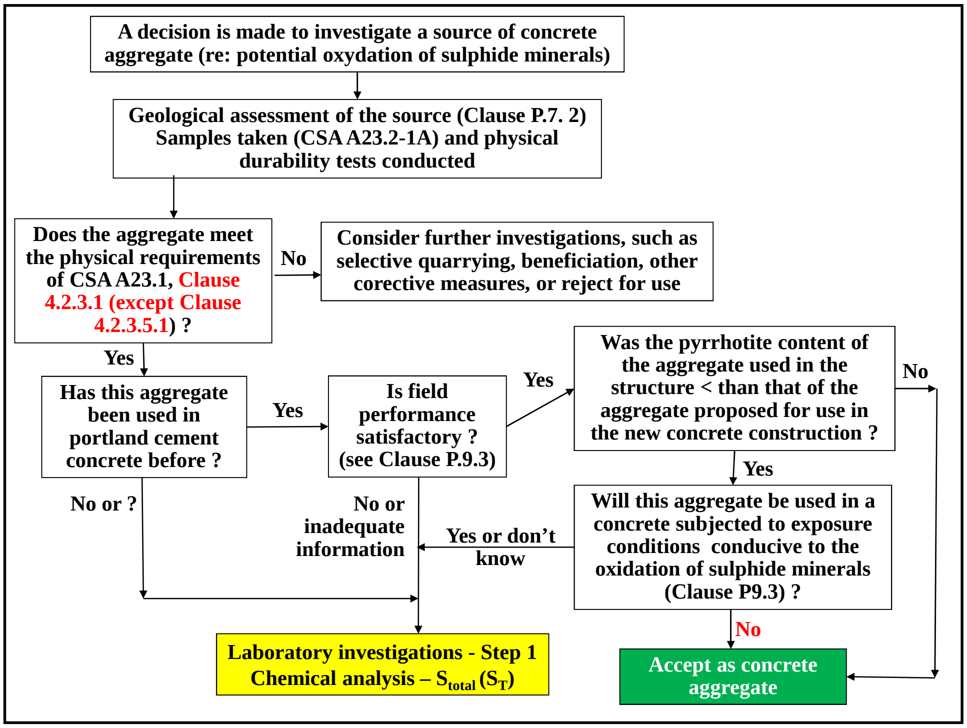
Geological assessment of the aggregate source

Field performance survey

Chemical analysis Ss

O_2 consumption

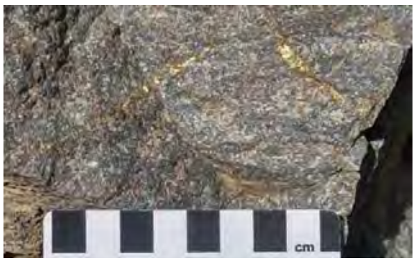
Mortar bar expansion



Performance testing program – Step 1

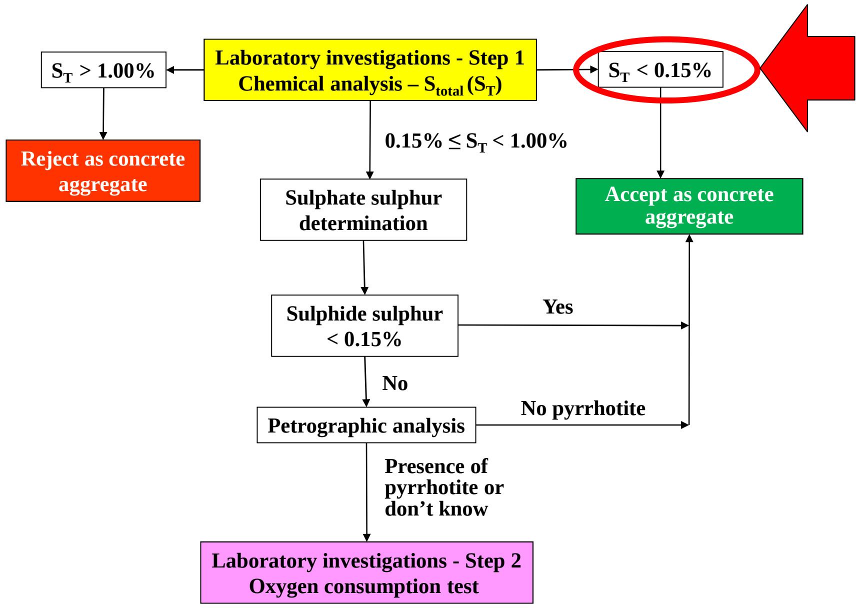
Screening tests

- Chemistry → Sulphur content
- Petrography → pyrrhotite



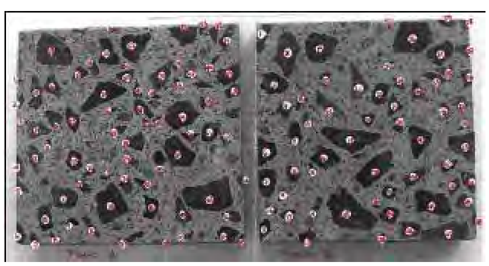
1

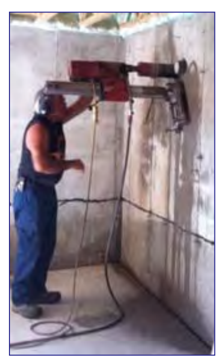
Protocol for testing sulphide-bearing aggregates



Defense experts in TR case (as per April 2018)

- S_T in coarse aggregate from cores





- Numbering of all particles > 2 mm in size
- Estimate the % of sulphides (0, 0.1, 0.5, 1, 2, 3, 5, 10%…)
- Particles > 0.5%: proportion of Py, Po and Chalcopyrite
- Average % of the surface corresponding to ≠ iron sulphides in the coarse aggregate
- Calculator (typical cement & aggregate contents, S_T for cement & sand…) → estimated S_T in the coarse aggregate

Defense experts in TR case (as per April 2018)

Petrographic determination of sulphide minerals on a polished concrete section - Calculator

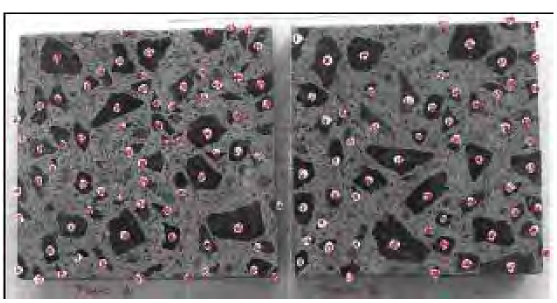
File no :	31112	Diameter (mm):	100	Note on the oxidation condition of Po grains
Core no :	C-3	Sample no :	1	

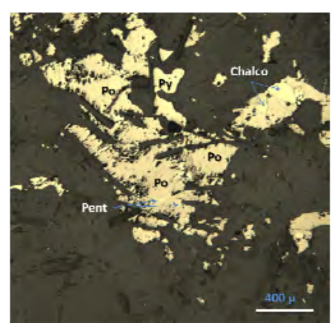
Particle no.	Rock type: gabbro	granit.	limestone	others	Total (%)	Ratio of sulphides (%): Po	Py	Cp	embedded in the particle	In contact with paste
1	1				0					
2	1				0,1					
3	1				0					
4	1				3	100	0	0	none	slight
5	1				2	90	5	5	slight	fair
6	1				0					
7	1				0,1					
8	1				0					
9	1				15	75	20	5	none	none
10				1	0					
11…										
Nbr	38	0	0	2						
%	95%	0%	0%	5%						
Avg					1,26	78	19	3		
Aggregate particles (total):				40						

	Po	Py	Cp
Average % of the surface area corresponding to pyrrhotite	0,98		
Average % of the surface area corresponding to pyrite		0,24	
Average % of the surface area corresponding to chalcopyrite			0,03

Defense experts in TR case (as per April 2018)

- S_T determination in coarse aggregate from cores





- S_T in coarse aggregate for 10 damaged houses with lowest pyrrhotite contents (0.20 to 0.30% in volume)
  - 0.29 – 0.45%
  - On an average: Po/Py/Cp: 52/42/6

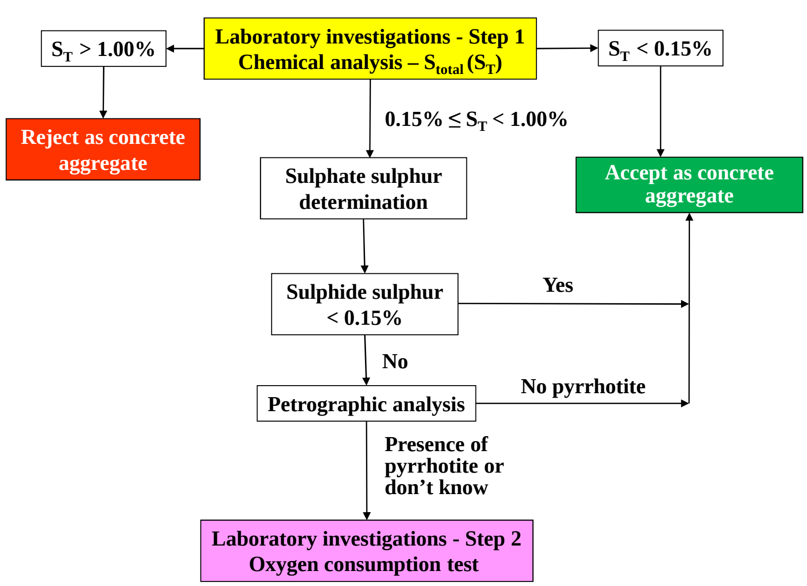
Experts en defense pour dossier TR

- Considering Po/Py/Cp: 52/42/6

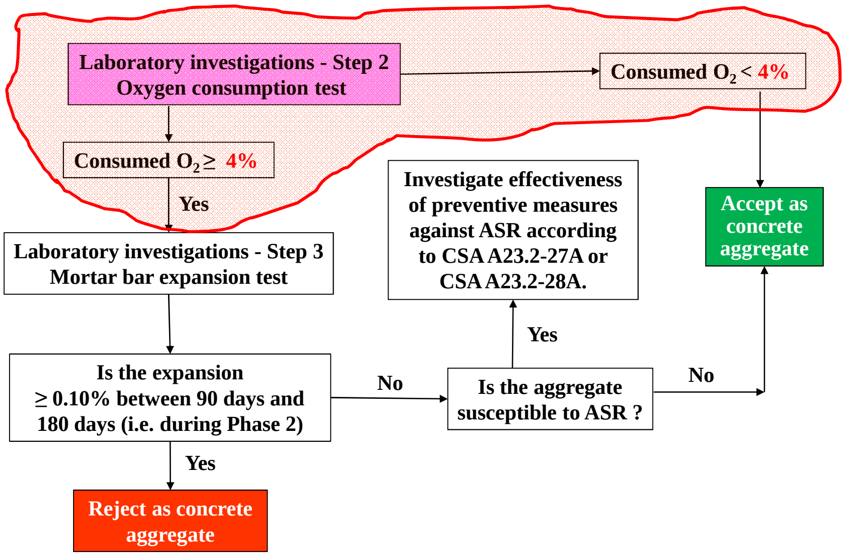
% Po (vol)	# damaged buildings	S_T in CA
0 – 0.099	0 / 10	Max 0.14%
0.10 – 0.199	0 / 48	Max 0.29%
0.20 – 0.299	10 / 59	0.29% - 0.43
0.30 – 0.399	13 / 46	0.43% - 0.58

- Proposal : use 0.15% for max S_T in CA for chemical analysis

Protocol for testing sulphide-bearing aggregates



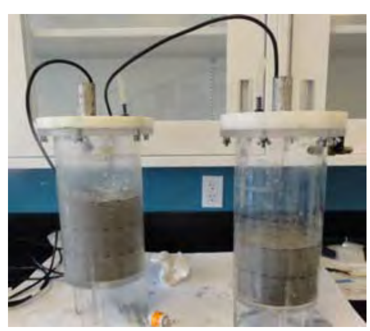
Protocol for testing sulphide-bearing aggregates



O_2 consumption Test

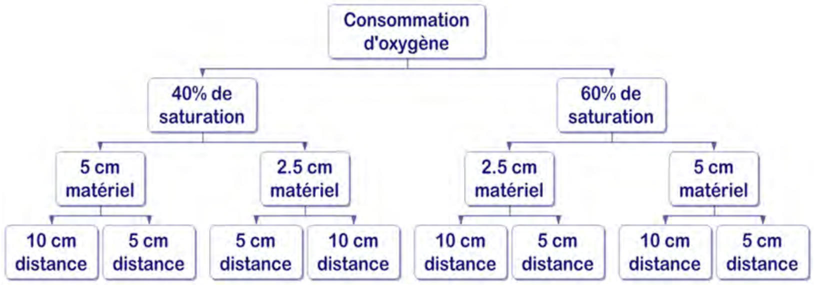
$$Fe_{1-x}S + (2-x/2)O_2 + xH_2O \rightarrow (1-x)Fe^{2+} + SO_4^{2-} + 2x\ H^+$$

- Column testing → O_2 consumed
- From Elberling et al. (1994) (acid rock drainage)
- Determination of sulphide oxidation rates



(Rodrigues et al. 2016)

O_2 consumption



O_2 consumption Test

- **Materials at 40% saturation**
- **10 cm materials (< 150 µm)**
- **10 cm of free space**

	Sulphide-bearing aggregates					Reference aggregates		
Aggregates → Parameters ↓	Sudbury	SB	SPH	SW	GGP	PKA	HPL	Dol
Flux (mole/m^2/yr)	2006	226	112	174	133	65	13	45
% O_2 consumed	57,0	10,7	6,2	8,2	5,4	2,6	1,7	3,0
S_{total}	13.86	0.87	0.32	0.07	0.25	0.04	0.02	0.12

(Rodrigues et al. 2016)

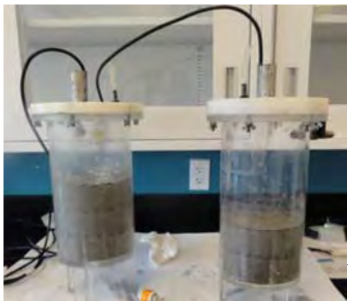
O_2 consumption - variability

- MSK material (< 150 µm)
- 40% saturation
- 10 cm materials
- 10 cm free space

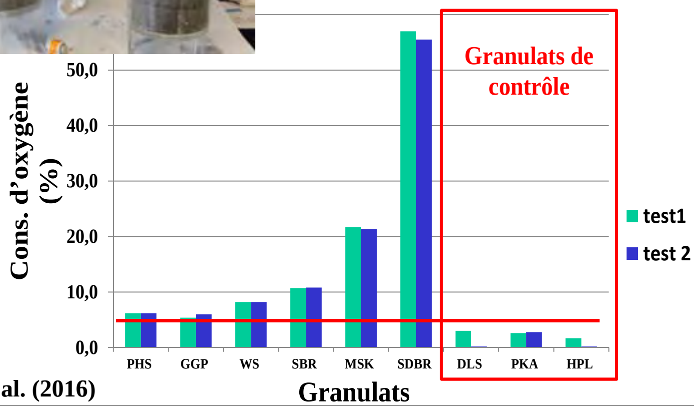
	Number of tests on companion aggregate samples							Moy.	CV
Aggregates→ Parameters ↓	1	2	3	4	5	6	7		
Flux (mole/m²/yr)	577	570	576	606	582	612	558	583	3.1
% O_2 consumed	21,7	21,8	21,9	22,7	21,8	22,8	21,4	22.0	2.2
S_{total}	0.99	1.05	1.07	1.15	1.09	1.13	1.11	1.10	4.6

(Rodrigues et al. 2016)

Oxygen consumption test

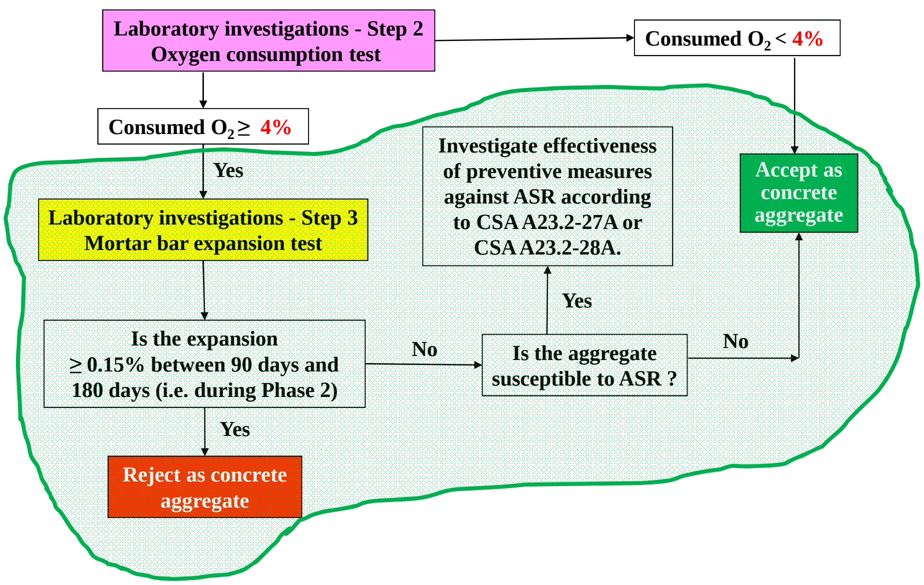


- Material at 40% saturation
- 10 cm of material (< 150 µm)
- 10 cm overhead
- O_2 consumption (3 hours)



Rodrigues et al. (2016)

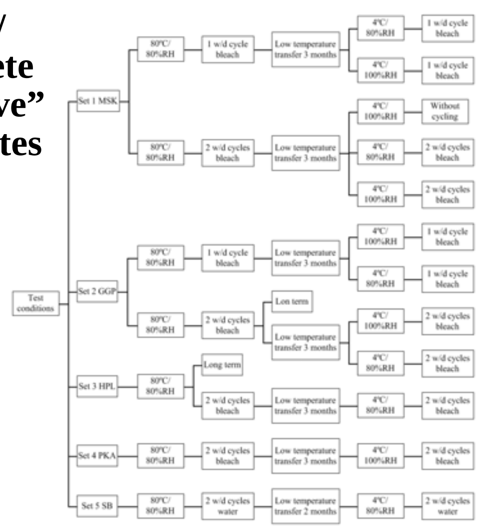
Protocol for testing sulphide-bearing aggregates



Mortar bar expansion test

Objectives

- Reproduce the expansion/ reaction process in concrete incorporating the "reactive" sulphide-bearing aggregates under lab conditions.



(Rodrigues et al. 2015)

Mortar bar test (based on ASR)

Cement:
440 g

Fine aggregate:
1200 g
(- 5mm + 160µm)

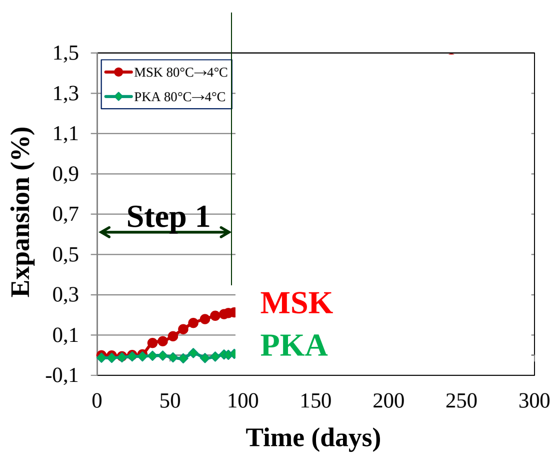
E/C: 0.65

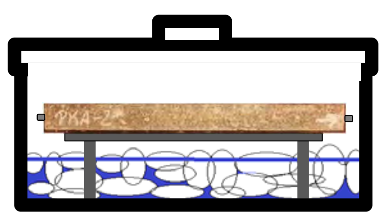
(Rodrigues et al. 2015)

Mortar bar test (Rodrigues et al. 2015)

Step 1: Oxydation of sulphides and internal sulfate attack

- **80°C, 80% R.H. + wetting in bleach (NaClO) 6% (2 x 3 hrs / week)**
- **Expansion and mass measurements (1x / week)**





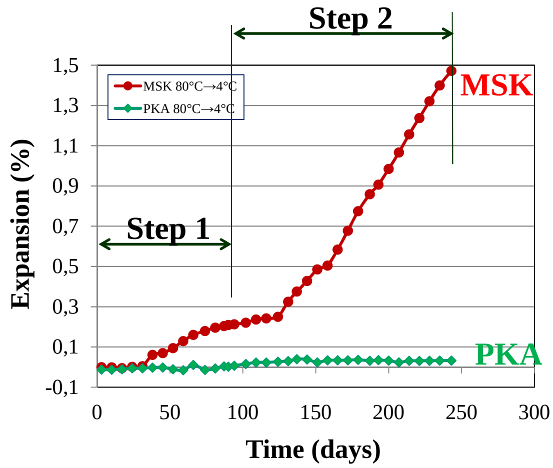
Bars above oversaturated solution of sodium chloride (NaCl)

3

Mortar bar test (Rodrigues et al. 2015)

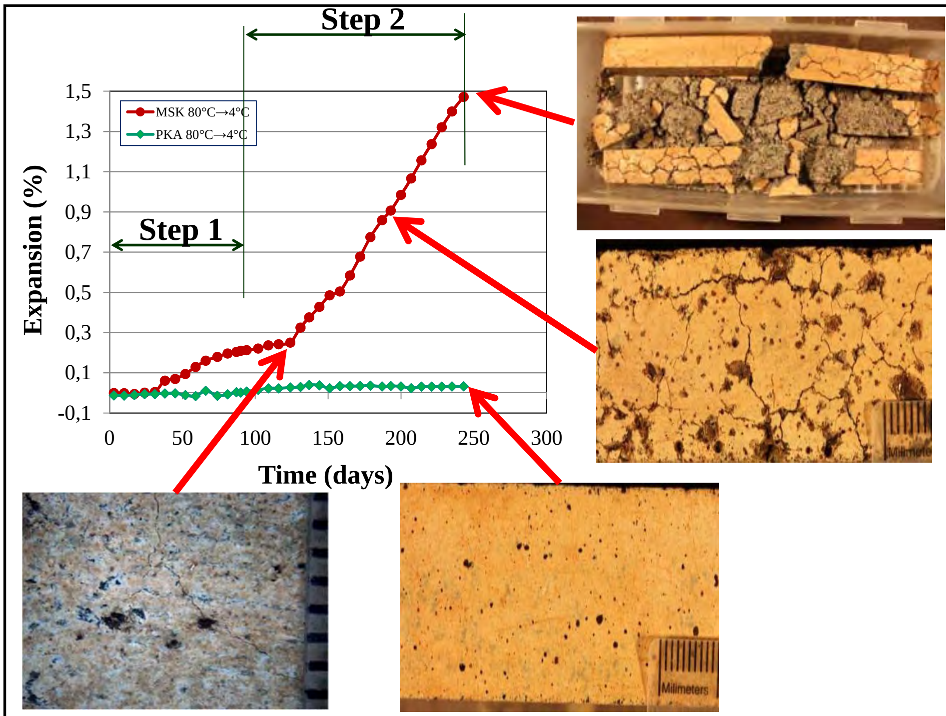
Step 1: Oxydation of sulphides and internal sulfate attack

- **80ºC, 80% R.H. + wetting in bleach (NaClO) 6% (2 x 3 hrs / week)**
- **Expansion and mass measurements (1x / week)**

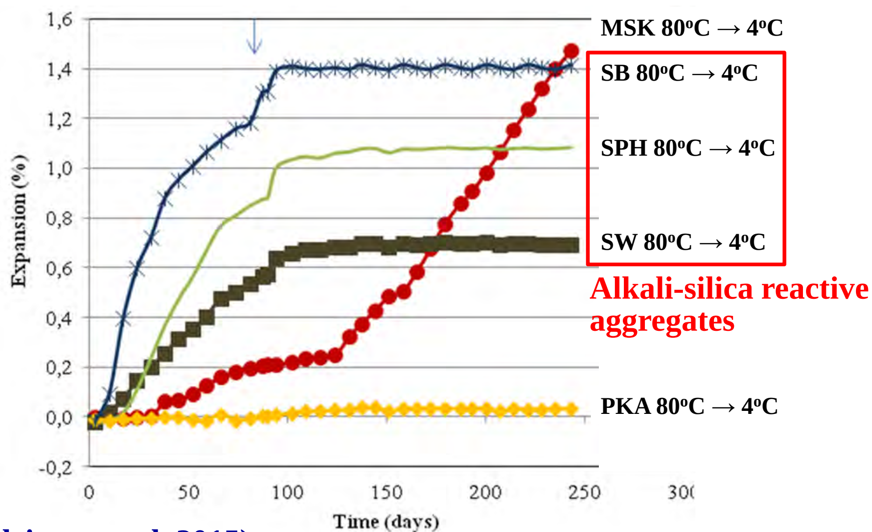


Step 2: Thaumasite Formation

- **4ºC, 100% R.H. + wetting in bleach 6% (2 x 3 hours / week)**
- **Expansion & mass measurements (1x / week)**

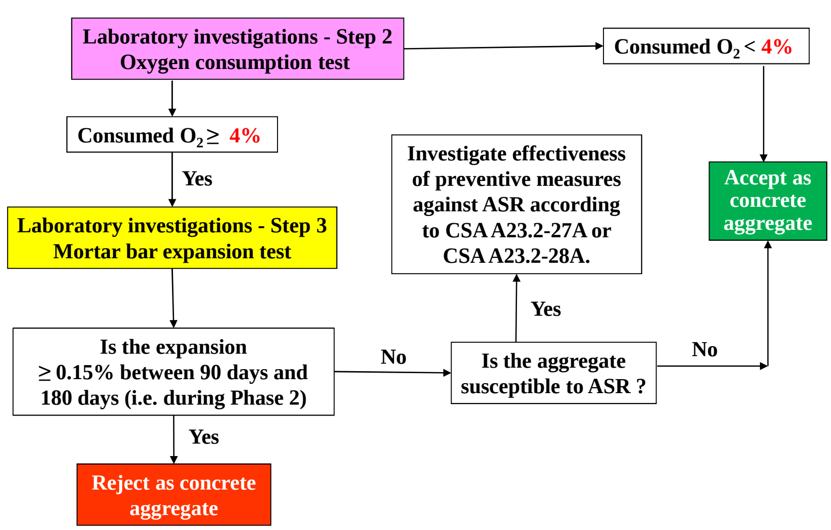


Development of expansion test (ASR vs sulphide-bearing)



(Rodrigues et al. 2015)

Protocol for testing sulphide-bearing aggregates



NRC·CNRC

NRC - U. Laval Pyrrhotite project

Colloque sur la pyrrhotite – 24-25 Sept. 2018

Jon Makar, Ph.D., P. Eng.

National Research Council Canada | Conseil national de recherches Canada

Canada

Project Partners

- NRC and Quebec Government are creating a research chair at Université Laval (2018-2022)
- 1 MSc student, 4 Ph.D.s, 1 Post-doc and a research professional at Laval U.
- Research carried out by NRC and Laval U.
- Research activities will extend across Canada (7 MSc's across the country)

Project Objectives

1. Determination of acceptable limits for the content of ≠ sulphides in Canadian concretes;
2. Rapid, inexpensive and reliable tests for detection of deleterious sulphide contents in Canadian concrete aggregates;
3. Development of preventive measures for the safe use of sulphide-bearing aggregates in concrete applications → mitigate the economic impact of sulphide content restrictions;

Project Objectives

4. Development of the technical capacity to carry out tests developed for results 1-3 in locations across Canada; and
5. Adoption of appropriate revisions to CSA A23.1/.2, based on the results of the project.

Project Tasks

1. Stakeholder engagement
2. Refinement of existing test methods for sulphides in concrete aggregate (+ new methods)
3. Estimation of frequency of occurrence of deleterious sulphides in Canadian aggregate
4. Determination of safe limits for sulphide sulfur and pyrrhotite contents in concrete agg.
5. Distribution of standardized test materials

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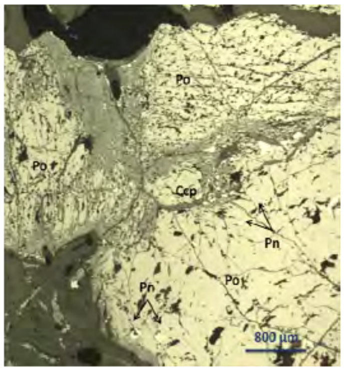
Final thoughts

- Lots of work still needed
  - Basic mechanisms and effect of various parameters (moisture content, concrete composition, sulphide mineral composition/ interactions, etc.)
  - What can we do to make sure that what happened in TR and Connecticut won't happen again → « engineering » !!!



People's aspects

Value of house
$ 500,000

Value of house
$ 0 !!!!

September 24th & 25th 2018 (TR)

PYRRHOTITE SYMPOSIUM

The situation in Mauricie and Connecticut

Québec

CAVP Coalition d'aide aux victimes de la pyrrhotite

crumbling BASEMENTS

Connecticut Coalition Against Crumbling Basements

Connecticut

Final thoughts – Connecticut (USA)

Not Covered by Insurance

- Since the early 2000s, insurance companies have been writing out coverage for a slow collapse, meaning a crumbling foundation is not covered despite paying premiums
- Cost to lift and replace concrete for a single-family home is $150,000-$300,000+ (sometimes exceeding the value of the home)

CCACB (2018)

Connecticut Coalition Against Crumbling Basements

Quebec (Canada)

- **Five-year warranty for new construction … but…**

Law suits – Quebec (Canada) (Soucy 2018)

- **Wave 1**
  - **$168 M of damage**
  - **Judgement given … minimum pyrrhotite content of 0.23% causing damage→ above 0.23%: basement foundations are replaced !**
  - **Appeal placed (71 questions raised, 8 weeks in court (Oct 2017- May 2018)… still waiting for decision … Supreme Court ???**
- **Wave 2 – more cases … but will depend of Wave 1 conclusions…**

Law suits– Quebec (Canada) (Soucy 2018)

- **Wave 3 → Pyrrhotite content < 0.23% volume**
  - **Housing foundations will not be replaced !**
  - **« Pressure » to confirm the minimum « pyrrhotite » content for damage generation**
  - **Test on « concrete » is needed → cores for potential for future expansion (# of cores ? → variability of aggregate composition…)**
  - **Set priorities for research … but fast ! → people are waiting !!**

Centre de recherche sur les infrastructures en béton

Montréal • Québec • Sherbrooke

Thank you for your attention !!

CRIB

Use of advanced mineral characterization techniques to quantify sulfides in rocks and aggregates, and to investigate deterioration of concrete containing sulfide-bearing aggregates

Kurt Aasly (1), Klaartje De Weerdt and Mette Geiker (2)
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An inaccurate quantification of the sulfur content and/or inaccurate or even incorrect identification of pyrrhotite may cause disqualification of otherwise highly qualified rock for aggregate production. This could have an enormous impact on the sustainable use of resources in the areas where sulfide alterations in rock occur. During the construction of the Follobanen tunnel for example, tunneling masses were intended to be used for the local production of the concrete lining. However, due to the detection of sulfur and pyrrhotite in the rock, the tunnel masses had to be disposed of and aggregates had to be transported in for the concrete production. This incident rose awareness about the knowledge gap regarding the testing methods and acceptance criteria for aggregates in concrete, and the performance of sulfide-bearing aggregates in high-quality concrete.

Pyrrhotite in rocks and aggregates

The requirements for aggregates for concrete (NS-EN 12620+NA) state that the total content of sulfur in aggregates and fillers should not exceed 1 wt-%. Special precautions apply when there are indications of the presence of pyrrhotite, in that case, the upper limit of the sulfur content is reduced to 0.1 wt-%. These low acceptance limits are challenging with regard to the characterization techniques. Qualified aggregates typically have sulfur and pyrrhotite content in the range of the detection limits of conventional analysis techniques.

Another aspect in the determination of sulfur and pyrrhotite in aggregates is the procedures for sampling and sample selection. Different rock types typically show different variations (inhomogeneity) throughout. Such inhomogeneity could be systematic (e.g. layering) or more random (e.g. veining) and could be primary or later stage effects of alteration. Hence, sampling of a raw material should be arranged to cover these inhomogeneities and as such determine the differences in sulfur content in different parts of the raw materials in order to ensure representative sampling of the rock mass

Pyrrhotite ($Fe_{(1-x)}S$) occurs mainly in basic igneous rocks but may also be found in several other of rock types (e.g. Deer et al. 2013) and it often occurs together with e.g. pyrite (FeS_2). Pyrrhotite occurs mainly as two principal types in nature, monoclinic pyrrhotite which is the magnetic species (also known as “4C”)/and hexagonal, none-magnetic species (NC). The magnetic pyrrhotite has a lower Fe content (46.5 - 46.8 %) compared with the none-magnetic form (47.4 – 48.3 %).

Determination and quantification of low concentrations of pyrrhotite is challenging. Today, differential thermal analysis (DTA) for mineral analyses and, according to NS-EN 1744-1, acid digestion or high temperature combustion are the methods for analyzing the sulfur content. At NTNU/SINTEF, a home built DTA from the 1950´s is considered the best instrument to determine the content of iron-sulfides and is capable of detecting iron sulfate contents down to one-tenth of a percent.

Optical petrography is always a mineralogist´s best friend and enables high detection limits (i.e. man is able to detect relatively small grains in any polished sample, it is only a question of patience and stamina), although quantification is more difficult and requires systematic, most likely automated methods, especially in such cases where contents of interesting minerals are very low (< 1%). Hence, future possibilities in developing quantitative analyses of iron sulfide minerals are seen in the evolving area of scanning electron microscopy (SEM). Two types of analyses show promising results when it comes to determination and quantifications of iron sulfide as shown by (Bunkholt, 2015). They used automated mineralogy and electron backscatter diffraction (EBSD) to determine and quantify different phases of pyrrhotite in sulfide bearing (calcite) marbles of high purity (i.e. >97% calcite). Although the challenge of determining pyrrhotite species was recognized by Becker (2009), later development has provided more accurate quantification of pyrite versus pyrrhotite. By using so called "sparse phase search" iron-sulfide grains may be identified and differentiation of pyrite and pyrrhotite is possible (e.g. Bunkholt, 2015). In cases where determination of pyrrhotite species is of interest, EBSD can be utilized. Although early attempts were not successful (Bunkholt, 2015) later development in technology could possibly enable improved recording and indexing of EBSD patterns.

At NTNU, a new state-of-the-art electron microscopy laboratory is under construction. The laboratory will have an electron- and optical microscopes for characterization of rocks and ores. A Zeiss Sigma 300 Mineralogic electron microscope for automated mineralogy can be utilized to identify and quantify iron sulfides in aggregates. The SEM is equipped with high-speed EBSD detector that can be used to differentiate between magnetic and none-magnetic pyrrhotite. However, sample preparation for optical- and electron-based methods are time consuming and limits representability of the sample as polished sections represent a narrow geographic selection. This is acceptable in research laboratories but other, more rapid sample preparation and analytical techniques should be considered in case the industry defines the analytical speed (including sample preparation) as critical.

Pyrrhotite in concrete

Pyrrhotite is potentially unstable in concrete. Upon exposure to oxygen from air and humidity pyrrhotite can oxidize and result in ferrous ions and sulfuric acid. The ferrous ions oxidize further to rust products such as ferrohydroxide. Whereas the sulfuric acid will upon reaction with the cement paste result in sulfate containing phases such as gypsum or ettringite, and in the presence of carbonates potentially in thaumasite. The rust products, as well as the formation of ettringite and thaumasite can lead to expansion, cracking and finally disintegration of the concrete. These phases have amongst others been found in heavily damaged concrete foundations containing pyrrhotite aggregate in buildings in the Trois-Rivières area in Canada (Rodrigues et al 2012).

Rodrigues et al. (2015) developed an accelerated mortar test to assess the potential deleterious effect of sulfide-bearing aggregate in concrete. The aim of the test is to accelerate the degradation mechanisms leading to the observed damage i.e. oxidation of the pyrrhotite and formation of ettringite and thaumasite. Hence, the test comprises an accelerated oxidation step where mortar bars are exposed twice a week for 3 hours to a 6% bleach solution (NaOCl) alternated with drying at 80 °C and 80% RH and this for a total of 13 weeks. In the next step the formation of thaumasite is accelerated by combining the exposure cycles to bleach with exposure to 4 °C and 100% RH. This accelerated mortar bar test was able to provoke expansion in mortars with reactive aggregate containing pyrrhotite and does not lead to expansion for mortars with non-reactive aggregates.

Guirguis et al. (2018) applied the accelerated mortar bar test to study the impact of lowering the water-to-binder ratio or using supplementary cementitious materials (SCMs) on the expansion due to the reaction of sulfide-bearing aggregates and found that both measures reduce the expansion of the mortar bars.

Further research focusing on the correlation between laboratory and field-testing is needed in order to validate the mortar bar test method for relevant concrete compositions and exposures. The final goal would be to develop a concrete performance test and set acceptance limits for the expansion. Such a performance test would enable us to evaluate whether aggregates are safe to use, or how we can adapt concrete recipes e.g. by reducing the water-to-binder ratio or using different binders in order to mitigate expansion in concrete containing sulfide-bearing aggregates.

The concrete group at NTNU could perform µXRF scans of cross sections of the mortar bars and thereby elucidate the ingress depth of the bleach (tracing e.g. chlorine) and potential leaching (tracing e.g. potassium) during accelerated testing of mortars with different binders or water-to-binder ratios. Techniques such as thermogravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscopy combined with energy dispersive spectrometry (SEM-EDS) can be used to investigate changes in the cement paste such as formation of gypsum, ettringite and thaumasite. By combining these methods both on laboratory and field exposed samples we can obtain a deeper understanding of the degradation mechanisms for concrete with sulfide-bearing aggregates and improve the reliability of potential performance tests.

Outlook

More accurate detection methods for sulfur and pyrrhotite in aggregates, and performance tests for concrete containing sulfide-bearing aggregates based on the fundamental understanding of the degradation mechanisms, would have a tremendous impact on the sustainable use of aggregates. It would enable the safe use of local aggregates (e.g. tunnel masses) and thereby reduce transport costs, unnecessary use of resources and deposition of waste.

Together with the Norwegian Public Road Administration, the Department of Geoscience and Petroleum and Department of Structural Engineering, Faculty of Engineering, NTNU is applying for funding of research on this topic within the Ferry free E39 project.

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The problem

- A lot has been said about sulphides in rocks these two days
- However, characterization of low contents of sulphides in rocks is not straight forward
- Hence, for us, characterization **is** the problem

Pyrite

- The sulphide problem occurs at very low S content in aggregates (<1 wt-%) – i.e. **ca 1.8 % pyrite** (FeS_2)
- Even more challenging when pyrrhotite occurs (S <0.1 wt-%) – i.e. as little as ca **0.25 wt-%** (FeS)

Pyrrhotite

- Locating and identifying sulphide minerals at these levels are challenging.

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Standard test methods

Chemical analyses:

- X-ray fluorescence (XRF):
  - Quantitative analyses
  - down to ppm level
  - Short lead time sample prep
  - Not suited for S
- Combustion method for S
  - e.g. Leco
  - Sub %
  - Short lead time sample prep
- Acid solubility/gravimetric
  - Sub % (?)
  - Short lead time sample prep

Mineralogy

- Petrography:
  - Qualitative analyses
  - down to sub one-thenths %
  - Long lead time sample prep
- X-ray diffraction (XRD):
  - around 1 wt-%
  - Short lead time sample prep
- Differential Thermal Analysis (DTA):
  - > one-tenths of wt-%
  - Short lead time sample prep

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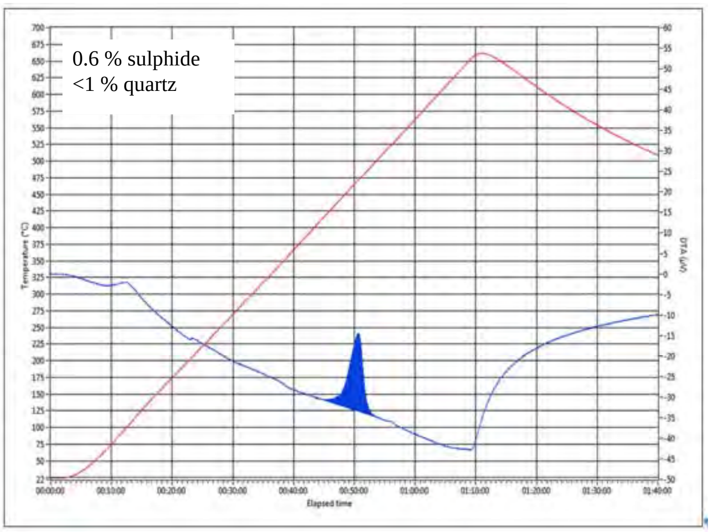
DTA analyses

DTA equipment at NTNU/SINTEF developed by Prof. Selmer-Oslen during 1950´s



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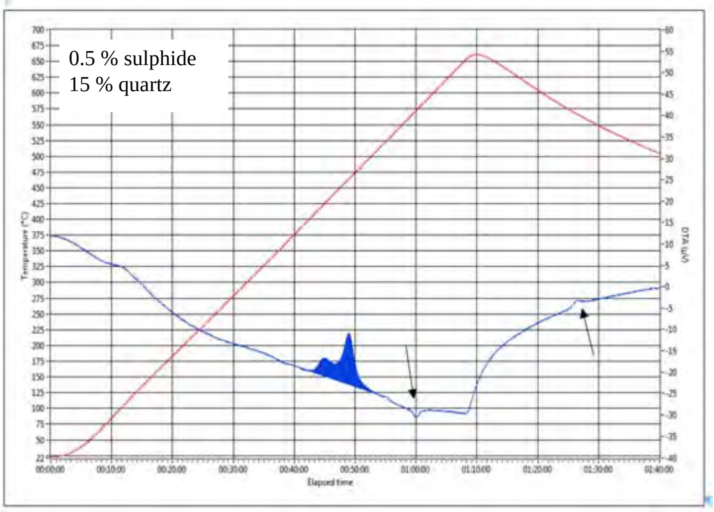
Pers. com.: Filip Dahl, SINTEF

DTA analyses

DTA equipment at NTNU/SINTEF developed by Prof. Selmer-Oslen during 1950´s



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Pers. com.: Filip Dahl, SINTEF

DTA analyses

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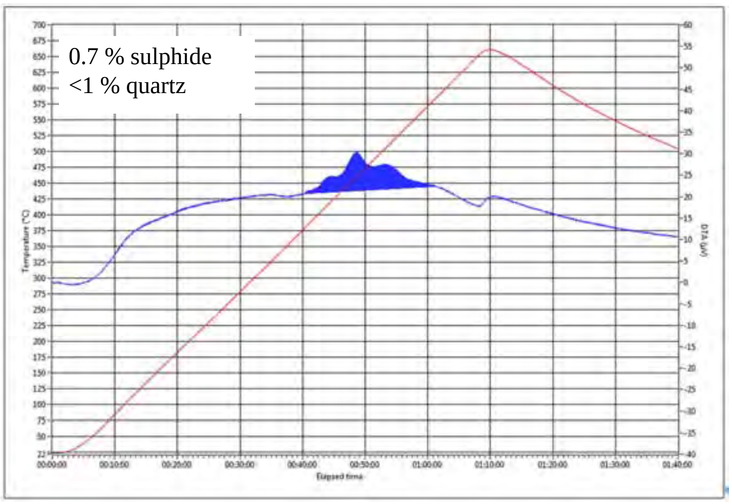

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Pers. com.: Filip Dahl, SINTEF

Relevant research

- In Ground Calcium Carbonate (GCC) production, whiteness is imperative
- It is known that sulphides degrade high whiteness calcite concentrates
- Bunkholt (2015) investigated pyrrhotite in calcite marble raw material
- The Norsk Mineral AS´ mine has a zone with sulphides
- Pyrrhotite present and most difficult to remove by traditional methods
- Used different techniques to check for pyrrhotite content and types of pyrrhotite present
- Significant for flotation results – rapid alteration of pyrrhotite made flotation difficult

Photo: Omya Hustadmarmor

Photo: Brønnøy Kalk, 2012

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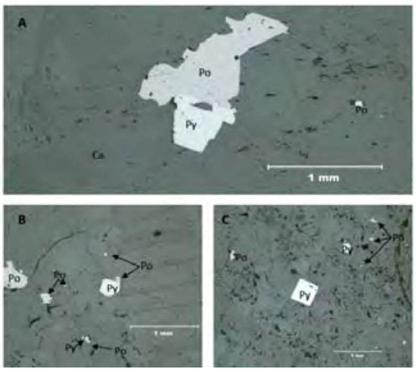
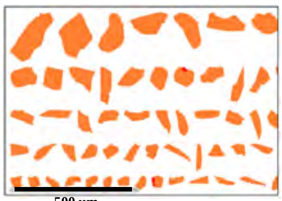
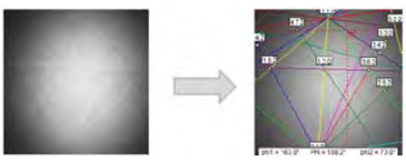




500 um

AMS:
- Define grains from BSE image
- Select grains for EDS analyses
- ID minerals based on EDS signature



EBSD:
- Measure crysallographic orientation
- Define grains and orientation
- ID minerals based on crystal structure

KA2

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Bunkholt (2015)

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Future thoughts

AMS

- Why AMS so promising (ID and characterization of sulphides)?
  - Able to detect even imperceptible amounts of sulphide minerals in samples
  - May quantify and identify different sulphide minerals
  - Able to define particle or grain size of different minerals
  - Imaging for visualization
  - All above from one analytical setup
  - Sample: polished slab up to 15x15 cm or thin section

- EBSD
  - To be used to identify different crystallographic species of pyrrhotite
  - Use crystallography to distinguish
  - Not dependent on minimal differences in chemical content

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MiMaC
Norwegian Laboratory for Mineral and Materials Characterisation

Aims to establish a world class Norwegian laboratory for structural characterization and high-sensitivity chemical analyses of minerals, metals and advanced nanomaterials in Trondheim.

Multi-scale (atom-scale to micro-meter scale)
Multi-dimensional (1D-3D)
Equipment for 70 MNOK
53 MNOK from the Norwegian Research Council
17 MNOK from the host institutions

Instruments:
- 3D Atom probe
- EPMA
- AMS
- LA-SS-MC/QqQ-ICP-MS
- LA-QqQ-ICP-MS

GEOLOGICAL SURVEY OF NORWAY
- NGU -
SINTEF
NTNU
Forskningsrådet

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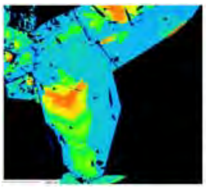
Node: NTNU Department of Geoscience and Petroleum

Electron Probe Micro Analyzer (EPMA)



The JEOL JXF-8530F PLUS is a field emission (FE) microprobe equipped with 5 wavelength (WDS)- + 1energy (EDS) dispersive spectrometers; panchromatic CL detector. The microprobe does low ppm element analyses on µm scale spatial resolution

Field of use

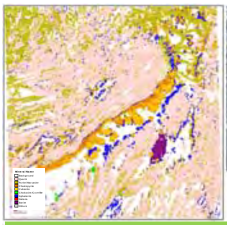
- In-situ none destructive chemical analyses of solid samples
- Quantitative analyses to ppm level
- Element mapping (zonations etc)
- Spatial resolution to µm level
- Rapid analyses of minerals, rocks, others solid materials

Complementary laboratories near by:

- IGP Mineral processing lab
- NTNU Paleo- and Rock Magnetic laboratory
- IGP Chemical- mineralogical lab
  - XRF; XRD; ICP-MS
- Automated mineralogy system
- Advanced optical microscopy lab
  - Fluid inclusion system; Heating stage;

Node: NTNU Department of Geoscience and Petroleum

Automated Mineralogy System



Zeiss Sigma 300 field emission SEM with Mineralogic software for Quantitative Mineralogical Analyses rocks and ores. Equipped with Bruker EDS; panchromatic CL; High-speed EBSD

Field of use

- Quantitative mineralogical analyses
- Automated analyses for mineralogy and petrography
- Mineral liberation analyses
- Textural analyses of rocks and ores
- Rare phase search

Complementary laboratories near by:

- IGP Mineral processing lab
  Bench scale- and pilot scale mineral processing equipment
- NTNU Paleo- and Rock Magnetic laboratory
- IGP Chemical- mineralogical lab
  XRF; XRD; ICP-MS
- Electron Probe Micro Analyzer
- Advanced optical microscopy lab
  Fluid inclusion system; Heating stage;

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Lab facilities – IGP/NTNU

Existing labs
- XRD
- XRF
- DTA (co-op with SINTEF)
- SEM and EPMA
- Petrographic microscopes

- + various magnetometry analysis

New labs
- *MiMaC laboratory*
  - Norwegian Laboratory for Mineral and Materials Characterisation
- *Automated Mineralogy System*
  - *Zeiss Sigma 300VP Mineralogic*
- *Electron Probe Micro Analyser (EPMA)*
  - JEOL JXA8530F PLUS

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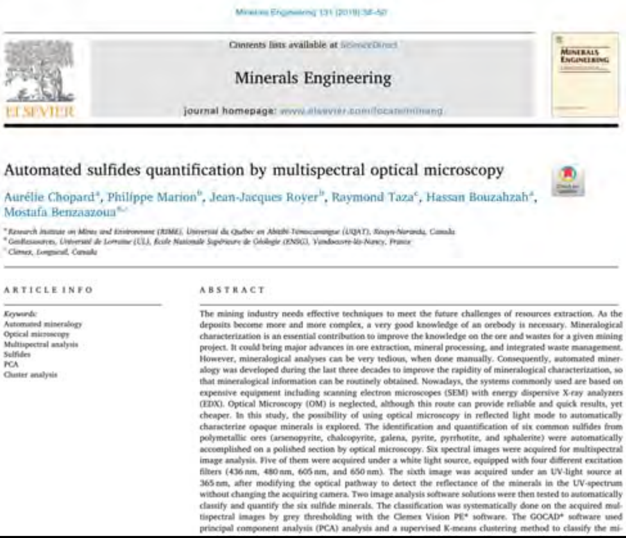
Fresh from the press



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Automated sulfides quantification by multispectral optical microscopy

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ARTICLE INFO

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Optical microscopy
Multispectral analysis
Sulfides
PCA
Cluster analysis

ABSTRACT

The mining industry needs effective techniques to meet the future challenges of resources extraction. As the deposits become more and more complex, a very good knowledge of an orebody is necessary. Mineralogical characterization is an essential contribution to improve the knowledge on the ore and wastes for a given mining project. It could bring major advances in ore extraction, mineral processing, and integrated waste management. However, mineralogical analyses can be very tedious, when done manually. Consequently, automated mineralogy was developed during the last three decades to improve the rapidity of mineralogical characterization, so that mineralogical information can be routinely obtained. Nowadays, the systems commonly used are based on expensive equipment including scanning electron microscopes (SEM) with energy dispersive X-ray analyzers (EDX). Optical Microscopy (OM) is neglected, although this route can provide reliable and quick results, yet cheaper. In this study, the possibility of using optical microscopy in reflected light mode to automatically characterize opaque minerals is explored. The identification and quantification of six common sulfides from polymetallic ores (arsenopyrite, chalcopyrite, galena, pyrite, pyrrhotite, and sphalerite) were automatically accomplished on a polished section by optical microscopy. Six spectral images were acquired for multispectral image analysis. Five of them were acquired under a white light source, equipped with four different excitation filters (436 nm, 480 nm, 605 nm, and 650 nm). The sixth image was acquired under an UV-light source at 365 nm, after modifying the optical pathway to detect the reflectance of the minerals in the UV-spectrum without changing the acquiring camera. Two image analysis software solutions were then tested to automatically classify and quantify the six sulfide minerals. The classification was systematically done on the acquired multispectral images by grey thresholding with the Clemex Vision PE* software. The GOCAD* software used principal component analysis (PCA) analysis and a supervised K-means clustering method to classify the mi-

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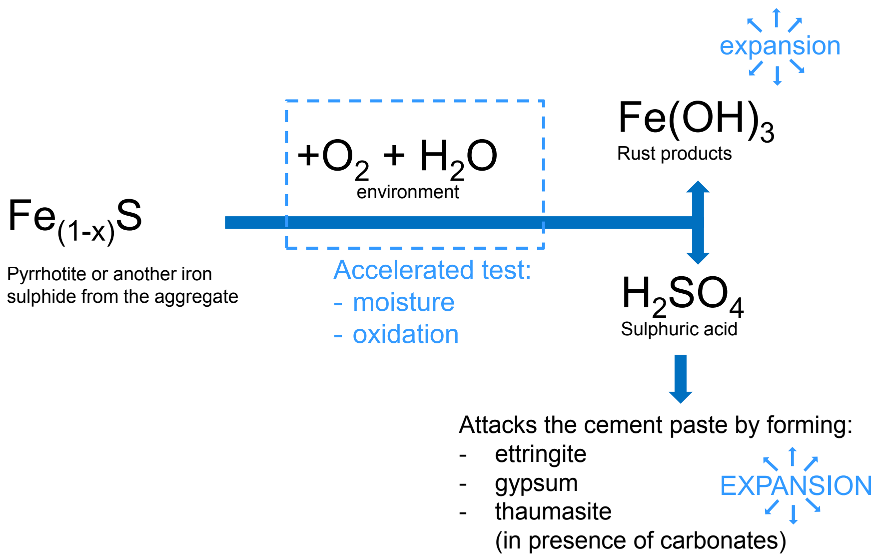
What happens with Pyrrhotite in concrete?



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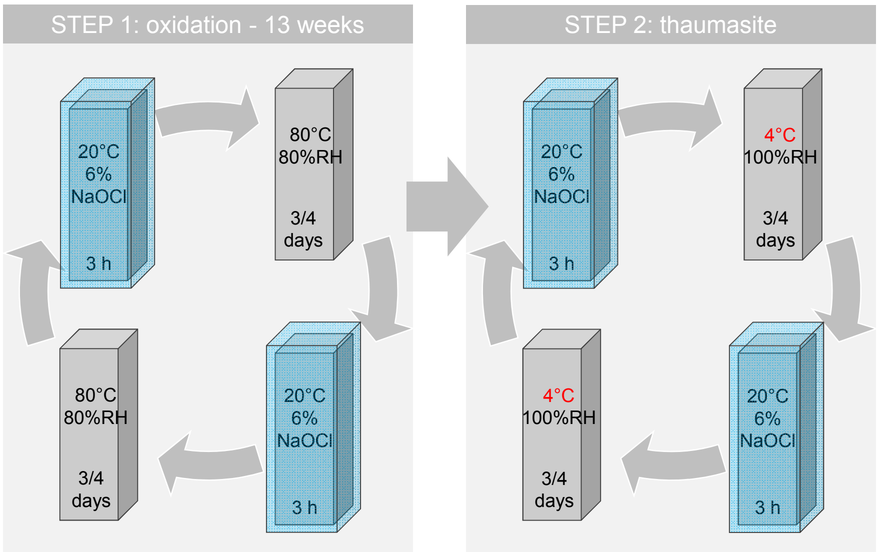
Accelerated test for iron-sulphide minerals



Rodrigues Duchesne Fournier (2015) CCR

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Accelerated test for iron-sulphide minerals

The accelerated test method can potentially be used to assess the impact of:

- Supplementary cementitious materials
- w/b ratio
- ..

Remaining questions:

- Risk for delayed ettringite formation (80C)
- Impact of chlorides on ASR

- Correlation laboratory expansion – field?
- Do we test the same mechanisms?
- Do we get the same reaction products?
- Is the test applicable on all kinds of concretes?

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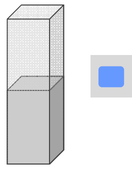
Validate test method

Tools:

- µXRF



- Verify ingress of bleach during accelerated testing
- Chloride and sulphate transport

- SEM-EDS, XRD, TGA
- Phase assemblage before and after exposure

- Verification with samples from field? Exposure site?

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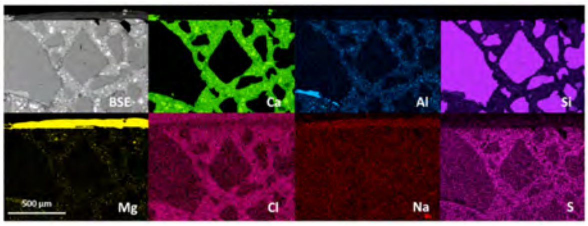
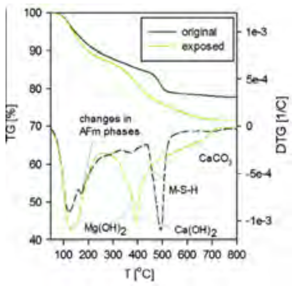
Example - sea water exposure

SEM-EDS maps - mortar

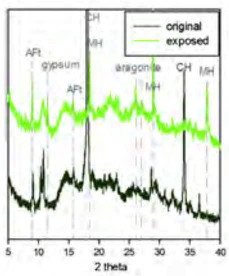


De Weerdt et al. 2018 CCR

TGA cement paste



XRD cement paste



Justnes and De Weerdt 2015 CCC

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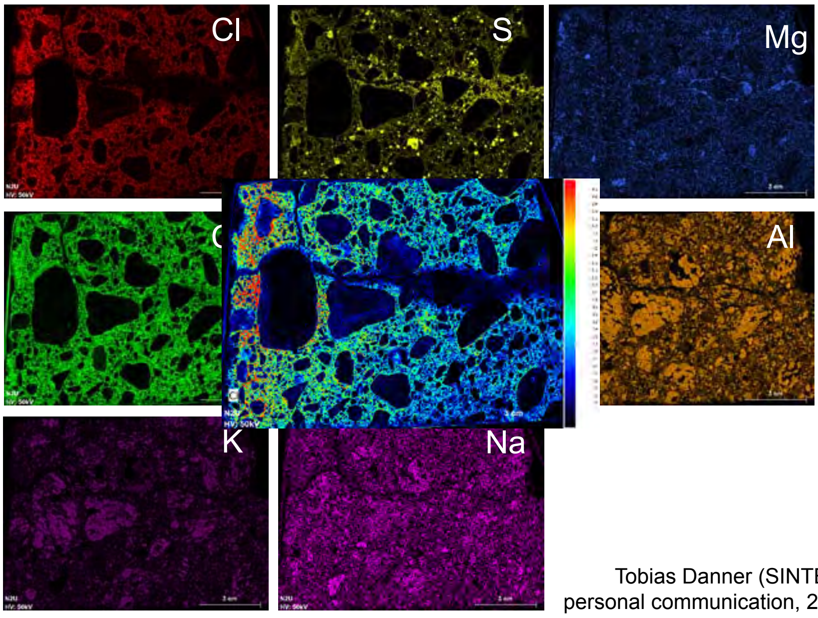
Example µXRF – seawater exposed concrete with crack



Tobias Danner (SINTEF), personal communication, 2018

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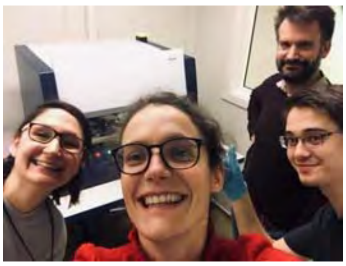
Example µXRF



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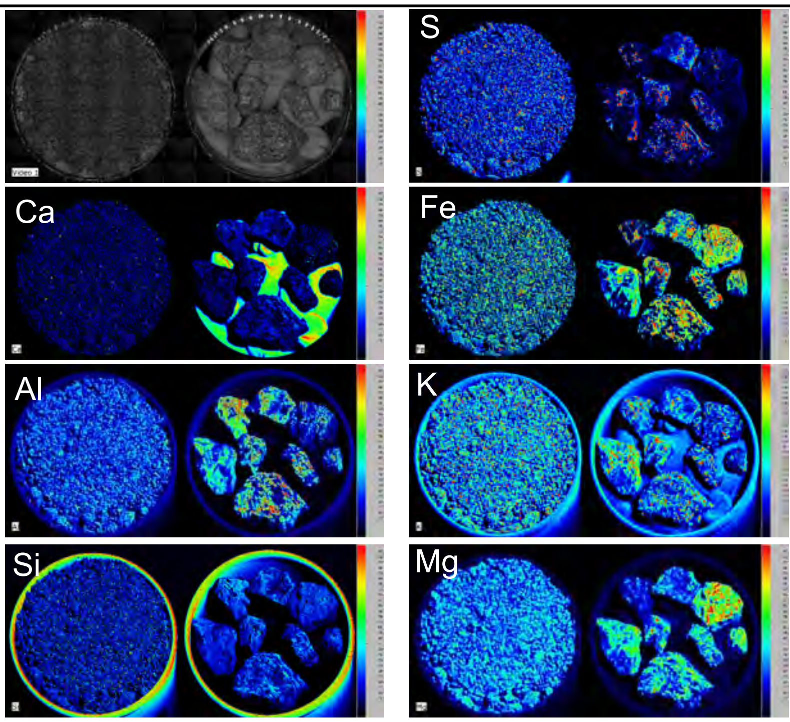

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Future research focus:

1. development of a methodology for identifying, characterizing and quantifying sulphides in aggregates;
2. contribute to understand the geological processes for the formation of sulphide-bearing minerals
3. development of accelerated performance test method and acceptance limits for sulphide containing aggregates in concrete
4. investigate the potential mitigating effect of measures such as reduced water-to-binder ratio, SCM, or alternative binders
5. contribute to the development of categorizing system for different sulphide minerals regarding the potential reactivity in concrete.

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Applications for project support

Ferry Free E39 - Pyrrhotite in aggregates for concrete

- Time frame: 2019-2022
- Budget: 15 MNOK
- Partners: NTNU, NPRA, SINTEF, HeidelbergCement Northern Europe, NGU, NHM, BaneNor (?), tilslagsprodusenter ..
- PhD students: 3 (Petter Hemstad)


Statens vegvesen
PROSJEKTFORSLAG FoU

- Goal:
  - We will develop methods to identify and quantify the sulphide- and pyrrhotite content and practical acceptance test for aggregates
  - We will develop reliable performance test for concrete enabling safe use of sulphide-bearing aggregates in concrete.

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Applications for project support

Potential funding through Norwegian Research Council

- To be submitted as KPN proposal in 2019?
- Centre(s) for Research-based Innovation (2019)
- Small clusters or individual companies as IPN?

KPN proposal – 2019

- Draft prepared and submitted 2018
- Final proposal not submitted
- Focus on all aspects from geology to concrete testing
- Applied research with fundamental aspects
- KPN aims at integration of results into partner operations

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A list of previous and upcoming Nordic workshops is available on www.nordicconcrete.net